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Linking trace gas measurements and molecular tracers of organic matter in aerosols for identification of ecosystem sources and types of wildfires in Central Siberia

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Abstract. Summer 2012 was one of the extreme wildfire years in Siberia. At the surface air monitoring station “ZOTTO” (60°48’N, 89°21’E, 114 m a.s.l.) in Central Siberia we observed biomass burning (BB) influence on the ongoing atmospheric measurements within more than 50 % of the time in June-July 2012 that indicates a 30 times greater wildfire signal compared to previously reported ordinary biomass burning signature for the study area. While previous studies thoroughly estimated a relative input of BB into aerosol composition (i.e. size distribution, physical and optical parameters etc.) at ZOTTO, in this paper we characterize the source apportionment of the smoke aerosols with molecular tracer techniques from large-scale wildfires occurred in 2012 in the two prevailing types of Central Siberian ecosystems: complexes of pine forests and bogs and dark coniferous forests. Wildfires in the selected ecosystems are highly differed by their combustion phase (flaming/smoldering), the type of fire (crown/ground), biomass fuel, and nature of soil that greatly determines the smoke particle composition. Anhydrosugars (levoglucosan and its isomers) and lignin phenols taken as indicators of the sources and the state of particulate matter (PM) inputs in the specific fire plumes were used as powerful tools to compare wildfires in different environmental conditions and follow the role and contribution of different sources of terrestrial organic matter in the transport of BB pollutants into the pristine atmosphere of boreal zone in Central Siberia.

1. Introduction

Biomass burning aerosols are one of the least understood aspects of the modern climate system. Biomass burning (including landscape fires) emits 2-4 versus 7.2 Pg C yr⁻¹ released by fossil-fuel combustion and thus produces up to 50% as much carbon dioxide (CO₂) as fossil-fuel combustion [1,



2] and caused up to 65% of the variability in the CO₂ growth rate between 1997 and 2001 [3]. Consisting of a complex mixture of inorganic and organic compounds organic aerosols comprise up to 90% of the submicron particulate mass in BB emissions [4] and their physicochemical and optical properties vary within fuel types and combustion conditions. Biomass burning aerosols released from Siberian wildfires dominating other BB sources at high latitudes may have significant impacts on regional direct radiative forcing and also may be transported deep into the Arctic regions. Previous studies found that wildfires in Russia and Siberia substantially contributed to the Arctic aerosols [5]. From modeled trajectory analyses [6], Stohl estimated that in summer, during years with average biomass combustion rates, wildfires in boreal forests are able to contribute more aerosol black carbon (BC) to the Arctic compared to anthropogenic sources. Despite the concerns of environmental significance of PM emitted by Siberian wildfires, systematic observations were performed only in some places in Western and North-Eastern Siberia [7, 8]. Therefore, the assessments of BB emissions from Siberian boreal forests and their attribution to potential adverse effects are very sparse.

This gap is to be partially filled with continuous trace gas and aerosol measurements at the background surface air monitoring station “ZOTTO” (Zotino Tall Tower Observatory, 60°48'N, 89°21'E, 114 m a.s.l.) in Central Siberia that operational since late 2006. While previous studies made by Vasileva et al. [9], Heintzenberg et al. [10] and Chi et al. [11] thoroughly estimated a relative input of BB into annual variability of carbon monoxide (CO) mixing ratios and aerosol composition (i.e. size distribution, physical and optical parameters etc.) at ZOTTO, in this study we concentrate mainly on the source apportionment of the smoke aerosols with molecular tracer techniques that we studied in large-scale wildfires occurred in 2012 in the two prevailing types of Central Siberian ecosystems: complexes of pine forests and bogs and dark coniferous forests. Wildfires in the selected ecosystems are highly differed by their combustion phase (flaming/smoldering), the type of fire (crown/ground), biomass fuel, and soil type that highly determines the smoke particle composition. Anhydrosugars (levoglucosan and its isomers) and lignin phenols taken as indicators of the sources and the state of particulate matter inputs in the specific fire plumes were used as powerful tools to compare wildfires in different environmental conditions and follow the role and contribution of different sources of terrestrial organic matter (OM) in the transport of BB pollutants into the pristine atmosphere of boreal zone in Central Siberia.

1.1. The monitoring site

The monitoring site (figure 1) is located in Krasnoyarsk krai, 20 km west of the Yenisei River at the eastern edge of the West Siberian Lowland and lies in a vast region of forests and bogs, relatively undisturbed by anthropogenic influences and relatively inhospitable because of its continental climate.

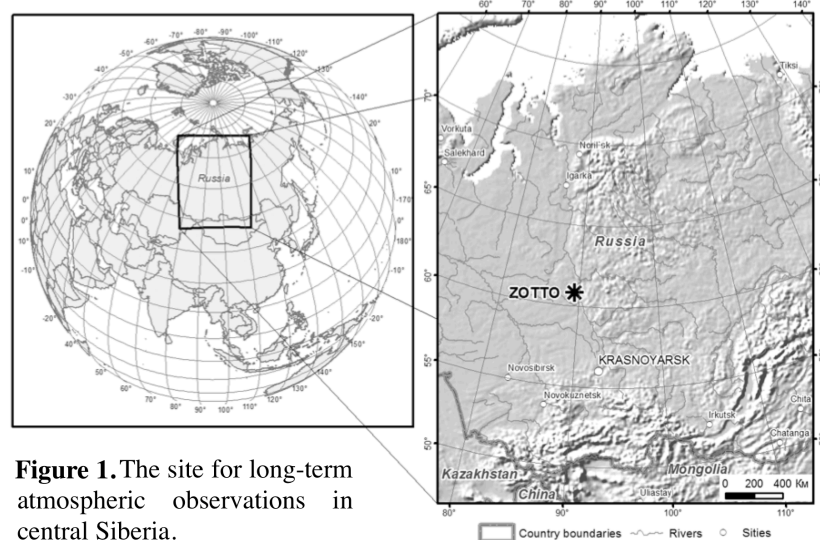


Figure 1. The site for long-term atmospheric observations in central Siberia.

The surrounding area is a flat with small hills and ridges. The climatic conditions of a mean annual temperature of 3.8 °C and a total precipitation of 536 mm derived from the weather station at Bor about 100 km northeast of ZOTTO (61°36' N, 90°01' E, 58 m a.s.l.) indicate a rather cold continental climate [12]. A temperature trend of around +3°C/100 yr was observed within the period of 1950-1999, which is representative for the larger territories of

Siberia [13]. The region is mostly influenced by Atlantic air masses traveling across the European part of the continent and a cold polar air from North-Eastern Siberia and the Arctic regions [14]. The vegetation of the study area consists of a mosaic of ecosystems that are representative for Central Siberia: large complexes of pine forests (18%) and bogs (16%), dark coniferous forests (26%), mixed forests (27%), broadleaf (5%) and larch (around 2%) forests. The monitoring station “ZOTTO” comprises a 300-m tall mast with inlets installed at the profile of heights (300 m, 227 m, 158 m, 92 m, 52 m and 4 m a.g.l.), where air is sampled and streamed to the analyzers located inside a partly underground laboratory bunker. The tall tower was developed for long-term atmospheric boundary layer (ABL) observations in Siberia that are representative for a very large spatial area. A detailed description of the site is given by Kozlova et al. [15] and Winderlich et al. [16].

1.2. Wildfires in Siberia within the last 20 years (1992-2012)

Within the last 20 years boreal forests in Siberia several times (1996, 2003 and 2012 y.) were greatly influenced by wildfires. In 1996 the Federal statistical service (EMISS; <http://www.fedstat.ru>) estimated up to 1.03 millions hectares of forests disturbed by wildfires (figure 2) with the most fires occurred in Krasnoyarsk krai (0.3 million hectares) and Irkutsk region (0.4 million hectares). In 2003

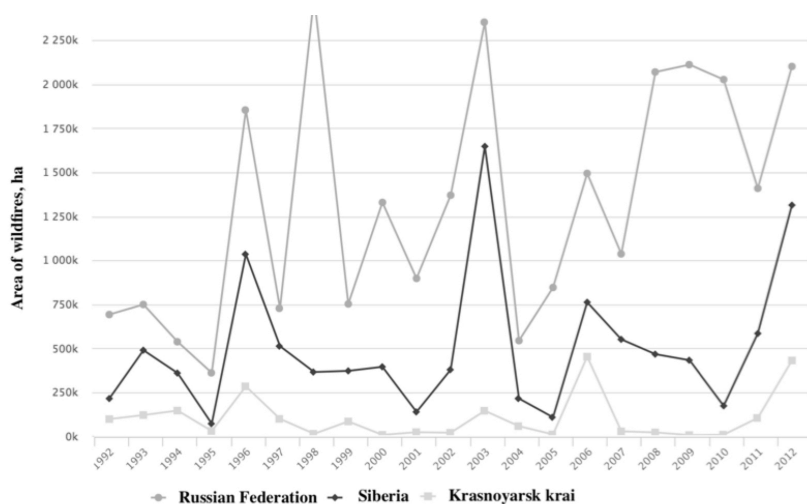


Figure 2. Areas of wildfires in Russia and Siberia within the last 20 yrs (1992-2012).

Russia achieved as much as 2.1 million hectares with up to 50 % of wildfires (1.3 million hectares) occurred in Siberia, the satellite-derived data might 2-3 times exceed the official statistics [19]. These large-scale fires within 2 months (June-July 2012) overlapped with the background surface atmospheric measurements at monitoring station “ZOTTO” in Central Siberia and demonstrated a 30 times stronger wildfire signal compared to previously reported ordinary BB signature for study area [20].

1.3. The instrumental setup and methods

Analysis of air composition in the specific fire plumes was based on the time series of CO₂/CH₄/CO mixing ratios measured at 300 m a.g.l. at monitoring station “ZOTTO”. The CO₂, CH₄, and H₂O measurements were performed by an EnviroSense 3000i analyzer (Picarro Inc., USA, CFADS-17) based on the cavity ring-down spectroscopy technique (CRDS) [21]. Carbon monoxide mixing ratios were measured by an APMA-370 ambient carbon monoxide monitor (Horriba Inc., Japan). The number of meteorological sensors recorded meteorological variables in a vertical profile on the tower. The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model [22], developed by the National Oceanic and Atmospheric Administration (NOAA), was used to compute 24-hrs backward trajectories for air probes sampled from the specific wildfires. The driving meteorological

data fields for the model were obtained from the National Center for Environmental Prediction (NCEP) Global Data Assimilation System (GDAS, global, 2006 – present). Active fire spots were detected from Terra/Aqua MODIS satellite data. The fire behavior associated with emissions was characterized using the Combustion Efficiency (CE) - index describing the relative amount of flaming and smoldering combustion in a wildland fire. As the molar ratio of CO_2 emitted to the total moles of carbon emitted, CE was calculated as the ratio of excess moles of carbon emitted as CO_2 to the molar sum of carbon released [23]. Chemical analysis of samples of atmospheric particulate matter at 300 m a.g.l. was performed in the specific fire plumes for identifying biomarkers, or compounds indicative of a unique biological source, and thus served as a powerful tool to trace the origin and transformations of organic matter. Anhydrosugars (levoglucosan and its isomers) were analyzed based on the gas chromatography-mass spectrometry (GC/MS) [24]. Lignin analysis was carried out according to the CuO oxidation method suggested by Hedges and Ertel [25] with modifications as described by Kaiser and Benner [26]. The Lignin Phenol Vegetation Index (LPVI) as a quantitative parameter representing the entire characteristics of the vegetation was applied as an additional tool to partition OM among end-member sources [27].

2. Results

Levoglucosan (1,6-anhydro- β -D-glucopyranose) and its isomers (mannosan and galactosan) are dehydro-monosaccharide derivatives formed exclusively from the thermal breakdown of cellulose and hemicellulose, respectively, during biomass burning [28]. Thus, they are source specific and can be used as a qualitative marker of biomass combustion in atmospheric particles [24] and as a tracer allowing quantitative apportionment of biomass combustion in the atmosphere. In the aerosol filter probes we found out concentration of levoglucosan in the specific fire plumes ranged from 1.19 up to 33.3 $\mu\text{g m}^{-3}$ (figure 3a), with a mean value of $9.22 \pm 9.66 \mu\text{g m}^{-3}$.

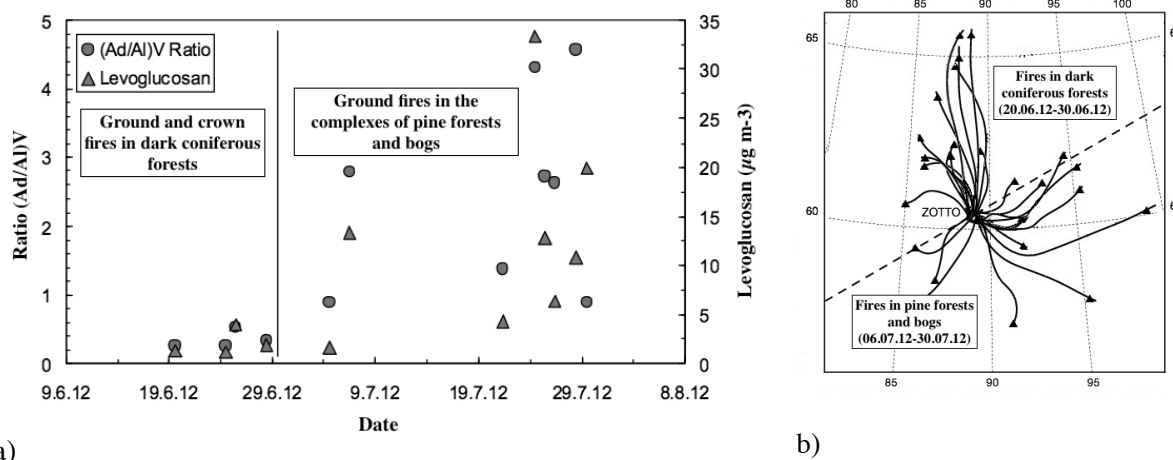


Figure 3. Time series of levoglucosan and the aldehyde to acid derivatives ratio versus vanillin ((Ad/Al)V) in the period of large-scale wildfires (20.06.2012-30.07.2012) occurred near “ZOTTO” monitoring station (a) and 24-hrs backward trajectories computed for the period of BB detection (b).

The backward trajectory analysis (figure 3b) demonstrates levoglucosan concentration considerably increased from $2.06 \pm 1.29 \mu\text{g m}^{-3}$ when air mass travelled from highly intensive ground and crown fires occurred in dark coniferous forests (20.06.2012-30.06.2012) 15-20 km northwest of the measurement site up to $14.59 \pm 10.67 \mu\text{g m}^{-3}$ when wind direction changed and we observed a BB signal produced by less severe ground fires occurred in the complexes of pine forests and bogs (06.07.2012-30.07.2012) 12-15 km southeast of the monitoring station. Mannosan and galactosan showed emission trends similar to levoglucosan.

Thermal degradation of fuels occurs ahead and along the fireline, while pockets of intermittent open flame often persist well behind the flaming front. To characterize emissions, wildfire behavior can be described based on the presence or absence of an open flame: “flaming” or “smoldering” combustion

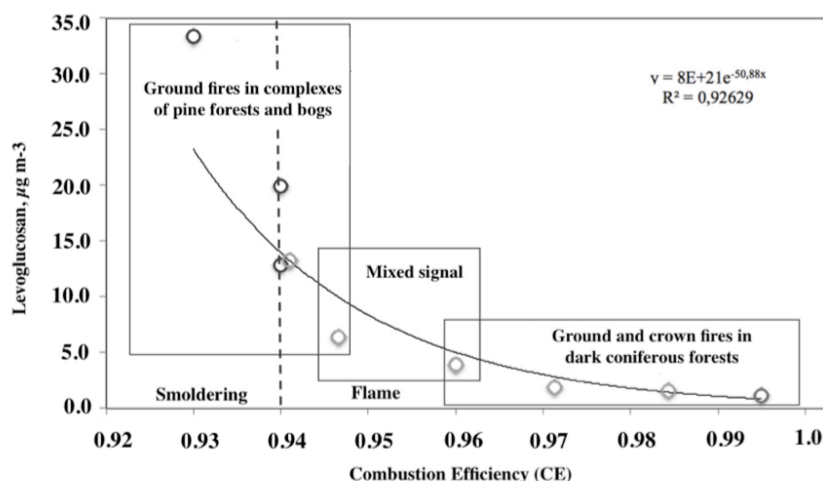


Figure 4. Levoglucosan versus Combustion Efficiency (CE) in the period of large-scale wildfires (20.06.2012-30.07.2012) occurred near «ZOTTO» monitoring station.

occurred in dark coniferous forests with greater values of CE (0.96-0.99) when mainly flaming combustion dominates and fine fuels completely engulfed in flame compared to a signal derived from ground fires in complexes of pine forests and bogs with CE values ranged from 0.93 (smoldering) to 0.95 (flaming) that finally indicates a stronger contribution of a smoldering duff in the fuel bed of the bogs into wildfire smoke.

In turn, the fuel characteristics (type, structure, loading, chemistry etc.) are primarily ecosystem vegetation specific properties that are strongly influenced by environmental conditions. Among molecular properties of organic compounds, lignin biomarkers are a unique proxy for distinction of the

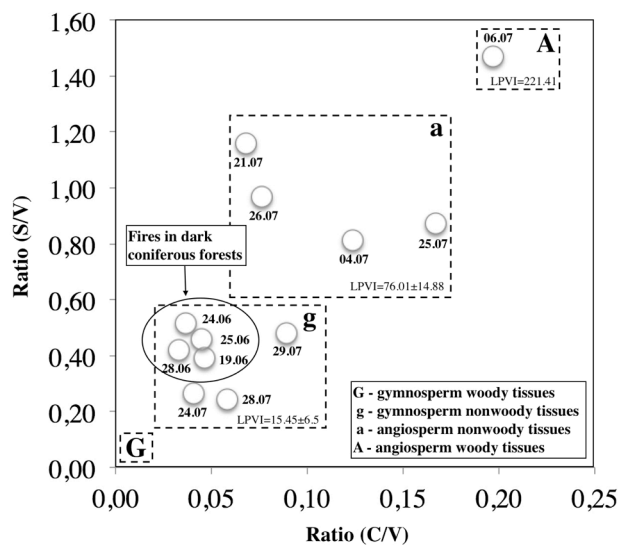


Figure 5. Relationship between lignin index-phenols (V, S and C): syringyl-based (S) to vanillyl-based (V) phenols ratio (S/V) versus cinnamyl-based (C) to vanillyl-based (V) phenols ratio (C/V).

vegetation type, because they are specific to individual or a restricted group of plants [27]. To distinguish a relative input of different taxonomical plant groups and tissue types in the OM appeared in smokes throughout the BB we used the differences in abundance of vanillyl (V), syringyl (S) and cinnamyl (C) structural groups [31, 32]. Vanillyl-based phenols are produced by all vascular plants, being the exclusive component in gymnosperm woody tissue. Syringyl-based phenols are produced by angiosperms and found in both woody and nonwoody tissue, although trace levels are found in gymnosperm nonwoody tissue. Cinnamyl phenols are present in the nonwoody tissues of gymnosperms and angiosperms. We used the composition of these three phenol groups to estimate contributions of terrestrial plant tissues. The lignin index-phenols (V, S and C) were defined as total concentration of three V-phenols, three S-phenols and two C-

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phenols normalized to 100 mg of OC, respectively. The S/V value, a measure of relative contributions made by gymnosperm ($S/V < 0.6$; $LPVI = 15.45 \pm 6.5$) and angiosperm ($S/V > 0.6$; $LPVI = 103.29 \pm 62.3$) plants, demonstrates an average value of 0.67 ± 0.38 throughout the wildfires (figure 5). Generally this value indicates nearly the equal input of both taxonomical plant groups, however applied backward trajectory analysis reflects the contribution of solely gymnosperms ($S/V = 0.45 \pm 0.05$) during wildfires occurred in dark coniferous forests. The C/V ratio that differentiates woody and non-woody vegetation [31] is relatively small and values are concentrated in a narrow range (0.04 ± 0.01) that simply illustrates the main contribution into particulate matter during BB in dark coniferous forests is made by gymnosperm nonwoody tissues. In turn the C/V ratio within wildland fires occurred in highly mosaic complexes of pine forests and bogs ranged from 0.04 up to 0.20. Besides of the gymnosperm woody tissues, whose contribution was not found, this range indicates a wide spectrum of terrestrial OM appeared in wildfire smokes contributed by both vascular tissue types (woody/nonwoody) and taxonomical (gymnosperm/angiosperm) plant groups. We found out a relatively equal input of gymnosperm nonwoody ($C/V = 0.06 \pm 0.02$; $LPVI = 15.45 \pm 6.5$) and angiosperm woody tissues ($C/V = 0.11 \pm 0.04$; $LPVI = 76.01 \pm 14.88$) in wildfire smokes, while the contribution of angiosperm nonwoody tissues ($C/V = 0.20$; $LPVI = 212.4$) is rather negligible.

Finally, we observed the changes in lignin phenol decomposition state in the OM appeared in wildfire smokes. Lignin decomposition state was estimated using the acid-to-aldehyde (Ad/Al) ratios of lignin phenols, as during microbial decomposition of plant-derived soil organic matter aldehyde forms of lignin phenols are oxidized to their acid derivatives [33]. Thus, increasing Ad/Al ratios reflects an enhancement of decomposition state of organic matter. For observed BB signals we found out sharply increased Ad/Al ratios of vanillin derivatives (Figure 3a) from 0.33 ± 0.27 detected during ground and crown fires in dark coniferous forests up to 2.52 ± 1.36 within ground fires occurred in complexes of pine forests and bogs. These changes reflect distinct sources of burned OM. Particularly there was “fresh” lignin input under intensive flaming combustion in dark coniferous forests: the domination of live biomass combustion. Highly decomposed OM was released to the atmosphere by the smoldering combustion of organic matter accumulated on the soil surface of pine forests and in the bogs: the domination of degraded soil organic matter combustion.

3. Conclusions

Anhydrosugars (levoglucosan and its isomers) and lignin phenols taken as indicators of the sources and the state of particulate matter inputs in the specific fire plumes were used as powerful tools to compare wildfires in different environmental conditions and follow the role and contribution of different sources of terrestrial organic matter (OM) in the transport of BB pollutants into the pristine atmosphere of boreal zone in Central Siberia.

In the observed wildfires we found out a considerable growth of the levoglucosan concentration when air masses travelled upwind to the measurement site from highly intensive ground and crown fires occurred in dark coniferous forests to less severe ground fires in complexes of pine forests and bogs. Mannosan and galactosan showed emission trends similar to levoglucosan. The strong feedback of the levoglucosan concentration to combustion efficiency illustrates stronger thermal degradation of lignocellulosic biomass within intensive ground and crown fires in dark coniferous forests with greater values of CE when mainly flaming combustion dominates and fine fuels completely engulfed in flame compared to a signal derived from ground fires in complexes of pine forests and bogs with CE values ranged from 0.93 (smoldering) to 0.95 (flaming) that finally indicates a stronger contribution of smoldering duff in the fuel bed of the bogs into wildfire smoke.

The ratio of syringyl-based phenols to vanillyl-based phenols (S/V) generally indicates nearly the equal input of both taxonomical plant groups into particulate matter in the wildfire smokes, however applied backward trajectory analysis reflects the contribution of solely gymnosperms under wildfires occurred in dark coniferous forests. The ratio of cinnamyl-based phenols to vanillyl-based phenols (C/V) illustrates the main contribution during BB in dark coniferous forests is made by gymnosperm nonwoody tissues. In turn the C/V ratio within ground fires in highly mosaic complexes of pine forests

and bogs indicates a wide spectrum of terrestrial OM appeared in wildfire smokes contributed by both vascular tissue types (woody/nonwoody) and taxonomical (gymnosperm/angiosperm) plant groups. We found out a relatively equal input of gymnosperm nonwoody and angiosperm woody tissues while the contribution of angiosperm nonwoody tissues into particulate matter is rather negligible.

The growth of the acid-to-aldehyde (Ad/Al) ratios of lignin phenols that coincides with change of air mass transport from wildfires occurred in dark coniferous forests to BB signal from complexes of pine forests and bogs upwind to the measurement site reflects an enhancement of decomposition state of organic matter. These changes reflect distinct sources of burned OM. Particularly there was “fresh” lignin input under intensive flaming combustion in dark coniferous forests: the domination of live biomass combustion. Highly decomposed organic matter was released to the atmosphere by the smoldering combustion of organic matter accumulated on the soil surface of pine forests and in the bogs: the domination of degraded soil organic matter combustion.

Acknowledgments

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