We thank the anonymous referees for their comments. Our responses are noted here in blue text; revisions in quoted text are indicated with bold text. We reference page/line numbers in the original manuscripts as 'OM' and in the revised manuscript as 'RM'.

Referee #1

This paper presents detailed measurement of semi- and intermediate-volatility S/I-VOC compounds from laboratory burns of a range of wildland fuels using a novel approach, which employs Teflon membrane in front of solid-phase extraction (sorbent-infused) filters to capture particle and vapor-phase fractions, respectively. Derivatized extracts from these media are analyzed using high-resolution 2-D GC-MS and the resulting chromatograms are analyzed in several ways to provide insights into similarities and differences between I/SVOC profiles from the different fuels. For example, analysis points out that different benzenediol isomers (that would not be separately resolved by other analytical techniques) have distinctive emission profiles across the different fuels/burns. The authors also explore the volatility distribution of the analyzed compounds. This is an interesting and well written paper, and I believe it should be published. I include some minor comments/clarifications below. My main concern is that this is more of a 'methods' paper (and so perhaps more appropriate for AMT than ACP) as it explores the application and some evaluation of a new and interesting method to a range of test burns. It does include a 'survey' of analysis across a few dimensions but does (and perhaps can't) go as far as actually yielding quantitative estimates of emissions the may be of most interest to the ACP audience. The main contribution is to show the promise of this new measurement approach and give a 'sampling' of some of the insights that its application yields. In short, while it is definitely an important contribution, it is more exploratory than broadly quantitative. The paper itself generally makes this orientation clear, but perhaps the title and abstract could be slightly reframed to emphasize the nature of the study.

We generally agree with the referee's assessment of the scope of the manuscript and also considered whether to submit it to AMT or ACP. Ultimately, we decided that the lack of a fully optimized, quantitative analysis protocol meant this work was better suited to ACP as the majority of the discussion focuses on the chemical insights gained from the filter analyses. Although qualitative, many of the findings, such as isomer-dependent emissions and partitioning of compound classes in biomass burning samples, have not been previously reported and will be of interest to the ACP community.

We feel that the title is a concise and accurate representation of the work that does not overstate the scope of the manuscript; thus we have opted not to revise it. However, we have revised the abstract in response to this referee's comments. We have added a note that the analysis is qualitative in the following sentence: "Emitted I/SVOCs were collected onto Teflon filters and solid-phase extraction (SPE) disks to **qualitatively** characterize particulate and gaseous I/SVOCs, respectively" (Page 1, Line 20, RM). We have also modified the objectives listed in the introduction to better emphasize the qualitative nature of the study "(1) **demonstrate the potential of** SPE filters for the untargeted analysis of compounds with a wide range of volatilities; (2) **qualitatively** investigate the **diversity** of I/SVOCs emitted from biomass burning across a range of fuel types…" (Page 3, lines 16-17, RM)

Specific points

P1, Line 23 – The abstract discusses 'speciation profiles', but the paper later specifies (P. 8, L25) that it will not provide speciation profiles (at least as this term is typically applied). As noted above, the abstract could be re-worked to clarify the scope/intent of the study.

We have changed 'speciation profiles' in the abstract to '**observed chromatographic** profiles' (page 1, line 23, RM) to make it clearer that we are considering the differences in observed chromatographic peaks between samples rather than identified compounds. We agree that is an important distinction.

P7, L20 – 'error estimated to be approximately a factor of two' – this phrasing doesn't make that much sense, especially given that you reference RSDs of ~80%. Is it really indending to say an uncertainty of 200%?

A factor of 2 uncertainty is effectively equivalent to 100% RSD, which is consistent with our conservative estimate based on maximum RSDs of 80%. To avoid further confusion, we have revised the text to:

"Further, the relative standard deviation (RSD) for each compound was conservatively estimated to be approximately **100 %** based on the maximum RSDs determined in the recovery tests (**80 % and 64 %** for the PTFE and SPE tests…)" (Page 7, Lines 33-34, RM).

P8, L25 – This framing, 'investigating the diversity of emissions' – should be more emphasized early in the paper, or else some effort should be made to present profiles (even in relative/approximate form). In general, I think there would be interest in having access to actual profiles in a supplement, as this is the key product that might be applied by the interested research community (apart from demonstrating the method). Are there are least some compounds for which you could provide emission ratios or C2 factors?

We have now used the preferred framing when introducing the goals of the study on page 3, line 17 (RM): "(2) **qualitatively** investigate the **diversity of** I/SVOCs emitted from biomass burning across a range of fuel types."

We have posted all PTFE and SPE filter data to the NOAA FIREX archive that is now publicly available. A note has been added describing the data availability (Page 17, lines 19-20, RM).

Considering the analysis issues affecting some samples and the lack of recovery and internal standards noted throughout the text, we prefer to remain conservative and provide qualitative, rather than potentially incorrect quantified data.

P10, L33 – Why is this difference likely too large? Need to justify statement.

This response assumes the referee is referring to Pg 12, line 33 (OM): "…for comparison, $C^*_{\mathrm{Cat}}/C^*_{\mathrm{HQ}}$ = 51 using the Verevkin and Kozlova (2008) ΔHvap data, which is likely too large of a volatility difference between the two isomers." We have added the following justification (page 13, lines 11-12, RM): "which is likely too large of a volatility difference between the two isomers **based on a comparison with hexane- and cyclohexane- diols (Capouet and Muller, 2006)."**

P13, L29-32 – I'm not sure this statement is supported. Doesn't this depend on the lifecycle of the VOC? Couldn't either of these be mostly reacted in the gas-phase if they don't find themselves around liquid water?

We have toned down this discussion and now suggest that differences in oxidation phase may, rather than will, be different between the two isomers. The text now reads: "Overall, the partitioning estimates calculated in this work support the conclusions of Smith et al. (2015) that **aqueous/condensed phase** SOA production mechanisms **are more likely to occur for hydroquinone than catechol**, for which gas-phase oxidation will dominate SOA production **based on its low condensed-phase fraction** (Figure 5)…" (Page 14, Lines 7-9, RM)

P14, L14-15 – How is it possible that particles in only one or other phase should be in a middle volatility bin? This needs justification.

We have added the following explanation: "It is possible that such compounds could belong in one of the middle volatility bins **if, for example, the compound was actually present in both phases, but was below detection limit/peak selection criteria in either the PTFE or SPE filter sample."** (Page 14, Lines 25-26, RM)

P14, L24-31 – It would make sense to renormalize your distribution to the same C* range when making this comparison – it is good to show your entire distribution, but doing the higher volatility bins are presumably 'invisible' in the May distribution, so I would advise a version of this plot making the comparison with a version of your distribution normalized to the same range as the May et al. distribution. Also, note that the fuel and burn conditions are different, and this is another source of variability (in addition to different analytical approaches). This discussion also falls into the category of 'descriptive/exploratory'.

We disagree that the bins should be rescaled to the May et al. volatility distribution, which was derived based on particle-phase measurements alone. A key motivation for this work was to measure compounds with volatilities intermediate to those accessible using the commonly applied particle- and gas-phase measurements. Rescaling our data to particle-phase measurements would diminish those efforts. We have modified the following sentence to make that point: "The trends observed in bins $\log C^*$ = 2-4 are nominally similar between the two studies, although the fractions are lower in this work due to allocation of some mass into bins >4 and **illustrates that the SPE filters enabled**

measurement of higher volatility compounds, although the relative abundances of such compounds are likely underestimated" (Page 15, lines 8-9, RM)

We have also added that the fires represented in the two distributions are different: "the agreement is reasonable considering the two very different analytical approaches… **and the different fires included in each distribution.**" (Page 15, lines 12-13, RM)

Minor/technical corrections
P9, L32 – minor quibble, but using 'fuels' where you mean 'burns' should be avoided for clarity. . .

We agree and have made the suggested change.

P10, L12 – I believe this should be 10ˆ3, not 10ˆ-3?

We thank the referee for catching this typo (on Pg 12, L12). We have corrected the text.

Referee 2:
This manuscript describes the analytical methodology associated with a relatively novel sampling strategy, analyte extraction/recovery, and analysis by two-dimensional gas chromatography for biomass combustion aerosol sampled at the Fire Science Laboratory. The authors have apparently studied a wide number of samples using a new analytical method without sufficient preliminary validation to understand the potential method errors associated with intermediate- and semi-volatile organic compounds (I/SVOC). For example, samples were dried under N2 to exchange solvents one or two times and the authors noted sample losses during storage. These are very significant errors leading to incorrect quantities of I/SVOC components. Some of these errors are discussed, but the associated limitations in the results interpretation is not sufficient. Overall, the paper is quite long including 3 major goals: (1) test the application of untargeted analysis to the new sampling strategy, (2) compare the I/SVOC speciation profiles, and (3) assess the accuracy of the measurements. Unfortunately, I did not understand how the accuracy was assessed. Considering the method errors, it is very difficult to have a meaningful discussion of the I/SVOC profiles, which I thought was the main point of this paper. I think the authors could do a better job of eliminating the analytes must susceptible to evaporative losses, and then proceed with the comparison of the profiles and their correlation. I would like to see the paper strongly revised with careful attention to the limitations associated with the method errors/assumption. At the same time, I think the paper should be substantially shortened to focus on the most valuable results.

Regarding the comment: "…without sufficient preliminary validation to understand the potential method errors associated with intermediate- and semi-volatile organic compounds (I/SVOC)." We have added to the Supplement (page S6, RM) a discussion of additional quality control tests we performed to investigate potential volatilization losses, which demonstrate that the variability is likely within the factor of 2 uncertainty we proposed on page 7, line 20 (OM). With those additional tests, we have provided method validation in the form of (1) potential recovery biases associated with the SPE filters using a broad range of standards (Section 3.1, page 6, OM); (2) breakthrough/collection efficiency of the SPE filters (page 8, lines 12-17, OM); and (3) the impact of sample mass/absorbing phase on volatilization losses (page S6, RM), where (1) and (2) were addressed in the original manuscript and (3) was added in response to the referee's comments. We believe this is sufficient validation to demonstrate the feasibility of this relatively novel method; we have been clear in the original and revised manuscripts that the results are qualitative rather than quantitative and the limitations of our conclusions have been clearly reported. We have refrained from calling this a "methods" paper and submitting to a methods journal, as we entirely agree that further method optimization and validation are needed to achieve quantitative analysis, and have stated as such throughout the text (e.g., see response to Referee #2's comment #10 below). Furthermore, we were very conservative in presenting only results that likely were not significantly impacted by the noted errors and uncertainty. When introducing each analysis of the fire samples, we discussed the justification and/or potential errors associated with that specific analysis (e.g., page 8, lines 30-34, OM; page 11, lines 3-5, OM; and page 14, lines 5-11, OM).

Regarding the comment: "…3) assess the accuracy of the measurements. Unfortunately, I did not understand how the accuracy was assessed," as written the referee has significantly broadened the scope of objective 3 relative to that stated in the manuscript. Our objective 3 was specific to investigating gas-particle partitioning (page 3, lines 18-19, OM): "(3) assess the accuracy of phase-separated SPE measurements to predict gas-particle partitioning of compounds". We have done that through a detailed comparison of the filter-based benzenediol (Figure 5, Section 3.2.1, OM) and levoglucosan (page 15, lines 12-17, OM) volatility estimates with available thermodynamic/volatility data. These two examples reflect compounds with volatilities differing by several orders of magnitude. We have added 'specific' before 'compounds' in objective 3 to further make this clear (pg 3, line 19, RM). We additionally acknowledged that further optimization would improve the partitioning measurements (page 12, lines 7-8, OM): "Future use of recovery standards and further method optimization will help to correct for any sample-to-sample inconsistencies in the extraction efficiency and ultimately better constrain the partitioning estimates."

Regarding the manuscript length, from a general perspective, the length is well within limits of previously submitted manuscripts by Hatch and/or Barsanti to ACPD. The current paper, as formatted for ACPD, is 30 pages; other manuscripts, also as formatted for ACPD and published post 2015 since formatting has changed, range from 22-36 pages. Two recent FIREX publications by other authors are 34 and 44 pages in ACPD, neither of which introduces a new method. Further, referee #2 has provided no specific comments in their review related to which results s/he found to be most valuable vs. confusing/unnecessary. The justification for substantially shortening the manuscript is not clear, as all of the specific comments seek additional information regarding the methods. We believe the manuscript in its current form satisfactorily addresses each of our stated objectives: demonstrating the feasibility of a new analytical approach and presenting results on gaseous emissions profiles as a function of fuel type and partitioning of I/SVOCs in smoke, which are of general interest to the atmospheric community. We have made an effort to be as concise as possible in presenting our approach and findings, while also addressing current uncertainties and limitations (which we agree are a critical component), but have not shortened the manuscript by any significant measure.

Specific comments:
1) Please specify how the blank subtraction was performed.

The background/blank subtraction was explained on page 5, lines 3-6 (OM): "Background correction was performed separately on the PTFE and SPE filters. Within each filter group, the maximum signal of a given peak observed on any *blank or background sample* was multiplied by 2 to ensure that all artifact peaks arising from the extraction and derivatization procedures were entirely removed; that value was subsequently used for background correction of all corresponding fire samples." As the referee did not specify which additional details s/he is looking for, we have attempted to provide further clarity by revising the sentence to (page 5, lines 3-7, RM):

"Within each filter group, the maximum **peak area** of each peak observed **across the full set of corresponding blank and background samples** was multiplied by 2 to ensure that all artifact peaks arising from the extraction and derivatization procedures would be entirely removed. **Those adjusted values were subsequently used to background correct all associated peaks in the corresponding fire samples; only 16 (PTFE) and 32 (SPE) peaks in the fire samples required background correction**."

2) MeOH extraction was performed prior to BSTFA derivatization and BSTFA derivatizes hydroxyl groups. Unfortunately, this can lead to unexpected variations in the amount of BSTFA that is available for reaction with the analytes, since the relative reaction rates are expected to be much slower for carboxylic acids compared to primary alcohols. This limitation should be noted.

We assume the referee is suggesting that the methanol solvent consumed some of the derivatization agent. However, the extracts were fully dried down prior to derivatization; thus we do not believe availability of BSTFA was a limiting factor in the derivatization of carboxylic acids. We have also revised the text accordingly (Page 4, lines 19-20, RM):

"For derivatization, each aliquot was dried completely under nitrogen **to avoid reactions between the solvent and derivatizing agent**."

3) Drying extracts leads to substantial losses of components depending on their specific volatility and can increase the possibility of solvent reaction artifacts (e.g., ester and hemiacetal formation). This limitation must be made clear along with appropriate caveats in the interpretation of the results.

We are aware of this limitation and discussed the potential for variable volatilization losses in the Supplement (Page S2, OM): "As seen in all figures (especially Figures S1 and S2), the recovery from both PTFE and SPE filters decreases with decreasing retention time (increasing volatility), likely due to losses during the drying periods. In both the PTFE and SPE tests, recovery increases for later-eluting compounds, although in the "transition" region where recovery gradually increases for each subsequent compound (e.g., tetradecane – heptadecane, Figure S1; guaiacol, Figure S3), *the measured recoveries were highly variable, as indicated by the large error bars. Despite such variability, we have retained these compounds in the biomass burning dataset and assume a factor of 2 uncertainty to account for this observation*".

We also provided relevant caveats in the main text when introducing relative abundance (Page 8, lines 29-35, OM): "The peak area fractions are used as an indication rather than an absolute measure of the % abundance *because the individual compounds have not been corrected for recovery or differences in instrument response.* This approach is reasonable for the qualitative assessment sought here because *many of the most volatile compounds were still observed with high relative abundance*. For example, cresols likely exhibited poorer recovery (<0.3) than guaiacol (Figure S3) due to their higher volatilities, yet were still among the most abundant of the observed compounds. However, *the relative abundance for volatile compounds should be considered a lower limit."*

In the revised manuscript, we have added the following additional discussions and caveats regarding volatilization losses:
-Page 6, lines 15-19, RM: "**However, there is no clear relationship between the poor recovery of these four compounds and oxygenated compounds that elute in the same primary retention time window. For example, heptanoic acid displayed significantly better recovery in the PTFE test (0.86±0.06, Figure S4) than tridecane (0.14±0.07, Figure S1) despite eluting significantly earlier (1045 s vs. 1190 s). As a result, the poor recovery of the volatile alkanes/naphthalene was not extrapolated to other relatively polar oxygenated compounds present at similar retention times in the fire samples"**
-Page 14, line 31-32, RM: "**Additionally, the relative fractions of the higher volatility bins (i.e., logC^* bins ≥5) would likely increase following correction of the relatively poor recovery exhibited by such compounds."**
-Page 15, lines 8-9, RM: **"…which illustrates that the SPE filters enabled measurement of higher volatility compounds, although the relative abundance of such compounds are likely underestimated."**
-Page 16, lines 26-29, RM: "However, **SPE-induced** extraction biases were generally consistent for each compound class and could be corrected, **although recovery was low for the most volatile compounds due to volatilization during blow down.** Future improvements in the extraction protocol, **specifically testing additional solvents and drying time, in addition** to the use of recovery, internal, and external standards, should enable quantification of compounds collected onto SPE filters."

We have also added to the revised Supplement a discussion of additional tests that were conducted to further probe the recovery of the relatively volatile compounds encountered in the SPE samples. We find that the variability in the recoveries of volatile compounds to be within the uncertainty stated above (Pages S6-S8, RM).

In the original Supplement (page S4, OM), we had also discussed extensively the observation of methyl ester derivatives that formed by reaction of methanol with aldehydes during storage of the standard mixtures. We further assessed the likelihood that such reactions impacted the biomass burning samples with the following discussion:

"Because acids were observed in the SPE and PTFE fire samples, extraction and subsequent storage of methanol extracts may have caused some conversion of aldehydes to methyl esters, although we expect this artifact to be relatively minor. For example, the peak area of methyl vanillate was ~3.5% that of vanillin in the dung SPE sample. Artifacts resulting from methanol extraction have also been previously observed (Sauret-Szezepanki and Lane, 2004). Therefore, further optimization of the extraction solvent should be conducted to limit potential reaction products, as well as to improve the recovery of hydrocarbons, as discussed in the main text (Section 3.1)."

However, we agree that the potential for analyte-solvent reactions was not clearly addressed in the main text. We have therefore added the following discussion to the main text (Page 7, lines 12-16, RM):

"**Because other artifacts resulting from methanol extraction have been previously observed (Sauret-Szezepanki and Lane, 2004), further characterization of methanol-extraction-related artifacts and/or further optimization of the extraction solvent may be needed for studies seeking to accurately identify/quantify certain compounds. However, given the consistency of the observed HMF reactions, potential solvent-analyte interactions likely did not substantially impact the observed differences in the chromatographic profiles of the biomass burning samples discussed below**."

4) An interesting point of discussion that could be elaborated here relates to the meaning of untargeted and targeted analysis. What is the actual certainty associated with the NIST library matches? I would expect them to have variations, especially with consideration to derivatized components. What happens to the analyte signals without library matches? What fraction of the overall signal do they represent?

We assume the referee is referring to the following text on page 5, lines 10-13 (OM): "For other peaks, a compound name was assigned and considered *tentatively identified* if the match similarity with the NIST library hit was >800 in any sample that contained that peak and the identified structure was consistent with the derivatization approach used here (i.e., contained trimethylsilyl groups where applicable)."

A recent paper assessed the accuracy of NIST library matches and found that the likelihood of an incorrect match was ~30% in the match range of 800-900 and even lower for matches >900. We have incorporated these details and the reference into the manuscript: "**Worton et al. (2017) have recently demonstrated that the probability of an incorrect NIST library match is ~30% for matches between 800-900 and 14% for matches >900"** (page 5, lines 14-15, RM). We emphasize that these compounds are considered tentatively identified, as we specified in the original manuscript (see quote above).

We are not entirely clear what the referee means by "variations" in the library matches. If s/he is referring to variability in the similarity values, such variability could arise depending on the quality of the analyte spectra (e.g., influence of background signal in low abundance peaks). For that reason, we allowed a tentative identification for a given peak if the library match was >800 in any sample. If s/he is referring to variability in the actual compounds matched, that could occur if there are a number of library compounds available with comparable match similarity values, in which case the best match may differ from sample to sample due to slight variations in the individual similarity values. We did not find that to be the case for the few tentatively identified compounds noted in the text. Because electron ionization is performed at an industry standard -70 eV specifically to minimize variability in the generated mass spectra, there shouldn't be any additional variability introduced by derivatization. However, compounds for which TMS-derivatives are not included in the library will not be identified, which thus explains the large number of unknown compounds within the fire samples: of the 1488 compounds observed across the full set of samples, only 24 were tentatively identified and 66 were positively identified. Because we have noted relatively few tentatively identified compounds in the text, and in the interest of keeping the text concise, we do not elaborate on the potential error in the tentative identifications.

The NIST library match was used to tentatively identify a few additional compounds (beyond those for which standards were available); the identification is independent of the analyte signal. Compounds for which the NIST match similarity was <800 were still retained, they are just considered as unknown identity. The NIST match has no influence on the analyte peak area.

5) Extraction efficiency tests include a test named PTFE test, but this test doesn't have anything to do with the PTFE filter. Please rename the tests. See also figure 1, where PTFE recovery is used to assess the SPE recovery. What is the slope of the fit? What are the outliers in the plot with red symbols?

When introducing these tests on page 5, lines 19-21 (OM) we were clear that the "PTFE test" was meant as a proxy for the PTFE filters and provided the reasons those tests were conducted as they were: "standard was spiked into 7 mL of methanol (HPLC grade) as a *proxy* for the PTFE extractions (hereafter called "PTFE test"; *standards were not spiked directly onto a PTFE filter due to the potential for rapid evaporation of the relatively volatile standard constituents*)." This approach implicitly assumes no recovery bias was introduced by the PTFE filter, which we have added to the sentence:

"…standards were not spiked directly onto a PTFE filter due to the potential for rapid evaporation of the relatively volatile standard constituents (Dhammapala et al., 2007); **this approach assumes no recovery biases are introduced by the PTFE filter**;" (Page 5, line 25, RM)

Because the PTFE test was used as the benchmark for comparison with the SPE filters, that assumption would overestimate rather than underestimate potential biases introduced from the SPE filters.

The regression parameters of the fit in Figure 1a were given on page 6, lines 14-16 (OM): "Linearity with a *correlation coefficient* (*R^2*) *of 0.72* was observed between the SPE tests and PTFE tests (Figure 1a); however there is clearly a negative bias in the extraction from SPE filters compared to the PTFE tests, *with a slope of ~0.75."* We have added these details to the Figure 1 caption in the revised manuscript so they are easier to find.

There are two red outliers in Figure 1a. The outlier with the square marker near the 1:1 text is one of the carboxylic acids that exhibited artifacts from the extraction/derivatization procedure, which was noted on page 6, line 25 (OM). The other red outlier with a circle marker at ~1.0 along the x-axis is an alkane, for which we discussed the under-recovery from the SPE filters on Page 7, line 5 (OM).

6) Please discuss the possibility of positive and negative sampling artifacts with respect to your sampling scheme.

We assume the referee is referring to filter adsorption artifacts. We pointed this out on page 12, lines 27-28 (OM): "…considering that the estimated Ci* values are more likely to be underestimated rather than overestimated due to adsorption of I/SVOCs to the PTFE filter (Mader and Pankow, 2001)." We also discussed the potential for sample-line losses on page 13, lines 14-24 (OM).

7) The threshold for poor recovery is quite low at 20%; I recommend raising it toward 50% for the discussion.

For the qualitative demonstration of the SPE method sought here, we have opted to use a relatively low threshold in order to illustrate the types of compounds that can be collected on the SPE filters. We have stated this rationale on page 7, lines 28-29 (RM): "As the interest at this stage is in assessing the full diversity of I/SVOCs in smoke **and demonstrating the range of compounds collected by SPE filters,** all observed compounds (except those explicitly noted above) were retained without correction for recovery."

We have tried to be very clear that the recovery of relatively volatile compounds is low (e.g., page 8, line 34, OM: "the relative abundance for volatile compounds should be considered a lower limit."). We have also adopted relatively large error (100% RSD) to account for the potential variability in the recoveries of the relatively volatile compounds; all tests that we have conducted indicate such uncertainty is reasonable, as shown/discussed in the Supplement, as well as on Page 7, lines 20-24 (OM). Additionally, relatively few standard compounds included in the SPE tests exhibited recovery below 50 % (Figures S1-S5) and thus we do not feel that we have enough information to adequately map the recoveries of peaks that eluted early in the chromatogram (where recoveries were poorest), as retention time alone is not a sufficient

proxy. Thus any changes in the compounds included in the analysis would largely be arbitrary without analyzing a wider range of standards. We have added some discussion to that effect (page 6, line 15-19, RM):
"However, there is no clear relationship between the poor recovery of these four compounds and oxygenated compounds that elute in the same primary retention time window. For example, heptanoic acid displayed significantly better recovery in the PTFE test (0.86±0.06, Figure S4) than tridecane (0.14±0.07, Figure S1) despite eluting significantly earlier (1045 s vs. 1190 s). As a result, the poor recovery of the volatile alkanes/naphthalene was not extrapolated to other relatively polar oxygenated compounds present at similar retention times in the fire samples."

8) Several specific compounds were poorly recovered from the SPE tests. To what degree are these recovery issues related to the various method errors (solvent evaporation steps, sampling artifacts, or derivatization artifacts).

In the original manuscript, we pointed out examples of specific compounds/classes that exhibited clear experimental bias and the likely method error responsible for each bias. On pages 6-7 (OM), we discussed the following specific cases:

a) Poor recovery of the most volatile compounds that "likely volatilized during the drying periods." (Page 6, line 10, OM)
b) Palmitic and stearic acid were over-recovered and "are likely an artifact of the extraction/derivatization procedure." (Page 6, line 26, OM)
c) Maltol was significantly under-recovered from the SPE filters and state "The reason for this large SPE bias for maltol is currently unknown." (Page 6, line 30, OM)
d) 5-Hydroxy methyl furfural reacted during extraction in both the PTFE and SPE tests. (Page 6, line 32, OM)
e) All hydrocarbons were poorly recovered compared to oxygenates and suggest that "it is possible that hydrocarbons were more strongly bound to the non-polar octadecane-based sorbent material than more polar compounds resulting in lower recovery." (Page 7, line 6, OM)
f) Octadecane was over-recovered in the SPE tests "likely due to degradation of the SPE sorbent material during extraction" (Page 7, line 9, OM)

We additionally offered further discussion of the recovery results in the supplement (Section S1, OM) and therefore believe we have fully explained the results related to the observed SPE biases. As the referee did not specify which other compounds require explicit discussion or which explanation(s) s/he found inadequate, we cannot provide further clarity.

9) Extracts for I/SVOC analysis should never be allowed to dry. Practically speaking, there are variations in the N2 flow rate and there are sample matrix differences that affect the rate of solvent evaporation. The two practical considerations contribute to variations in time the dried solute is exposed to the N2 thus varying the extent of analyte losses. This is a very important limitation that is poorly addressed.

In this case, it was necessary to completely dry the solvent to avoid reactions between methanol and the BSTFA derivatization agent. As the referee noted in comment #2, such reactions could limit the amount of BSTFA available to derivatize analytes. We agree that drying to completeness is not ideal for maximizing recovery of I/SVOCs and should be one variable considered in future method optimization, which would necessarily require testing different non-protic solvents or other derivatization agents. We have added that as an additional optimization parameter for future experiments on Page 8, Lines 30-31 (RM): "**For example, other non-protic solvents could be tested to enable derivatization without the need to completely dry the samples, which would help to minimize volatilization losses**."

To further address the volatilization losses, additional quality control tests are now discussed in the Supplement (pages S6-S8, RM). Although the goal of the tests was to assess the role of the amount of absorbing phase on the recovery of relatively volatile compounds, the results provide some insights into the effects of drying time and matrix effects. Because of the different volumes used for those tests (100-500 uL), the drying time varied considerably (although was not controlled). We did not observe variability outside the factor of 2 (100% RSD) that we assumed for the samples on page 7, line 20 (OM), as long as some absorbing phase was present, as would be the case in the biomass burning samples. We did observe evidence for potential matrix effects wherein a polar matrix reduced the recovery of an aliphatic hydrocarbon. However, we do not expect this to introduce major errors for this qualitative analysis. For example, we find much higher fractions of aliphatic compounds in peat smoke compared to sagebrush smoke (i.e., the example shown in Figure 4c). Based on complementary measurements from the same fires using sorbent tube collection followed by thermal desorption-GCxGC analysis, which are not subject to the same matrix effects (unpublished data, but similar protocol to that described in Hatch et al. 2015), we also find negligible aliphatic compounds in sagebrush compared to peat. We have added this discussion to the revised Supplement (Page S8, RM).

10) Were any internal standards used to monitor analyte losses?

No. This was noted several times throughout the manuscript in the context of future needs for quantitative analysis, specifically:

- Page 6, line 17 (OM): "Such bias could be corrected in future work through application of recovery standards."
-Page 7, lines 12-13 (OM): "Further method optimization (e.g., use of recovery, internal, and external standards) would be necessary for quantification."
-Page 12, lines 7-8 (OM): "Future use of recovery standards and further method optimization will help to correct for any sample-to-sample inconsistencies in the extraction efficiency and ultimately better constrain the partitioning estimates."
-Page 16, lines 12-13 (OM): "Future improvements in the extraction protocol, specifically the use of recovery, internal, and external standards, should enable quantification of compounds collected onto SPE filters."

11) Considering the method limitations, please justify how the analyte recovery from the SPE filters was determined to be satisfactory? For which analytes?

We have conducted a number of tests to characterize the recovery for a broad range of compounds from the SPE filters, as outlined in the main text (Section 3.1, OM) and Supplement (Section S1, OM). We found that several compounds exhibited very poor recovery regardless of filter type due to substantial volatilization losses, as discussed on page 6, lines 8-12 (OM) and possible activity effects, as now discussed on page 6, lines 12-14 (RM). We noted specifically which compounds were omitted from the analysis on page 6, lines 11-12 (OM) and page 7, line 10 (OM). For the other standard compounds, our tests indicated that the variability in recovery was within a factor of 2 (and significantly better for most compounds), which we noted on page 7, lines 20-24 (OM). We deemed this factor of 2 uncertainty as sufficient for the qualitative analysis sought here. We acknowledge that the absolute recovery is not consistent across all compounds and further characterization tests would be needed to adequately correct for that in order to achieve quantitative analysis. We stated as such on page 7, lines 13-15 (OM): "Characterization of the recoveries for more standards would also be necessary to adequately correct the recoveries for the wide range of compounds observed in untargeted analysis of biomass-burning smoke (including many unknown compounds), especially the most volatile observed compounds."

Please also see the responses to Referee #2's comments 3, 7, and 9 for additional discussion of the method limitations and the associated caveats we have noted in the text.

12) Again, the assessment of diversity in the I/SVOC is dependent on the assumption that the samples did not have losses associated with the sample preparation. What if some of the variation you see is due to solvent evaporation during storage or during the solvent exchange steps?

All samples were stored identically; we did not observe obvious solvent losses during storage. We noted volatilization losses in some samples during derivatization due to faulty vial caps and have attempted to correct for that artifact (Table S1, OM). We looked for and found no clear association between those losses and potential errors in the gas-particle partitioning estimates where such artifacts would have the greatest impact among the analyses presented in the manuscript. As we've noted above, we believe the variability in compound recovery is on the order of a factor of 2 or less. In the discussion of the results, we have specifically emphasized results that fall outside this factor of 2 uncertainty (e.g., in the discussions of Figure 3 and in Figures 4b,c).

13) Please define what is meant by composite chromatograms?

For additional clarity, we have revised the text to:
"Figure 2 shows a comparison of composite SPE and PTFE chromatograms **wherein peaks from all SPE and all PTFE samples are represented** (GasPedal, Decodon Gmbh, Greifswald, Germany) (Schmarr and Bernhardt, 2010)" (page 8, lines 5-6, RM). Readers are referred to the cited reference for additional information.

14) Please define the RI values ~ 1200-2100.

Retention index is a standard and commonly used chromatography parameter, and as such does not require further definition here. We have additionally provided the retention times for comparison to Figure 2 to put the noted RIs in context.

15) References on page 8 did not simply use PUF for SVOC collection. XAD has been frequently used and XAD is an SPE material.

We had noted as such on page 2, lines 30-31 (OM): "All of the off-line I/SVOC characterization studies cited above collected samples using a filter and polyurethane foam (PUF) plug (or PUF/*XAD-sorbent*/PUF sandwich". We agree that XAD should be noted on page 8 (OM), as well (page 9, line3, RM). The text now reads: "samples are largely consistent with the compounds reported from PUF/**XAD** measurements".

16) Figure 4 is quite complex. The effect of levoglucosan on the correlation is quite strong. Since levoglucosan is non-volatile, it could suggest that the more volatile components were more highly variable even between replicate burns. But, is this related to the sampling strategy, sample prep, or actual burn conditions? This makes me curious about other volatility bins and their correlations.

We investigate the referee's questions using the peat-sagebrush comparison shown in Figure 4c for visual reference and because sampling/analysis artifacts are more likely to lead to poorly correlated sample pairs than well correlated sample pairs. We have separated the data into two fractions-- compounds eluting before and after levoglucosan-- to investigate the correlations among different broad volatility classes. Of the 358 compounds present in only one of those fires, approximately 40% (by compound number and relative abundance) are attributed to compounds that elute after levoglucosan, indicating that there were significant differences in the compounds that are generally less volatile than levoglucosan. Additionally, although the correlation coefficient is very poor for both compound fractions, it is significantly lower among the less volatile compounds: 0.075 for compound eluting before levoglucosan and 1.7e-5 for compounds eluting after levoglucosan ($R^2 = 0.057$ including all data except levoglucosan). Thus the correlations are not driven solely by variability in the recoveries of volatile compounds. Furthermore, of the compounds that could be identified (positively or tentatively), the differences are consistent with previous studies. For example, the fact that peat smoke is uniquely rich in aliphatic compounds has been shown previously, as we stated on Page 10, lines 19-22 (OM): "Peat smoke was also poorly correlated with most other biomass-burning emission samples, largely due to a high abundance of aliphatic compounds, including *n*-alkanes and 1-alkenes, as has been observed previously (George et al., 2016; Hatch et al., 2015; Jayarathne et al., 2018)." In summary, we find no significant indication that the correlations in Figure 4 are dominated by sampling errors rather than real differences in the smoke samples.

17) What is the purpose/significance of figure 5?

The entirety of section 3.2.1 is devoted to discussion of the significance of the results shown in Figure 5. In particular, we illustrate the fuel dependence of the benzenediol isomer speciation (Figure 5a), which would not be observed by many of the instruments commonly used these days that are unable to resolve isomers (e.g., chemical ionization). We additionally used the benzenediols as an example to demonstrate the ability of the filters to capture phase separation and estimate saturation concentrations, C*. In Figure 5b, we show a comparison of the filter-based C* estimates with available thermodynamic data, as a means of testing the accuracy of the method, which was one of the objectives of the paper as outlined in the Introduction. Figure 5b further illustrates the significant differences in gas-particle partitioning between the two isomers, for which we have discussed the implications (i.e., potentially underestimating emission factors, differences in sample-line losses, and available reaction pathways) on page 13, lines 5-8, 29-32 (OM). As the referee did not specify what s/he found confusing or inadequate within the ~3 page discussion related to Figure 5, we cannot provide further clarity regarding the significance of that figure.

Measurements of I/SVOCs in biomass-burning smoke using solid-phase extraction disks and two-dimensional gas chromatography

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Abstract. Biomass-burning organic-aerosol (OA) emissions are known to exhibit semi-volatile behavior that impacts OA loading during plume transport. Because such semi-volatile behavior depends in part on OA composition, improved speciation of intermediate and semi-volatile organic compounds (I/SVOCs) emitted during fires is needed to assess the competing effects of primary OA volatilization and secondary OA production. In this study, 18 laboratory fires were sampled in which a range of fuel types were burned. Emitted I/SVOCs were collected onto Teflon filters and solid-phase extraction (SPE) disks to qualitatively characterize particulate and gaseous I/SVOCs, respectively. Derivatized filter extracts were analyzed using comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GC×GC-TOFMS). Quality control tests were performed using biomass-burning relevant standards and demonstrate the utility of SPE disks for untargeted analysis of air samples. The observed chromatographic profiles of I/SVOCs in coniferous fuel-derived smoke samples were well correlated with each other, but poorly correlated with other fuel types (e.g., herbaceous and chaparral fuels). Emissions of benzenediol isomers were also shown to be fuel dependent. The combined Teflon and SPE filter data captured differences in gas-particle partitioning of the benzenediol isomers, with hydroquinone having a significantly higher particle-phase fraction than catechol due to its lower volatility. Additionally, the speciated volatility distribution of I/SVOCs in smoke from a rotten-log fire was estimated to evaluate the composition of potentially volatilized primary OA, which was entirely attributed to oxygenated (or other heteroatomic) compounds. The isomer-dependent partitioning and the speciated volatility distributions both suggest the need for better understanding of the gas-phase and heterogenous reaction pathways of biomass-burning-derived I/SVOCs in order to represent the atmospheric chemistry of smoke in models.

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1 Introduction

Biomass burning emits high levels of carbonaceous material, including trace gases, black carbon, and primary organic aerosol (POA) (Akagi et al., 2011; Andreae and Merlet, 2001; Bond et al., 2004) that can significantly impact air quality (Kunzli et al., 2006; Liu et al., 2015; Naeher et al., 2007) and climate (Hobbs et al., 1997; Liu et al., 2014). The high concentrations of trace organic gases in smoke plumes suggest that their atmospheric processing could result in substantial production of secondary organic aerosol (SOA), as has been observed in a number of laboratory and field studies that investigated the photochemical aging of biomass-burning smoke (Cubison et al., 2011; DeCarlo et al., 2010; Grieshop et al., 2009a; Hennigan et al., 2011; Ortega et al., 2013; Tkacik et al., 2017; Yokelson et al., 2009). However, other studies have demonstrated negligible or even net loss of OA downwind of fires due to evaporative losses of POA (Akagi et al., 2012; Capes et al., 2008; Jolleys et al., 2012; May et al., 2015). Such observations are further supported by modelling studies, which have shown that significant SOA formation in biomass-burning plumes can be balanced by considerable losses of OA due to volatilization (Bian et al., 2017). In addition to affecting total OA mass, evaporation can impact oxidation rates and atmospheric lifetimes of traditional POA markers (e.g., levoglucosan in biomass burning smoke) (May et al., 2012). Therefore, better understanding the relative contributions of dilution-induced volatilization and SOA production requires speciation of the intermediate and semi-volatile organic compounds (I/SVOCs) in fresh biomass-burning smoke and estimation of their propensity to partition between gas and particle phases. Such measurements can further help to assess the available oxidation pathways of SOA precursors (i.e., gas-phase vs. heterogeneous oxidation).

Of the thousands of biomass burning-related emissions studies available in the literature, relatively few have targeted speciation of I/SVOCs in both gas and particle phases. Those few studies generally characterized emissions from either a narrow range of compound classes or fuel types. McDonald et al. (2000) reported the emissions from residential wood combustion for selected I/SVOCs, including polycyclic aromatic hydrocarbons (PAHs) and 8 methoxyphenols. Schauer et al. (2001) and Hays et al. (2002) have reported the most comprehensive speciation of gas- and particle-phase I/SVOCs to date, including hydrocarbons (alkanes, PAHs), alkanoic acids, substituted phenols, and anhydrosugars, among other more and less volatile compounds in the emissions of three types of residential wood combustion (Schauer et al., 2001) and burning of six foliar fuels (Hays et al., 2002). Mazzoleni et al. (2007) investigated I/SVOC emissions of methoxyphenols, levoglucosan, and organic acids across a range of fuel types and burning conditions, including laboratory, fireplace, and prescribed fires. Other studies have investigated I/SVOC emissions from selected fuel types, including wheat and Kentucky blue grass (Dhammapala et al., 2007). Gaston et al. (2016) conducted online measurements of ambient gas- and particle-phase emissions from residential wood combustion in real time, however without isomer speciation capability.

All of the off-line I/SVOC characterization studies cited above collected samples using a filter and polyurethane foam (PUF) plug (or PUF/XAD-sorbent/PUF sandwich) to trap particle- and gas-phase I/SVOCs, respectively. Due to the drawbacks of PUF/XAD sampling and analysis, including high solvent needs and relatively large physical size that exacerbates shipping costs and storage demands (Galarneau et al., 2006), alternative approaches, such as sorbent-impregnated filters (SIFs), have been investigated. Galarneau et al. (2006) custom coated glass-fiber filters with XAD resin and found that the collection and recovery of compounds from ambient samples compared well to PUF measurements. Similarly Paolini et al. (2016) functionalized glass-fiber filters with phenyl moieties for targeted collection of gaseous PAHs and found recoveries of PAHs comparable to PUF plugs. As with lab-coated SIFs, commercial solid-phase extraction disks (hereafter called SPE filters) consist of a sorbent material incorporated into filters; in one such SPE filter, Empore by 3M, the sorbent is integrated into polytetrafluorethylene (PTFE) fibrils and accounts for >90% of the filter mass (Erger and Schmidt, 2014). Although SPE filters have been designed and primarily utilized for extraction of organic compounds from aqueous samples (e.g., (Erger and Schmidt, 2014) and references therein), a few studies have demonstrated their efficacy for air sampling (Sanchez et al., 2003; Stuff et al., 1999; Tollback et al., 2006). In each of these studies, researchers simultaneously collected both gas and particle phases onto the SPE filter for targeted analysis of a specific class of compounds, including organophosphate esters (Tollback et al., 2006), nitroaromatic compounds (Sanchez et al., 2003), and chemical warfare agents (Stuff et al., 1999).

In this work, samples of biomass-burning smoke were collected onto tandem Teflon and SPE filters during the 2016 FIREX (Fire Influence on Regional and Global Environments Experiment) campaign at the US Forest Service Fire Sciences Laboratory (FSL). Two-dimensional gas chromatography (GC×GC-TOFMS) was used to analyze the I/SVOCs emitted during biomass burning and collected onto the filters. Leveraging the enhanced speciation capability of GC×GC-TOFMS, the goals of this work were threefold: (1) demonstrate the potential of SPE filters for the untargeted analysis of compounds with a wide range of volatilities; (2) qualitatively investigate the diversity of I/SVOCs emitted from biomass burning across a range of fuel types; and (3) assess the accuracy of phase-separated SPE measurements to predict gas-particle partitioning of specific compounds emitted from fires.

2. Materials and Methods

2.1 Laboratory Fires and Sample Collection

Selimovic et al. (2018) provided details of the FIREX laboratory experiment, including the fuels burned. The fire samples analyzed in this work are listed in Table 1. Composite fires were constructed to recreate the relevant ecosystem, including fuel components such as duff, litter, wood debris (e.g., twigs), and canopy; these fires are listed as the ecosystem without further designation (e.g., Engelmann spruce). Individual fuel components were also burned separately, as noted in Table 1 (e.g., Engelmann spruce duff). Also included in Table 1 are the reported modified combustion efficiencies (MCEs) (Selimovic et al., 2018), defined as fire-integrated $\Delta CO_2/(\Delta CO_2 + \Delta CO)$, where Δ indicates background-corrected mixing ratios (Yokelson et al., 1996). MCE provides a measure of the relative contributions of flaming and smoldering combustion, with values approaching 1 indicative of predominantly flaming combustion, values ~0.8 predominantly smoldering, and 0.9 an even mix of both flaming and smoldering (Akagi et al., 2011).

The FSL has been described in detail by Christian et al. (2004). Briefly, fires were burned beneath a 1.6 m diameter stack with an inverted funnel located above the fuel bed. The combustion chamber is pressurized and vented through the top of

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the stack to completely entrain the smoke and carry it to the measurement platform 17 m above the floor. Previous measurements have shown the smoke to be well mixed at platform height (Christian et al., 2004). To collect filter samples, a passivated (Inertium®, AMCX, PA) stainless steel tube (1.27 cm o.d., 20.3 cm long) was passed through the stack wall and into the well-mixed smoke. At the outlet of the tube, one PTFE and one SPE filter were placed in series within a single 47 mm Teflon filter holder such that the PTFE filter was contacted first by the sample stream. The SPE filters (47 mm Empore C18 bonded silica, 3M) were pre-cleaned prior to the campaign in a Büchner funnel with 2 × 5 mL washes of acetone followed by methanol (Tollback et al., 2006). The PTFE filters (47 mm, 1.2 µm pore size, Cole-Parmer) were used without pretreatment. Smoke was pulled through the filters at 10 LPM for the duration of each fire (7-41 min). Samples were collected from 18 fires that burned a range of fuel types (Table 1). Three background samples were also collected from the stack over 30-40 min, in addition to two blanks for each filter type. Samples were stored in foil packets in a freezer until extraction approximately 3 months following collection.

2.2 Sample Extraction and Analysis

SPE and PTFE filters were identically extracted at the Environmental and Molecular Sciences Laboratory of Pacific Northwest National Laboratory. The filters were inserted into glass vials and extracted in 7 mL of methanol (HPLC grade) under sonication for 1 h. The extracts were transferred to new vials then dried under ultra-pure nitrogen. The dried extracts were reconstituted in 1.2 mL of methanol, followed by centrifugation at 6500 rcf for 5 min to separate the SPE-filter residue; 0.7 mL of each extract was allocated for GC×GC-TOFMS analysis. These aliquots were stored at -80 °C for approximately one month followed by storage at -18 °C for up to 1.5 weeks until derivatization and analysis was completed at University of California-Riverside. For derivatization, each aliquot was dried completely under nitrogen to avoid reaction between the solvent and derivatizing agent. Trimethylsilylation derivatization was achieved by adding 100 µL of BSTFA (N,O-Bis(trimethylsilyl) trifluoroacetamide) and 50 µL of anhydrous pyridine to each residue followed by heating at 70 °C under mixing at 1200 rpm for 1 h. During incubation, faulty vial caps caused volatilization losses (~10-33%) for a few samples; affected samples are listed in Table S1. It is assumed that only derivatization agent evaporated resulting in more concentrated samples. The data for impacted samples were scaled according to the estimated volume loss (Table S1). All samples were analyzed within ~40 hours of derivatization.

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Derivatized extracts were analyzed on a Pegasus 4D GC×GC-TOFMS (Leco Corp., St. Joseph, MI) equipped with an autosampler (Agilent 7683). 1 µL of each extract was injected in splitless mode at 250 °C. GC×GC separations were performed with reversed polarity, i.e., using a mid-polarity primary column (Rxi-17SilMS, 30 m, 0.25 mm i.d., 0.25 mm film thickness, Restek, Bellefonte, PA) and a non-polar secondary column (Rxi-1MS, 1.1 m, 0.15 mm i.d., 0.15 mm film thickness, Restek, Bellefonte, PA). The primary oven was held at an initial temperature of 50 °C for 0.2 min, followed by a 3 °C/min ramp to 305 °C, with a final hold of 1 min. The secondary oven (modulator) was held at +5 °C (+25 °C) relative to the primary oven. The modulation period was 5 s. The transfer line was maintained at 250 °C. The ion source temperature was 225 °C; the mass spectrometer acquired at 200 Hz. A 450 s solvent delay was used.

2.3 Data Analysis

GC×GC-TOFMS raw files were processed using Chromatof (Leco Corp., St. Joseph, MI). Background correction was performed separately on the PTFE and SPE filters. Within each filter group, the maximum peak area of each peak observed across the full set of corresponding blank and background samples was multiplied by 2 to ensure that all artifact peaks arising from the extraction and derivatization procedures would be entirely removed. Those adjusted values were subsequently used to background correct all associated peaks in the corresponding fire samples; only 16 (PTFE) and 32 (SPE) peaks in the fire samples required background correction. Data were retained for analyte peaks with $S/N > 200$ and background-corrected peak area >100,000 A.U. To further avoid potentially spurious or insignificant peaks, any remaining compounds present in only one sample (PTFE or SPE) were omitted from further analysis unless its peak area accounted for >0.1 % of the total peak area for that sample (out of ~1100 singly observed peaks, ~120 were retained). Peaks corresponding to standard compounds (see Section 2.4) were considered positively identified. For other peaks, a compound name was assigned and considered tentatively identified if the match similarity with the NIST library hit was >800 in any sample that contained that peak and the identified structure was consistent with the derivatization approach used here (i.e., contained trimethylsilyl groups where applicable). Worton et al. (2017) have recently demonstrated that the probability of an incorrect NIST library match is ~30% for matches between 800-900 and 14% for matches >900.

2.4 Extraction Efficiency Tests

Potential biases in the SPE extractions, which would affect comparisons of measured compounds between the PTFE and SPE filters, were tested using a range of standard compounds relevant to biomass-burning emissions, including phenol derivatives, levoglucosan, *n*-alkanes, *n*-alkanoic acids, and PAHs. Three tests were performed using equivalent volumes of the standard mixture: (1) a control where the standard was derivatized without going through the extraction procedure (hereafter called "standard"); (2) standard was spiked into 7 mL of methanol (HPLC grade) as a proxy for the PTFE extractions (hereafter called "PTFE test"); and (3) the standard was spiked onto SPE filters, briefly allowed to dry, then extracted in 7 mL of methanol (hereafter called "SPE test"). Regarding the PTFE test, standards were not spiked directly onto a PTFE filter due to the potential for rapid evaporation of the relatively volatile standard constituents (Dhammapala et al., 2007); this approach assumes no recovery biases are introduced by the PTFE filter. The PTFE and SPE tests were performed in triplicate; the standard test was performed in duplicate. For the PTFE and SPE tests, the extraction and derivatization procedures were similar to that described above for the FSL samples with the main differences being that the extracts were filtered using PTFE-coated syringe filters (Titan3, Thermo-Scientific) rather than centrifugation, and MSTFA (*N*-Methyl-*N*-(trimethylsilyl)trifluoroacetamide with 1% trimethylchlorosilane) was used as the derivatizing agent rather than BSTFA. Standards derivatized with MSTFA showed no significant differences from those derivatized with BSTFA. GC×GC-TOFMS analysis was performed as described above. Additional standards (similar to those used in Hatch et al. (2015)) were derivatized and analyzed for identification purposes only.

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3 Results and Discussion

3.1 Extraction Efficiency

Because SPE filters have not reportedly been used for untargeted analysis of air samples, the extraction efficiency was assessed for a range of standard compounds with regard to both absolute recovery and potential biases compared to extraction from PTFE filters. The recoveries of standard compounds from SPE and PTFE filters are shown in Figure 1a for compounds relevant to the SPE fire samples described below, namely standards eluting at or before 3000 s (see Figure 2 for comparison); data for all individual standard compounds tested are shown and discussed in the Supplementary Information (SI, Figs. S1-S5). Most compounds displayed high recovery (~0.8-1.1) in the PTFE test (Figures S1-S5). Exceptions were observed for the most volatile standard compounds within each compound class (Figs. S1-S5). The compounds with the poorest observed recovery (<0.2) included naphthalene, undecane, dodecane, and tridecane and showed no obvious bias between the SPE and PTFE tests (Figures 1a, S2, and S2) indicating that these compounds are too volatile to survive the extraction procedure regardless of filter type and likely volatilized during the drying periods. Matrix effects likely also contributed to the very poor recovery of these volatile non-polar hydrocarbons, due to the high concentration of highly polar, oxygenated compounds present in the standard matrix (further discussed in the SI). Thus, these four compounds were omitted from further analysis. However, there is no clear relationship between the poor recovery of these four compounds and oxygenated compounds that elute in the same primary retention time window. For example, heptanoic acid displayed significantly better recovery in the PTFE test (0.86±0.06, Figure S4) than tridecane (0.14±0.07, Figure S1) despite eluting significantly earlier (1045 s vs. 1190 s). As a result, the poor recovery of the volatile alkanes/naphthalene was not extrapolated to other relatively polar oxygenated compounds present at similar retention times in the fire samples.

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Linearity with a correlation coefficient (R^2) of 0.72 was observed between the SPE tests and PTFE tests (Figure 1a); however there is clearly a negative bias in the extraction from SPE filters compared to the PTFE tests, with a slope of ~0.75. This is partly due to retention of ~0.5 mL (~7% of the total volume) of the extraction solvent by the SPE filters; thus 100% recovery from SPE filters cannot be achieved. Such bias could be corrected in future work through application of recovery standards. The general under-recovery of analytes from the SPE filter is likely also due in part to incomplete solvation of analytes from the sorbent material.

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The biases between the SPE and PTFE tests are further shown as a function of compound class in Figure 1b. Included in the box plot are all data that were used to determine scaling factors to facilitate comparison of the SPE and PTFE extracts, namely compounds eluting before 3000 s and with PTFE-derived extraction efficiency >0.15. For all compound classes, the recovery from SPE filters was lower than in the PTFE tests, however differences were observed between hydrocarbons and oxygenated compounds. The median recovery for oxygenated compounds was ~75 % that of the PTFE tests and was fairly consistent across different oxygenated classifications (0.74 for phenols, 0.75 for alkanoic acids, and 0.79 for miscellaneous oxygenates, Fig. 1b). Two outliers, palmitic acid and stearic acid, with recoveries >1 were observed for the alkanoic acid class (Figs. 1a, S4). These two compounds were observed in all biomass-burning sample blanks/backgrounds and are likely

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an artifact of the extraction/derivatization procedure. The largest SPE bias among all compounds tested was observed for maltol, for which the recovery in the PTFE test was 0.75 ± 0.04, but only 0.15 ± 0.01 in the SPE test (Figure S5). A repeat test was performed with a fresh maltol solution and resulted in similarly low recovery from SPE filters. The reason for this large SPE bias for maltol is currently unknown.

5-Hydroxy methyl furfural (HMF) displayed poor recovery in both tests (0.03 ± 0.007 and 0.09 ± 0.1 for the PTFE and SPE tests, respectively, Figure S5) and can be attributed to reaction of HMF during extraction, as the same reaction product (based on comparison of the mass spectra) was observed in the composite standard and a repeat test using a fresh HMF standard solution. HMF was the only standard compound to form an obvious reaction product during extraction; reactions of other aldehydes (e.g., vanillin) during extraction were negligible (see SI). The methyl ester of HMF was also present in the composite standard solution due to reaction with methanol solvent during storage of the standard and showed significantly improved recovery compared to the aldehyde (0.80 ± 0.08 and 0.56 ± 0.05 in the PTFE and SPE tests, respectively, Figure S5). Because other artifacts resulting from methanol extraction have been previously observed (Sauret-Szezepanki and Lane, 2004), further characterization of methanol-extraction-related artifacts and/or further optimization of the extraction solvent may be needed for studies seeking to accurately identify/quantify certain compounds. However, given the consistency of the observed HMF reactions, potential solvent-analyte interactions likely did not substantially impact the observed differences in the chromatographic profiles of the biomass burning samples discussed below.

Alkanes and PAHs were under-recovered by ~50% in the SPE test compared to the PTFE test (Fig. 1b). It is possible that hydrocarbons were more strongly bound to the non-polar octadecane-based sorbent material than more polar compounds resulting in lower recovery. Other solvents (e.g., hexane) and/or solvent mixtures could be tested in future work to improve the recovery of hydrocarbons from SPE filters. Octadecane displayed a large positive bias in the SPE tests (SPE / PTFE = 2.0 ± 0.6, Figure S1), likely due to degradation of the SPE sorbent material during extraction. Octadecane data have been omitted from Figure 1, as well as all FIREX SPE-filter data discussed below.

These results demonstrate that the recovery of compounds from SPE filters is satisfactory for qualitative assessment of the compounds measured in the biomass-burning samples. Further method optimization (e.g., use of recovery, internal, and external standards) would be necessary for quantification. Characterization of the recoveries and matrix effects for more standards would also be necessary to adequately correct the recoveries for the wide range of compounds observed in untargeted analysis of biomass-burning smoke (including many unknown compounds), especially the most volatile observed compounds. As the interest at this stage is in assessing the full diversity of I/SVOCs in smoke and demonstrating the range of compounds collected by SPE filters, all observed compounds (except those explicitly noted above) were retained without correction for recovery. However, corrections have been made for the observed biases between the SPE and PTFE filters. Based on Figure 1b, the peak areas for all known hydrocarbons detected in the FIREX SPE samples (alkanes, alkenes, and PAHs) were scaled 2× and the remaining compounds (largely oxygenates) were scaled 1.33×. Further, the relative standard deviation (RSD) for each compound was conservatively estimated to be approximately 100 % based on the maximum determined RSDs in the recovery tests (80 % and 64 % for the PTFE and SPE tests, respectively, not including the five

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omitted compounds mentioned above). This approach should account for much of the variability in analyte recovery during extraction and derivatization (see SI); however, it should be noted that on average the RSDs for most standard compounds were much lower than the maximum, with median RSDs of 8 % and 12% for the PTFE and SPE tests, respectively.

3.2 Biomass-Burning Samples

Figure 2 shows a comparison of composite SPE and PTFE chromatograms wherein peaks from all SPE and all PTFE samples are represented (GasPedal, Decodon Gmbh, Greifswald, Germany) (Schmarr and Bernhardt, 2010); chromatograms from individual fires are also included in the SI (Figs. S7-S24). The compounds observed on the SPE filters (shown in orange) are generally earlier eluting than the compounds observed on the PTFE filters (shown in blue). The vast majority (~97%) of compounds observed in the SPE filters correspond to first dimension Kovats retention indices (RI) in the range of ~1200-2100 (although even earlier eluting compounds were observed in the SPE samples, we restrict the analysis to only compounds eluting after 930 s, equivalent to an RI of 1200, Figure 2). The mean primary retention time of analytes on the SPE filters is ~1800 s (RI 1550) compared to ~2600 s (RI 1915) for the compounds eluting in the PTFE filter extracts. Although retention time is not a perfect indicator of volatility differences here, due to derivatization as well as variable activity of diverse analytes in the column stationary phase, these observations suggest that the compounds detected on the SPE filters were on average more volatile than those collected on the PTFE filters, which is consistent with particles being first trapped on the PTFE filter followed by gases (or desorbed POA) being collected on the SPE filters. As indicated by the Venn diagram inset of Figure 2, the majority of the compounds were found on only one filter type— across all samples, 543 and 581 compounds were detected solely on the SPE and PTFE filters, respectively. Because all standard compounds tested on the SPE filters could be observed to some degree (Figures S1-S5), it is unlikely that SPE-related extraction bias was the cause of the different compounds observed solely on one filter type. Compounds present in both phases were detected (shown in black, Figure 2); 364 compounds were found on at least one SPE and one PTFE filter sample. The numbers of compounds observed on each filter type for the individual fires are listed in Table 1.

The earliest eluting, positively identified compounds in the SPE-filter data correspond to benzonitrile, and *o*-, *m*-, and *p*-cresol. Potential breakthrough of such volatile compounds through the SPE filter was probed by collecting smoke samples from a campfire-style burn in Riverside, CA onto a PTFE-SPE-SPE sampling train. Any compounds present on the backup SPE filter were below detection limit despite very high concentrations observed on the front SPE filter, consistent with the negligible breakthrough observed in previous studies using sorbent-impregnated filters (Galarneau et al., 2006) and SPE filters (Tollback et al., 2006). These observations demonstrate the ability of SPE filters to trap relatively volatile compounds, although more work is needed to optimize the recovery and quantification of such compounds. For example, other non-protic solvents could be tested to enable derivatization without the need to completely dry the samples, which would help to minimize volatilization losses. Other positively and tentatively identified compounds observed from the FIREX SPE samples are largely consistent with compounds reported from PUF/XAD measurements (Hays et al., 2002; Mazzoleni et al., 2007; Schauer et al., 2001), including phenol derivatives (e.g., dimethyl phenols, guaiacols, benzenediols,

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vanillin, isoeugenol, acetovanillone), mono-carboxylic acids, dicarboxylic acids (e.g., methyl maleic acid), *n*-alkanes, and PAHs (e.g., fluorene, phenanthrene). With high trapping efficiency and similar observable compound classes, SPE filters appear to be a suitable alternative to PUF/XAD measurements for untargeted analysis of I/SVOCs in air samples. Because many of the identifiable compounds in the FIREX samples have been reported and quantified in previous studies (Hays et al., 2002; Mazzoleni et al., 2007; Schauer et al., 2001), the focus here is on investigating the diversity of emissions rather than providing detailed speciation profiles.

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Hereafter, the relative abundance (or % abundance) of a given compound is defined as the ratio of the peak area for compound *i* to the total observed peak area (using deconvoluted total ion current, DTIC) summed over all compounds present in either the corresponding SPE sample only or the combined SPE+PTFE samples (each case is explicitly noted where applicable). The peak area fractions are used as an indication rather than an absolute measure of the % abundance because the individual compounds have not been corrected for recovery or differences in instrument response. This approach is reasonable for the qualitative assessment sought here because many of the most volatile compounds were still observed with high relative abundance. For example, cresols likely exhibited poorer recovery (<0.3) than guaiacol (Figure S3) due to their higher volatilities, yet were still among the most abundant of the observed compounds. However, the relative abundance for volatile compounds should be considered a lower limit.

Figure 3 illustrates the number of SPE samples in which each compound was observed along with its median % abundance across the relevant set of samples (i.e., 0 % abundance values were ignored); for 2 or fewer samples, the maximum observed % abundance was used. Of the 907 total compounds observed across all 18 SPE samples, approximately half (452) were detected in 3 or fewer samples, demonstrating the abundance of unique compounds. In contrast, only 31 compounds were observed in all 18 samples; these ubiquitous compounds were also generally the most abundant. The red trace in Figure 3 denotes the median of the median % abundance values within each bin and demonstrates a general trend of increasing average relative abundance with increasing detection frequency. On average, the most ubiquitous compounds (*N*=18) account for ~10× greater % abundance than compounds observed in 13 or fewer samples. These highly abundant (median relative abundance >1 %), ubiquitous compounds include phenol derivatives (*o*-, *m*-, and *p*- cresols, guaiacol, methyl guaiacol, hydroquinone, 3- and 4-methyl catechol), methyl maleic acid, and several unknowns. Only catechol accounted for >1 % of the total SPE peak area in all 18 samples, ranging from 4.9 % (dung) to 15 % (ponderosa pine, burn 37) and was therefore the most universally abundant I/SVOC detected in the gas phase. Several highly abundant compounds were also present in 1-7 samples (Figure 3). For example, camphor was only detected in sagebrush smoke, at 4.3% of the total SPE peak area; a unique camphor signature was also observed during FIREX by (Sekimoto et al., 2018). Two other highly abundant compounds were present in only one sample; these are unknown compounds (but likely alcohols or organic acids based on mass spectral fragmentation patterns discussed below) and accounted for 1.1 and 2.3% abundance in sagebrush and peat smoke, respectively.

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Large variability is evident in the % abundances of a given compound across the SPE samples, as indicated by the marker sizes in Figure 3, which represent the ratio of the maximum observed value to the minimum observed non-zero value (ratios greater than ~2 are unlikely to be due entirely to experimental artifacts). Ratios as high as 150 were observed (values in Figure 3 have been capped at 50 for visual clarity), demonstrating the potential for high variability in the fraction of smoke accounted for by individual I/SVOCs. For example, there is wide variability in the relative abundances for many of the most ubiquitous compounds, with 35% displaying max/min ratios >25 and a median ratio of 15. Although there is an apparent trend of increasing median variability (red marker sizes in Figure 3) with increasing detection frequency, this is likely due in part to the higher relative abundance of more ubiquitous compounds. The variability of less frequently observed and generally less concentrated compounds was potentially truncated by the method detection limit and peak selection criteria (Section 2.3). This hypothesis is somewhat supported by the observation that the variability tends to be higher for the more abundant compounds within bins 2-7.

To explore the overall diversity of the speciated emissions among the smoke samples, correlation coefficients were calculated based on the combined (SPE+PTFE) % abundances of all individual observed compounds between pairs of fires (Figure 4a, R^2_{All}, lower half). For illustration, example correlation plots for highly and poorly correlated fire pairs are included in Figure 4b and c, respectively. Because levoglucosan was by far the most abundant compound in all burns except manzanita, accounting for between 7.6-43% of the total abundances (e.g., Figure 4b, c), this single compound had a large effect on the regression parameters. Therefore, the correlation coefficients calculated with the levoglucosan data omitted (R^2_{NoLevo}) are shown in the upper half of Figure 4a. This allows a better comparison of the less abundant compound signatures. For nearly all sample pairs, the R^2 values dropped significantly after removing levoglucosan (Figure 4a), with mean R^2_{All} of 0.67 compared to mean R^2_{NoLevo} of 0.33.

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The highest correlations were observed among the coniferous fuels (bounded by the white box in Figure 4a). Among conifers, the mean R^2_{All} is 0.91 and mean R^2_{NoLevo} is 0.62, both of which are significantly higher than the overall mean values reported above. Selimovic et al. (2018) also observed similarities among the VOC emissions from coniferous fuels. The conifer emissions were well correlated with conifer-derived decayed plant matter (rotten log and duffs) with mean R^2_{All} of 0.77 and mean R^2_{NoLevo} of 0.47. When levoglucosan was included in the regressions, excelsior (aspen wood shavings) smoke is well correlated with the coniferous fuels (R^2_{All} = 0.76-0.97). This is likely because excelsior smoke was dominated by levoglucosan (43 % of the total abundance), and emissions from coniferous fuels also contained higher average levoglucosan (mean f_{Levo} = 27 %) than other fuels (mean f_{Levo} = 14 %, not including excelsior). Jen et al. (2018a) similarly observed higher average levoglucosan emission factors among coniferous fuels from filter samples collected during FIREX. However, with levoglucosan removed from the regression, excelsior smoke is poorly correlated with conifer-derived smoke (R^2_{NoLevo} = 0.17-0.25), likely due in part to the much simpler overall composition of excelsior smoke compared to other samples (Table 1).

In general, emissions from the miscellaneous fuel types that were sampled in this work (peat – manzanita in Figure 4a) are poorly to moderately correlated with each other (mean R^2_{All} = 0.46, mean R^2_{NoLevo} = 0.22) and the coniferous fuel types (mean R^2_{All} = 0.53, mean R^2_{NoLevo} = 0.16). Of these, manzanita smoke was the least correlated with all other smoke samples

(R^2_{All}<0.32 and R^2_{NoLevo} <0.19); the unique signature of manzanita smoke is further discussed in Section 3.2.1. Peat smoke was also poorly correlated with most other biomass-burning emission samples, largely due to a high abundance of aliphatic compounds, including *n*-alkanes and 1-alkenes, as has been observed previously (George et al., 2016; Hatch et al., 2015; Jayarathne et al., 2018). The poor correlations are not driven solely by very low-abundance compounds. For example, in the peat-sagebrush comparison (Figure 4c), 15 and 187 compounds with >1% and >0.1% abundance, respectively, were present in only one of the smoke samples (i.e., well outside the factor of 2 uncertainty).

Although sufficient data are not available to differentiate the separate effects of fuel type and combustion efficiency on smoke composition, Figure 4a suggests that the diversity of I/SVOCs and their chromatographic profiles cannot be fully explained by combustion efficiency. For example, rice-straw smoke was much more strongly correlated to bear-grass smoke (R^2_{NoLevo} = 0.72), the only other herbaceous fuel sampled, despite significantly different MCEs (0.952 vs. 0.897, Table 1) than to the emissions of the two fires with the most similar MCEs (lodgepole pine, MCE=0.951, R^2_{NoLevo} = 0.12 and ponderosa pine litter, MCE=0.954, R^2_{NoLevo} = 0.15, Figure 4a).

3.2.1 Benzenediol Isomers

Benzenediols (catechol, hydroquinone, and resorcinol) are ubiquitous in smoke, as described above, and thus are used as a case study to probe the variability of isomers from different fuel types. All three isomers were positively identified, demonstrated consistent recovery (Figure S3), and are expected to exhibit similar instrument responses; therefore uncorrected experimental artifacts are not expected to significantly influence the comparison of these three compounds. Figure 5a shows the fraction of the total peak area (SPE+PTFE) from each burn attributed to the three benzenediol isomers. For nearly all samples, catechol was the dominant isomer and composed a relatively consistent fraction of the measured smoke, at 2.9-7.2% of the total peak area measured for each fire. In contrast, resorcinol constituted a negligible fraction of the total emissions in all samples. Hydroquinone emissions were much more variable than catechol (0.29 % - 33 % of the total measured emissions). Hydroquinone was overwhelmingly dominant in manzanita smoke, accounting for 33 % of the total measured peak area and with relative abundance ~10× that of catechol. Sagebrush smoke also showed relatively high emissions of hydroquinone, comparable to that of catechol. These similar hydroquinone signatures are likely one reason that manzanita smoke was best correlated with sagebrush smoke (Figure 4a). The data in Fig. 5a are arranged by increasing MCE and demonstrate that the variable isomer speciation was not likely due to effects of combustion efficiency, but rather arise from the fuel composition. For example, the hydroquinone signature from manzanita fires can be attributed to its high concentration of arbutin, which contains a hydroquinone group that breaks off during pyrolysis (Jen et al., 2018b). These results demonstrate that important fuel-dependent emissions signatures could be missed when emissions measurements are performed solely with non-isomer specific measurements.

The chromatographic data further indicate a significant difference in volatility among the benzenediol isomers. For compounds with similar functionality—i.e., similar activity coefficients in the column stationary phase—the retention factor is inversely correlated with vapor pressure (Dettmer-Wilde and Engewald, 2014). Hydroquinone and resorcinol both elute

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just after 4-methyl catechol in the first GC×GC dimension, which is significantly later than catechol, thereby suggesting significant differences in the volatilities of the benzenediol isomers. Because gas and particle phases were trapped separately on the SPE and PTFE filters, the gas-particle partitioning for each isomer can be investigated. The median gas-phase fractions of catechol and hydroquinone were 0.96 and 0.57, respectively (Figure 5a), consistent with lower hydroquinone volatility. Schauer et al. (2001) similarly observed isomer-dependent benzenediol partitioning in smoke from residential wood combustion.

The measured partitioning was used to estimate the saturation concentration (C_i^*) of catechol and hydroquinone from each fire, based on Pankow (1994) and following Donahue et al. (2006) (Equation 1):

$$f_\mathrm{p} = \frac{1}{1+\left(\frac{C_i^*}{C_{OA}}\right)} \,. \qquad (1)$$

The particle-phase fraction (f_p) of compound *i* was based on the measured peak area from the PTFE filter relative to the total (PTFE + SPE) peak area; OA concentrations (C_OA) were estimated using $\mathrm{PM}_{2.5}$ data for each fire that was scaled by the corresponding OC fraction based on OC/EC measurements (Jen et al., 2018a). The gas-phase fractions for individual fires as a function of C_OA are shown in Figure 5b. For both catechol and hydroquinone, the gas-phase fractions for fires 50 and 56 were anomalously low, likely due to an unidentified error or artifact in the filter measurements. It is possible that the recovered extraction volumes were lower from the corresponding SPE samples, however this was not tracked for each sample. Future use of recovery standards and further method optimization will help to correct for any sample-to-sample inconsistencies in the extraction efficiency and ultimately better constrain the partitioning estimates. Fires 50 and 56 were therefore omitted from the mean and standard deviation values of each compound to provide a best estimate of C_i^* (although fire 66 also appears to be an outlier for catechol, it is not a clear outlier for hydroquinone and so the data have been retained). Using data from the remaining fires (except burn 2 for hydroquinone because it was not detected in both phases), the calculated mean C_Cat^* is $(6.2 \pm 4.9)\times10^4$ µg m^{-3}, compared to C_HQ^* of $(3.6 \pm 1.7)\times10^3$ µg m^{-3} (including the outliers from burns 50 and 56 yields C_i^* values of $(5.6 \pm 4.9)\times10^4$ µg m^{-3} and $(3.3 \pm 1.8)\times10^3$ µg m^{-3} for catechol and hydroquinone, respectively). The parameterized phase distributions as a function of C_OA for hydroquinone and catechol using the mean C_i^* values ± one standard deviation are included in Figure 5b.

To evaluate the accuracy of the filter-based estimates, the mean C_i^* values were compared to those calculated using Antoine vapour-pressure coefficients (Burgess, 2018). The available Antoine coefficients are valid at elevated temperatures only (159-326 °C for hydroquinone and 118-245 °C for catechol), thus vapor pressures were estimated at the minimum valid temperature and extrapolated down to the average ambient FSL temperature (20.8 °C) using the Clausius-Clapeyron equation and reported ΔH_vap values. Literature values of ΔH_vap varied widely for both isomers. To represent this variability, feasible bounds of C_i^* were determined using two ΔH_vap values for each compound, one reported by NIST (70.5 and 62.2 kJ mol^{-1} for hydroquinone and catechol, respectively (Burgess, 2018)) and the other by Verevkin and Kozlova (2008) (84.4 and

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70 kJ mol^{-1} for hydroquinone and catechol, respectively). The resulting C_i^* values are summarized in Table 2 and the parameterized gas-particle partitioning for both literature assessments is shown in Figure 5b.

Although there is significant scatter in the filter-based C_i^* estimates, the mean values for both compounds fall within the two literature-based C_i^* estimates suggesting that on average the measured phase partitioning captured the differences in volatility between the two isomers and with reasonable accuracy. Further, considering that the estimated C_i^* values are more likely to be underestimated rather than overestimated due to adsorption of I/SVOCs to the PTFE filter (Mader and Pankow, 2001), the filter-based C_i^* estimates are more consistent with the Antoine + NIST ΔH_{vap} thermodynamic data. The Antoine + NIST C_i^* estimate displayed a consistent offset from the filter-based method for both compounds (i.e., Antoine C_i^*/filter-based C_i^* = 1.7 and 1.6 for catechol and hydroquinone, respectively) and a similar ratio between the isomers (C^*_{Cat}/ C^*_{HQ} = ~18 for both the measured and Antoine-based values); for comparison, $C^*_{\mathrm{Cat}}/C^*_{\mathrm{HQ}}$ = 51 using the Verevkin and Kozlova (2008) ΔH_{vap} data, which is likely too large of a volatility difference between the two isomers based on a comparison with hexane- and cyclohexane- diols (Capouet and Muller, 2006).

Based on their C_i^* values, benzenediols are classified as IVOCs (defined as C^* = 300-3×10^6 µg m^{-3} (Li et al., 2016)) and are therefore expected to reside almost entirely in the gas phase at ambient OA loadings (C_{OA} << 10^2 µg m^{-3}), consistent with the parameterizations shown in Figure 5b. However, at the high OA concentrations typical of biomass-burning smoke, considerable fractions of both catechol and hydroquinone—and by extension IVOCs in general—can partition to the particle phase in fresh emissions (Robinson et al., 2007). Therefore, single-phase measurements of such compounds in fresh/undiluted smoke may underestimate the total emissions by up to a factor of 2 and with significantly different potential errors across the I/SVOC volatility range as illustrated using the two isomers (Figure 5b). It is also likely that wall losses within sample lines are significantly greater for hydroquinone than catechol. For example, using the parameterization of Pagonis et al. (2017) and our mean filter-derived C_i^* values, delays in measurement response to benzenediols flowing through 3/16" i.d. Teflon tubing are calculated to be 2.2 and 39 min m^{-1} of tubing at a flow rate of 1 L min^{-1} for catechol and hydroquinone, respectively (1.4 and 26 min m^{-1} for catechol and hydroquinone, respectively using the Antoine + NIST ΔH_{vap} -derived C_i^* values). Transport delays increase further with decreasing flow rate and increasing tube diameter (Pagonis et al., 2017). Such large differences in transport times between the two isomers could have a considerable impact on the measured total benzenediol emissions for some fuels (e.g., sagebrush and manzanita). To evaluate any potential effects on the filter measurements, the estimated delay in hydroquinone transport through the sample tube used here was ~ 5 min (0.3 min for catechol; assuming the transport behavior of benzenediols through passivated stainless steel is similar to Teflon). Such time delays may have significantly impacted the hydroquinone measurements for rice straw and excelsior emissions, for which the fires lasted only 7-8 min. All other fires lasted 13-41 min and thus sample line wall effects are expected to have impacted the hydroquinone results from each fire by at most 12-38 %. The magnitude of the actual measurement impacts would depend in part on the timing of maximum hydroquinone emissions relative to the sampling period. Based on the emissions vs. time profiles of VOCs from online measurements of the FIREX fires (Sekimoto et al., 2018; Selimovic et al., 2018), maximum emissions generally occurred during the first half of the fire periods (or at least >5 min prior to the end

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of the filter sample) and therefore any effects of transport delays on the hydroquinone (and other I/SVOC) measurements were likely minimal for most fires.

The different phase distributions among the benzenediol isomers also suggest different oxidation and other reaction pathways could be available for catechol versus hydroquinone. Smith et al. (2015) determined that benzenediols can react rapidly in the aqueous phase with both triplet-state oxidants and OH radical yielding significant SOA mass (~75-100 % yield); hydroquinone is further susceptible to aqueous-phase self-photodegradation with ~90 % SOA yield. Overall, the partitioning estimates calculated in this work support the conclusions of Smith et al. (2015) that aqueous/condensed-phase SOA production mechanisms are more likely to occur for hydroquinone than catechol, for which gas-phase oxidation will dominate SOA production based on its low condensed-phase fraction (Figure 5). Rate constants and SOA yield estimates, however, are not available for gas-phase reactions of hydroquinone (or resorcinol).

3.2.2 Volatility Distribution

The benzenediol case study above demonstrates that the mean partitioning of individual compounds from SPE-PTFE comparisons can be estimated with reasonable accuracy to derive volatility distributions with decadal resolution. In this section, a single fire was used to investigate the overall volatility distribution of I/SVOCs in smoke following Equation 1 and the approach outlined above. Rotten-log smoke (fire 31) was chosen because it was the only sample for which compounds present in both phases constituted a majority of the overall abundance (73%). The estimated C_i^* values for benzenediol isomers from fire 31 were within a factor of 3 of the mean values suggesting sufficient accuracy for use within the volatility basis set (VBS) framework that is built upon order of magnitude volatility bins (Donahue et al., 2009). Therefore, among the available samples, the volatility distribution can be estimated most completely for the rotten log fire, although given the different I/SVOC chromatographic profiles observed for different fuels, as described above, the derived volatility distribution may not be broadly applicable.

The estimated volatility distribution for compounds observed in rotten log smoke is shown in Figure 6a. Saturation concentrations could not be estimated for compounds that were detected in only one phase; therefore, particle- and gas-phase only compounds were lumped into the logC^* ≤ 0 and ≥ 7 bins, respectively. It is possible that such compounds could belong in one of the middle volatility bins if, for example, the compound was actually present in both phases, but was below detection limit/peak selection criteria in either the PTFE or SPE sample. For compounds that were measured on both filters, volatilities were estimated in the logC^* = 1-6 range with the highest fractions of the emissions falling in the logC^* = 1 and 4 bins. The relative fractions could change following improved quantification and correction of experimental artifacts, as outlined above. For example, C^*_{Cat} from this fire falls within the logC^* = 4 bin whereas the mean value derived above would place catechol in the logC^* = 5 bin; we leave catechol in the logC^* = 4 bin here for consistency with the other unknown compounds in this sample. Additionally, the relative fractions of the higher volatility bins (i.e., logC^* bins ≥5) would likely increase following correction of the relatively poor recovery exhibited by such compounds. Regardless, our estimated volatility distribution demonstrates that the SPE-PTFE method enables analysis of gas-phase compounds with lower

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volatility than has been observed using PTR-TOFMS and sorbent-tube GC×GC-TOFMS analyses, where little material has been reported in logC^* bins <5 (Hatch et al., 2017; Koss et al., 2018) and is therefore a complementary approach to common gas-phase measurements.

May et al. (2013) estimated the volatility distribution of biomass-burning OA from isothermal dilution and thermodenuder-aerosol mass spectrometry measurements of laboratory fires. Their distribution could be constrained within the logC^* = -2-4 range and is included for comparison in Figure 6a. The trends observed in bins logC^* = 2-4 are nominally similar between the two studies, although the fractions are lower in this work due to allocation of some mass into bins >4, which illustrates that the SPE filters enabled measurement of higher volatility compounds, although the relative abundances of such compounds are likely underestimated. The relative fractions in the logC^* $\leq$0 and 1 bins are opposite, however the sum of the two bins is very similar between the two studies (42% in this work, 40% in May et al.). Although the relative fractions in each bin do not line up exactly, the agreement is reasonable considering the two very different analytical approaches (speciation of individual compounds in gas and particle phases vs. volatility measurements of bulk OA) and the different fires included in each distribution.

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The compound-class speciation for compounds observed in each volatility bin (for logC^* 1-6) is given in Figure 6c. For compounds that could not be positively or tentatively identified, compound classes were determined by mass-spectral fragmentation patterns (Lai and Fiehn, 2018): alcohols and carboxylic acids were defined by significant m/z 75 or 147 (and occasionally 103, 117, or 131) peaks; spectra for phenol derivatives contained large m/z 73, negligible m/z 75, and presence of higher m/z peaks, indicative of resonance-stabilized aromatic structures; anhydrosugars and related compounds were characterized by m/z 204 and 217; and "other" compounds were underivatized oxygenates or N/S-containing compounds (no mass spectral trimethylsilyl or hydrocarbon signatures) and eluted early in the secondary GC×GC dimension, consistent with higher polarity than derivatized compounds. Only one hydrocarbon (a PAH) was observed in rotten-log smoke within the characterized volatility range.

The logC^* = 2-6 bins are dominated by alcohols/acids and phenolic compounds, with increasing fractions of anhydrosugars with decreasing volatility (Figure 6c). "Other" compounds were predominantly found in the highest volatility bin for which speciation was characterized (logC^* = 6); the absence of derivatization for such compounds implies that they lack –OH (or –NH, –SH) groups and therefore lack vapor-pressure lowering hydrogen-bonding functionality (Ziemann, 2011). Only two compounds were binned into the logC^* = 1 bin: levoglucosan and its unidentified isomer. May et al. (2012) and Booth et al. (2011) both report measured sub-cooled liquid vapor pressures for levoglucosan equivalent to C_i^* of ~13 μg m^{-3} at 298 K. These reported values are within ~25 % of our estimated levoglucosan C_i^* of 16 μg m^{-3}, demonstrating with the benzenediol isomer C_i^* estimates above that our volatility estimates are reasonable over 4 orders of magnitude, encompassing both predominantly gas-phase and predominantly particle-phase compounds and providing greater confidence in the overall estimated volatility distribution. Whereas our estimated benzenediol C_i^* values appeared to be underestimated, our estimated value for levoglucosan could be higher than literature estimates because the levoglucosan peak in the PTFE samples was overloaded on the GC×GC and may be out of the linear quantification range resulting in an underestimated particle-phase fraction. It is also possible that levoglucosan was only observable on the SPE filter due to its extremely high abundance, as only 0.3% of the total levoglucosan signal was found on the SPE filter for the rotten log fire. Other compounds with similar gas-particle partitioning but much lower abundance would likely fall below the detection limit on the SPE filters and such compounds would therefore be lumped into the logC^* ≤ 0 bin in Figure 6.

As smoke dilutes in the atmosphere, a considerable fraction of OA is expected to volatilize (Bian et al., 2017; Donahue et al., 2006; Grieshop et al., 2009b; Robinson et al., 2007). Figure 6b shows the predicted gas-particle partitioning following a theoretical 100-fold evaporation of rotten-log smoke POA (~4400 to 44 µg m^{-3}) and demonstrates that approximately 40 % of the particle-phase I/SVOCs would evaporate following such perturbation (ignoring potential OA activity effects). Comparison with Figure 6a illustrates that compounds in the logC^* = 3 and 4 bins volatilized completely (as expected for IVOCs), in addition to a significant fraction of the logC^* = 1 and 2 bins. The framed pie chart of Figure 6c shows the speciated compound classes of the POA that would theoretically volatilize following dilution (including all volatility bins). Of this material newly accessible to gas-phase oxidation, 41 % is attributable to anhydrosugars (levoglucosan and several isomers/related compounds), 38 % to phenol derivatives (catechol, vanillic acid, 4-methyl catechol, pyrogallol, 3-vanilpropanol) and 21 % to alcohols/acids (unknowns), where the identifiable compounds that account for >5 % of the corresponding class of volatilized material are listed in descending order parenthetically. These speciated volatility measurements provide a first approximation of the types of I/SVOCs that can evaporate from POA and react as non-traditional SOA precursors. All such compounds were oxygenated and will therefore exhibit very different chemistry and SOA yields than I/SVOCs in vehicular emissions, which have generally been characterized as almost entirely hydrocarbons, particularly alkanes (Tkacik et al., 2012; Zhao et al., 2014; Zhao et al., 2016). Of the identified compounds, only catechol has been studied with respect to gas-phase oxidation and SOA formation (Finewax et al., 2018; Nakao et al., 2011; Yee et al., 2013). Therefore more work is needed to better understand the relative importance of gas-phase vs. heterogeneous reaction pathways for biomass-burning-derived I/SVOCs.

4 Conclusions

This study demonstrates the use of SPE filters for untargeted analysis of gas-phase I/SVOCs in biomass-burning smoke samples. Based on extensive analysis of standard compounds, the extraction recovery was generally lower from SPE filter than PTFE filters. However, SPE-induced extraction biases were generally consistent for each compound class and could be corrected, although recovery was low for the most volatile compounds due volatilization during blow down. Future improvements in the extraction protocol, specifically testing additional solvents and drying time, in addition to the use of recovery, internal, and external standards, should enable quantification of compounds collected onto SPE filters. Further, negligible breakthrough was observed through SPE filters, demonstrating their high trapping efficiency. Therefore, SPE filters appear to be a suitable alternative to PUF/XAD measurements for untargeted analysis of I/SVOCs in air samples.

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Analysis of biomass-burning smoke PTFE and SPE filter samples collected during laboratory fires demonstrated that particle- and gas-phase compounds were separately trapped on the respective filter types, with most of the observed compounds detected on only one filter type. The GC×GC-TOFMS-derived chromatographic profiles of I/SVOCs showed significant diversity among the different fuel types tested, with high correlations observed only among emissions from coniferous fuels. The chromatographic profiles did not appear to be strongly related to combustion efficiency.

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Of the compounds observed on the SPE filters, catechol was the most common, highly abundant compound detected and was generally the dominant benzenediol isomer. However, fuel-dependent signatures were observed among the benzenediol isomers, with hydroquinone the most abundant isomer in manzanita smoke. Further, hydroquinone was shown to be significantly less volatile than catechol ($C^*_{\mathrm{Cat}}/\ C^*_{\mathrm{HQ}} \sim 18$), which can lead to considerable differences in sampling-line losses, as well as in gas-particle partitioning and oxidation chemistry between these isomers. This demonstrates the need for isomer speciation to achieve a holistic understanding of biomass-burning emissions and plume chemistry.

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Based on the phase-specific measurements enabled by PTFE and SPE filter samples, the speciated volatility distribution of Douglas fir rotten log smoke was estimated. Detection of compounds with logC^* ~1-4 demonstrates that the SPE-PTFE method enables analysis of gas-phase compounds with lower volatility than has been observed using PTR-TOFMS and sorbent-tube GC×GC-TOFMS analyses. Effectively 100 % of the compounds observed in both phases were oxygenates (or contained other heteroatoms). The POA likely to volatilize during plume dilution was attributed to anhydrosugars, phenol derivatives, and unidentified alcohols/acids, for which gas-phase chemistry has not been extensively studied.

Data Availability. All PTFE and SPE filter data are available for download from the NOAA FIREX archive at https://esrl.noaa.gov/csd/groups/csd7/measurements/2016firex/FireLab/DataDownload/

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Table 1. Summary of sampled fires

Fire number	Fuel Type	MCE[1]	# of Compounds Total (SPE, PTFE, Both)
02	Ponderosa pine	0.931	256 (157, 74, 25)
16	Ponderosa pine, litter	0.954	503 (191, 255, 57)
22	Douglas fir, litter	0.945	376 (221, 128, 27)
28	Manzanita, canopy	0.963	357 (152, 155, 50)
31	Douglas fir, rotten log	0.781	722 (269, 270, 183)
36	Engelmann spruce, duff	0.871	470 (280, 142, 48)
37	Ponderosa pine	0.940	733 (299, 354, 80)
42	Lodgepole pine	0.951	482 (257, 175, 50)
47	Subalpine fir	0.932	630 (311, 253, 66)
49	Excelsior	0.971	141 (84, 46, 11)
50	Yak dung	0.899	881 (378, 360, 143)
52	Engelmann spruce	0.957	597 (357, 194, 46)
55	Indonesian peat	0.831	547 (94, 402, 51)
56	Subalpine fir, duff	0.886	683 (232, 280, 171)
60	Rice straw	0.953	190 (146, 30, 14)
62	Bear grass	0.897	518 (307, 154, 57)
65	Jeffrey pine, duff	0.877	449 (215, 182, 52)
66	Sagebrush	0.919	317 (183, 113, 21)

[1] MCE values from Table S1 of Selimovic et al. (2018)

Table 2. Measured and literature-derived C_i^* (μg m^{-3}) values of benzenediol isomers

	Catechol	Hydroquinone
This work	$(6.2 \pm 4.9)\times10^4$	$(3.6 \pm 1.7)\times10^3$
Antoine + NIST ΔH_{vap}[1]	1.05×10^5	5.70×10^3
Antoine + Verevkin ΔH_{vap}[1]	4.76×10^4	9.26×10^2
Mean – Antoine Estimates	7.63×10^4	3.31×10^3

[1] Calculated from vapor pressures estimated using Antoine coefficients (Burgess, 2018) scaled to ambient temperature using ΔH_{vap} data from NIST (Burgess, 2018) or Verevkin and Kozlova (2008).

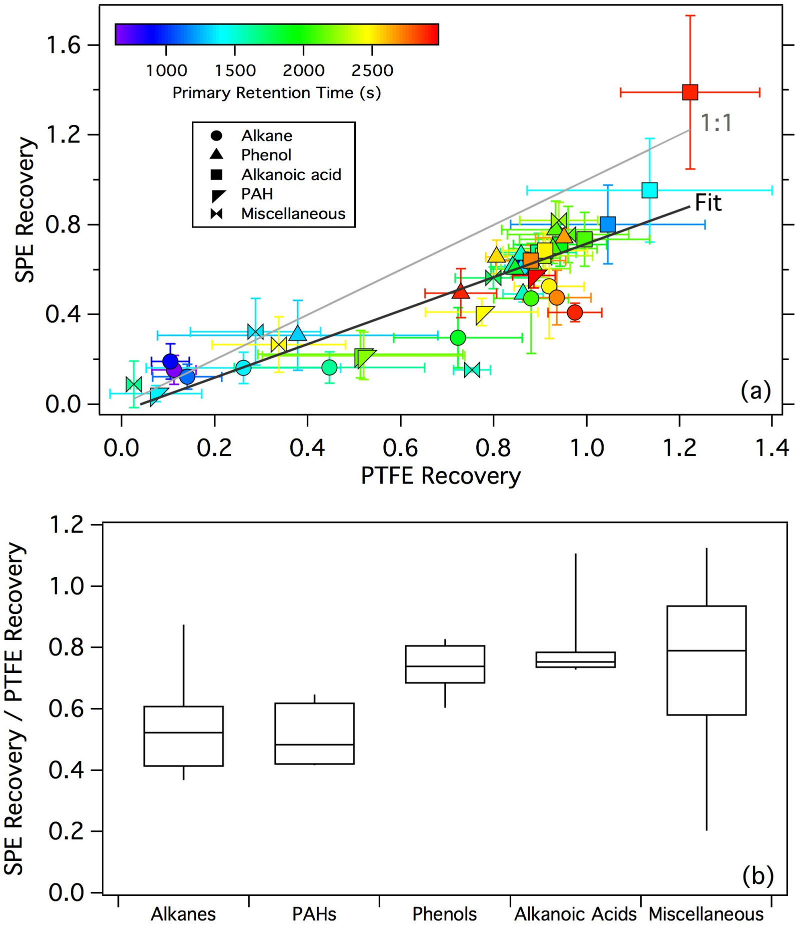

Figure 1. (a) Comparison of the extraction recoveries of standard compounds in the SPE and PTFE tests. For the linear regression, R^2 = 0.72 and slope = 0.75. (b) SPE extraction bias as a function of compound class.

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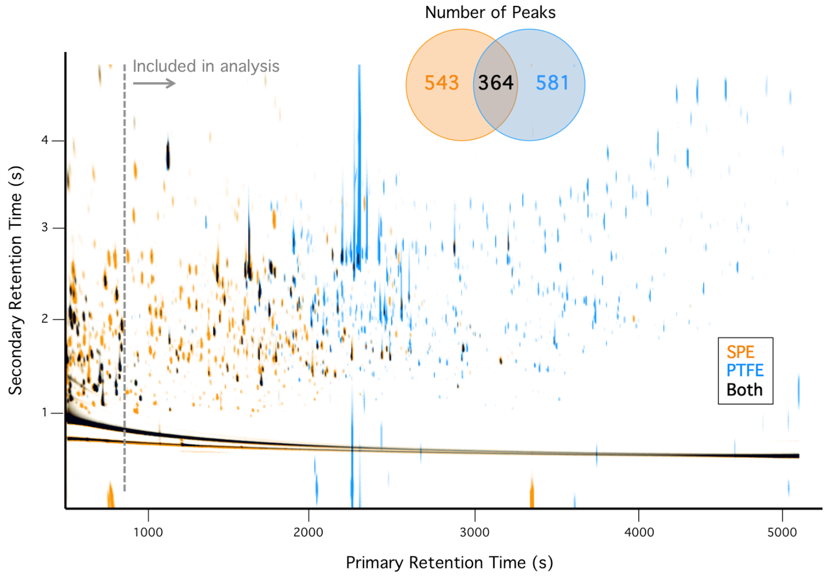

Figure 2. Overlay of composite chromatograms for all SPE and all PTFE smoke samples. Inset shows the number of peaks observed on each filter type.

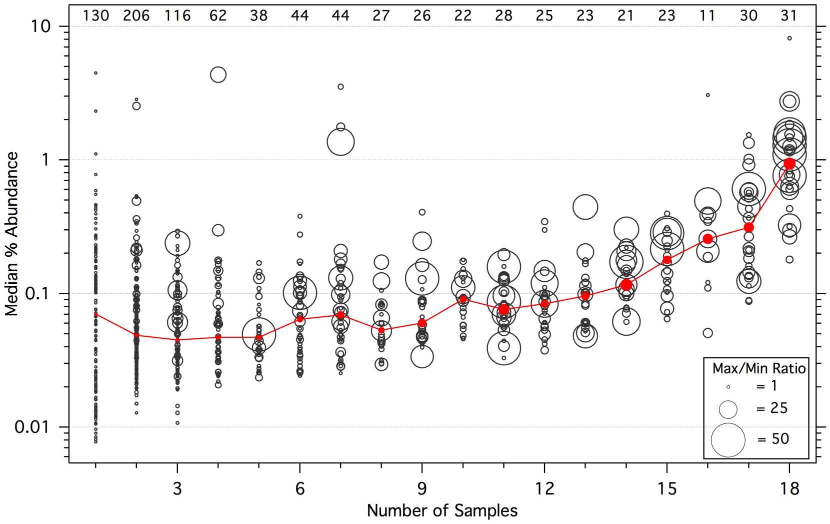

Figure 3. The black circles represent the median percentage (ignoring zeros) of the total SPE peak area for each observed compound as a function of the number of SPE samples that contained that compound; for compounds observed in only one or two samples, the maximum percent abundance was used in place of the median. Marker size is proportional to the range of percent abundances observed for each compound (capped at 50), calculated as the ratio of the maximum value to the minimum non-zero value. The red trace represents the median of the values shown for each number of samples, with the marker sizes corresponding to the median max/min ratio. The numbers along the top represent the number of compounds observed within each bin.

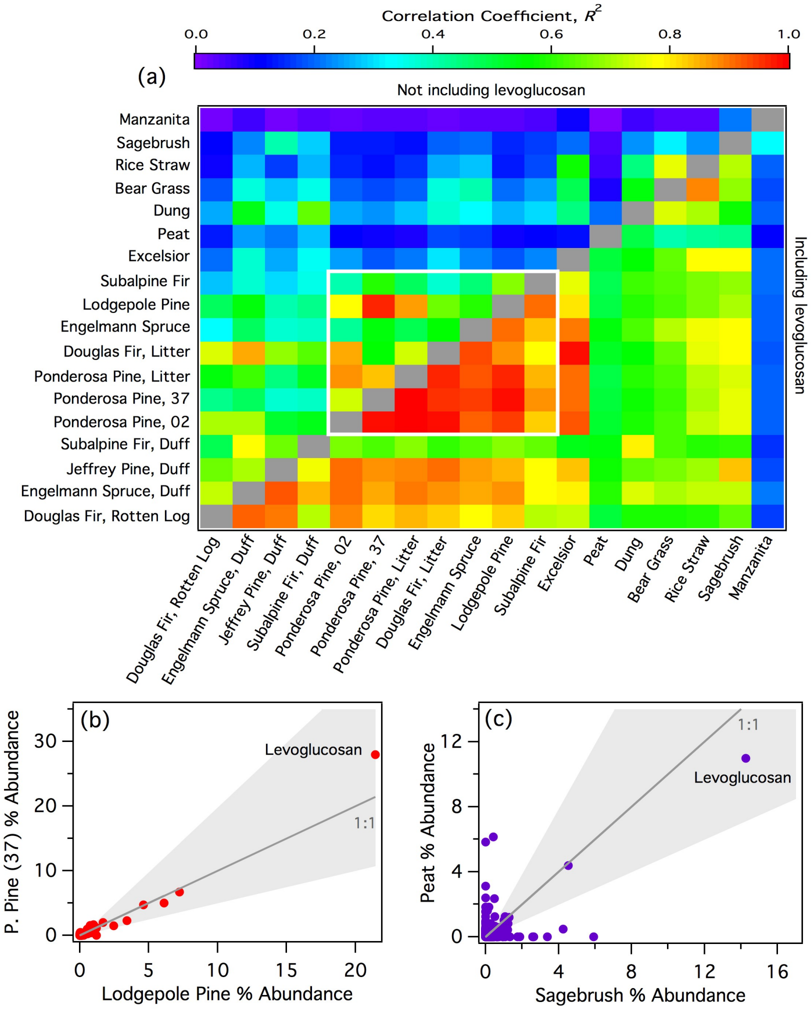

Figure 4. (a) Correlation coefficients (R^2) for each fire pair based on the total (SPE+PTFE) % abundance for each observed compound. For the ponderosa pine replicates, the fire number is indicated. Regression values below the diagonal were calculated including all observed compounds; above the diagonal, levoglucosan was omitted. The white box bounds the conifer fires. (b) Example scatter plot of a highly correlated fire pair. (c) Example scatter plot of a poorly correlated fire pair. In (b) and (c), each point represents a single compound and the shaded areas denote a factor of two from the 1:1 line.

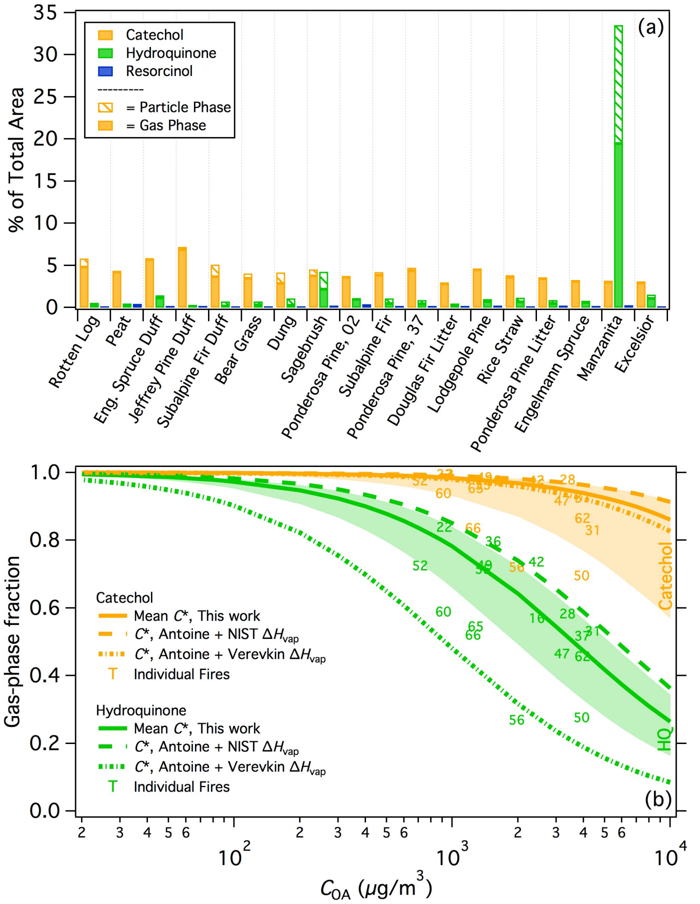

Figure 5. (a) The percentage of the total (SPE+PTFE) peak area attributed to benzenediol isomers for each fire. Samples are arranged with increasing modified combustion efficiency (MCE) left to right. Fire numbers are indicated for the two ponderosa pine burns. (b) Calculated partitioning of catechol and hydroquinone (HQ) as a function of organic aerosol concentration (C_{OA}). Solid lines indicate the partitioning based on the mean C^* values calculated in this work, with the shaded areas indicating plus/minus one standard deviation of the mean C^*. Dashed lines represent the partitioning calculated from vapor pressures estimated using Antoine coefficients and scaled to ambient temperature using ΔH_{vap} data from NIST (Burgess, 2018) and Verevkin and Kozlova (2008).

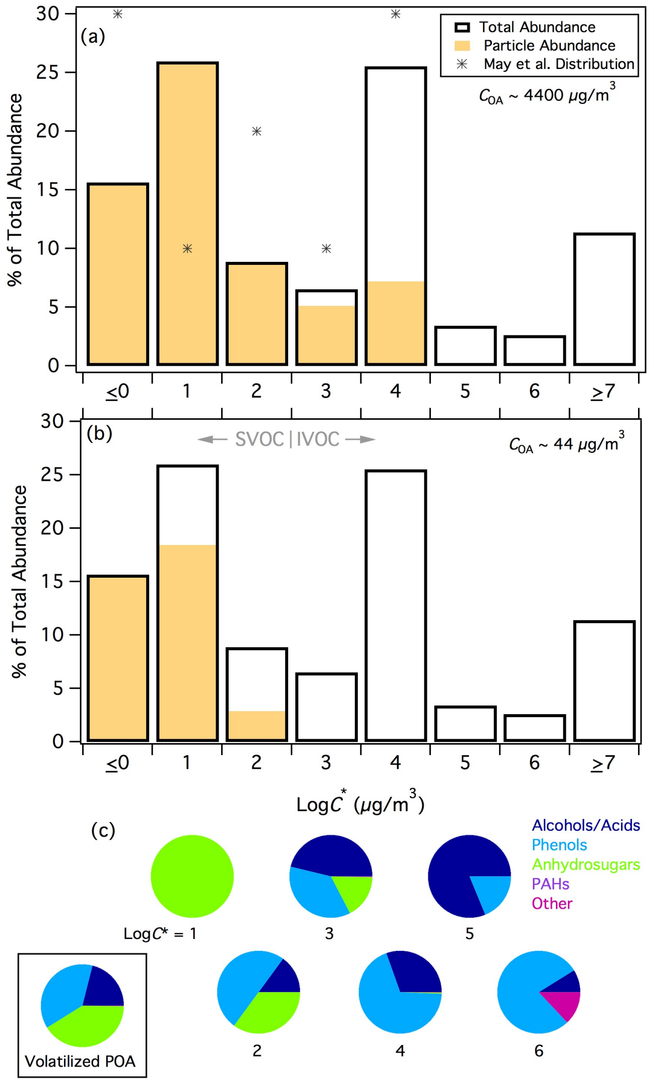
(a)
Total Abundance
Particle Abundance
May et al. Distribution
C_{OA} ~ 4400 μg/m^3
% of Total Abundance
30
25
20
15
10
5
0
≤0
1
2
3
4
5
6
≥7
(b)
SVOC | IVOC
C_{OA} ~ 44 μg/m^3
% of Total Abundance
LogC^* (μg/m^3)
(c)
Alcohols/Acids
Phenols
Anhydrosugars
PAHs
Other
LogC^* = 1
3
5
Volatilized POA
2
4
6

Figure 6. (a) Volatility distribution of compounds observed in fresh rotten log smoke. Markers represent the derived volatility distribution for biomass-burning smoke organic aerosol from (May et al., 2013). Particle- (gas-) phase only compounds are lumped into the logC^* ≤0 (≥7) bin. (b) As in panel one, for a theoretical 100-fold evaporation of POA. (c) Speciation of the compound classes contributing to each volatility bin with measurable C^* values. The pie chart bounded by the box shows the speciation of the I/SVOCs that were predicted to volatilize from the particle phase across all volatility classes following evaporation of POA represented in panel b.

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Supporting Information

Measurements of I/SVOCs in biomass-burning smoke using solid-phase extraction disks and two-dimensional gas chromatography

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S1. Extraction Efficiency

The extraction recoveries for all individual standard compounds (see Section 2.4 of the main text for experimental details) are given in Figures S1-S5, grouped by compound class. Within each class, the compounds have been arranged with increasing retention time (i.e., decreasing volatility) left to right. As seen in all figures (especially Figures S1 and S2), the recovery from both PTFE and SPE filters decreases with decreasing retention time (increasing volatility), likely due to losses during the drying periods. In both the PTFE and SPE tests, recovery increases for later-eluting compounds, although in the "transition" region where recovery gradually increases for each subsequent compound (e.g., tetradecane – heptadecane, Figure S1; guaiacol, Figure S3), the measured recoveries were highly variable, as indicated by the large error bars. Despite such variability, we have retained these compounds in the biomass burning dataset and assume a factor of 2 uncertainty to account for this observation. We also note that the recovery from SPE filters often decreases relative to the PTFE recovery and error bars increase for the least volatile compounds tested (e.g., Figure S3-S5). Although not important for this work because such compounds were trapped on the PTFE filters, it may have implications for future studies seeking to co-sample gas- and particle-phase compounds onto a single SPE filter. Such sampling approaches have already been used for the targeted analysis of air samples collected onto SPE filters (Sanchez et al., 2003; Stuff et al., 1999; Tollback et al., 2006); future work should investigate the viability of such approaches for untargeted analysis.

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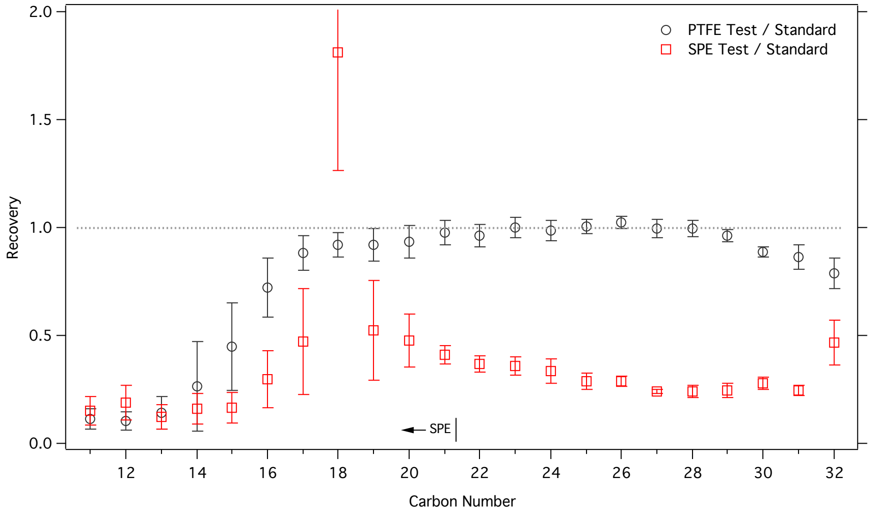

Figure S1. Recoveries of individual *n*-alkanes from the PTFE and SPE tests. Compounds are listed with increasing primary retention time (left to right). The cutoff for standard compounds relevant for biomass-burning SPE samples (i.e., primary retention time <3000 s) is indicated.

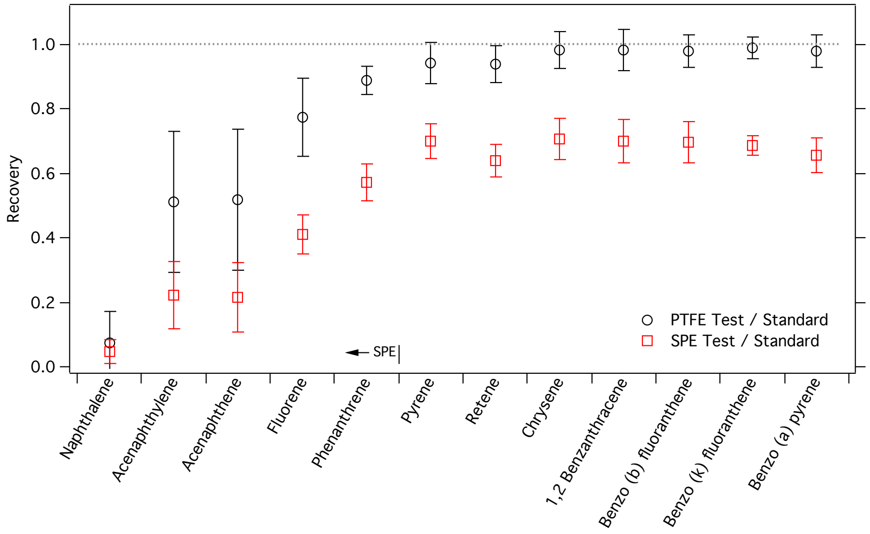

Figure S2. As in Figure S1, for polycyclic aromatic hydrocarbons (PAHs).

Methyl ester derivatives were observed for all standard compounds containing an aldehyde functional group (vanillin, syringaldehye, sinapaldehyde, Figure S3; 5-hydroxy methyl furfural, Figure S5). These byproducts were attributed to reaction with methanol solvent during storage (in a freezer), as the standard mixture was prepared more than 1 year prior to use in these tests. The age of the standard otherwise did not affect the results because all extraction tests were referenced to the derivatized standard analyzed at the same time. We present the data for these compounds as "aldehyde + byproduct" and note that the error bars are larger for the SPE tests than PTFE tests (Figure S3). To ensure no aldehyde/methyl ester artifacts occurred due to the SPE filters, fresh solutions were prepared separately for vanillin and methyl vanillate and run through the same tests outlined for the composite standard (Section 2.4, main text). No methyl vanillate was observed in any vanillin test; vanillin was observed in one methyl vanillate test on the SPE filters, but accounted for <0.2% of the combined peak area, which was well within the stated purity of neat methyl vanillate (≥98%, Sigma-Aldrich). Therefore, we expect no SPE-induced artifacts to have impacted aldehyde measurements in the biomass burning samples. However, the conversion of aldehydes to esters appears to depend on the presence of acids, which were included in the standards analyzed here (Figure S4-S5). We observed similar conversion of furfural and benzaldehyde in solutions containing phthalic acid that were prepared in methanol whereas negligible aldehyde to ester conversion was observed for benzaldehyde and furfural in methanolic solutions prepared without organic acids (data not shown). Similarly, no methyl vanillate was observed in a methanolic solution containing vanillin and no acids, even after storage for ~ 3 months. Because acids were observed in the SPE and PTFE fire samples, extraction and subsequent storage of methanol extracts may have caused some conversion of aldehydes to methyl esters, although we expect this artifact to be relatively minor. For example, the peak area of methyl vanillate was ~3.5% that of vanillin in the dung-smoke SPE sample. Artifacts resulting from methanol extraction have also been previously observed (Sauret-Szezepanki and Lane, 2004). Therefore, further optimization of the extraction solvent should be conducted to limit potential reaction products, as well as to improve the recovery of hydrocarbons, as discussed in the main text (Section 3.1).

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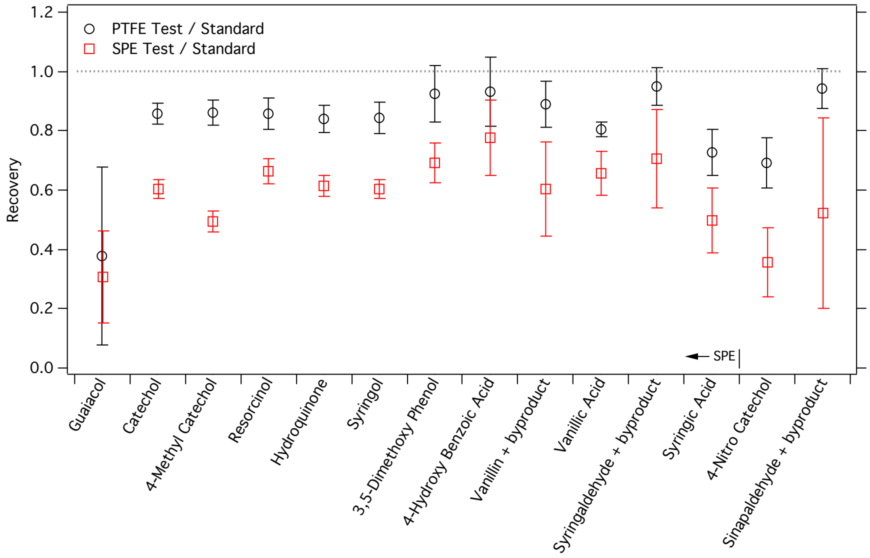

Figure S3. As in Figure S1, for individual phenol derivatives. 'Byproduct' refers to the methyl ester product of the indicated aldehyde that formed through reaction with methanol during storage of the standard.

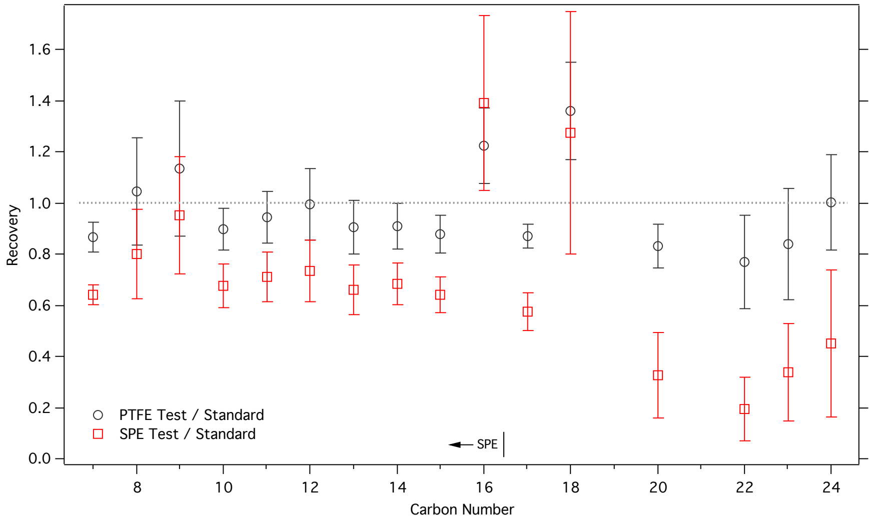

Figure S4. As in Figure S1, for individual *n*-alkanoic acids

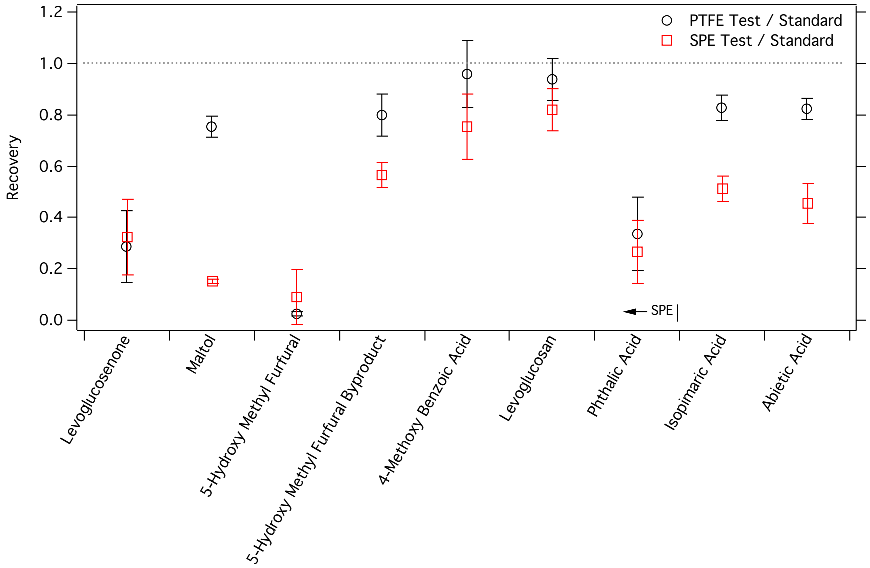

Figure S5. As in Figure S1, for miscellaneous oxygenates. ‘Byproduct’ refers to the methyl ester product of 5-hydroxy methyl furfural that formed through reaction with methanol during storage of the standard.

We also tested for potential differences in evaporative losses of the more volatile compounds due to differences in the mass of the less volatile material present in the samples that could act as an absorbing phase during drying, which could be variable based on the amount of sample collected. For these tests, a mixture was prepared of representative volatile compounds, which eluted early in the SPE samples, and included guaiacol, 1,13-tetradecadiene, 2,5-dimethyl phenol, camphor, and acenaphthene each at ~50 ng/µL. We created a separate mixture to represent the lower volatility absorbing phase. These compounds were chosen based on available standards relevant for biomass burning and included vanillin, isoeugenol, 2,6-dimethoxy phenol, myristic acid, phthalic acid, and fluorene each at ~50 ng/µL; they eluted late in the SPE filter samples indicating they are less likely to volatilize during blow down. Five tests were then conducted in duplicate using a constant volume (100 µL) of the volatile compound solutions with varying amounts of the lower volatility mixture (from 0-400 µL). The mass of the absorbing phase (assuming no volatilization during drying) ranged from 0 - 122 µg; for

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comparison the mass of the standard compounds used in each SPE and PTFE tests was ~87 μg of mostly lower-volatility material. Each sample was dried down and derivatized similarly to the "Standard" test described in the main text. In Figures S6, we show the average peak area (± 1σ) of each volatile standard compound as a function of the available absorbing mass.

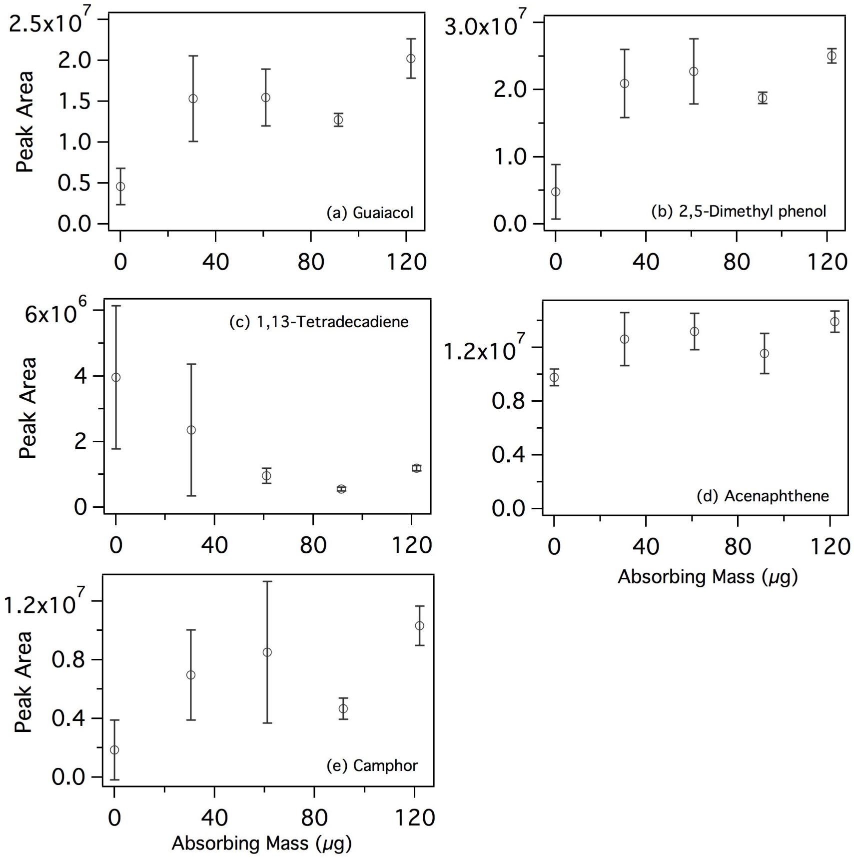

Figure S6. The effect of absorbing mass on the recovery of volatile analytes.

Figure S6 indicates that volatile compounds were very poorly recovered in the absence of a residue containing lower volatility compounds, although all volatile compounds were recovered to some extent even in the absence of other absorbing

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material. Such poor recovery is expected with low residual mass because there is little to no absorbing phase in which the relatively volatile compounds can exist.

At higher amounts of absorbing mass, which is more representative of the biomass burning samples, sufficient lower volatility mass exists to act as an absorbing phase, and compounds are more strongly retained in that condensed phase, thereby improving recovery. For all compounds except 1,13-tetradecadiene, the recovery improved significantly with addition of the absorbing phase and the average peak area was fairly consistent across all residue masses tested (Figure S6). Of those four compounds, the mean peak areas varied between 8 % (acenaphthene) and 37 % (camphor) across the four tests that included absorbing mass. However, the recovery was more variable at lower residue mass (i.e., 30 and 60 µg). For example, the relative standard deviations (RSDs) were highest for camphor (Figure S6e), with 44 % and 56 % RSDs at 30 and 60 µg of residue, compared to 15 % and 30 % RSDs at 91 and 122 µg of residue. These results indicate that the recovery of relatively volatile compounds can vary based on the mass of other absorbing compounds in the sample, and the variability is well within the 100 % uncertainty estimate outlined in the main text based on the SPE and PTFE tests.

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In contrast to the other compounds, 1,13-tetradecadiene displayed poorer recovery with increasing absorbing mass (Figure S6c). We attribute this behavior to activity effects wherein the overwhelmingly polar nature of the residue matrix used here resulted in greater volatilization of the non-polar hydrocarbon. This result could explain why the light hydrocarbons (undecane-tridecane, naphthalene) displayed the lowest recoveries in the SPE and PTFE tests (Figures S1 and S2) and why few alkanes/alkenes were observed in most fire samples: the high abundance of oxygenated compounds in biomass burning smoke may have enhanced the volatilization of aliphatic hydrocarbons. However, such matrix effects were not likely sufficient to obscure the qualitative trends in I/SVOCs between fuel types. For example, we find much higher fractions of aliphatic compounds in peat smoke compared to sagebrush smoke. Based on complementary measurements from the same fires using sorbent tube collection followed by thermal desorption-GC×GC analysis, which are not subject to the same matrix effects (unpublished data, similar protocol to that described in (Hatch et al., 2015)), we also find negligible aliphatic compounds in sagebrush compared to peat.

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S2. Biomass-burning samples

For a few sample extracts, vial caps did not remain sealed during incubation causing evaporative losses. The affected samples are listed in Table S1 along with the estimated volume loss. The resulting GC×GC data were subsequently scaled using the indicated factor.

Table S1. Samples impacted by volatilization losses during derivatization

Fire number	Filter type	Volume loss	Scaling factor
22	SPE	25%	0.75
42	SPE	10%	0.9
47	SPE	25%	0.75
65	PTFE	10%	0.9
66	PTFE	33%	0.66

Overlays of chromatograms (Schmarr and Bernhardt, 2010) from SPE and PTFE filter extracts of individual burns are included below, in the same order as Figure 4 (main text).

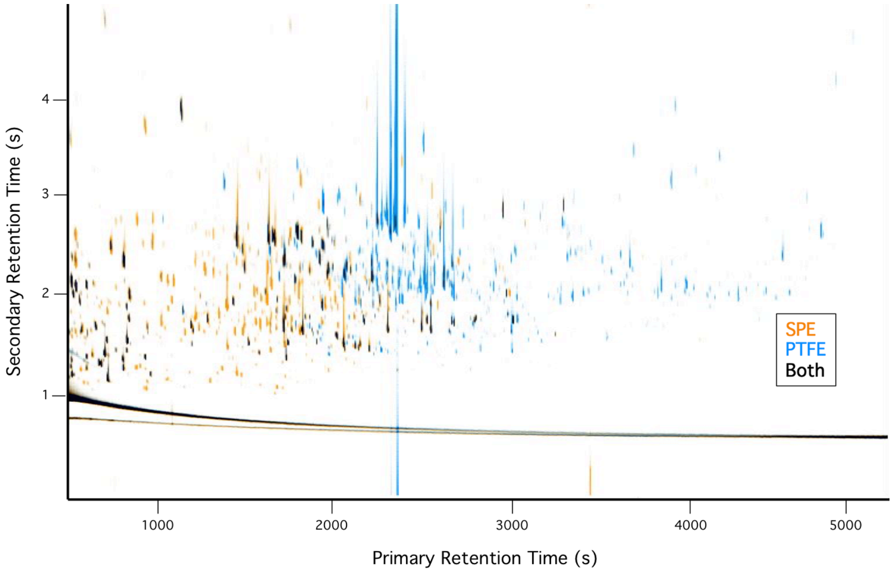

Figure S7. GC×GC chromatogram of the SPE extract (orange) from a Douglas fir rotten log fire (#31) overlaid on the corresponding chromatogram of the PTFE extract (blue). Peaks with black shading were observed in extracts from both filters.

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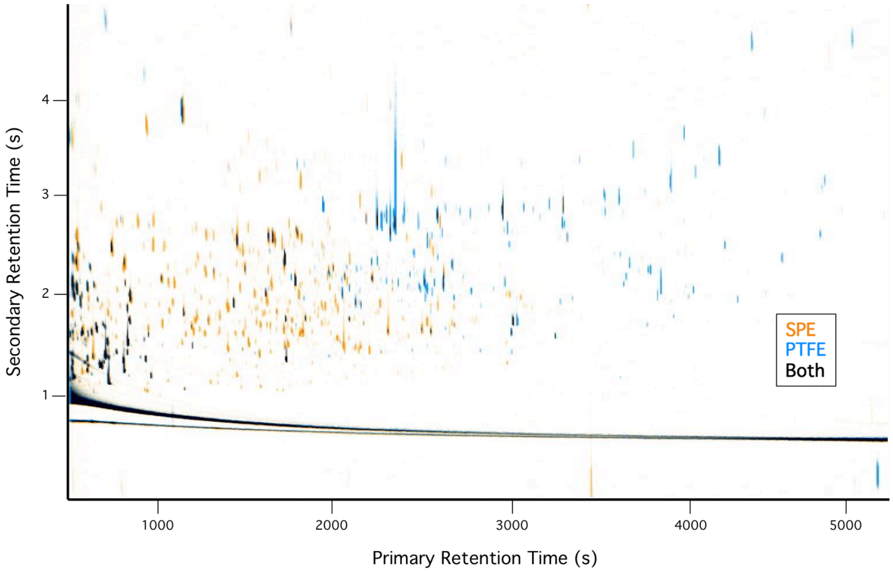

Figure S8. As in Figure S7, for an Engelmann spruce duff fire (#36).

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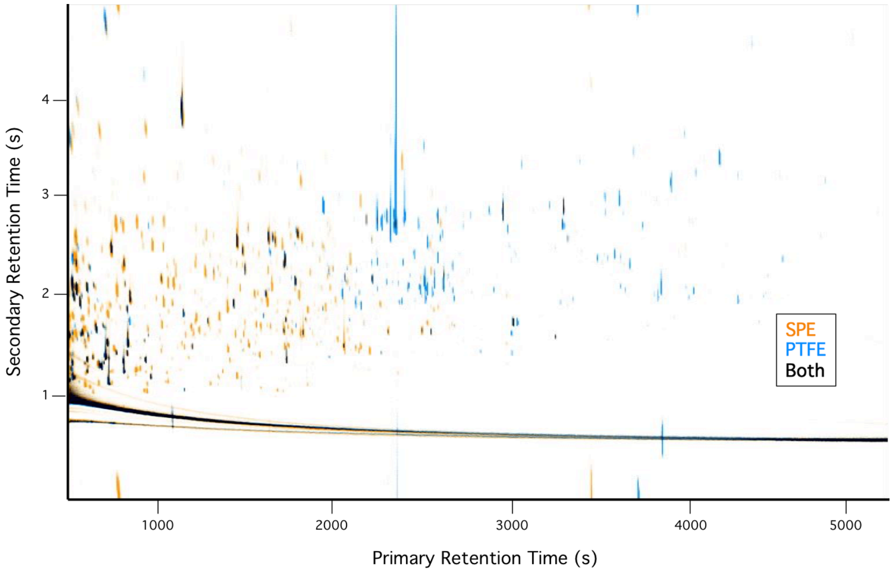

Figure S9. As in Figure S7, for a Jeffrey pine duff fire (#65).

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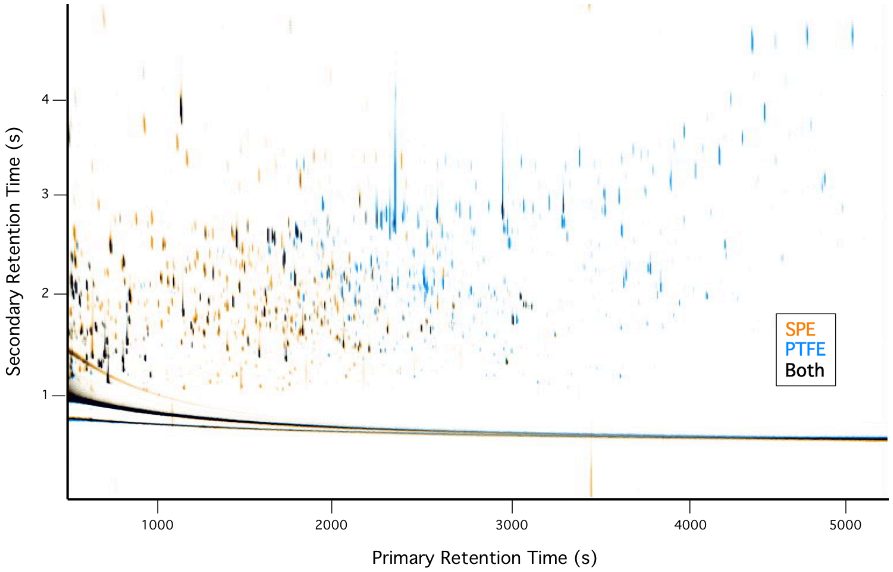

Figure S10. As in Figure S7, for a subalpine fir duff fire (#56).

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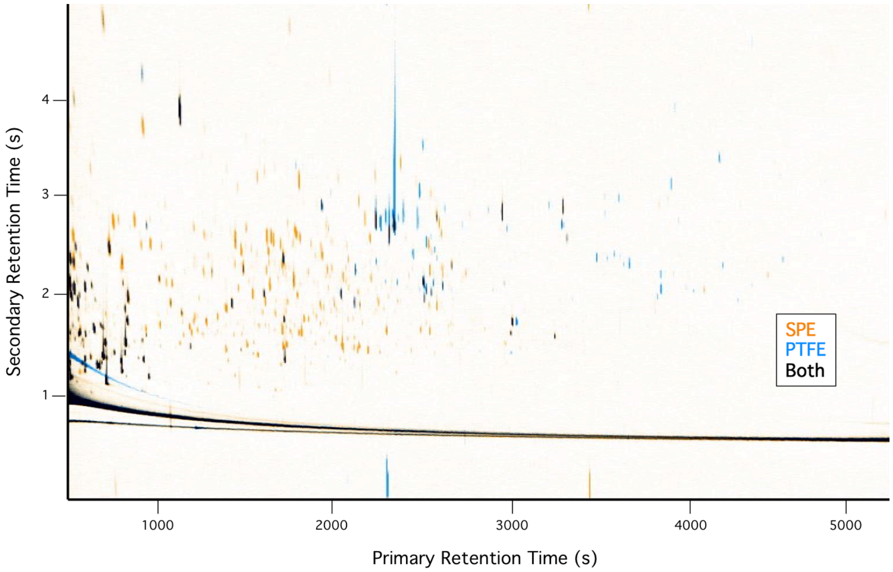

Figure S11. As in Figure S7, for a ponderosa pine fire (#02).

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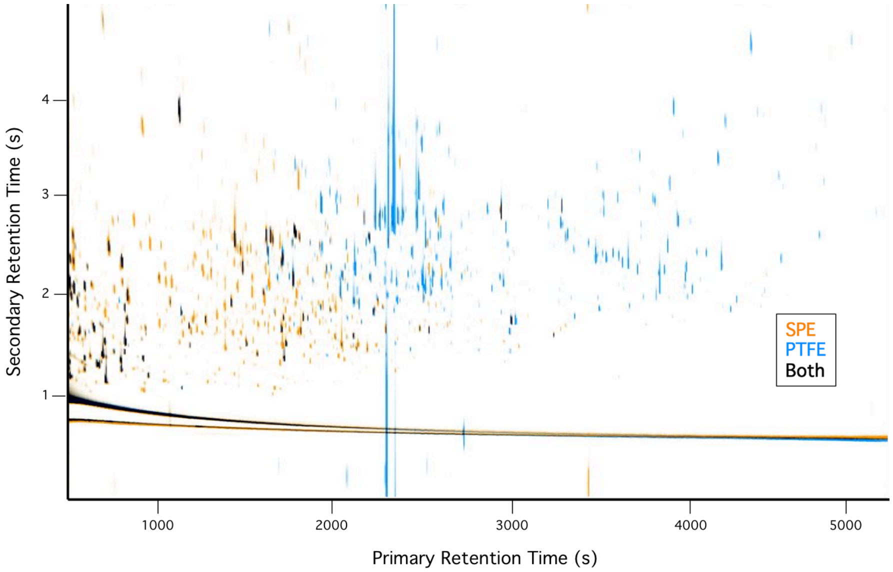

Figure S12. As in Figure S7, for a ponderosa pine fire (#37).

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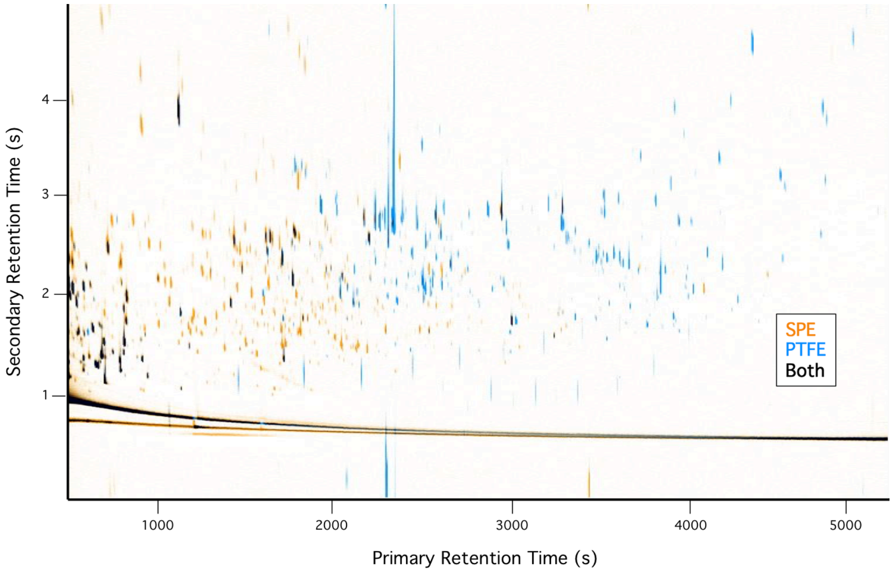

Figure S13. As in Figure S7, for a ponderosa pine litter fire (#16).

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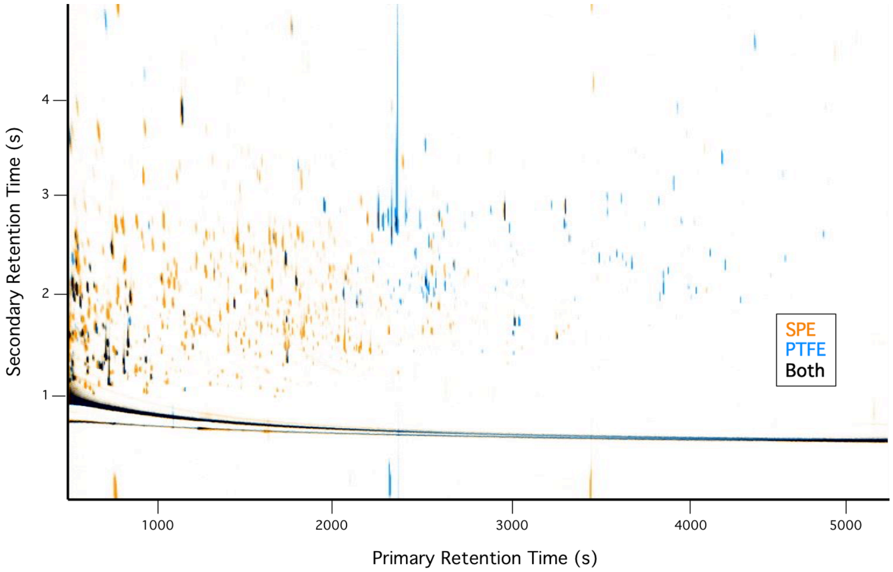

Figure S14. As in Figure S7, for a Douglas fir litter fire (#22).

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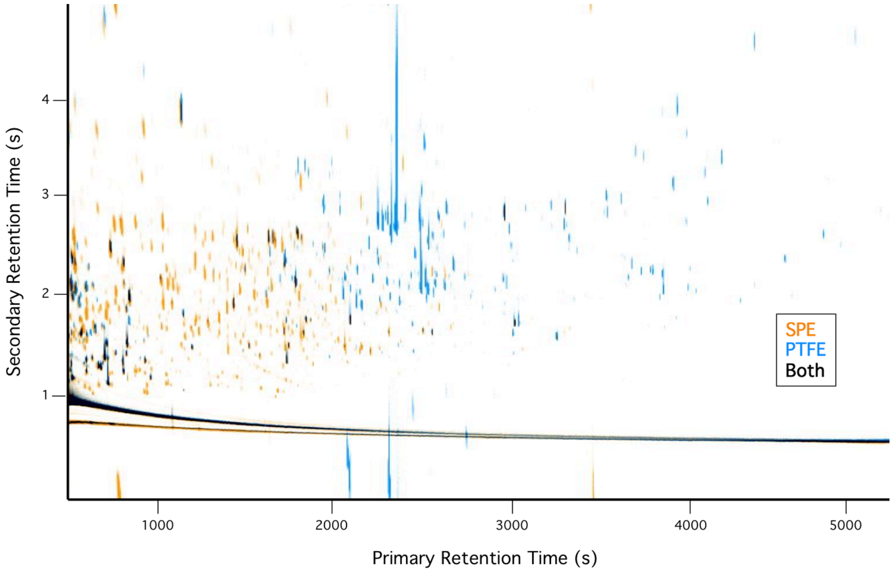

Figure S15. As in Figure S7, for an Engelmann spruce fire (#52).

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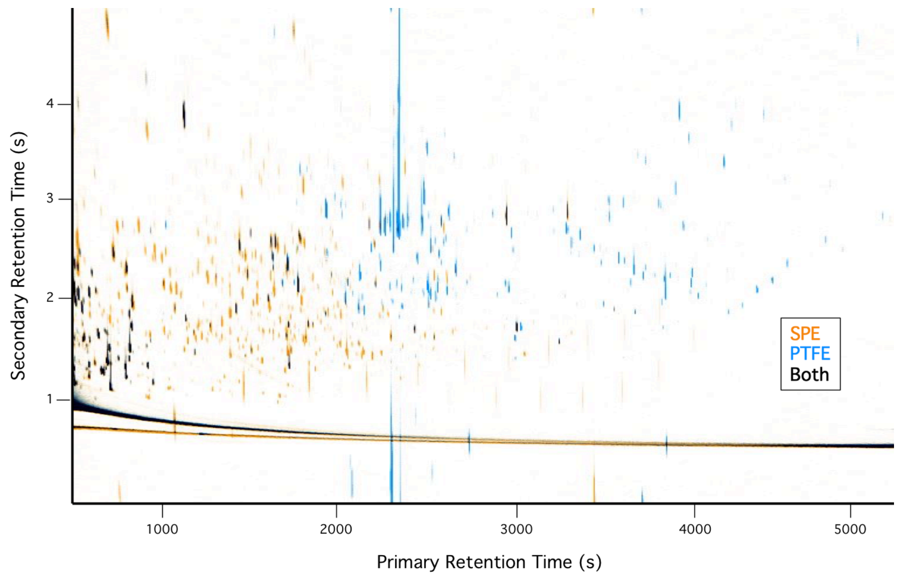

Figure S16. As in Figure S7, for a lodgepole pine fire (#42).

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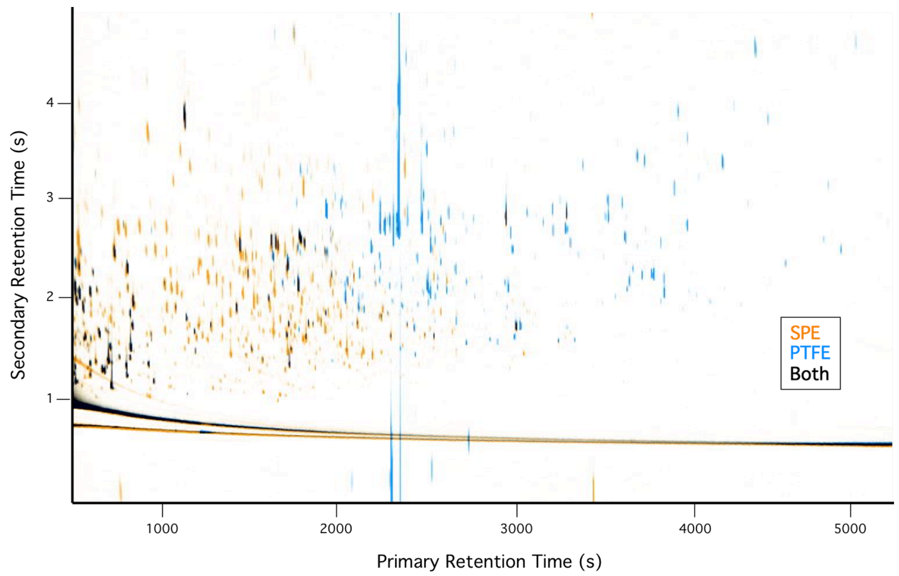

Figure S17. As in Figure S7, for a subalpine fir fire (#47).

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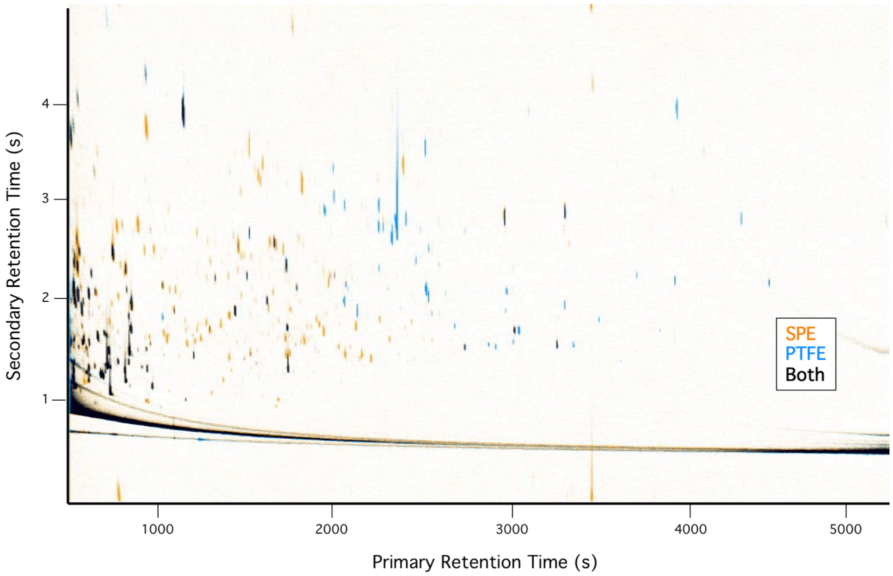

Figure S18. As in Figure S7, for an excelsior fire (#49).

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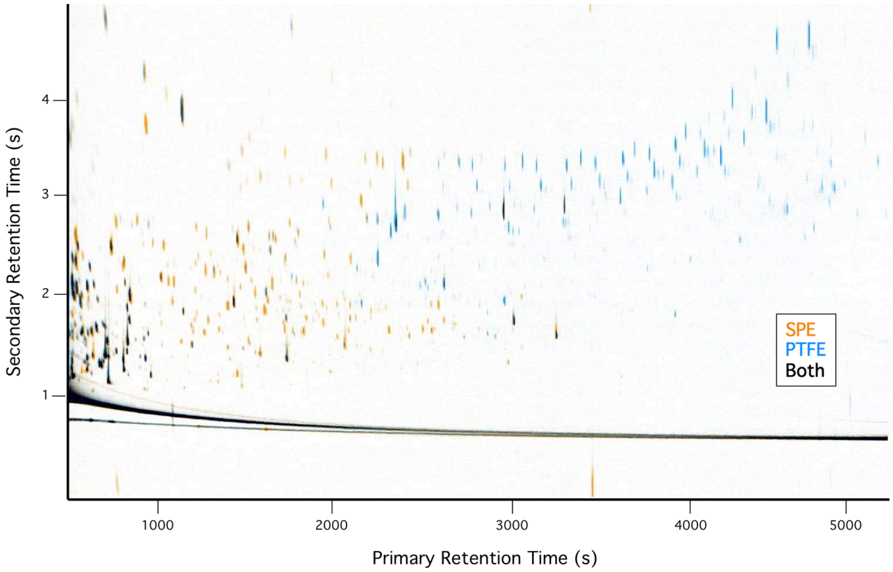

Figure S19. As in Figure S7, for a peat fire (#55).

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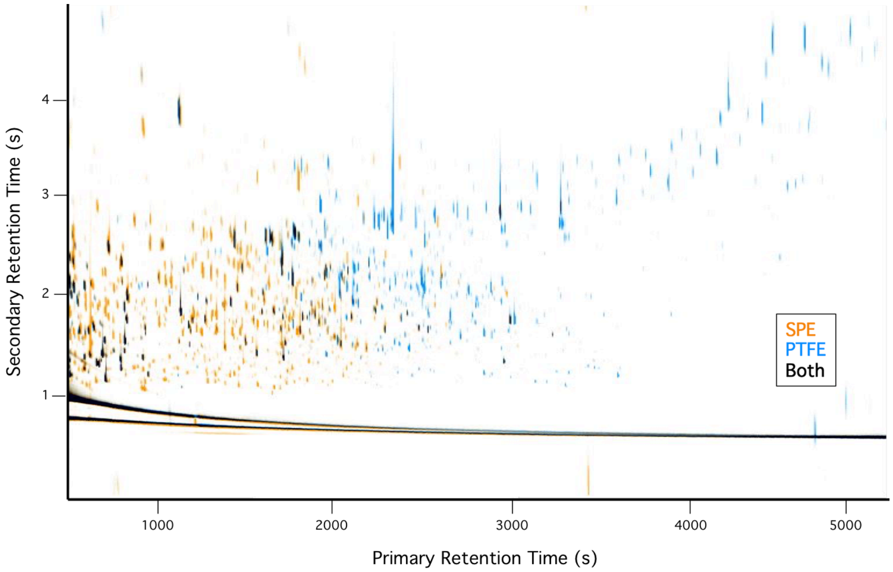

Figure S20. As in Figure S7, for a yak dung fire (#50).

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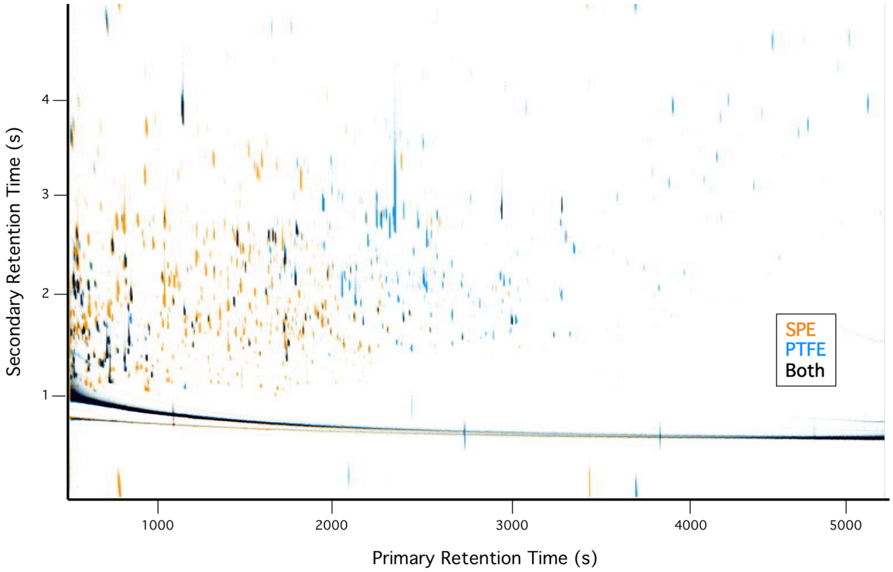

Figure S21. As in Figure S7, for a bear grass fire (#62).

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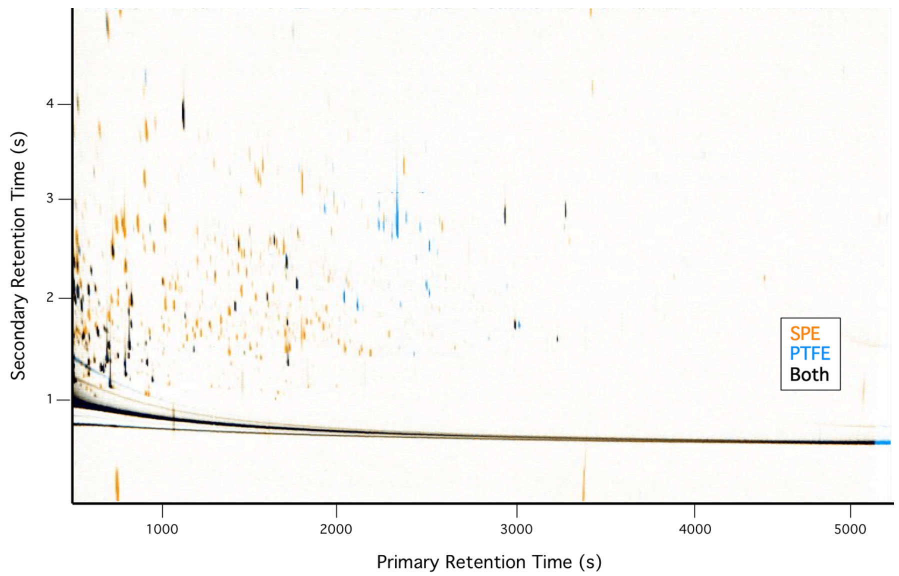

Figure S22. As in Figure S7, for a rice straw fire (#60).

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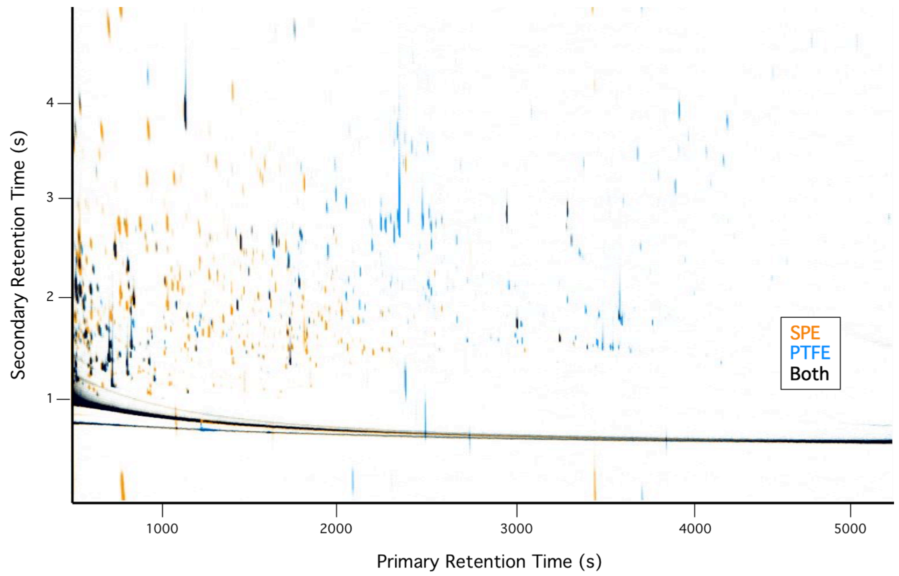

Figure S23. As in Figure S7, for a sagebrush fire (#66).

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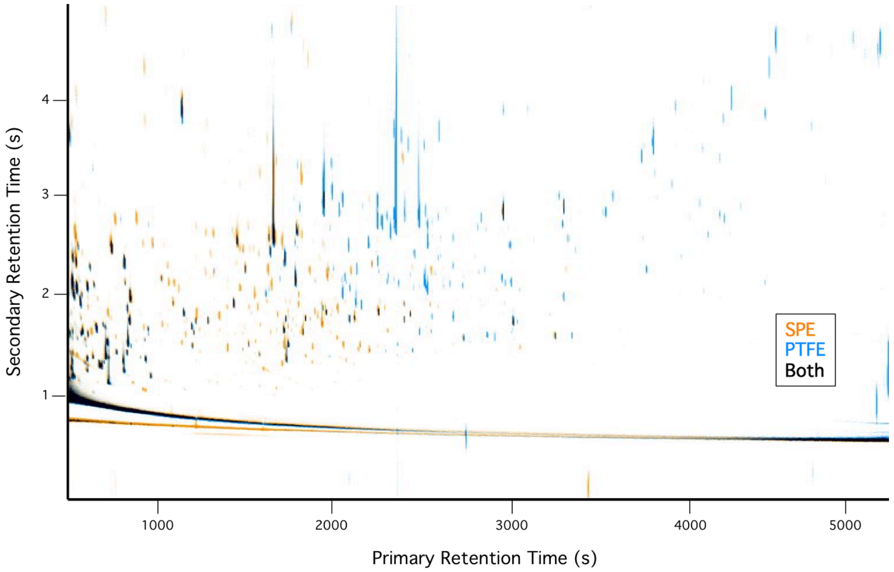

Figure S24. As in Figure S7, for a manzanita fire (#28).

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