

Supplementary Information

Table S1 Polycyclic aromatic hydrocarbons (PAHs) analyzed in this study. Pyrogenic PAHs are grouped into low, medium, and high molecular weight. Selected Reaction Monitoring (SRM) transitions are reported for each compound.

Elution Group	Compound Name	Mass	Product Ion (m/z)
LMW	Naphthalene	128	128/102
	2-Methylnaphthalene	142	142
	Acenaphthylene	152	152
	Acenaphthene	154	153/154
	Fluorene	166	166
	Phenanthrene	178	178
	Anthracene	178	178
MMW	Fluoranthene	202	202
	Pyrene	202	202
	Retene	234	234/219
	Benzo[a]anthracene	228	228
	Chrysene	228	228
HMW	Benzo[k]fluoranthene	252	252
	Benzo[a]pyrene	252	252
	Indeno[1,2,3-c,d]pyrene	276	276
	Dibenzo[a,h]anthracene	278	278
	Benzo[g,h,i]perylene	276	276

Table S2. Modern vegetation samples collected from TANB and surrounding areas for leaf wax n-alkane analysis.

Sample ID	Vegetation group	Scientific name	Common name	Dry weight (mg)
TANB_pl_01	Gymnosperm	<i>Picea mariana</i>	Black spruce	792
TANB_pl_02		<i>Larix laricina</i>	Tamarack	461
TANB_pl_03	Angiosperm (graminoid)	<i>Eriophorum vaginatum</i>	Tussock cottongrass	652
TANB_pl_04	Angiosperm (herb)	<i>Symphyotrichum novi-belgii</i>	New York aster	483
TANB_pl_05	Angiosperm (Shrub)	<i>Rhododendron viscosum</i>	Swamp azalea	552
TANB_pl_06		<i>Chamaedaphne</i>	Leatherleaf	349

		<i>calyculata</i>		
TANB_pl_07		<i>Kalmia polifolia</i>	Bog laurel	445
TANB_pl_08		<i>Andromeda polifolia</i>	Bog rosemary	621
TANB_pl_09		<i>Ilex verticillata</i>	Winterberry	385
TANB_pl_10		<i>Cephalanthus occidentalis</i>	Buttonbush	472
TANB_pl_11	Mosses	<i>Sphagnum</i>	Bog mosses	362

Table S3. Permutation ANOVA results for environmental variables constraining PAH assemblages in the RDA

Variable	Category	Variance	F	P
P _{aq}	n-alkane/carbon	0.0581	11.65	0.001***
aCAR	n-alkane/carbon	0.0085	1.70	0.164
CPI	n-alkane/carbon	0.0636	12.75	0.001***
TAR	n-alkane/carbon	0.0068	1.37	0.225
ACL	n-alkane/carbon	0.0101	2.03	0.111
Broadleaf (%)	Pollen	0.0252	5.07	0.011*
Conifers (%)	Pollen	0.0179	3.59	0.019*
Herbs (%)	Pollen	0.0331	6.63	0.002**
Bog heath shrubs (%)	Pollen	0.0031	0.63	0.566
Wetland taxa (%)	Pollen	0.0367	7.37	0.001***

TANB pollen-based vegetation CONISS zonation

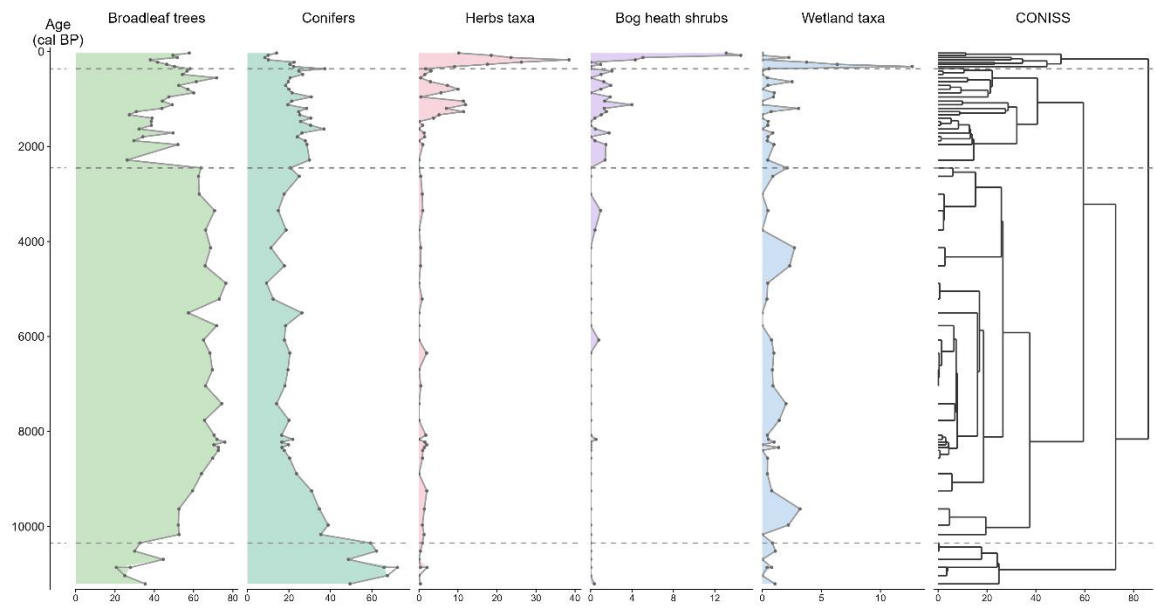


Figure S1. Pollen-based vegetation stratigraphy of the TANB peat core. Profiles show the relative abundances of broadleaf trees, conifers, herb taxa, bog heath shrubs, and wetland taxa plotted with calibrated age (cal yr BP). The pollen data come from Cai and Yu (2011)'s study. The dendrogram on the right presents the results of stratigraphically constrained cluster analysis (CONISS) based on these vegetation groups. Dashed horizontal lines indicate the boundaries of the four pollen-defined CONISS zones.

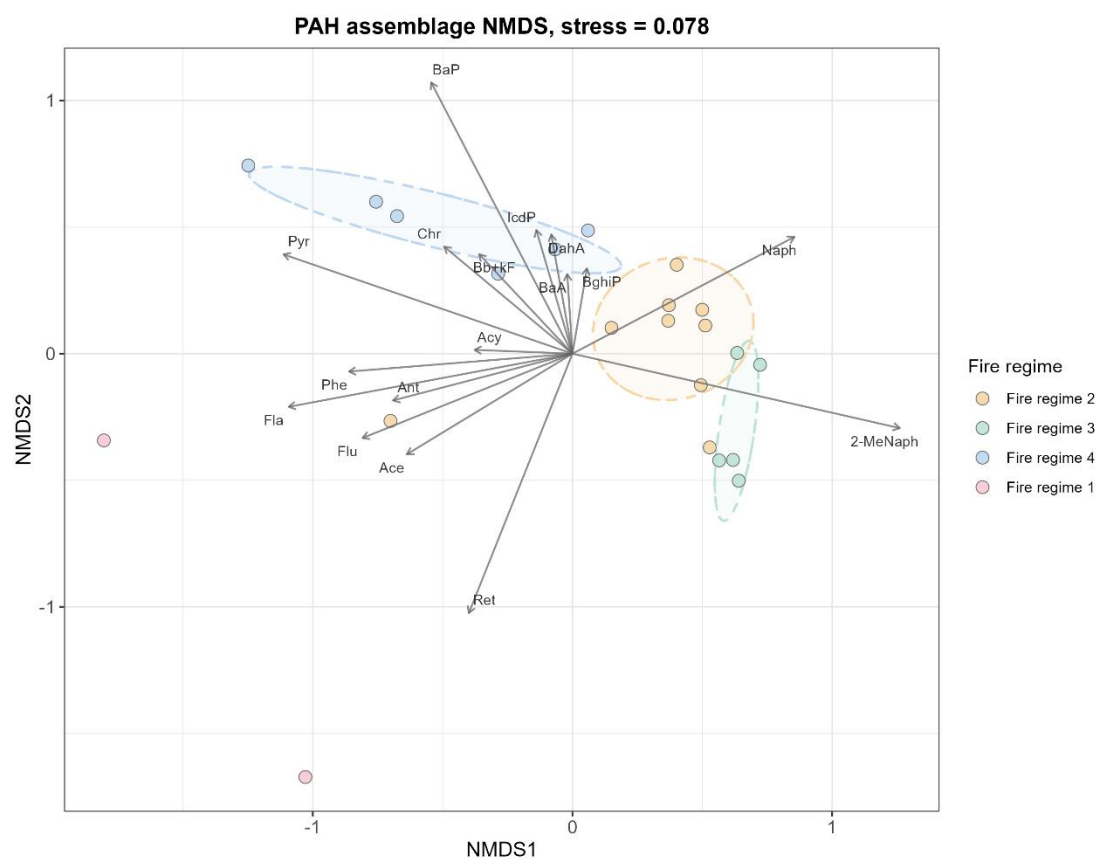


Figure S2. NMDS ordination of PAH assemblages from the TANB peat core. Symbols represent individual samples and colors indicate fire-system states identified by clustering analysis. Arrows show the contributions of individual PAH compounds to the ordination. Ellipses indicate the distribution of samples within each fire-system state.

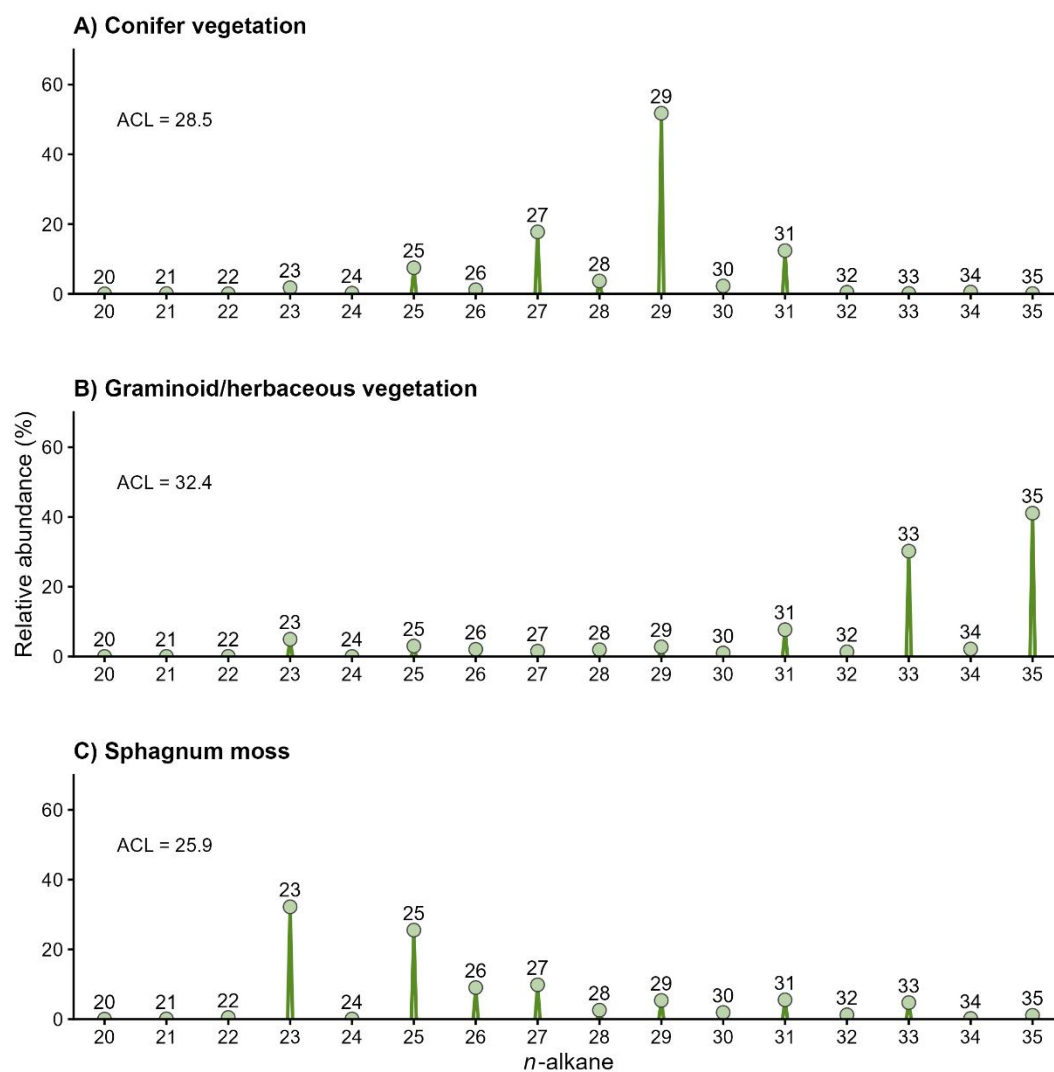


Figure S3. Relative abundances of odd-chain n-alkanes (C20–C35) in modern vegetation samples collected from TANB. Mean distributions are shown for (A) conifer vegetation, (B) graminoid/herbaceous vegetation, and (C) *Sphagnum* moss.

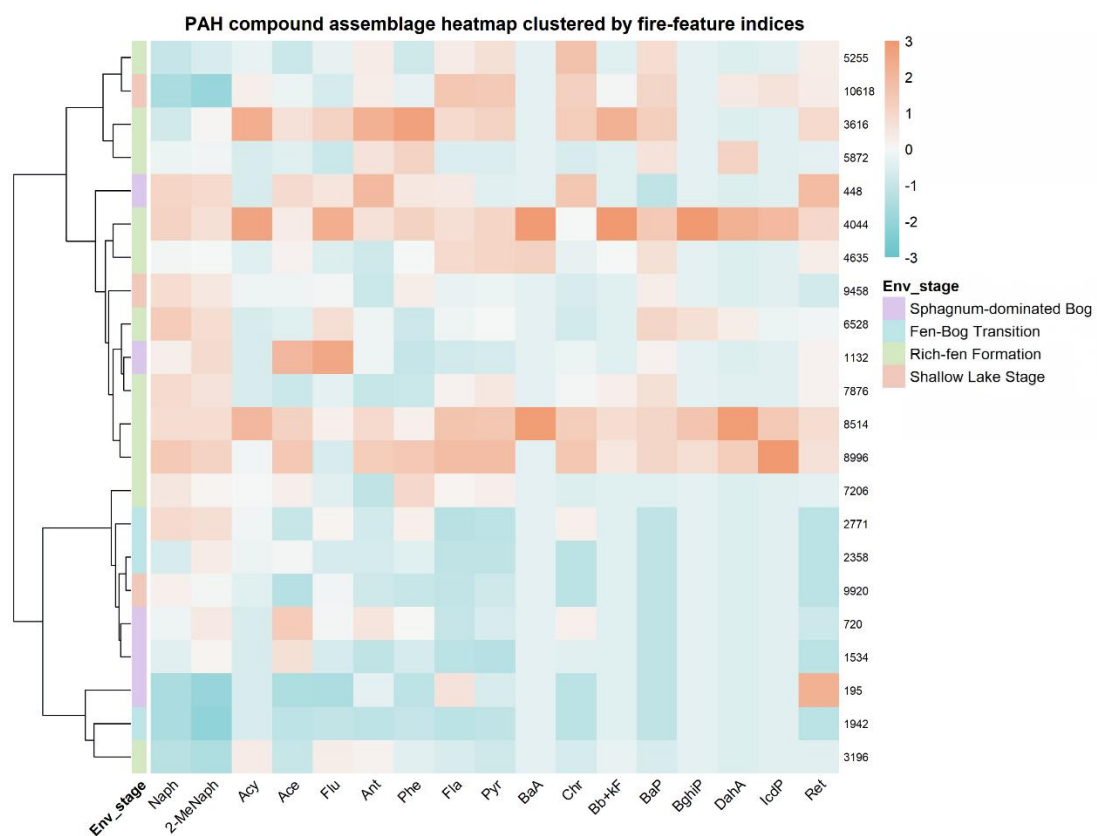


Figure S4. Heatmap of PAH compound assemblages at TANB clustered by fire-feature indices. Hierarchical clustering based on total PAH flux, LMW/Total PAH ratio, MMW%, HMW%, and retene-derived indices groups samples with similar combustion characteristics. The left annotation bar (Env) denotes the four stages of environmental development inferred from n-alkane and carbon accumulation proxies.

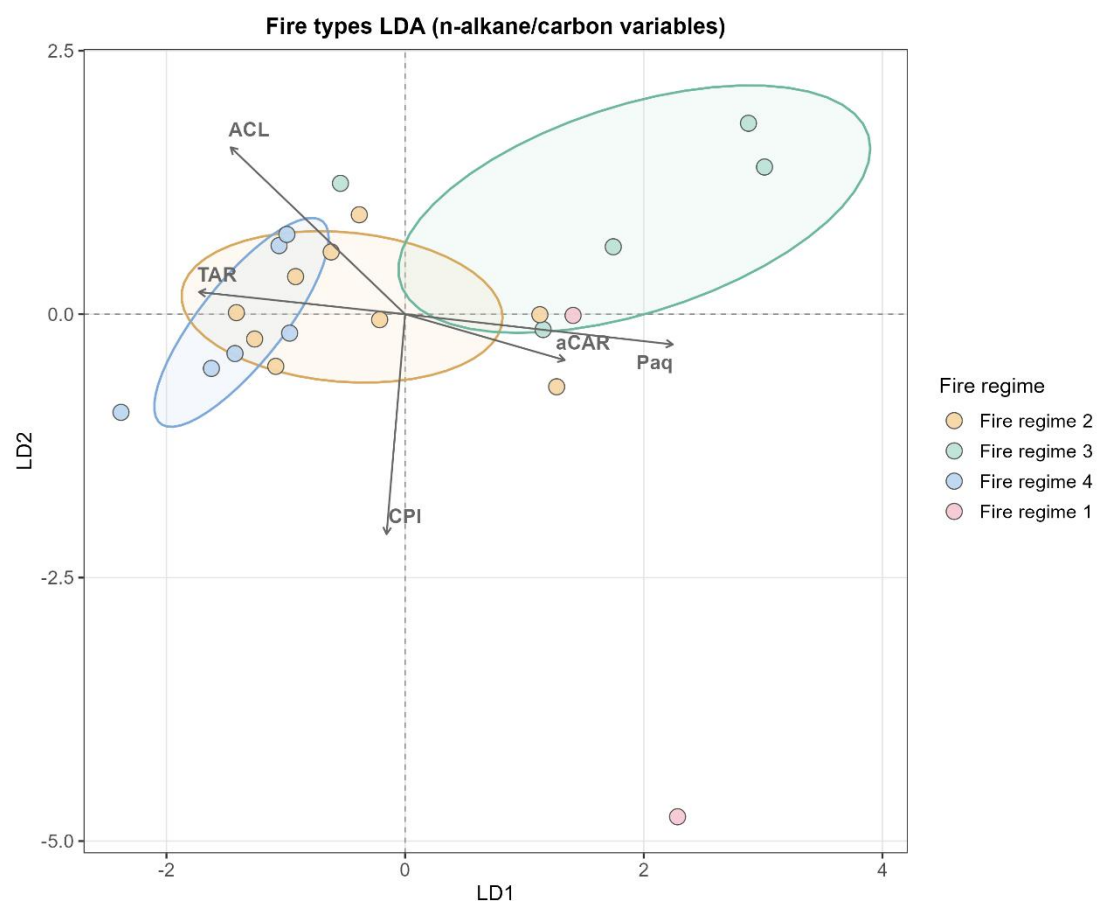


Figure S5. Linear discriminant analysis (LDA) of fire regimes constrained by n-alkane and carbon-related environmental variables from the TANB peat core. Symbols represent individual samples and colors indicate fire regimes identified by clustering analysis. Arrows show the contributions of environmental variables to the discriminant axes, including ACL, TAR, P_{aq} , aCAR, and CPI. Ellipses indicate the distribution of samples within each fire regime.

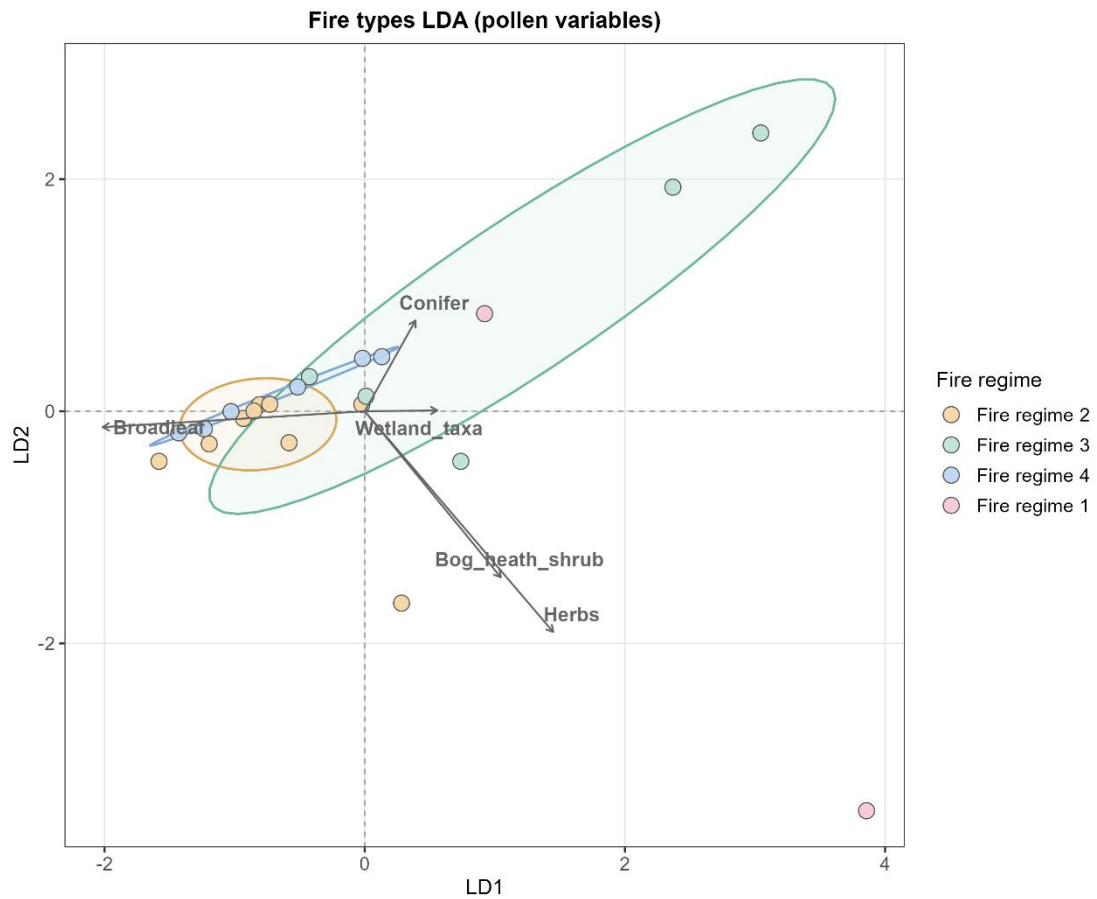


Figure S6. Linear discriminant analysis (LDA) of fire regimes constrained by pollen-derived vegetation variables from the TANB peat core. Symbols represent individual samples and colors indicate fire regimes identified by clustering analysis. Arrows show the contributions of vegetation variables to the discriminant axes, including Broadleaf trees, Conifers, Herbs, Bog heath shrubs, and Wetland taxa. Ellipses indicate the distribution of samples within each fire regime.

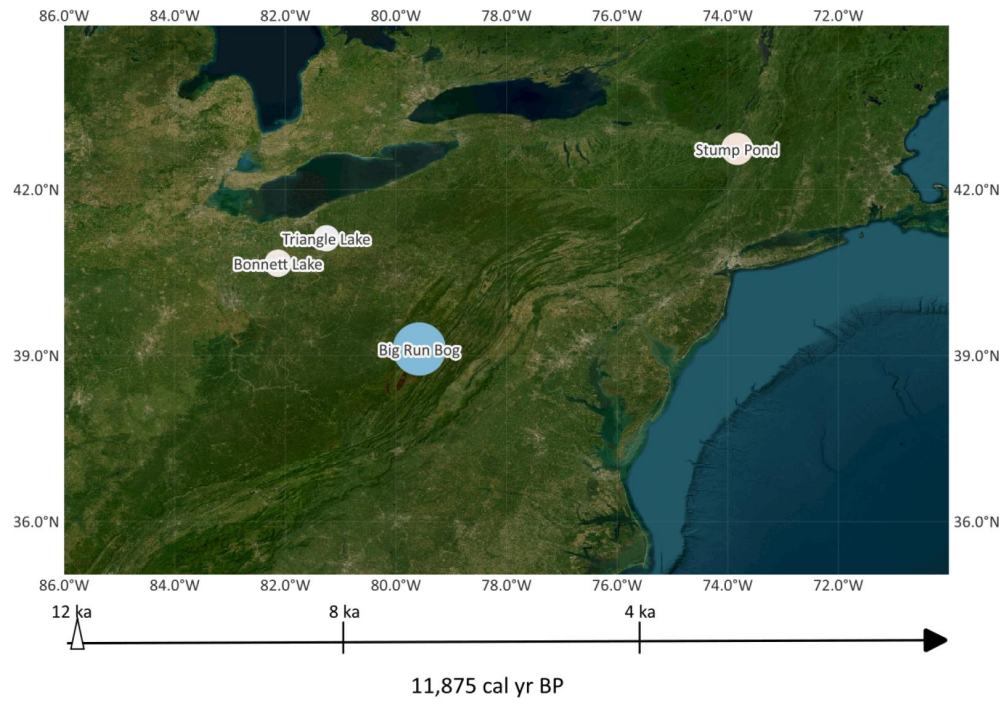


Figure S7. Spatiotemporal visualization of Holocene fire activity across the northeastern Appalachian region. Circle size and color represent standardized fire-proxy values at individual paleofire sites for each time step. Basemap source: Esri World Imagery. Sources: Esri and its data providers | Powered by Esri.