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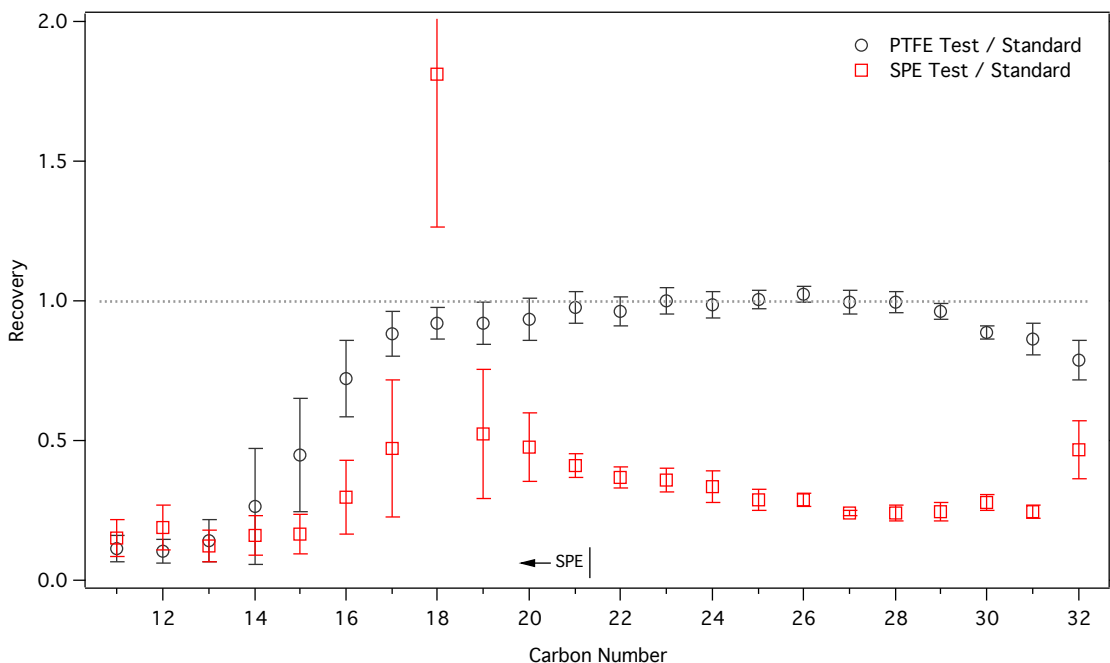
Figure S1. Recoveries of individual *n*-alkanes from the PTFE and SPE tests. Compounds are listed with increasing primary retention time (left to right). The cutoff for standard compounds relevant for biomass-burning SPE samples (i.e., primary retention time <3000s) is indicated.
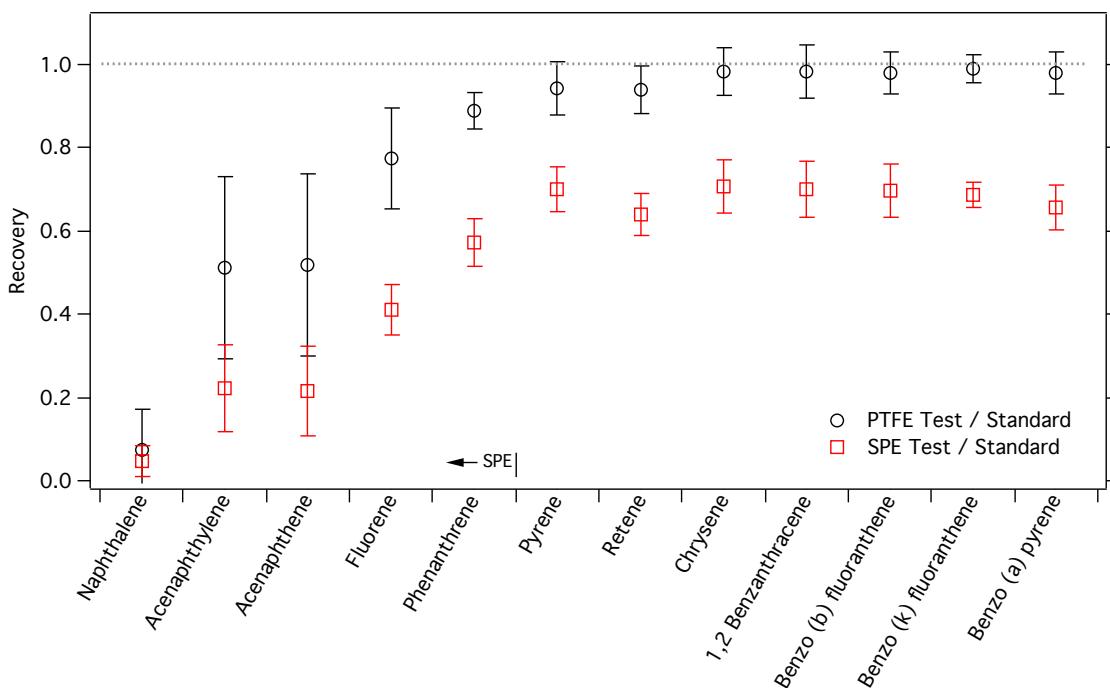

Figure S2. As in Figure S1, for polycyclic aromatic hydrocarbons (PAHs).

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 was otherwise not an issue 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 as a result of 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 $\sim$ 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 ~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).
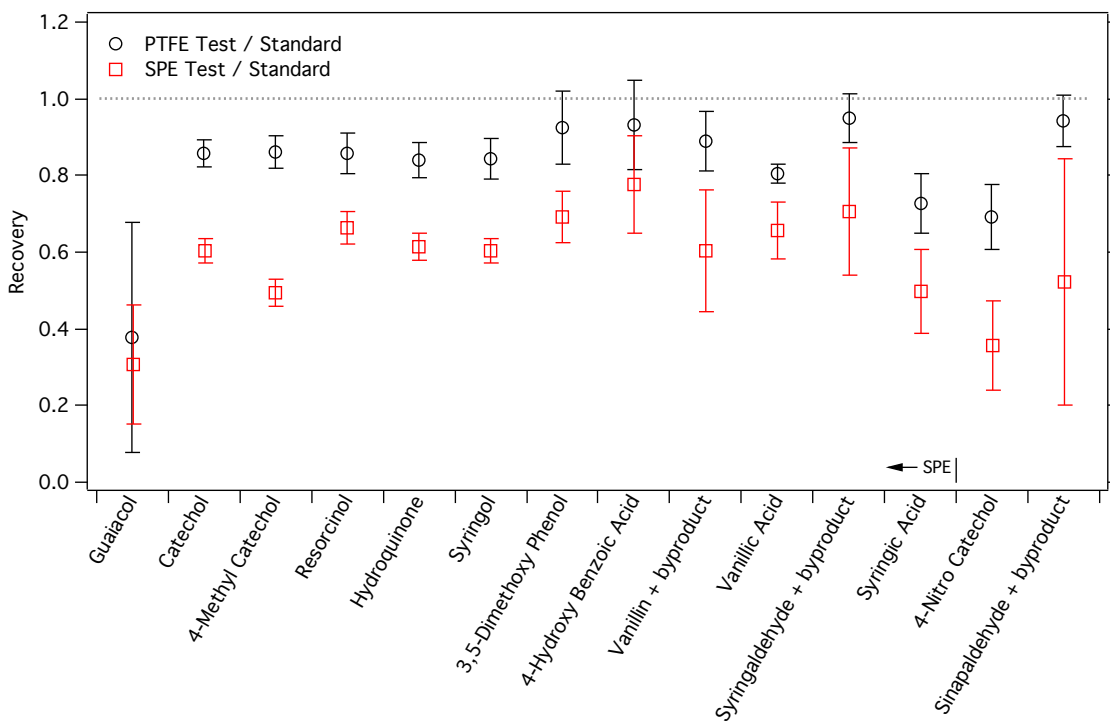
Figure S3. As in Figure S1, for individual phenol derivatives. 'Byproduct' refers to the methyl ester product of the indicated aldehyde that formed through reaction with methanol during storage of the standard.
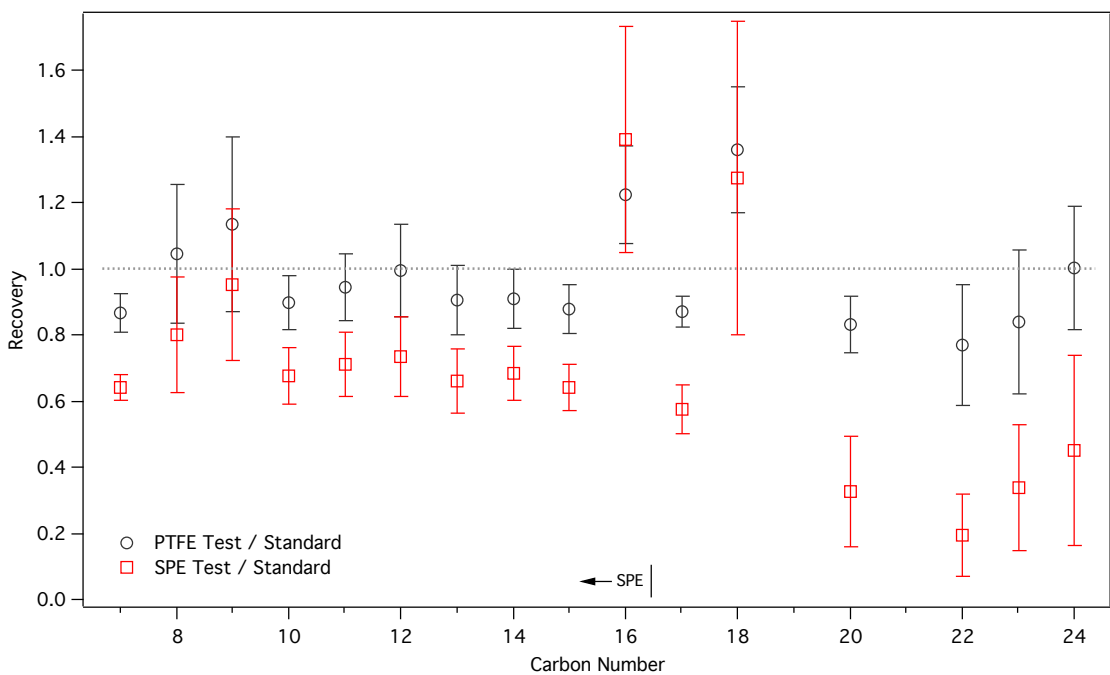

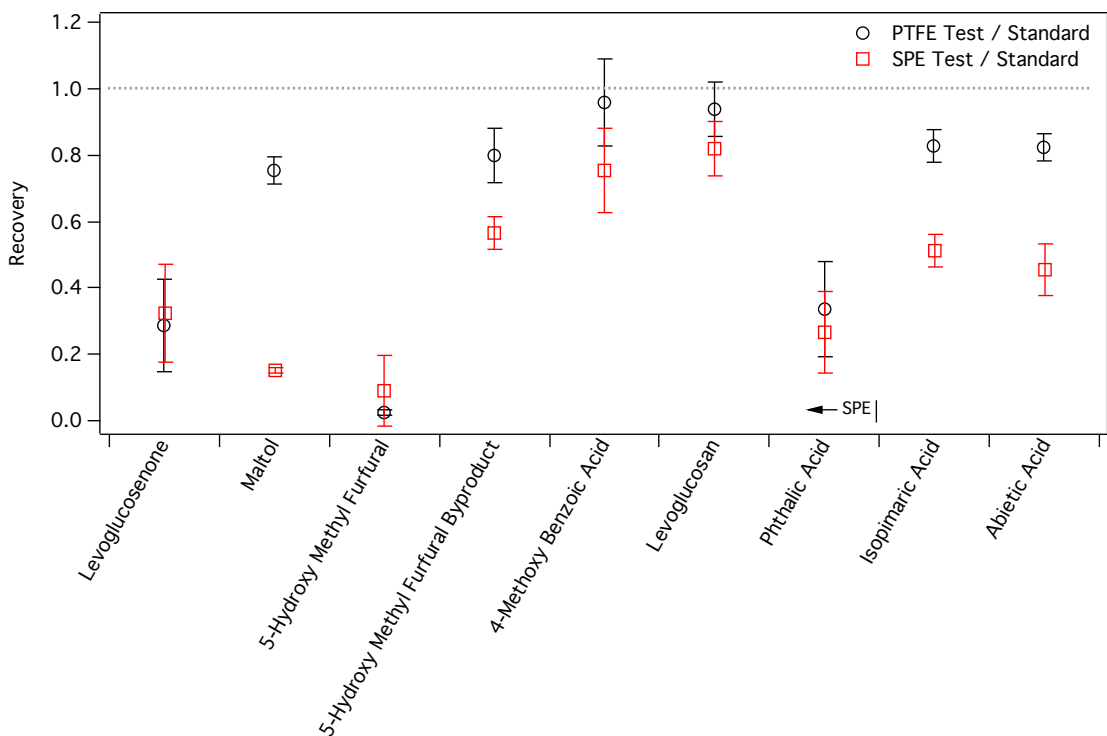Figure S4. As in Figure S1, for individual *n*-alkanoic acids

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.

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).
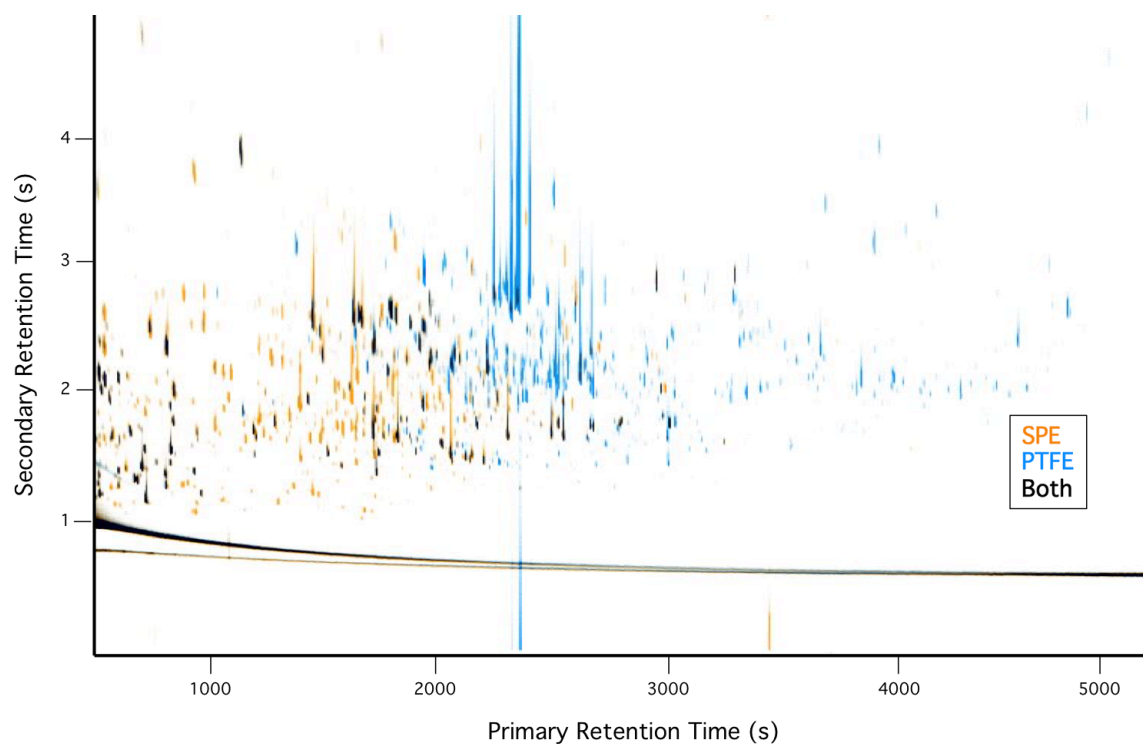
Figure S6. GC×GC chromatogram of the SPE extract (orange) from a Douglas fir rotten log fire (#31) overlaid on the corresponding chromagram of the PTFE extract (blue). Peaks with black shading were observed in extracts from both filters.
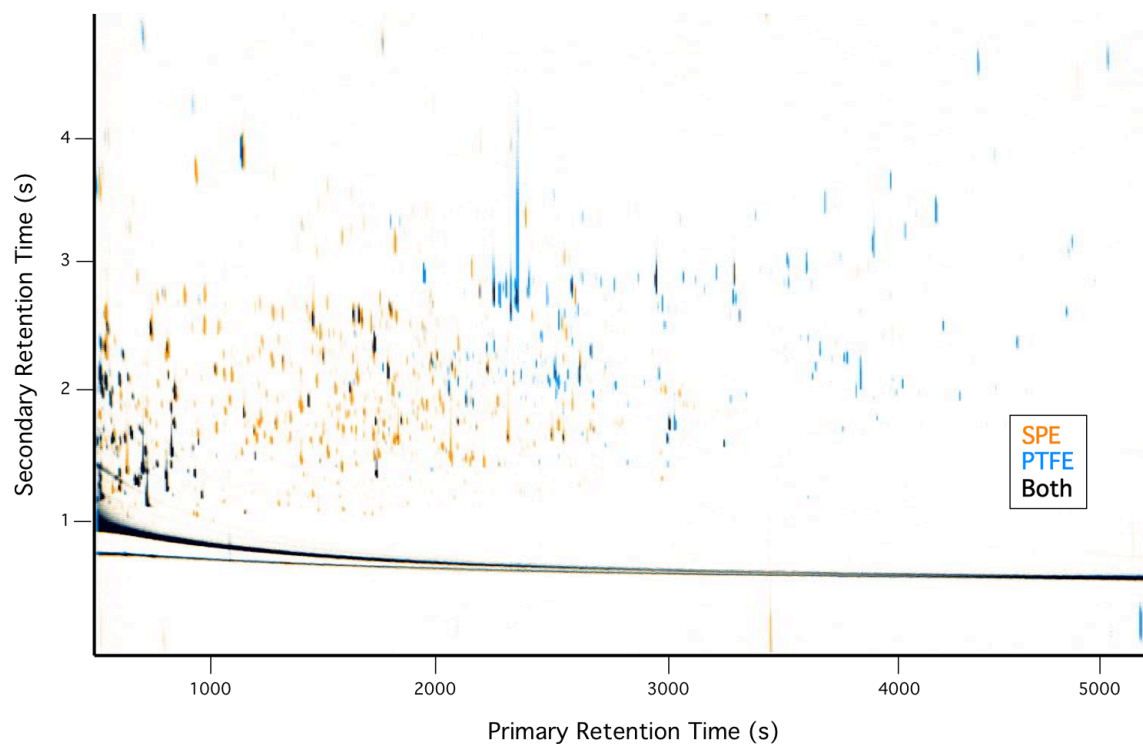
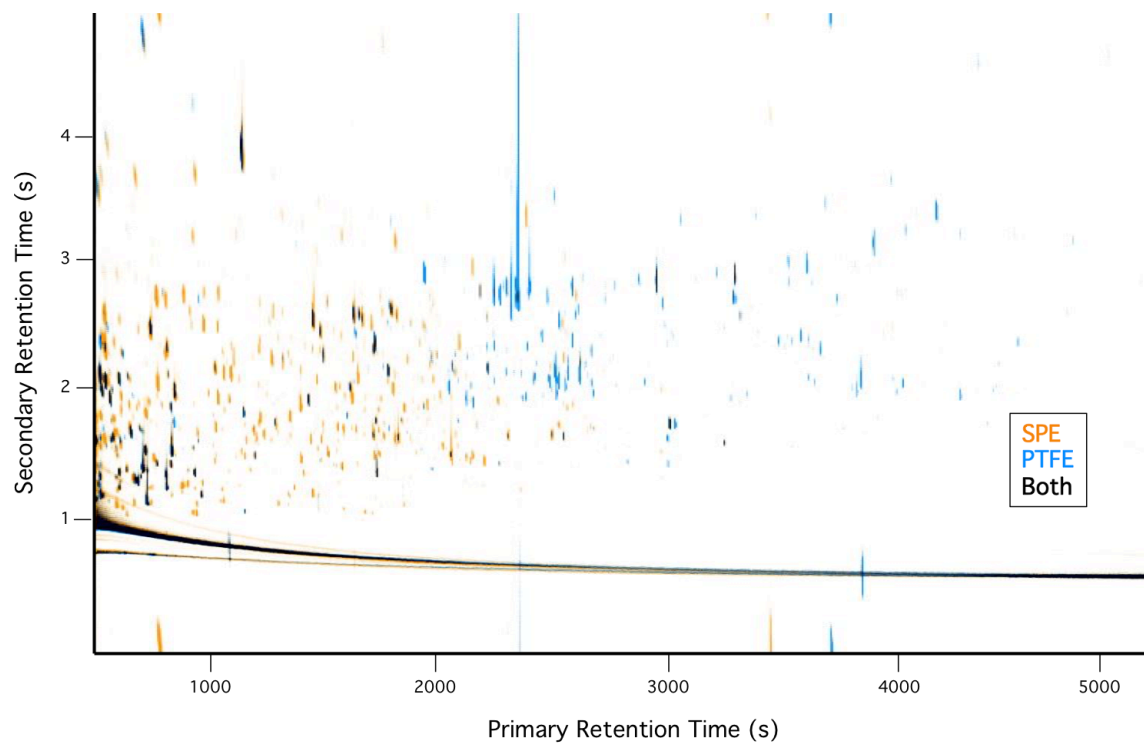Figure S7. As in Figure S6, for an Engelmann spruce duff fire (#36).

Figure S8. As in Figure S6, for a Jeffrey pine duff fire (#65).
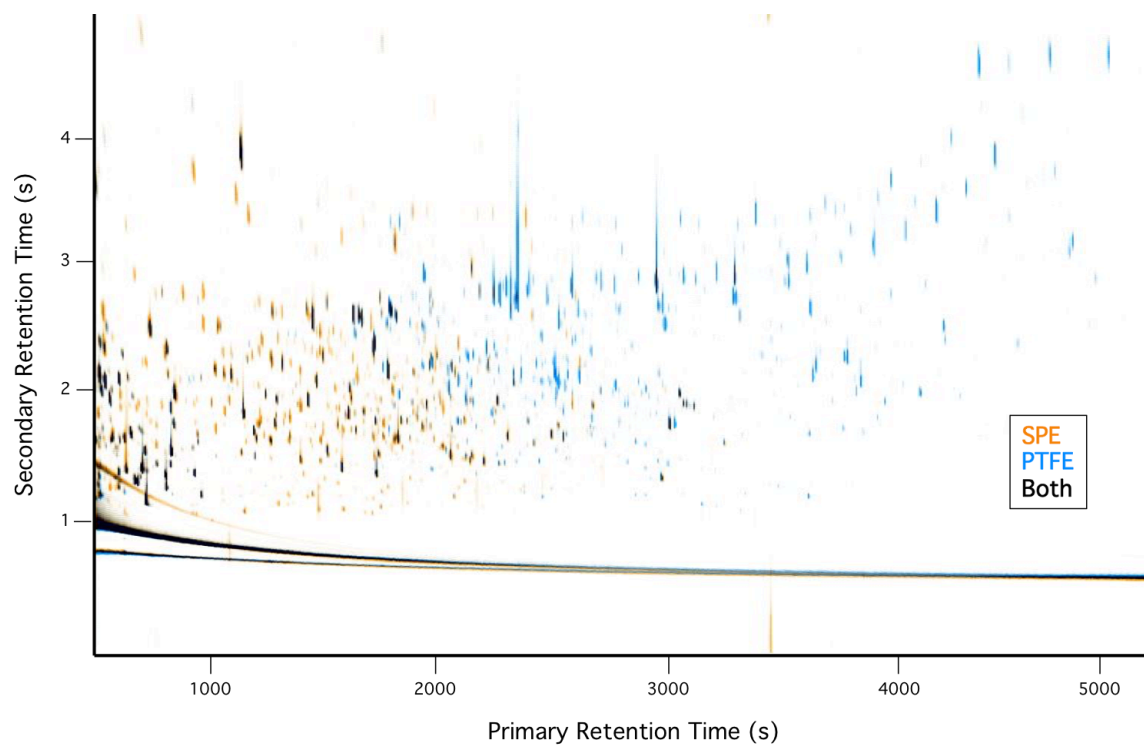

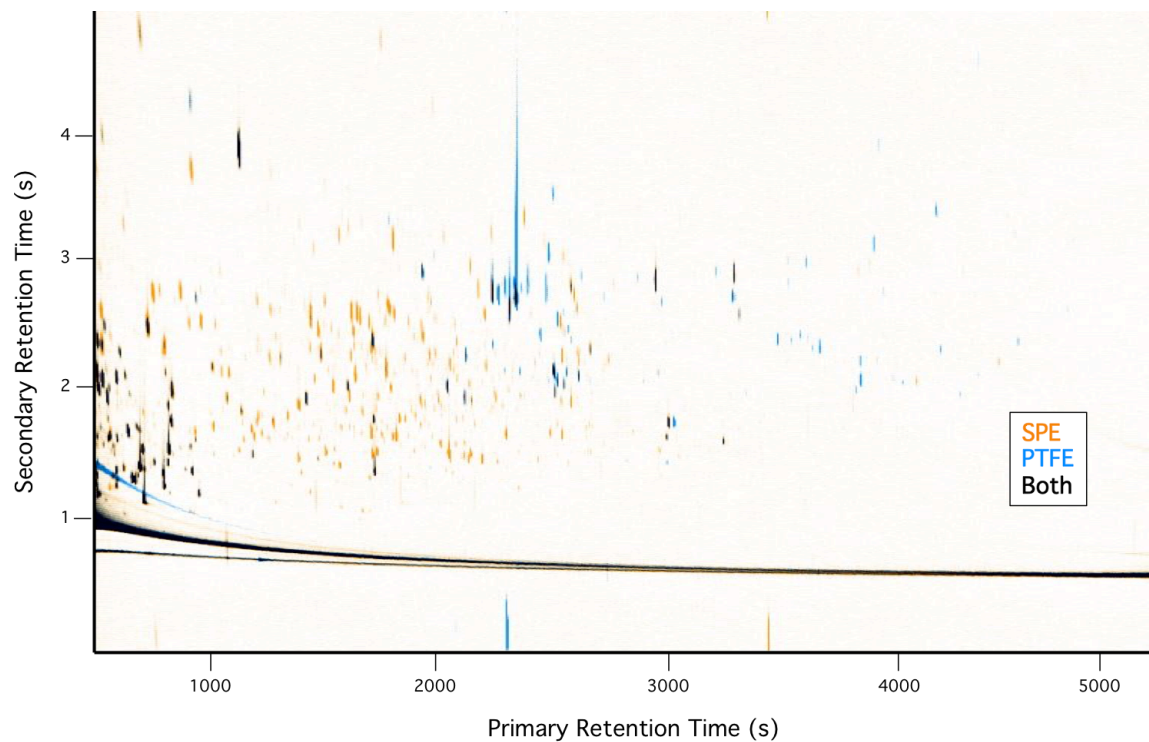Figure S9. As in Figure S6, for a subalpine fir duff fire (#56).

Figure S10. As in Figure S6, for a ponderosa pine fire (#02).
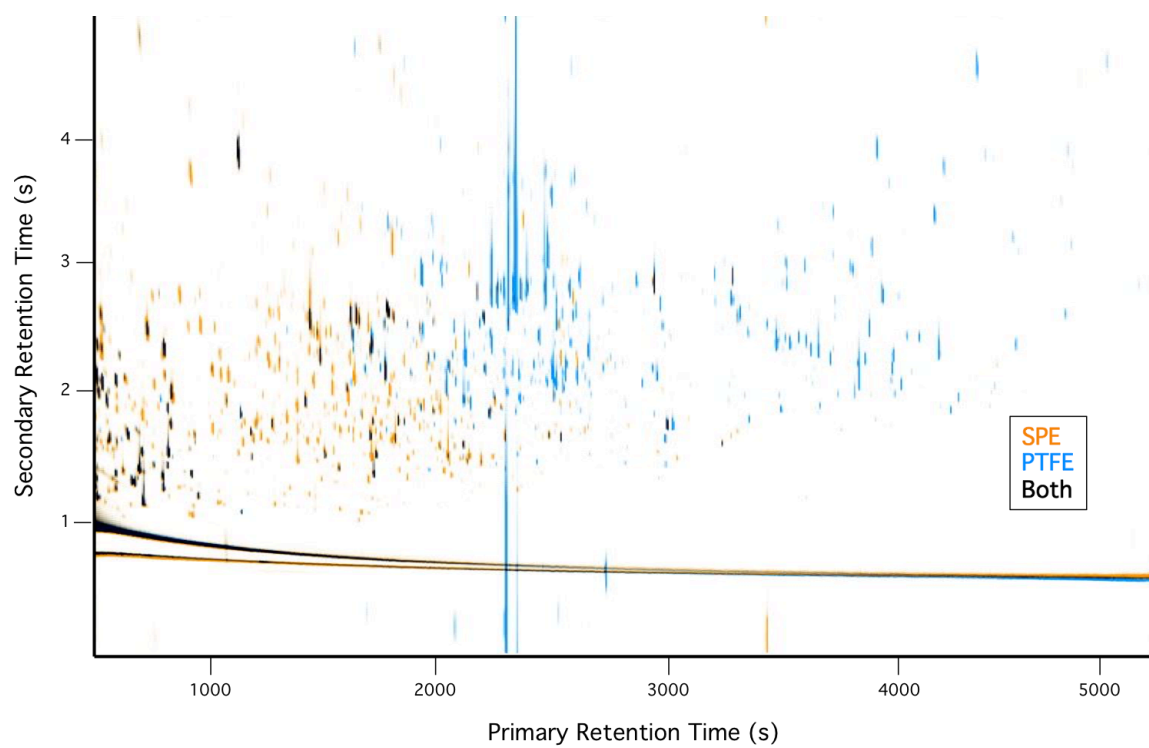
Figure S11. As in Figure S6, for a ponderosa pine fire (#37).
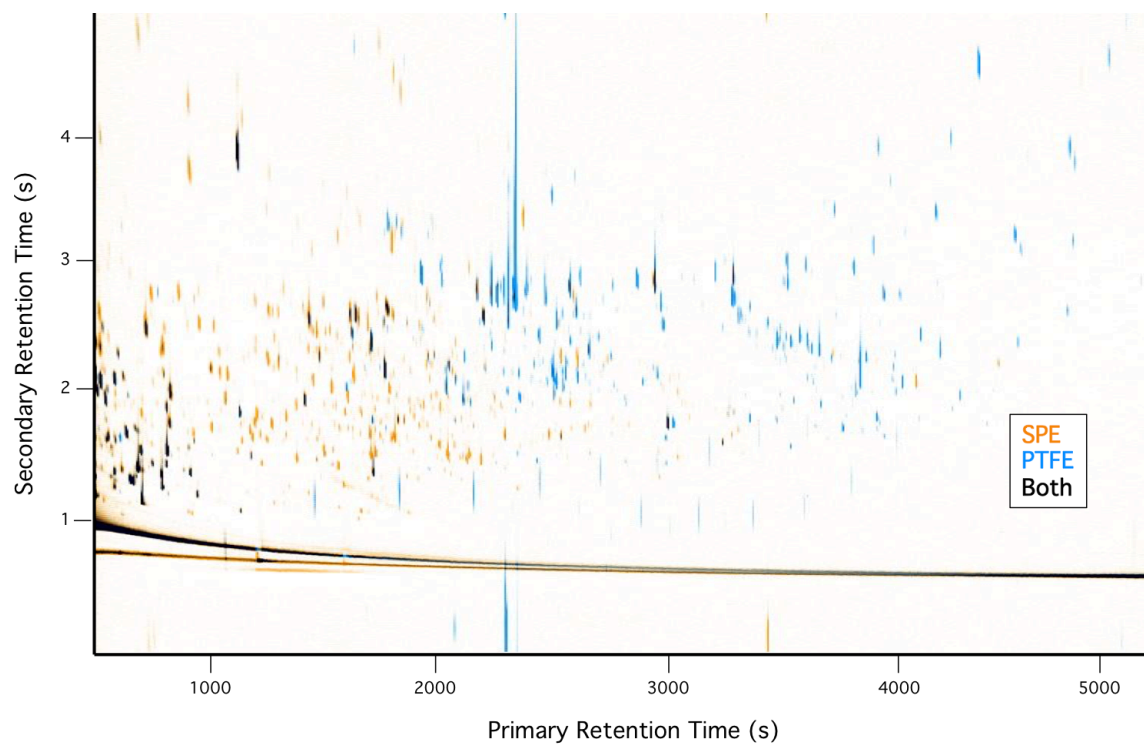
Figure S12. As in Figure S6, for a ponderosa pine litter fire (#16).
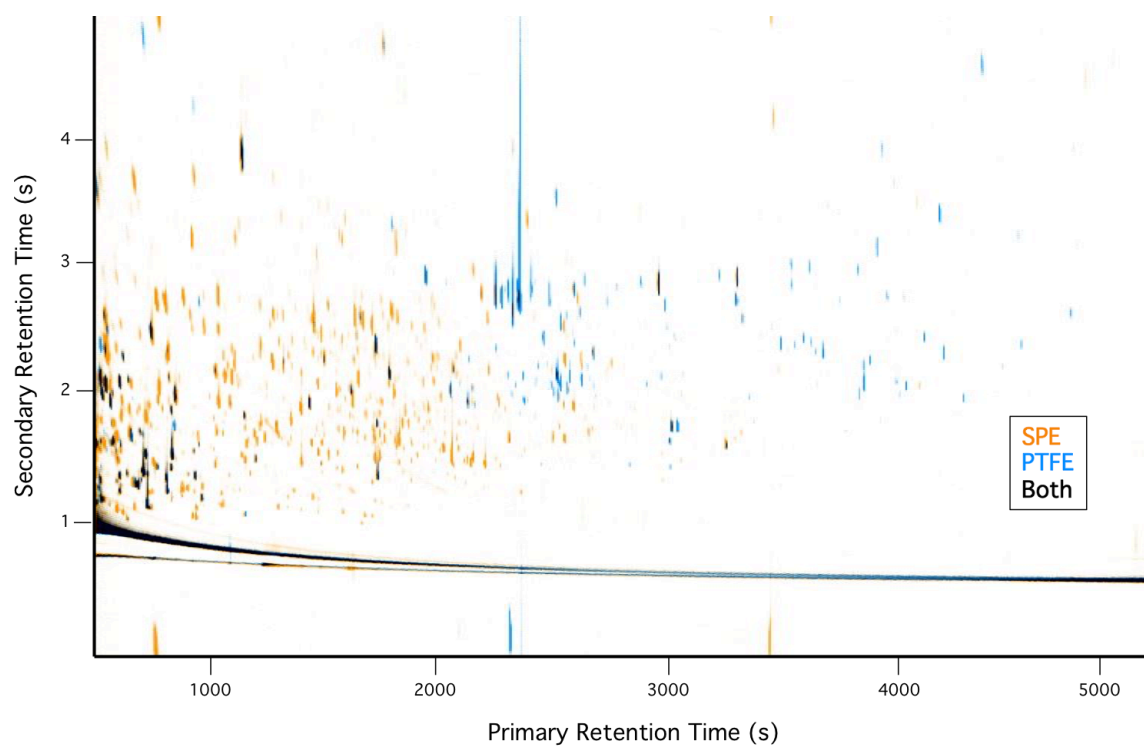
Figure S13. As in Figure S6, for a Douglas fir litter fire (#22).
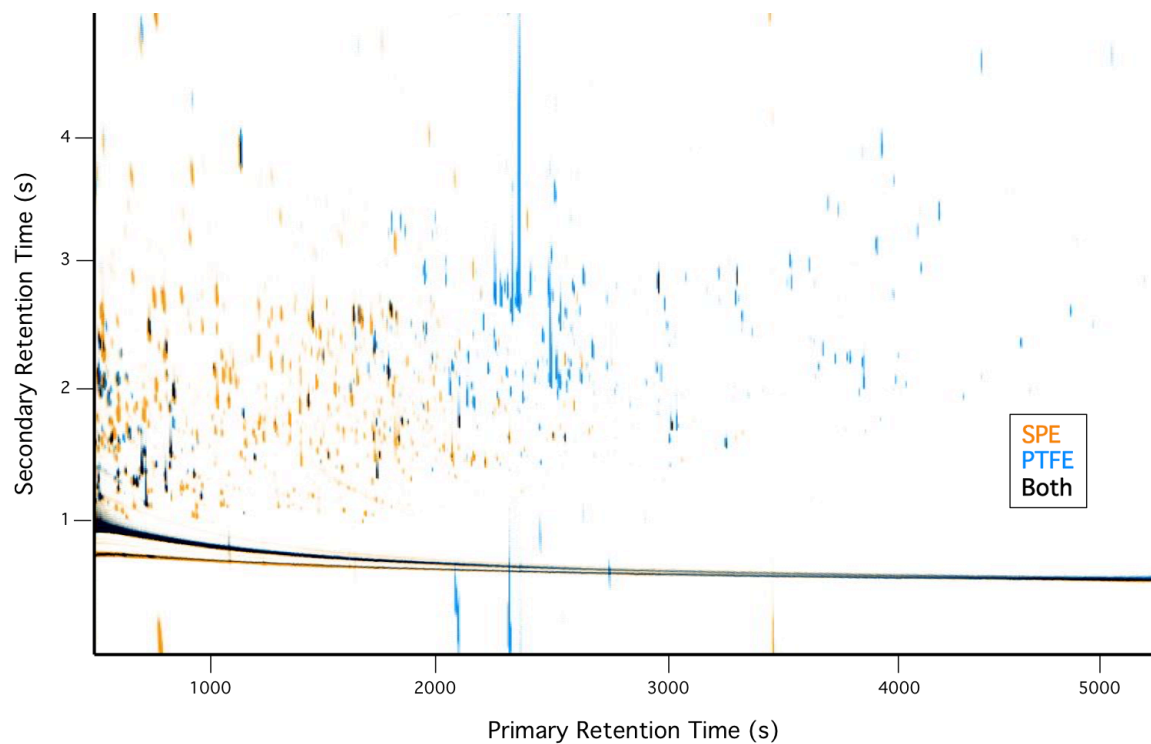
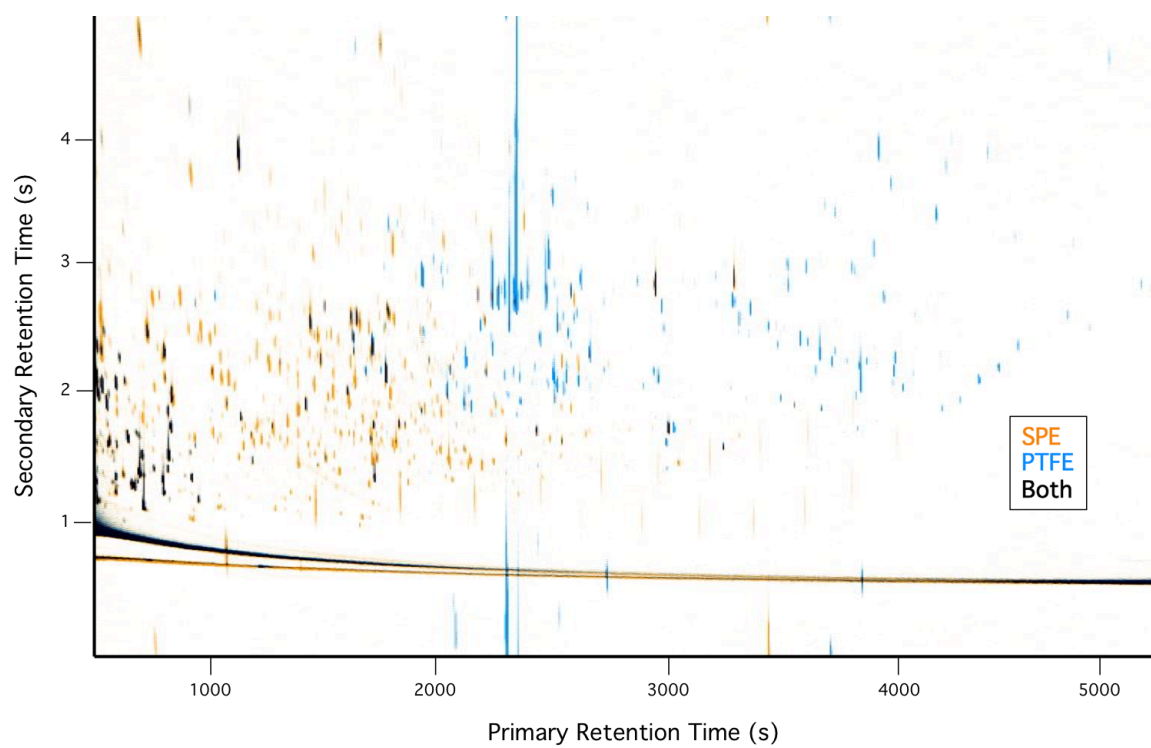Figure S14. As in Figure S6, for an Engelmann spruce fire (#52).

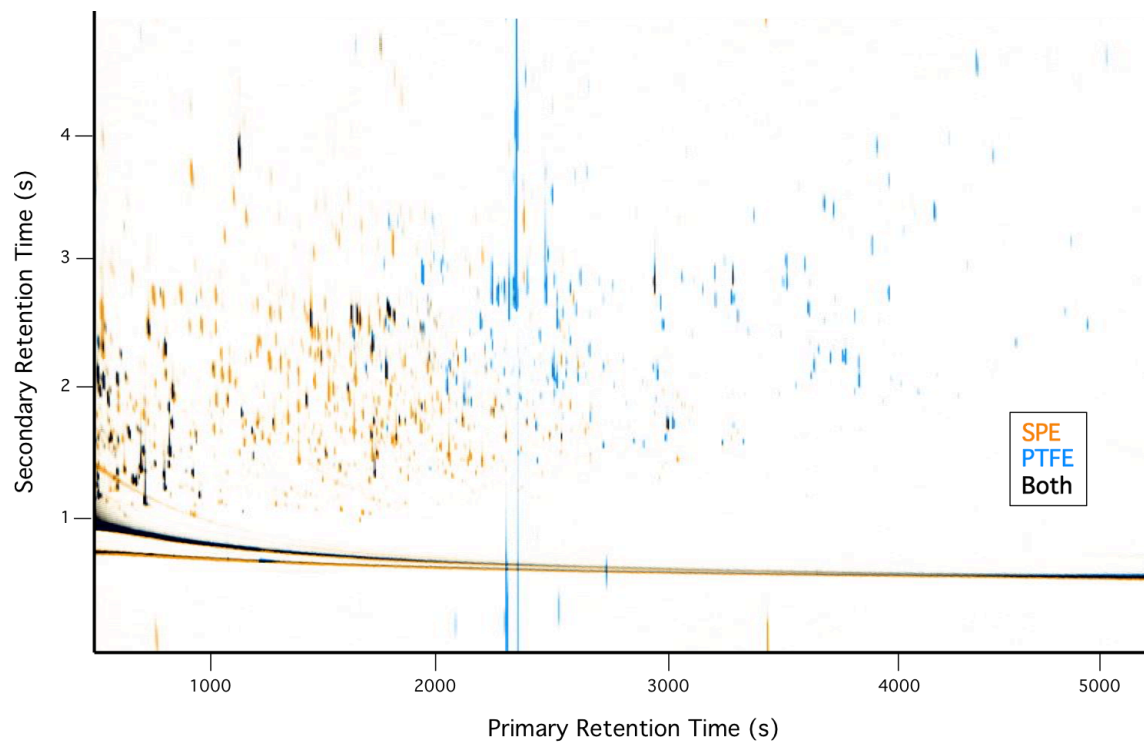Figure S15. As in Figure S6, for a lodgepole pine fire (#42).

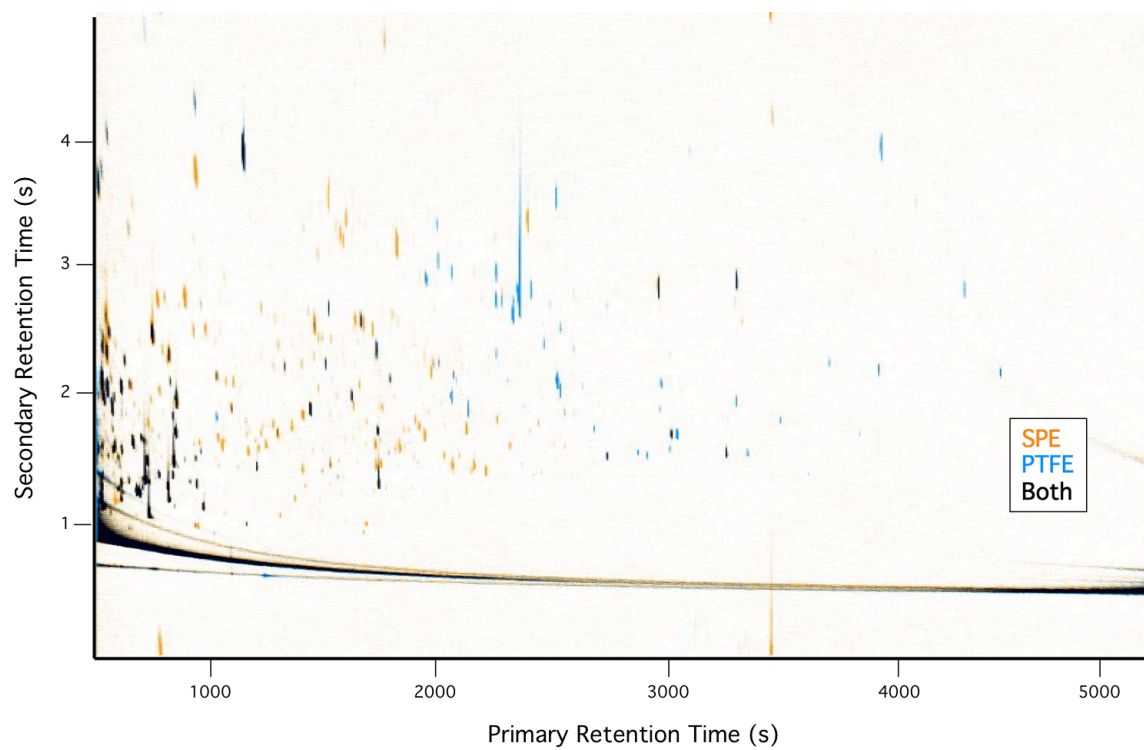Figure S16. As in Figure S6, for a subalpine fir fire (#47).

Figure S17. As in Figure S6, for an excelsior fire (#49).
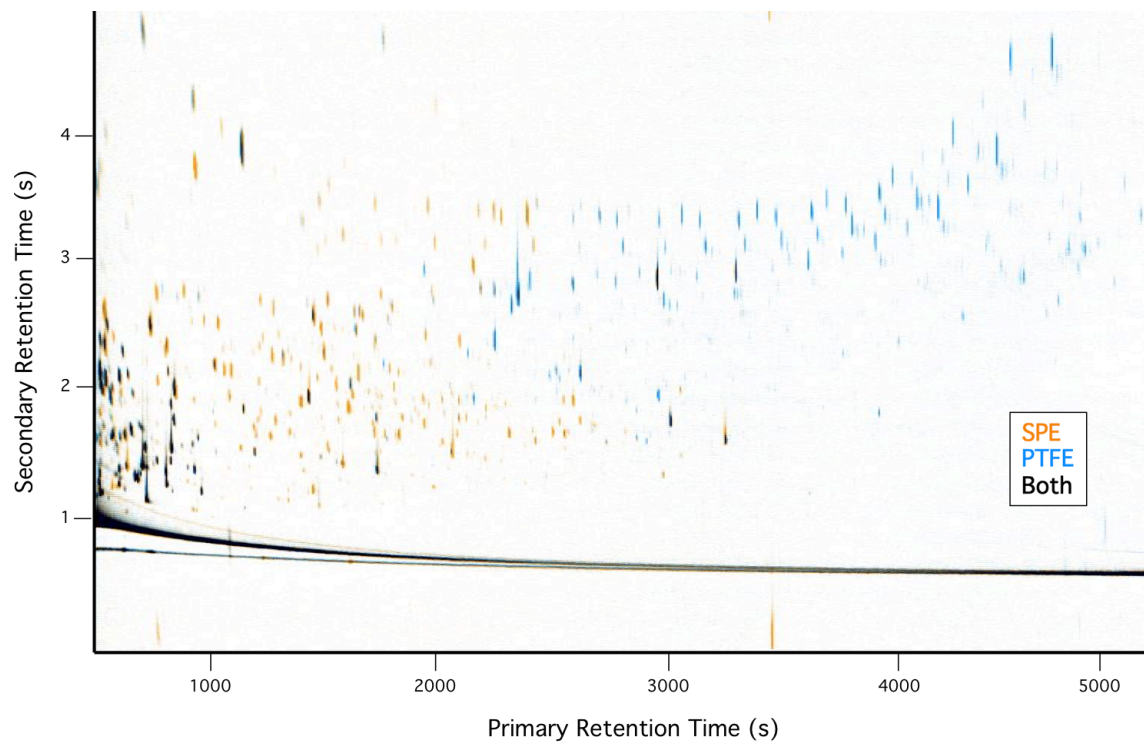
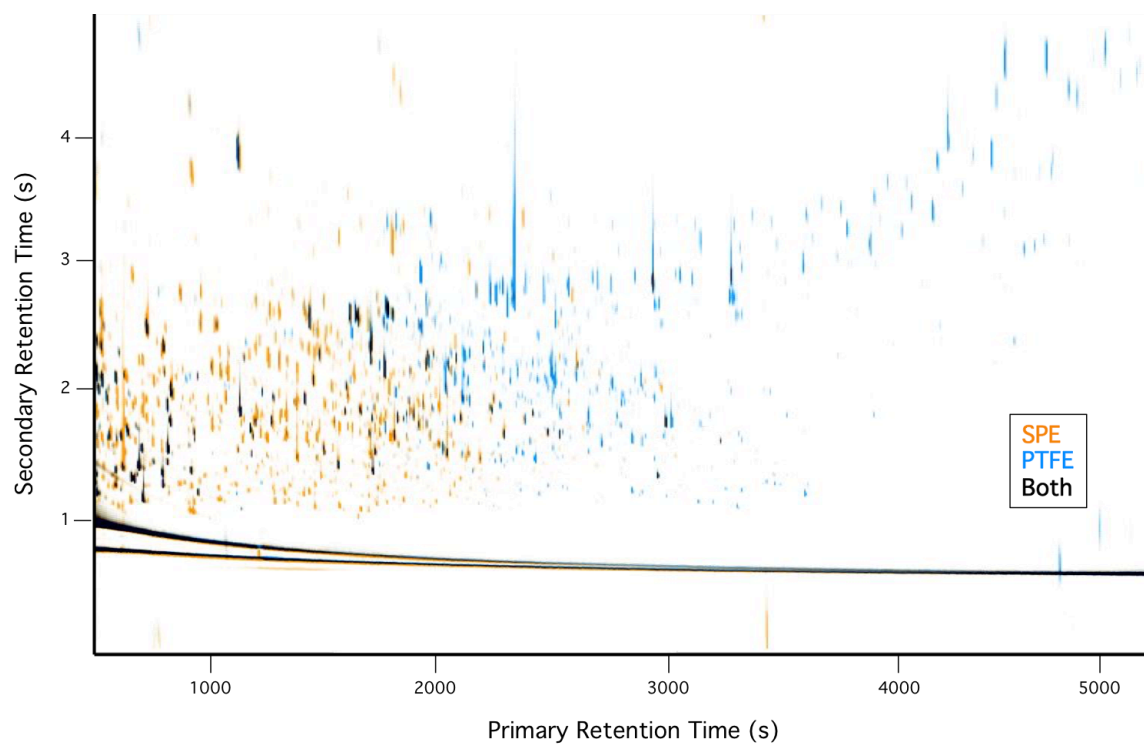Figure S18. As in Figure S6, for a peat fire (#55).

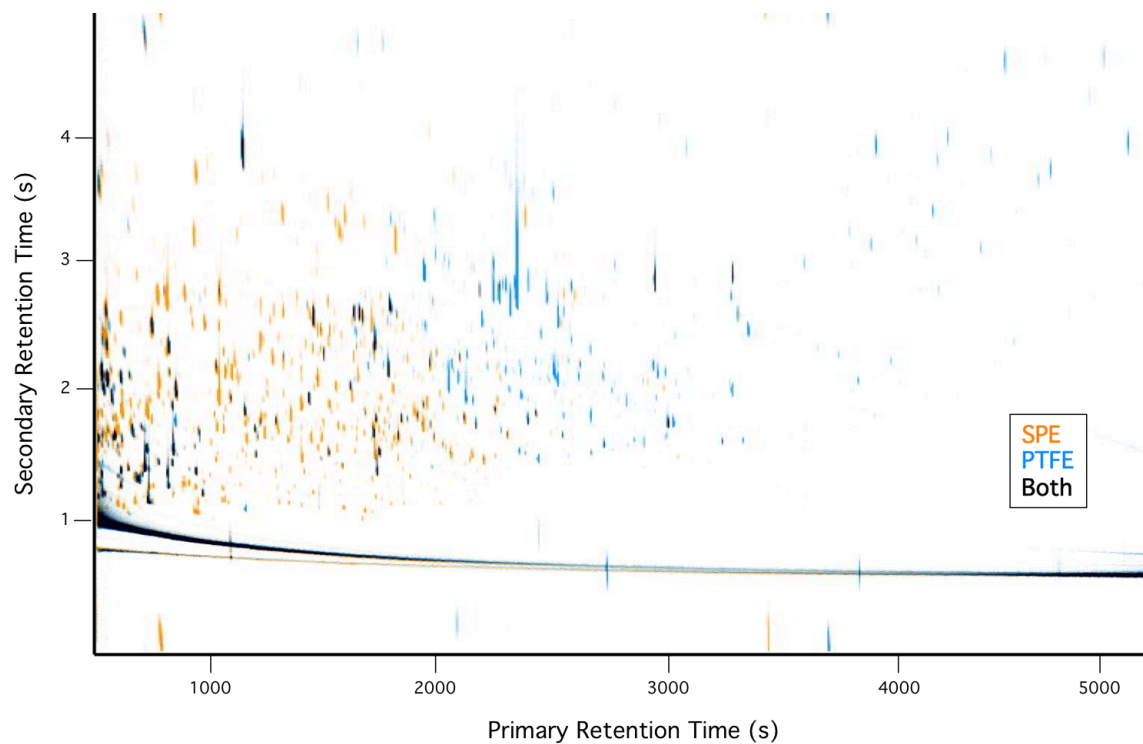Figure S19. As in Figure S6, for a yak dung fire (#50).

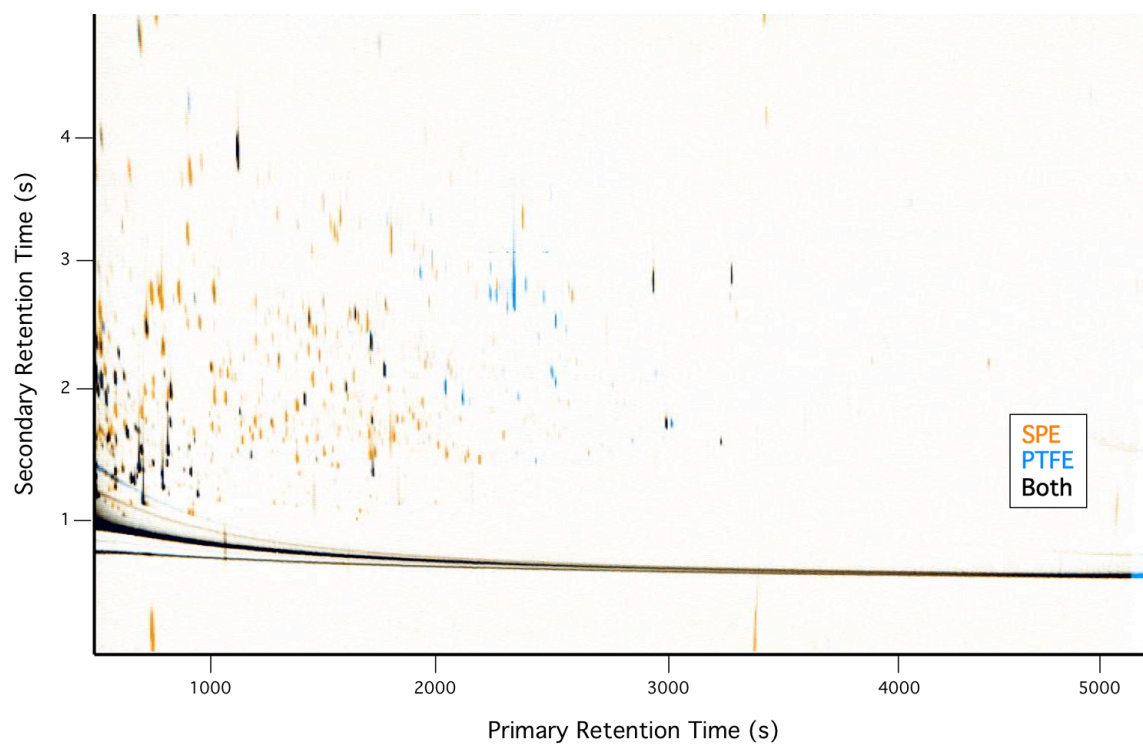Figure S20. As in Figure S6, for a bear grass fire (#62).

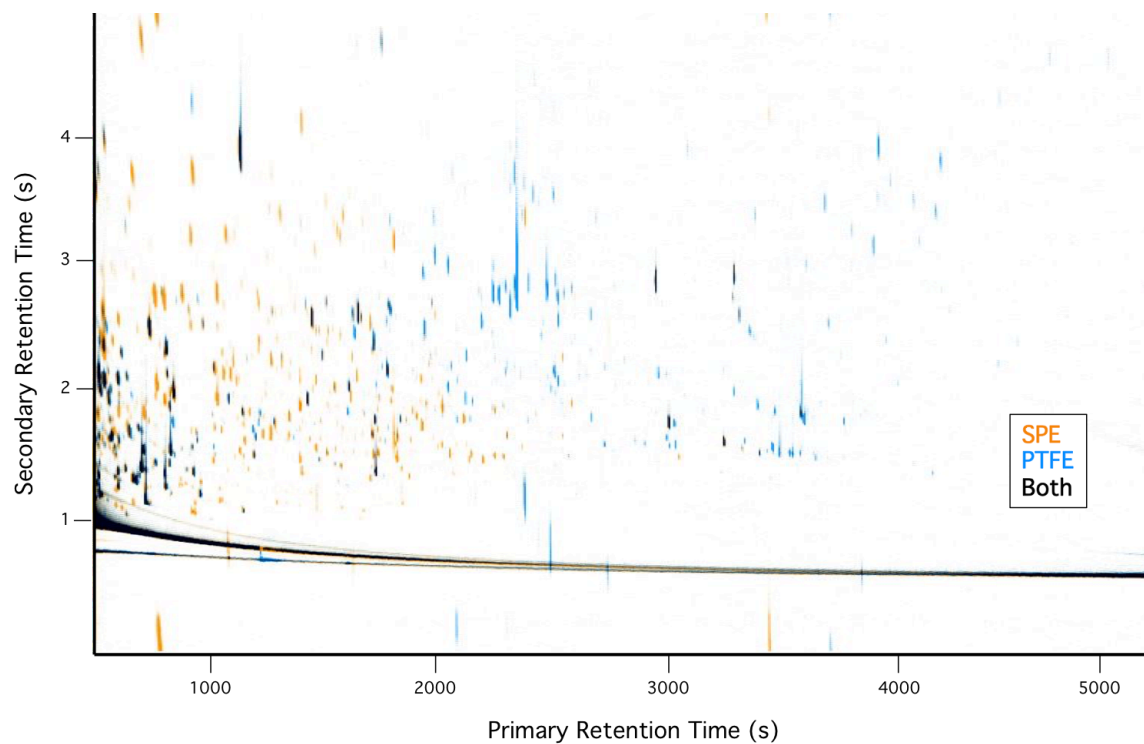Figure S21. As in Figure S6, for a rice straw fire (#60).

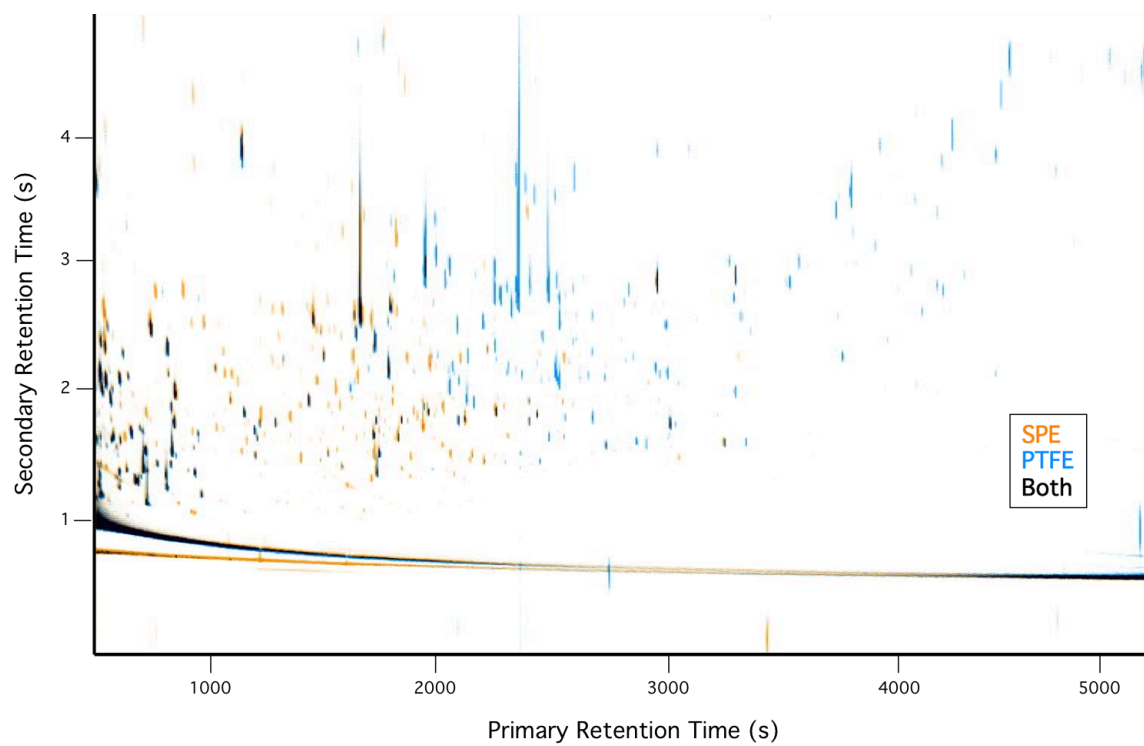Figure S22. As in Figure S6, for a sagebrush fire (#66).

Figure S23. As in Figure S6, for a manzanita fire (#28).

References

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