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*Supplement of*

## **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.

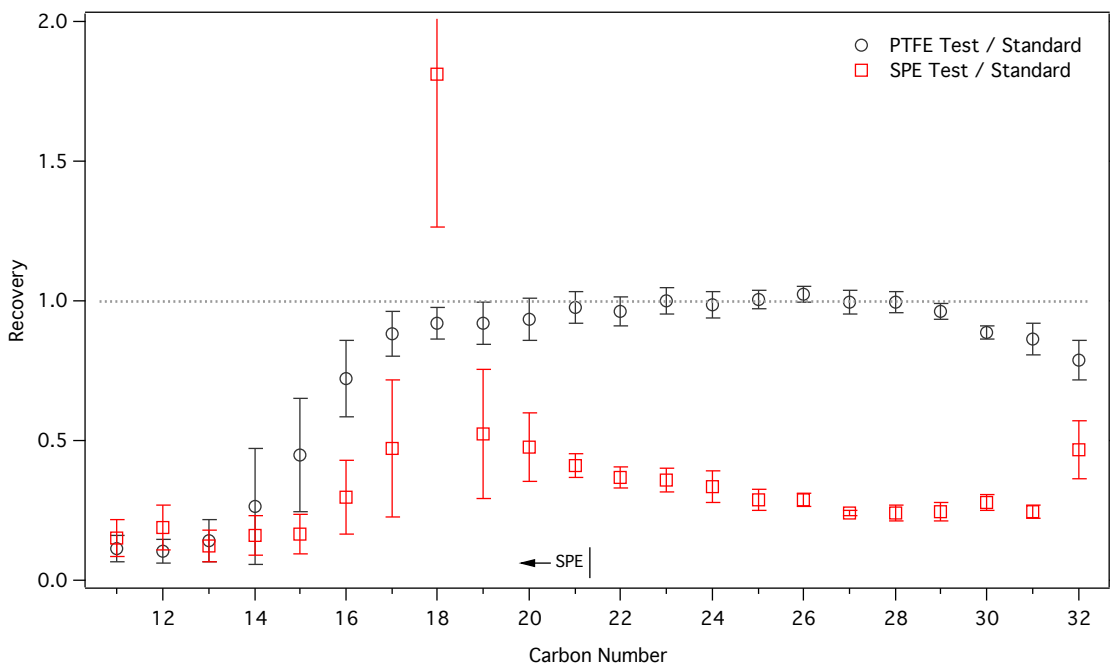


Figure S1. Recoveries of individual *n*-alkanes from the PTFE and SPE tests. Compounds are listed with increasing primary retention time (left to right). The cutoff for standard compounds relevant for biomass-burning SPE samples (i.e., primary retention time <3000 s) is indicated.

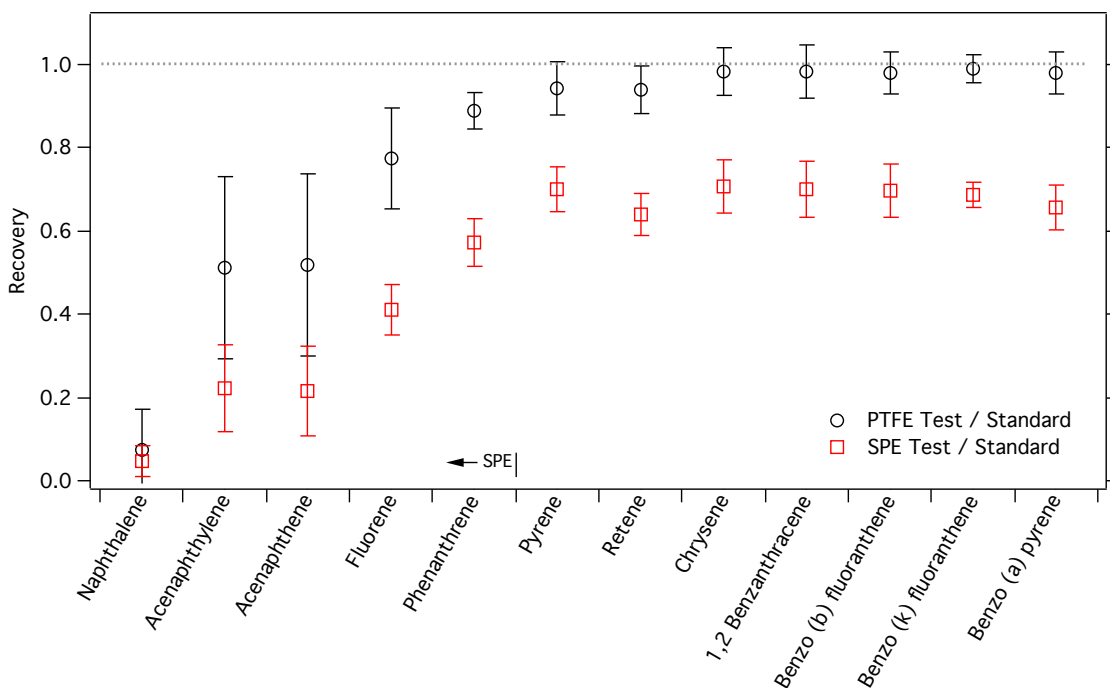


Figure S2. As in Figure S1, for polycyclic aromatic hydrocarbons (PAHs).

Methyl ester derivatives were observed for all standard compounds containing an aldehyde functional group (vanillin, syringaldehyde, 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 ( $\geq 98\%$ , 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  $\sim 3$  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  $\sim 3.5\%$  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).



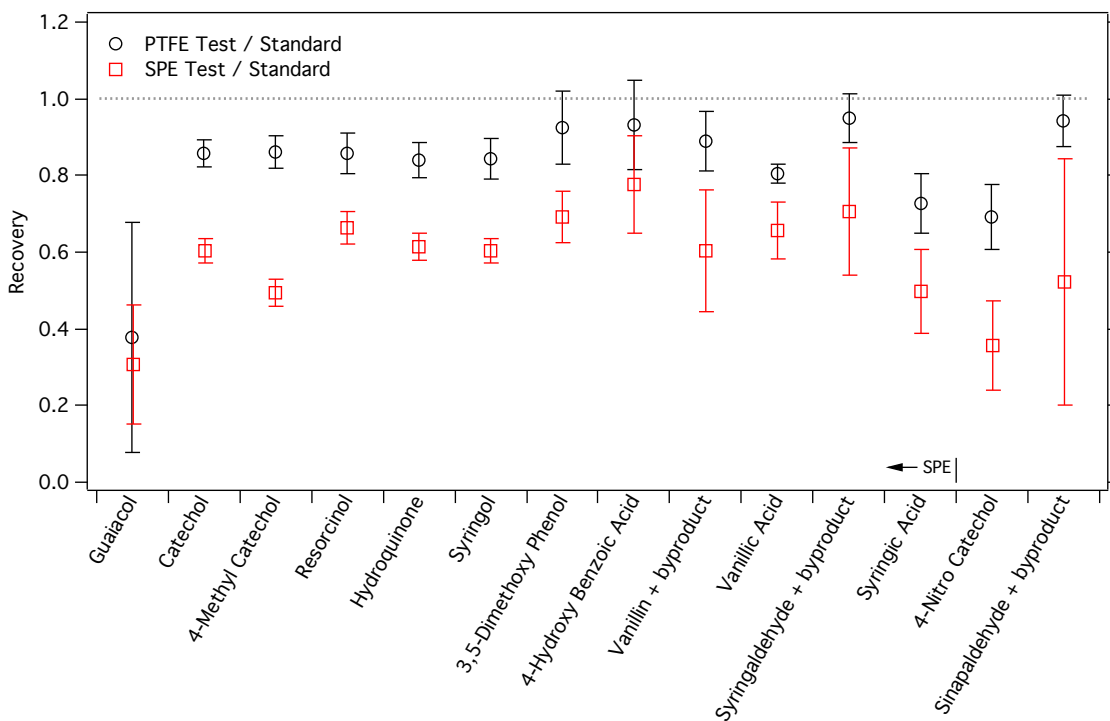


Figure S3. As in Figure S1, for individual phenol derivatives. 'Byproduct' refers to the methyl ester product of the indicated aldehyde that formed through reaction with methanol during storage of the standard.

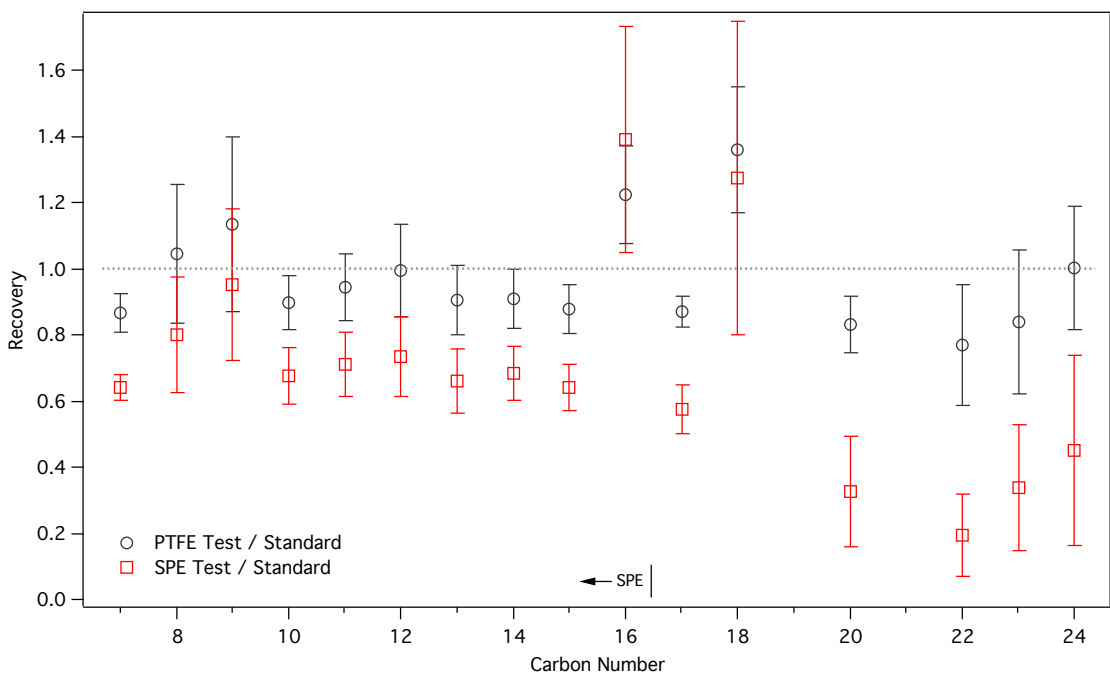


Figure S4. As in Figure S1, for individual *n*-alkanoic acids

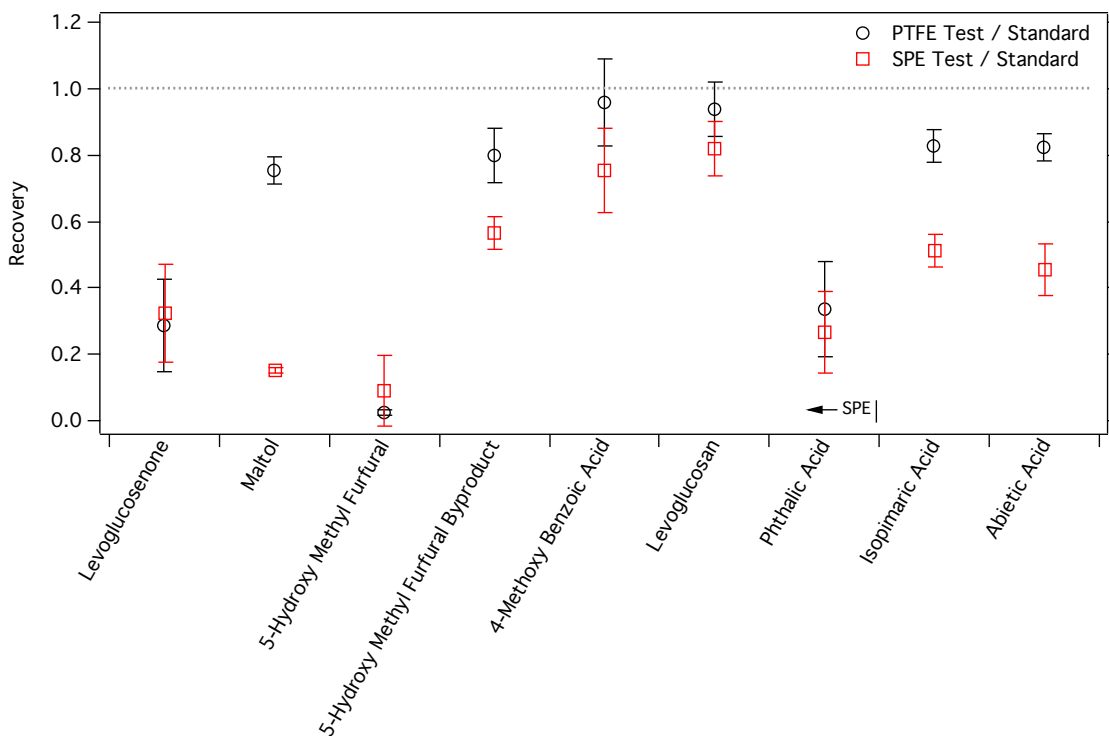


Figure S5. As in Figure S1, for miscellaneous oxygenates. 'Byproduct' refers to the methyl ester product of 5-hydroxy methyl furfural that formed through reaction with methanol during storage of the standard.

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  $\sim 50$  ng/ $\mu$ L. 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  $\sim 50$  ng/ $\mu$ L; 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  $\mu$ L) of the volatile compound solutions with varying amounts of the lower volatility mixture (from 0-400  $\mu$ L). The mass of the absorbing phase (assuming no volatilization during drying) ranged from 0 - 122  $\mu$ g; for

comparison the mass of the standard compounds used in each SPE and PTFE tests was  $\sim 87$   $\mu\text{g}$  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 ( $\pm 1\sigma$ ) of each volatile standard compound as a function of the available absorbing mass.

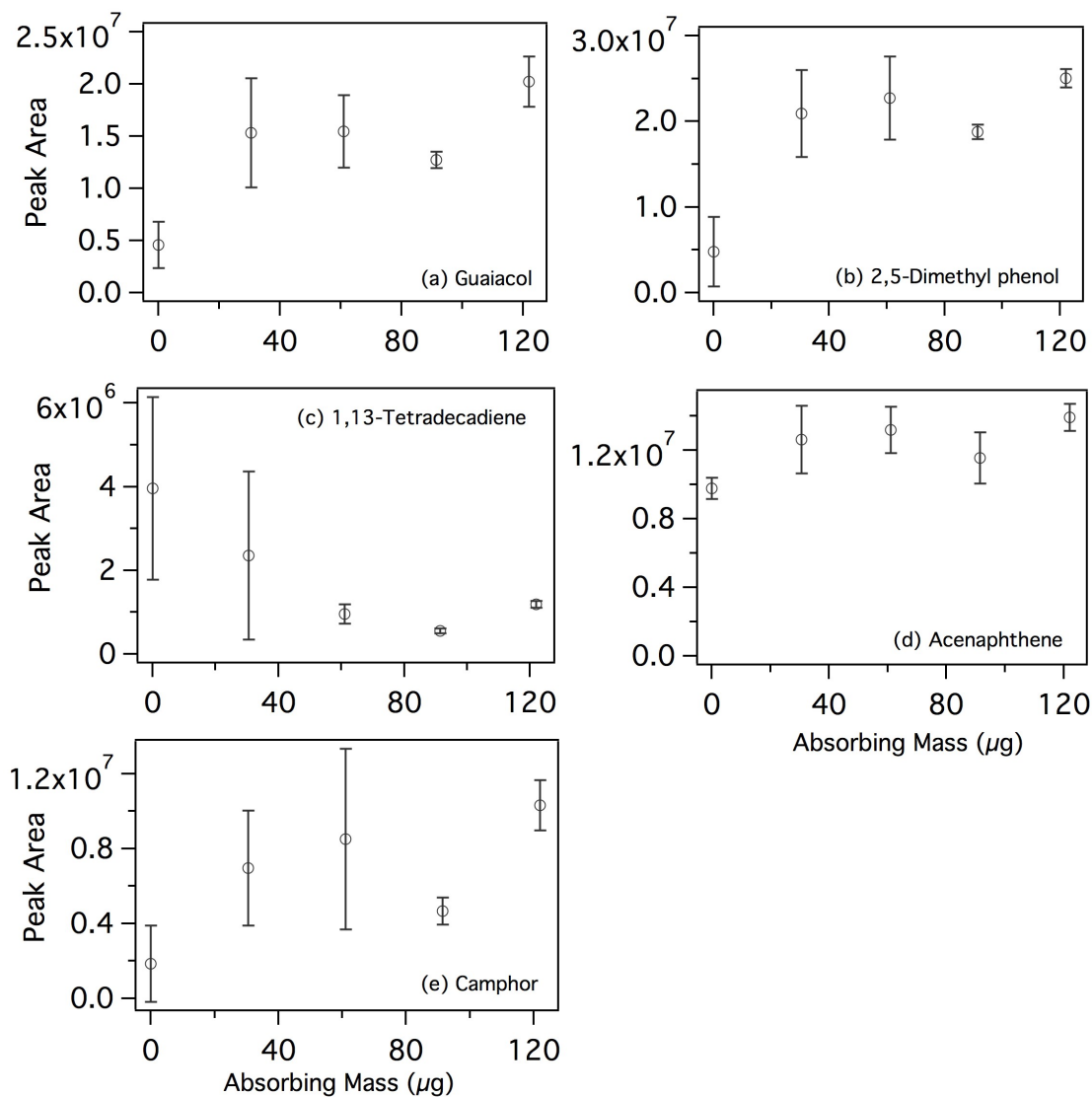


Figure S6. The effect of absorbing mass on the recovery of volatile analytes.

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

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  $\mu\text{g}$ ). For example, the relative standard deviations (RSDs) were highest for camphor (Figure S6e), with 44 % and 56 % RSDs at 30 and 60  $\mu\text{g}$  of residue, compared to 15 % and 30 % RSDs at 91 and 122  $\mu\text{g}$  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.

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 $\times$ 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.

## 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).

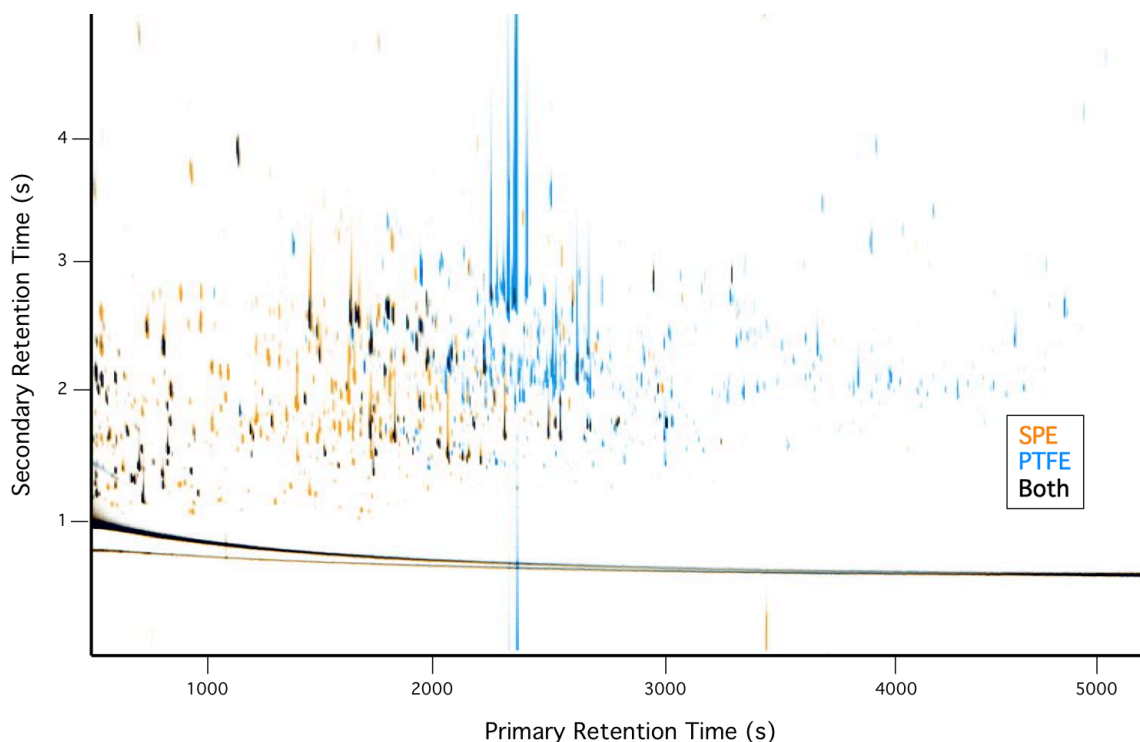


Figure S7. GC×GC chromatogram of the SPE extract (orange) from a Douglas fir rotten log fire (#31) overlaid on the corresponding chromatogram of the PTFE extract (blue). Peaks with black shading were observed in extracts from both filters.

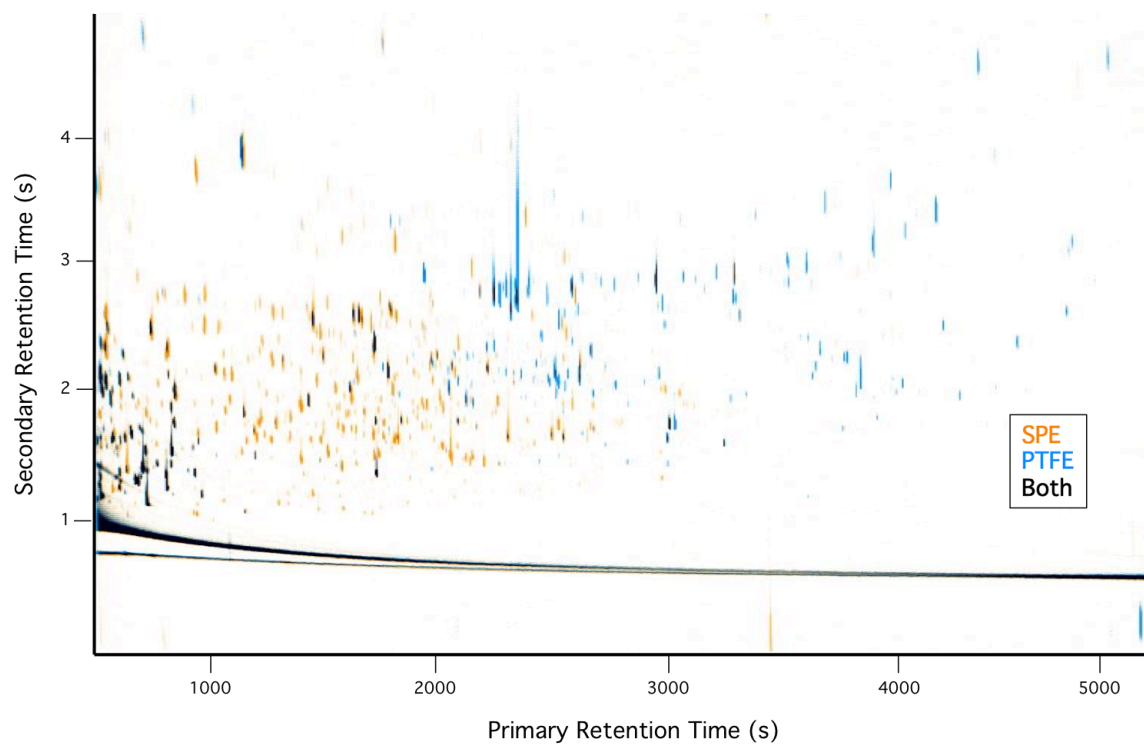


Figure S8. As in Figure S7, for an Engelmann spruce duff fire (#36).

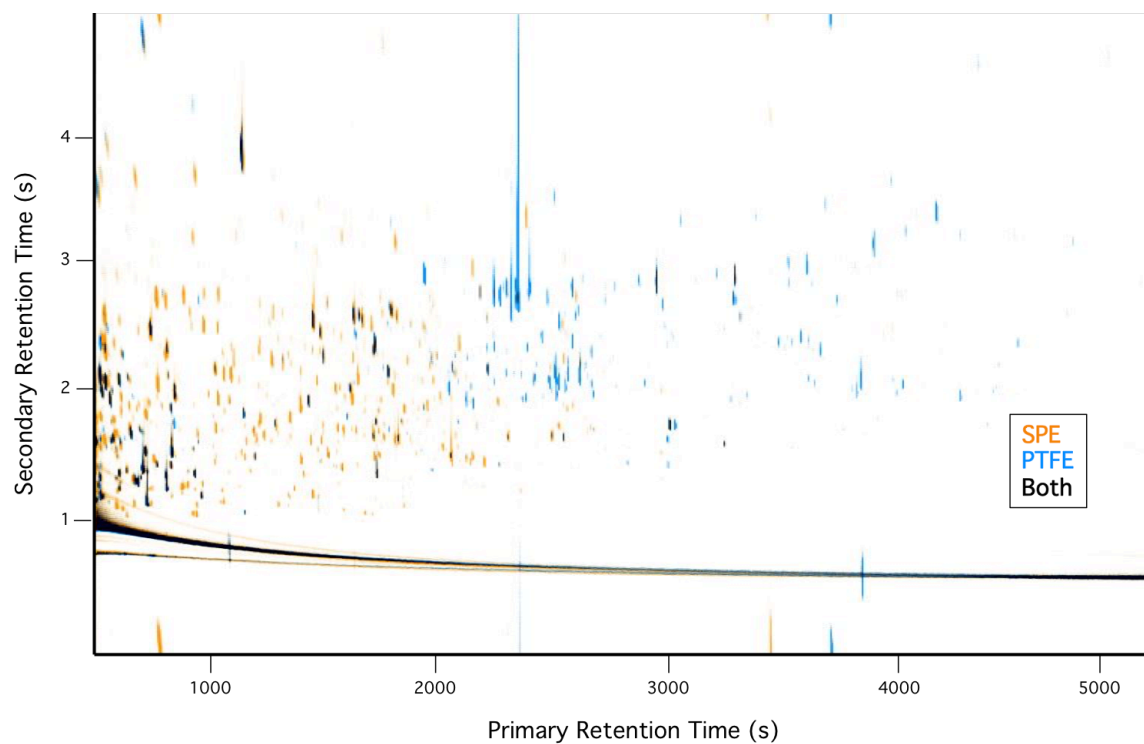


Figure S9. As in Figure S7, for a Jeffrey pine duff fire (#65).

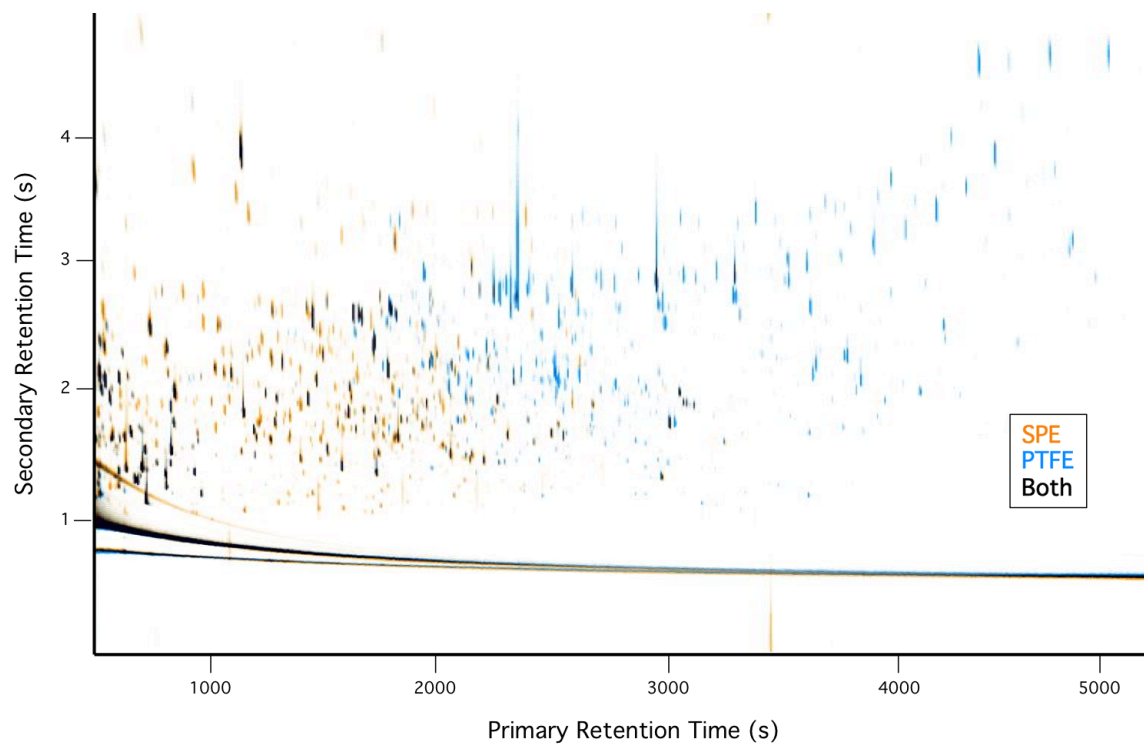


Figure S10. As in Figure S7, for a subalpine fir duff fire (#56).

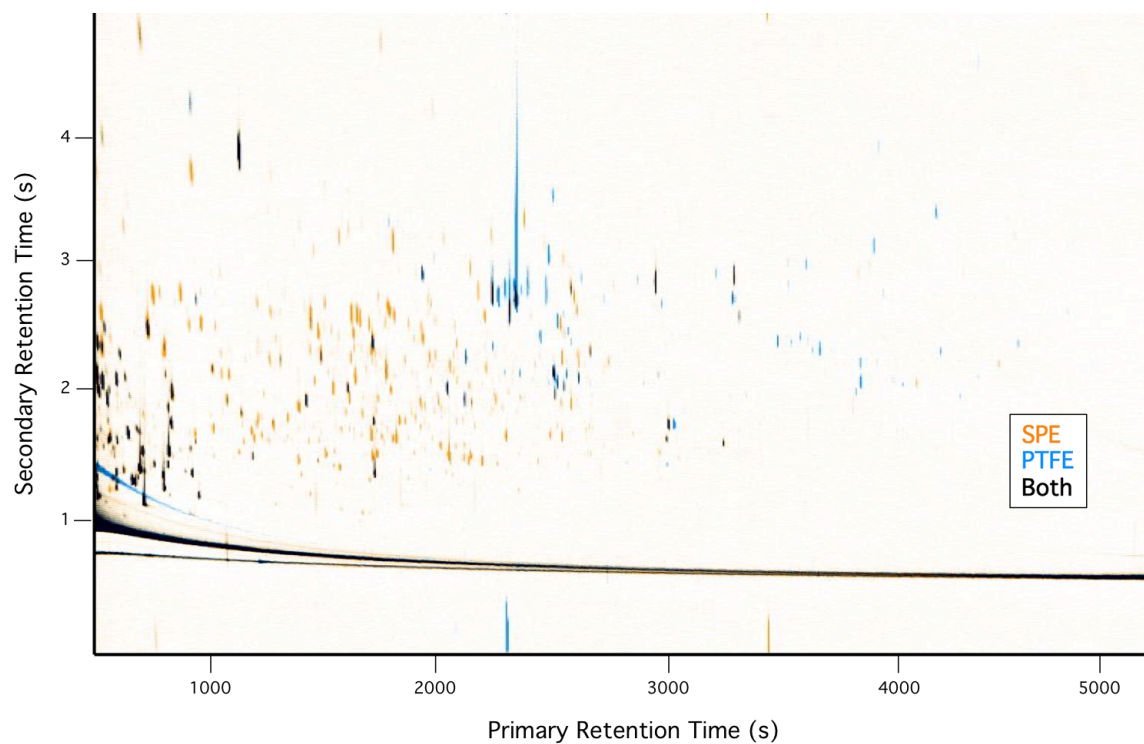


Figure S11. As in Figure S7, for a ponderosa pine fire (#02).

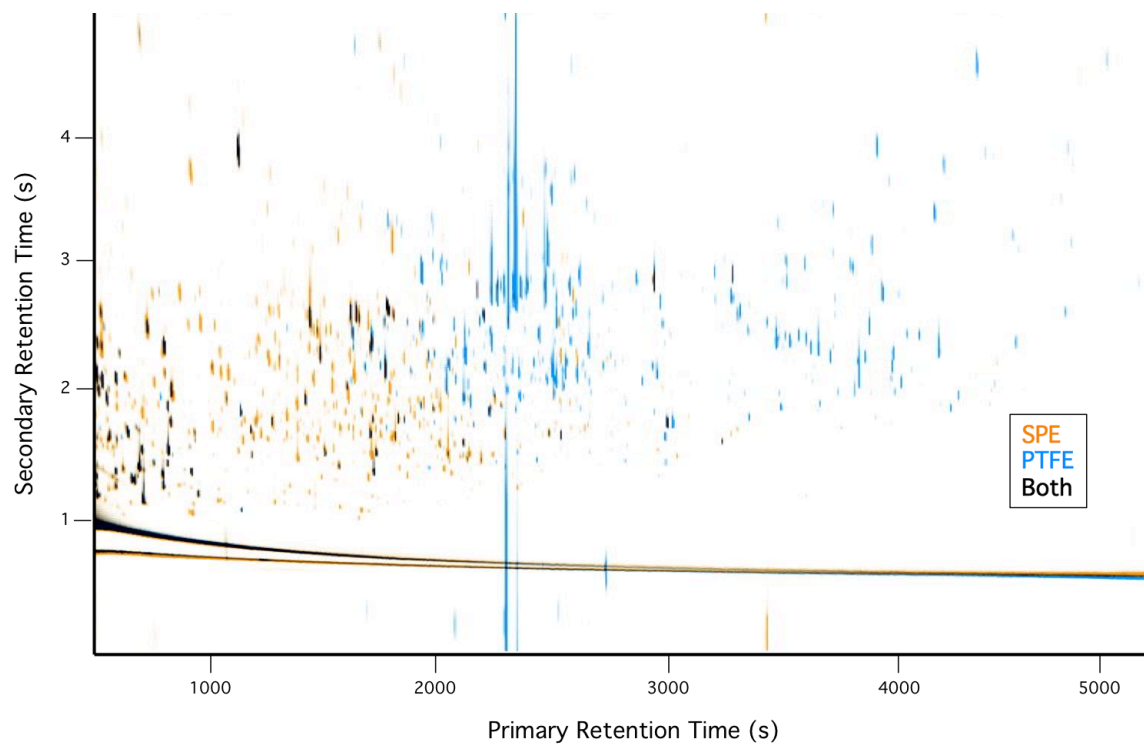


Figure S12. As in Figure S7, for a ponderosa pine fire (#37).

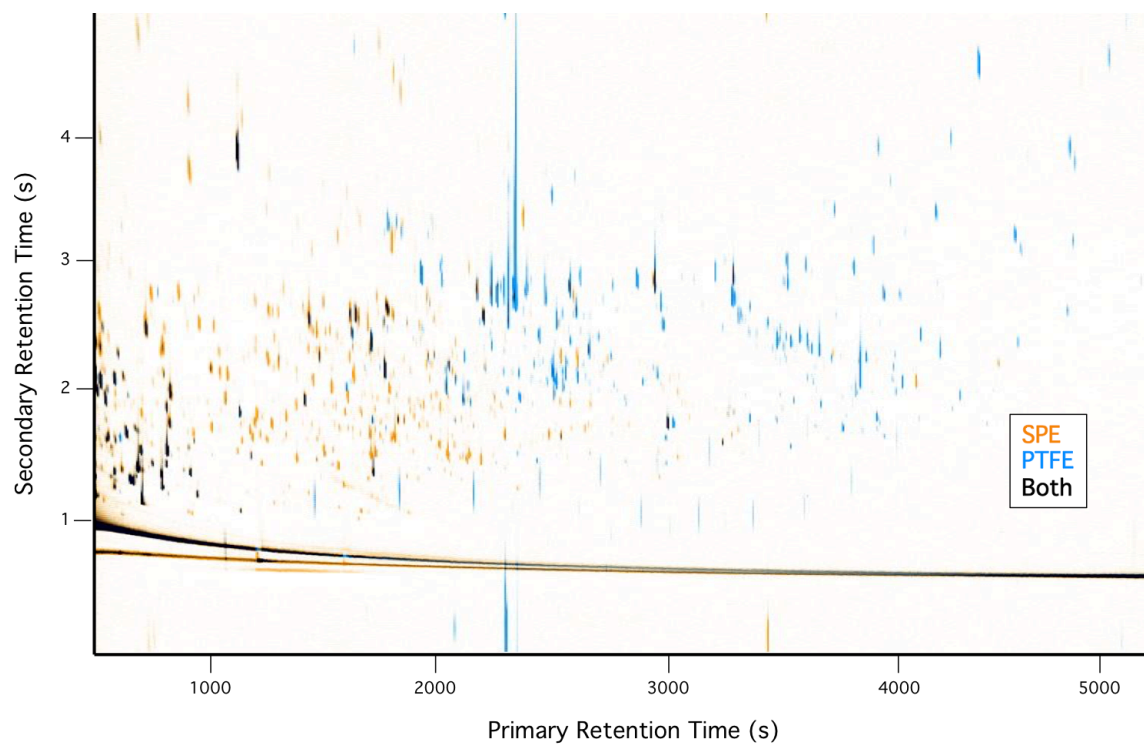


Figure S13. As in Figure S7, for a ponderosa pine litter fire (#16).



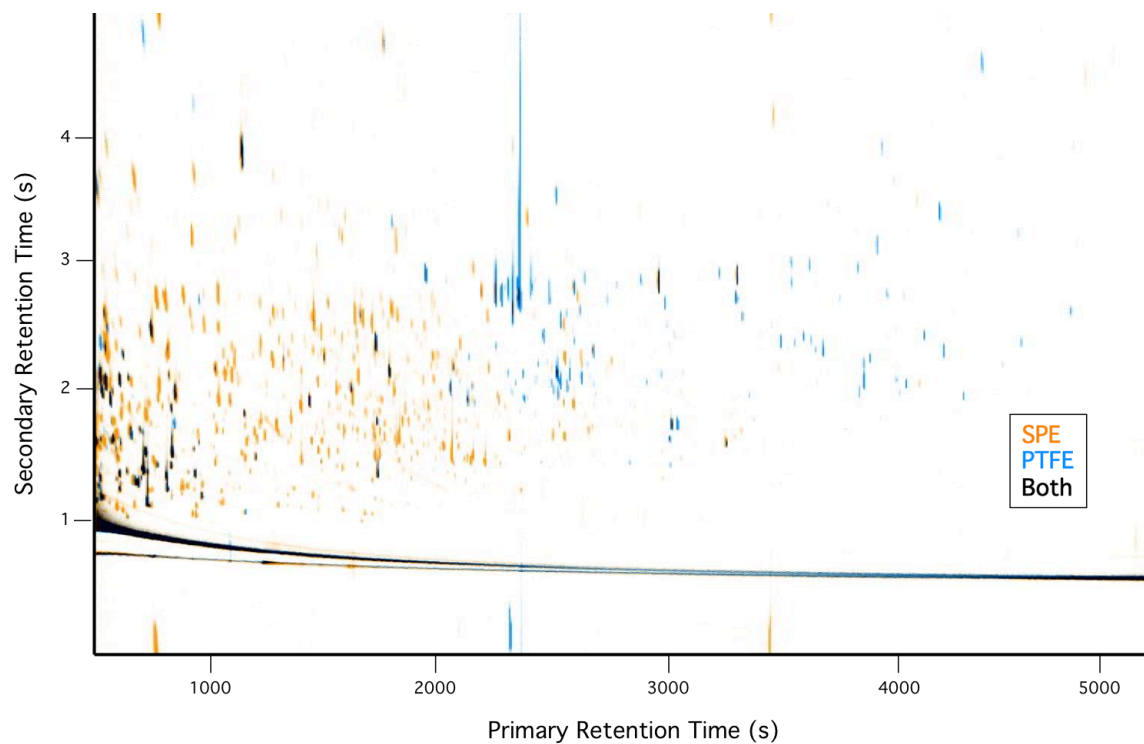


Figure S14. As in Figure S7, for a Douglas fir litter fire (#22).

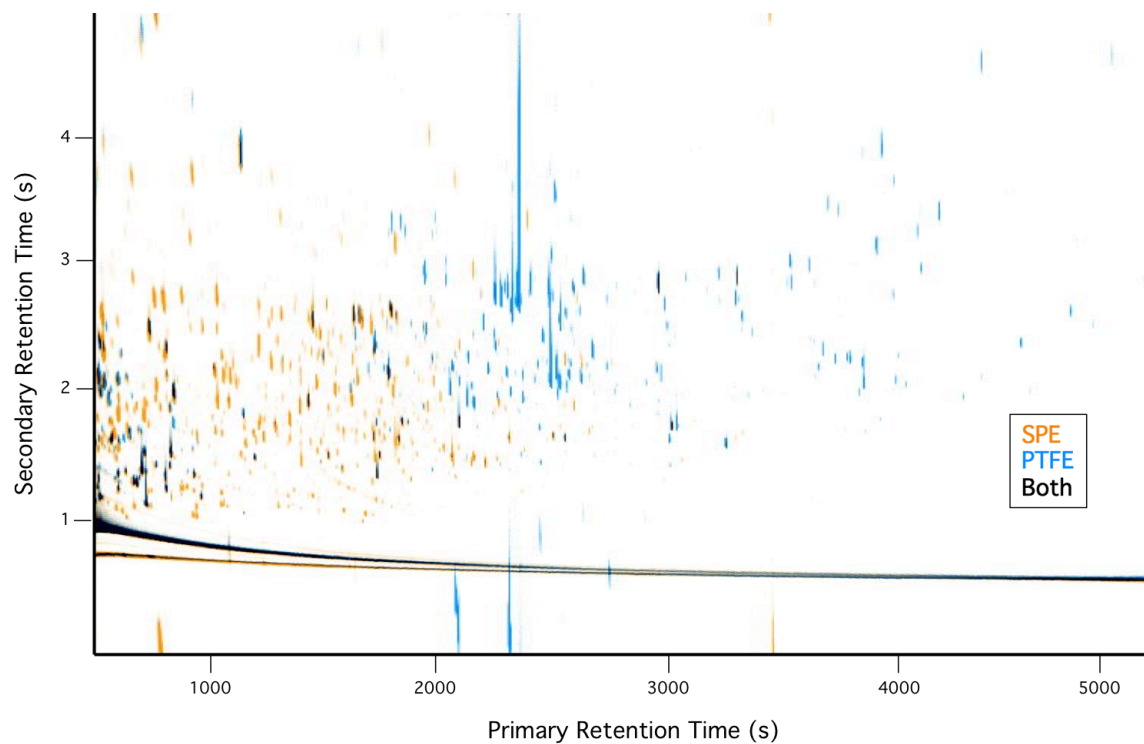


Figure S15. As in Figure S7, for an Engelmann spruce fire (#52).

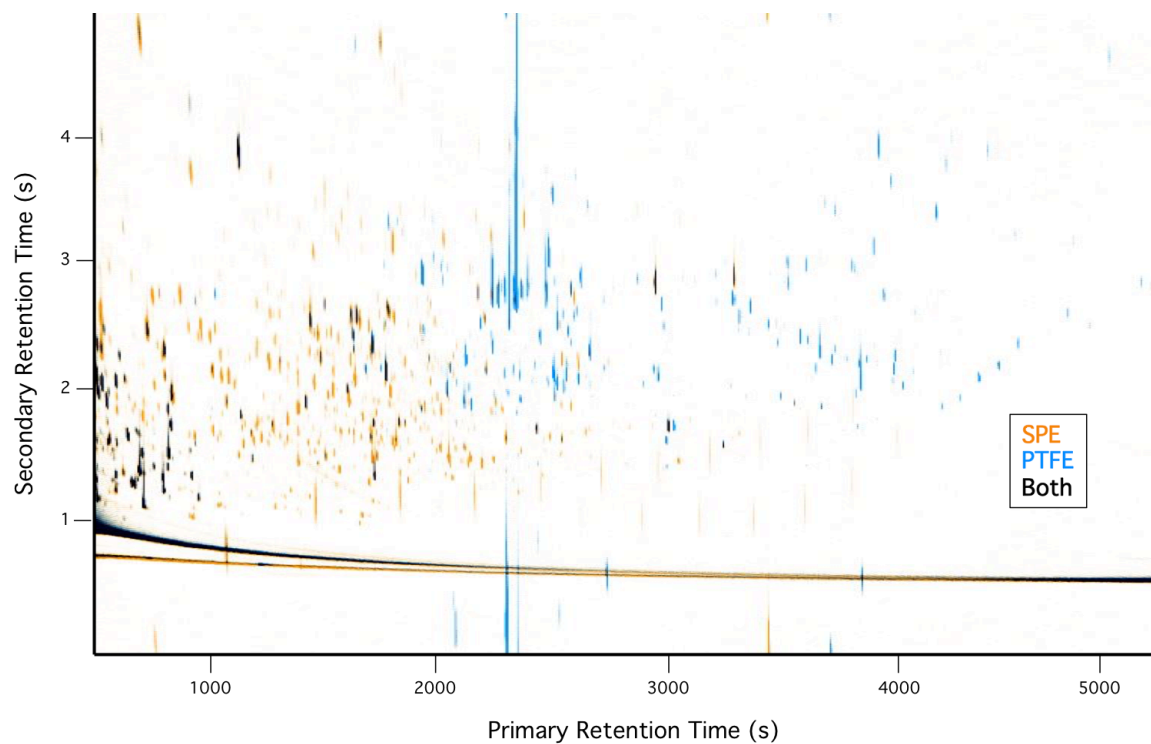


Figure S16. As in Figure S7, for a lodgepole pine fire (#42).

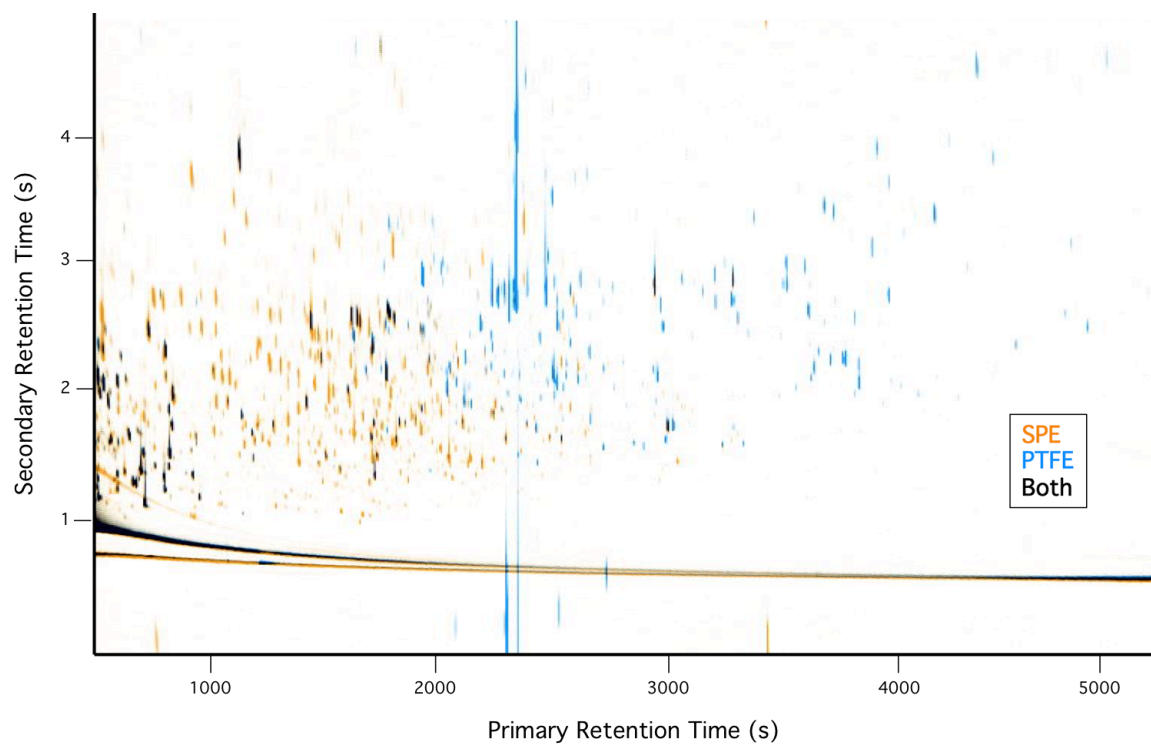


Figure S17. As in Figure S7, for a subalpine fir fire (#47).

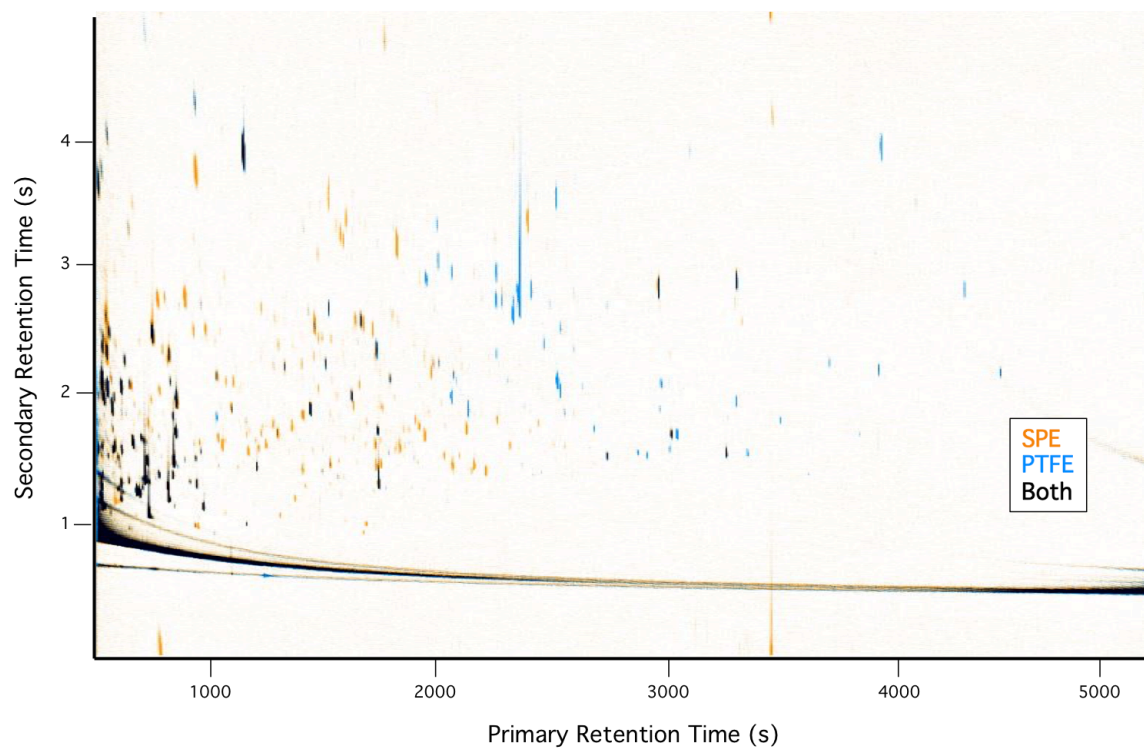


Figure S18. As in Figure S7, for an excelsior fire (#49).

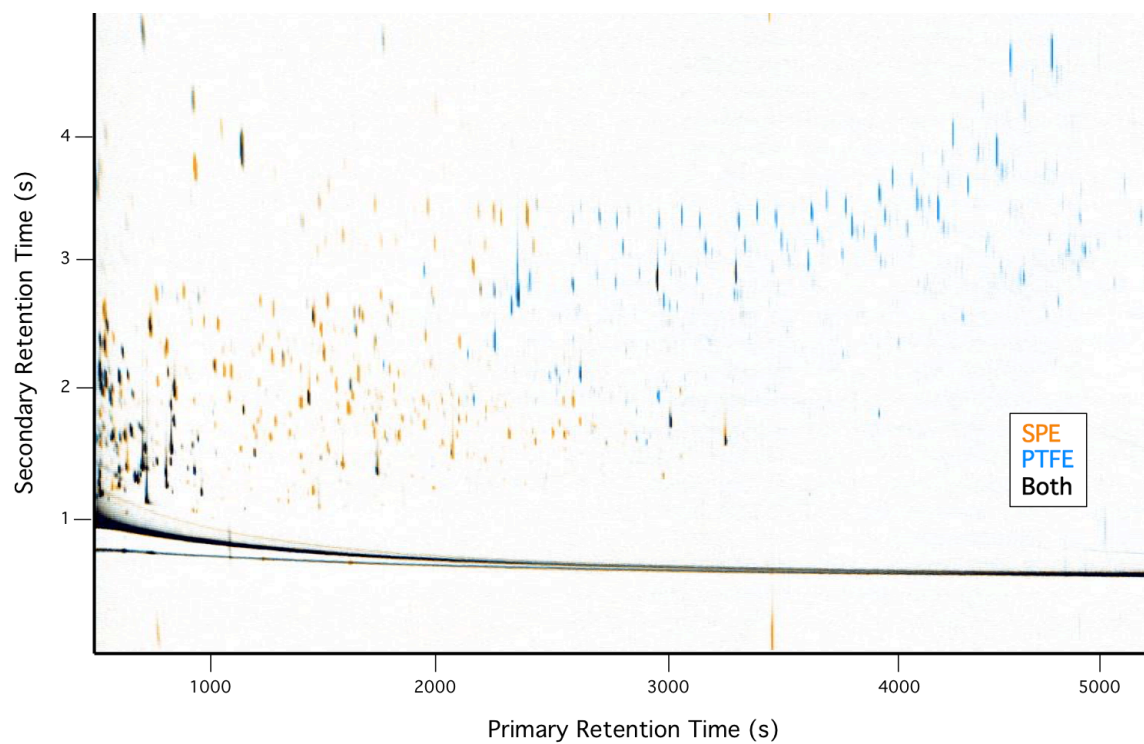


Figure S19. As in Figure S7, for a peat fire (#55).

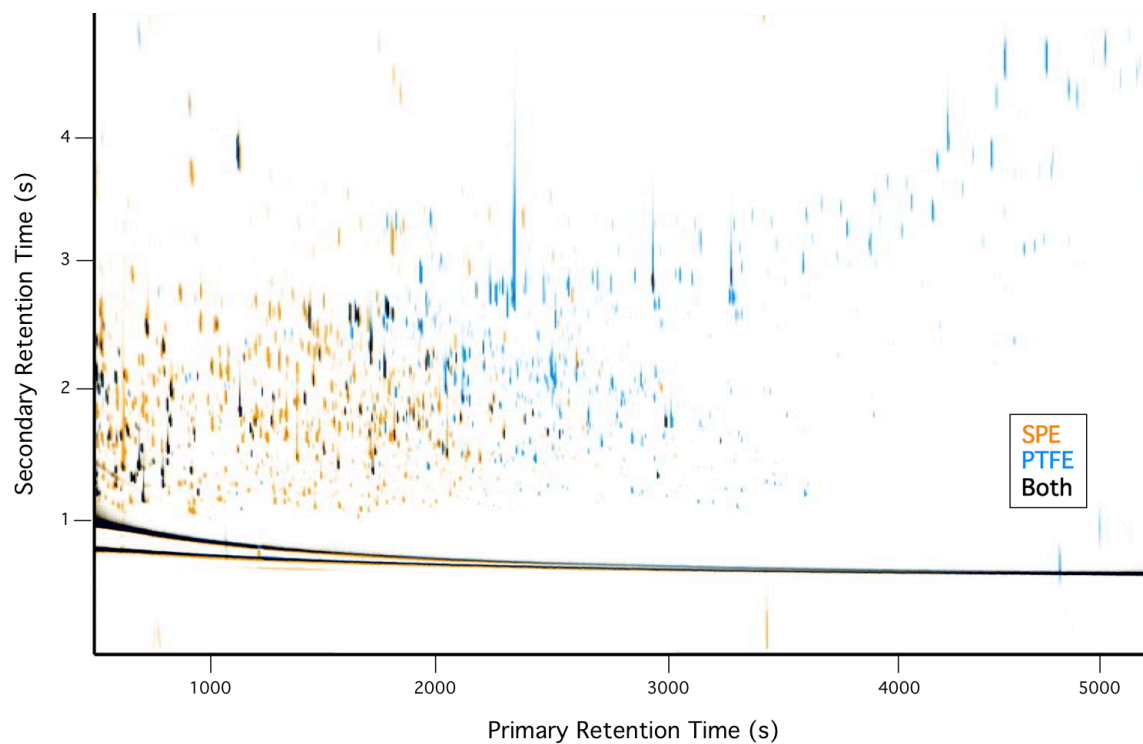


Figure S20. As in Figure S7, for a yak dung fire (#50).

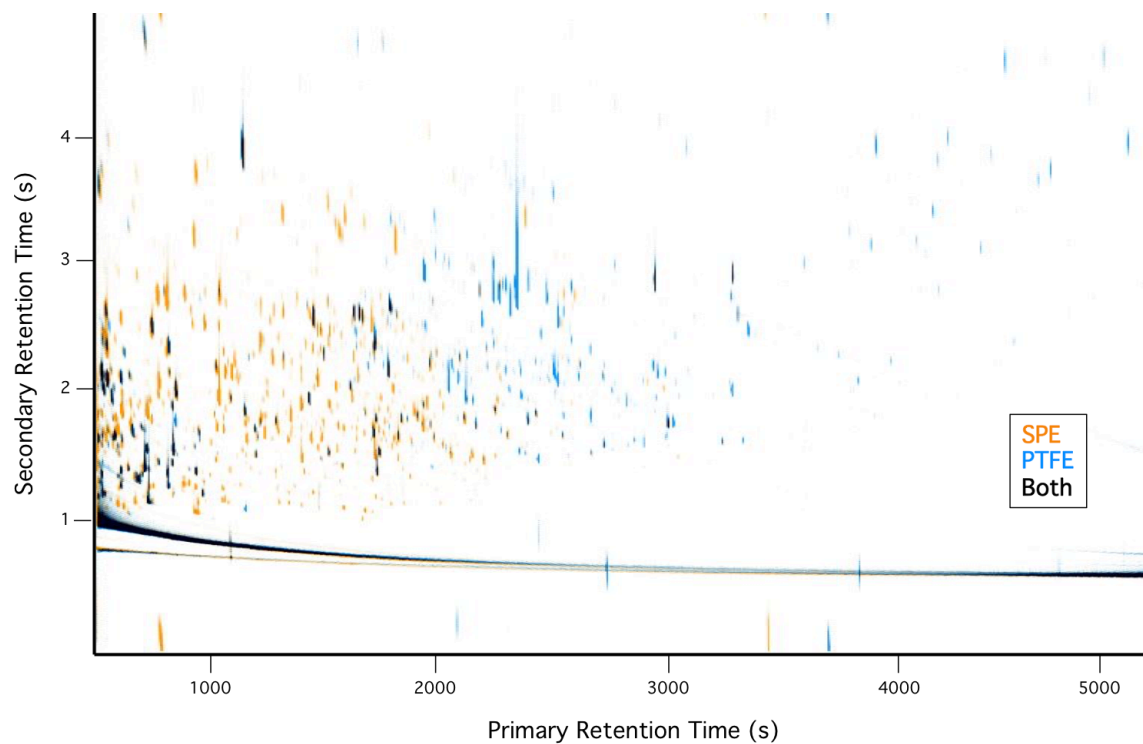


Figure S21. As in Figure S7, for a bear grass fire (#62).

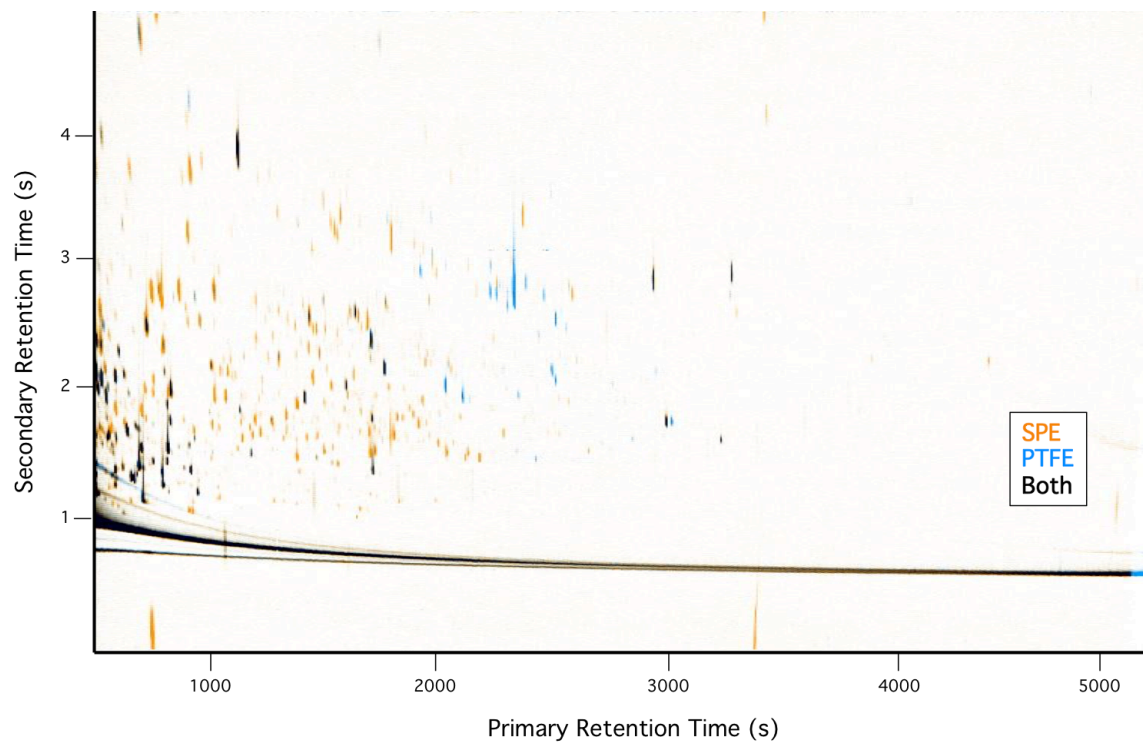


Figure S22. As in Figure S7, for a rice straw fire (#60).

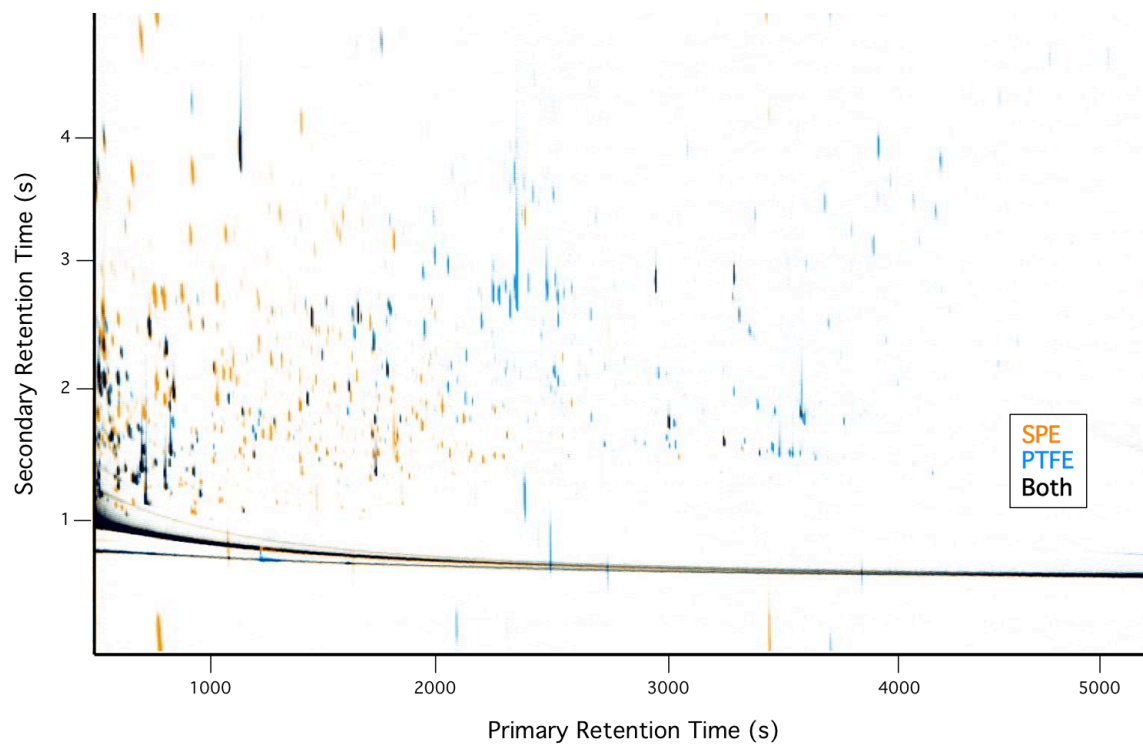


Figure S23. As in Figure S7, for a sagebrush fire (#66).



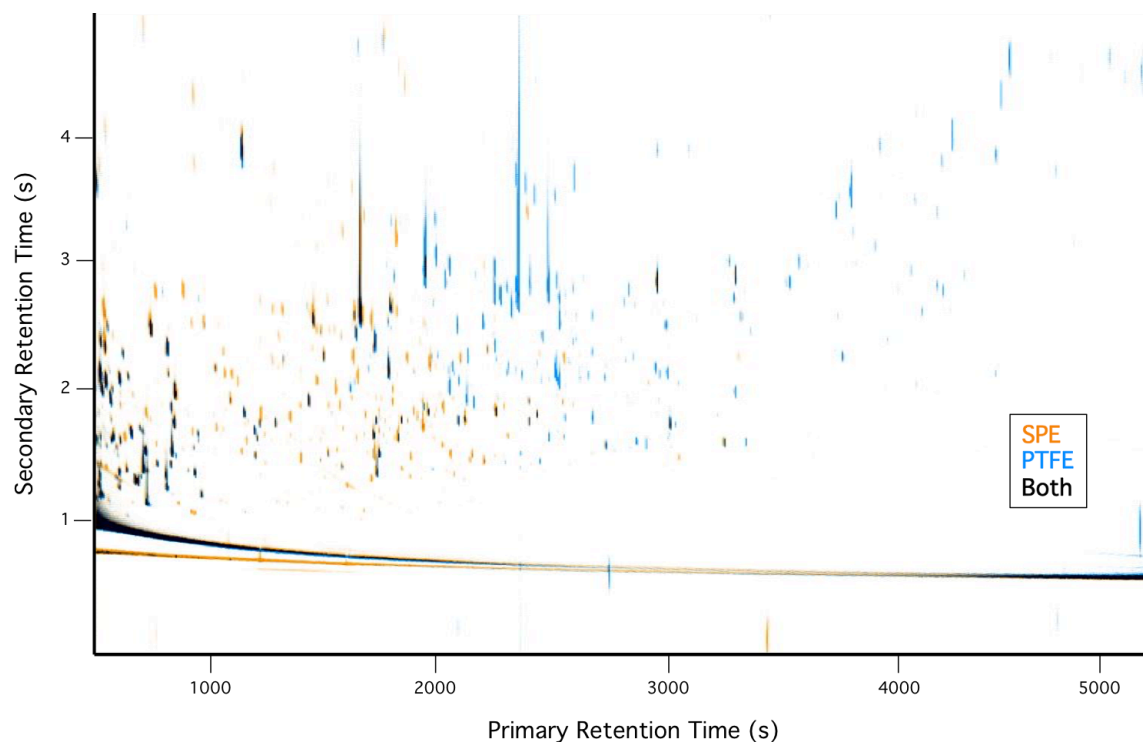


Figure S24. As in Figure S7, for a manzanita fire (#28).

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