

**Sugars as Source Indicators of Biogenic Organic Carbon in Aerosols  
Collected Above the Howland Experimental Forest, Maine**

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**Abstract**

Bulk aerosols ( $> 1 \mu\text{m}$ ) were collected continuously above the canopy at the Howland Experimental Forest, Maine, USA from May to October 2002. Each sample integrated over an approximately two-week period. Mono- and disaccharide sugars were extracted using a microscale technique and were analyzed as their TMS derivatives by GC-MS. Concentrations of total aerosol sugars ranged from 10 to  $180 \text{ ng m}^{-3}$ . Glucose was the most abundant sugar (40-75% of the total sugars). The monosaccharides arabinose, fructose, galactose, mannose, arabitol and mannitol, and the disaccharides sucrose, maltose and mycose (aka trehalose) were also present in lower concentrations. The sugar composition in the aerosols varied seasonally. Fructose and sucrose were prevalent in early spring and decreased in relative abundance as the growing season progressed. Sugar polyols (arabitol and mannitol) and the disaccharide mycose (a fungal metabolite) were more prevalent in autumn during the period of leaf senescence. The changes in the sugar composition in the aerosol samples appear to reflect the seasonality of sugar production and utilization by the ecosystem. Plant waxes were present as significant components also indicating an input from biogenic background.

Smoke plumes from Quebec forest fires passed over the Howland site in early July 2002. Levoglucosan, a biomarker of biomass burning, increased by an order of magnitude in the aerosol samples collected during this time. Glucose, mannose, arabinose, galactose, and also, plant waxes increased in concentration by factors of 2-5 in the smoke-impacted samples, indicating that wildfires enhance atmospheric emissions of uncombusted organic compounds. In contrast, concentrations of fructose, sugar polyols and disaccharides were not significantly higher in the smoke-impacted samples and indicated that biomass burning was not a significant source of these compounds in the aerosols.

**Keywords:** Sugars, aerosol, biomarkers, smoke, plant wax, biogenic, Howland Experimental Forest.

## 1. Introduction

Atmospheric particles contain organic tracers that are characteristic of their sources, mode of formation and subsequent alteration during transport downwind (Simoneit, 1977, 1984, 1989; Marty and Saliot, 1982; Mazurek and Simoneit, 1984; Schauer et al., 1996; Fang et al., 1999; Simoneit et al., 1999; Conte and Weber, 2002; Kawamura et al., 2003; Simoneit et al., 2004a and references therein). Organic matter in aerosol particles is derived from four major sources and is admixed depending on environmental conditions. These particle sources are: (1) natural biogenic detritus (e.g., plant wax, microbes, pollen, etc.), (2) anthropogenic emissions (oil, soot), (3) soil organic matter, and (4) biomass burning (natural and anthropogenic).

The biogenic biomarkers in atmospheric samples consist of homologous series of *n*-alkanoic acids, *n*-alkanols and *n*-alkanes derived from epicuticular waxes and related lipids of higher plants (Simoneit, 1977, 1978), with lesser amounts of other oxygenated homologous species, such as *n*-alkanedioic acids and *n*-alkan-2-ones (Simoneit and Mazurek, 1982; Abas and Simoneit, 1996; Fang et al., 1999; Simoneit, 1989, 1999; Conte and Weber, 2002; Kawamura et al., 2003). Other primary biogenic biomarkers observed in atmospheric samples include sterols (cholesterol, campesterol and sitosterol), triterpenoids (e.g.,  $\alpha$ - and  $\beta$ -amyrone), diterpenoids (e.g., dehydroabietic acid) and sugars (mono- and disaccharides) (Simoneit, 1999; Simoneit et al., 1999; Graham et al., 2002; Simoneit et al., 2004a-c).

Sugars or saccharides represent the major form of photosynthetically assimilated carbon in the biosphere. They comprise up to 75 wt. % of vascular plant tissues as

structural polysaccharides like cellulose, hemicellulose and pectin (Sjöström and Reunanen, 1990). In aerosols, the saccharides are comprised of three main groups: (1) primary saccharides consisting of mono- and disaccharides, (2) saccharide polyols (reduced sugars), and (3) anhydrosaccharide derivatives such as mainly levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose) (Simoneit et al., 1999; 2004a-c).

The dominant primary saccharides in aerosols are comprised of  $\alpha$ - and  $\beta$ -glucose, sucrose and mycose (trehalose), with various other minor components (e.g., fructose, xylose and inositols). The sources of these compounds are innumerable and include microorganisms, plants and animals (Pigman and Horton, 1970; Bielecki, 1982; Simoneit et al., 2004a). Glucose is the most common monosaccharide present in vascular plants (Cowie and Hedges, 1984) and is an important source of carbon for soil microorganisms, such as fungi and bacteria (Paul and Clark, 1996). CO<sub>2</sub> fixed in leaves moves into the phloem of trees primarily as the disaccharide sucrose (glucose + fructose) and reaches the root cells in this form (Martin et al., 1988). However, in symbiotic fungal tissues (mycorrhizal fungi), sucrose is replaced by mycose (glucose + glucose) as the most common disaccharide (Martin et al., 1988; Niederer et al., 1989). Mycose is present in a large variety of microorganisms (fungi, bacteria, yeast), a few higher plants and invertebrates (Elbein, 1974) where it can serve as a reserve carbohydrate and a stress protectant (Crowe et al., 1984; Wiemken, 1990).

Saccharide polyols are produced in large amounts by many fungi, and several functions have been proposed for these compounds, such as storage or transport carbohydrates, and intracellular osmoregulatory solutes (Wong et al., 1993). Polyols are also the major soluble carbohydrates in lichens (Dahlman et al., 2003), often found on the

bark of trees, branches and leaves. Bacteria can also form and accumulate polyols (e.g., sorbitol) in order to overcome osmotic stress (Loos et al., 1994).

Levoglucosan, with minor mannosan, galactosan and 1,6-anhydro- $\beta$ -D-glucofuranose (levoglucosan isomer) are the primary thermal alteration products produced during biomass combustion of cellulose and hemicellulose and, therefore, are key tracers for smoke particulate matter from burning biomass (Simoneit et al., 1999). Levoglucosan and other anhydrosaccharides produced during biomass burning have been found in aerosols over the ocean, attesting to their stability during long-range transport (Fraser and Lakshmanan, 2000; Simoneit and Elias, 2000; Simoneit et al., 2004b,c).

Saccharides are ubiquitous in urban, rural, and remote aerosols (Simoneit et al., 1999; Simoneit and Elias, 2000; Nolte et al., 2001; Graham et al., 2002; Zdráhal et al., 2002; Simoneit et al., 2004a-c) and, therefore, are potentially powerful tools in elucidating organic carbon sources and atmospheric transport pathways. In addition, sugars and other water-soluble compounds are believed to regulate the hygroscopicity of aerosols and, thus, potentially play an important role in the regulation of climate (Kanakidou et al., 2005).

This study presents the atmospheric concentration and composition of sugars and plant waxes in aerosol samples collected over the 2002 growing season at Howland Experimental Forest, an ecotonal boreal forest in central Maine, USA. During the collection period, a large smoke plume from wildfires in northern Quebec passed over the sampling site.

## 2. Experimental Methods

### 2.1. Sample location and collection

The Howland Experimental Forest (Maine, USA) is located in a transitional northern hardwood-boreal conifer forest (45.2°N, 68.7°W, 60 m above sea level) with natural stands about 20 m tall (Hollinger et al., 1999). The major tree species at Howland are red spruce (*Picea rubens* Sarg.), eastern hemlock (*Tsuga Canadensis* (L.) Carr.), balsam fir (*Abies balsamea* (L.) Mill.), white pine (*Pinus strobus* L.), northern white cedar (*Thuja occidentalis* L.), red maple (*Acer rubrum* L.) and paper birch (*Betula papyrifera* Marsh.). Forests to the south are dominated by the typical northern hardwood forest assemblage species such oaks (*Quercus ssp.*), red maple (*Acer rubrum*), American beech (*Fagus grandifolia* ehrh.) and birches (*Betula ssp.*). The growing season typically averages slightly more than 200 days, with the first date for soil thaw about day 90 of the year and mean date of first frost about day 280 (Hollinger et al., 1999). The first frost in 2002 occurred on day 282 (October 9).

Bulk aerosols were collected over the 2002 growing season (May to October). The sampler was located just above the tree canopy (~30 m above the forest floor). Aerosols were filtered onto pre-combusted (380°C) Gelman A/E glass fiber filters (1 µm pore size, 90 mm diameter) fitted in dual Teflon filter holders. Each sample was collected continuously over a nominal two-week period to obtain a sample with a mean aerosol composition that integrated over the prevailing air masses. The sampled air volumes filtered ranged from 2644 to 3675 m<sup>3</sup>. Filters were transferred to pre-cleaned, combusted, solvent rinsed glass jars equipped with Teflon cap liners and stored at -30°C until

laboratory analyses. Blank filters (installed but no airflow) were also collected during the course of the study.

## 2.2. Chemical analyses

The saccharides were analyzed on filter sub-samples (~1.40% of the total filter) that were extracted using a direct microscale technique. Filters were sonicated for 15 min in a 1 mL mixture of dichloromethane:methanol (2:1, v/v). The solvent extract was evaporated to dryness using a stream of filtered nitrogen gas. The total extracted compounds were converted to their trimethylsilyl derivatives using N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS) and pyridine (70°C, 3 h). An aliquot of 1  $\mu$ L of each sample was analyzed within 24 hours by gas chromatography-mass spectrometry (GC-MS).

The silylated total extracts of the aerosols were analyzed in the splitless mode using a HP6890 gas chromatograph interfaced with a HP5973 MSD. The injector temperature was set to 300°C. A DB5-MS capillary column (30 m x 0.25 mm i.d. and film thickness of 0.25  $\mu$ m, Agilent) was used, with helium as carrier gas. The column temperature program consisted of injection at 65°C and hold for 2 min, temperature increase of 6°C  $\text{min}^{-1}$  to 300°C, followed by an isothermal hold at 300°C for 15 min. The MSD was operated in the electron impact mode with an ionization energy of 70 eV. The scan range was set from 50 to 650 daltons.

Data were acquired and processed with the HP-Chemstation software. Individual compounds were identified by comparison of mass spectra with literature and library data, comparison of mass spectra and GC retention times with those authentic standards

and/or interpretation of mass spectrometric fragmentation patterns. Compounds were quantified using total ion current (TIC) peak area, and converted to compound mass using calibration curves of external standards (glucose for monosaccharides, sorbitol for reduced sugars, sucrose for disaccharides, and levoglucosan for derivative saccharides).

Plant waxes in the aerosols were analyzed using the methods previously published in Conte and Weber (2002). Briefly, waxes were ultrasonically extracted from the total filters using dichloromethane. An internal standard mixture consisting of 21:0 *n*-alkanol, 23:0 *n*-acid, 36:0 *n*-alkane and 5 $\alpha$ -cholestane was added prior to the initial extraction step. The filters were then acidified using 1N methanolic HCl and re-extracted. The total combined extract was evaporated to dryness, resuspended in 4:1 dichloromethane:methanol and passed through a minicolumn containing Na<sub>2</sub>SO<sub>4</sub> to remove any residual water. The extract was then evaporated, a small amount of toluene added to resuspend the lipids, and the sample transesterified using 5% methanolic HCl (55°C, 12 h). The transesterified products were extracted in hexane, dried, and then trimethylsilylated under N<sub>2</sub> using BSTFA + 1% TMCS in pyridine (55°C, 1 h). The individual compounds were then quantified using a Fisons 8000 series GC fitted with a Chrompack CPSil5CB column (60 m x 0.25 mm, 0.25  $\mu$ m film thickness). The temperature programming was 50 to 150°C at 10°C min<sup>-1</sup> and from 150 to 320°C at 4°C min<sup>-1</sup> with a 30 min isothermal hold at 320°C.

### 2.3. Back-trajectories

Back-trajectories were calculated using NOAA's Air Resources Laboratory's (ARL) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Model with the



National Center for Environmental Prediction's (NCEP) final model run (FNL) meteorological data set (Draxler and Rolph, 2003). Four-day back-trajectories (6-10 July, 2002) were calculated at an ending altitude of 90 m (the approximate elevation of the sampling site) in a 6h interval. The plume's fate and transport were further assessed qualitatively through publicly available satellite images acquired with the Moderate Resolution Imaging Spectroradiometer (MODIS).

### **3. Results and Discussion**

#### **3.1. Long-range transport of smoke from Quebec wildfires**

Fires broke out in northern Quebec during the dry summer of 2002. According to the Canadian Forest Service, there was more than a 100-fold increase in hectares of boreal forest burned during the month of July for the forest fire season of 2002 (Sapkota et al., 2005). Forest stands included shade-intolerant deciduous species such as aspen (*Populus tremuloids* Michx.) and paper birch (*Betula papyrifera* Marsh.), as well as conifer species such as black spruce (*Picea mariana* (Mill.) BSP.), balsam fir (*Abies balsamea* (L.) Mill.), jack pine (*Pinus banksiana* Ait.) and white spruce (*Picea glauca* (Moench) Voss) (Bauhus and Messier, 1999). Smoke plumes were advected over the northeastern US in early July, 2002. The smoke plume transport across the eastern seaboard was evaluated by a satellite image (MODIS) taken on July 8 showing a smoke plume extending from the forest fires in Quebec to the northeastern US (Fig. 1a). Figure 1b shows air mass back-trajectories computed using the HYSPLIT model over the period from 6 to 10 July

(at an ending height of 30 m above ground level or 90 m above sea level), which also indicate transport of the smoke to the sampling site at Howland, Maine.

### 3.2. Sugar concentrations

Individual concentrations of the primary monosaccharides glucose, fructose, arabinose, mannose, galactose, as well as sugar polyols (arabitol and mannitol), anhydrosugars (levoglucosan, galactosan and mannosan), and disaccharides (sucrose, maltose and mycose) in aerosol samples taken from the Howland Experimental Forest are shown in Table 1. Total sugar concentrations (two week integrated averages) varied from approximately 10 to 180 ng m<sup>-3</sup> with maximum concentrations found in samples affected by the passage of the smoke plume from the Quebec wildfires (25 June-23 July). Minimum concentrations were observed in two samples collecting in late summer (6 August-5 September). A secondary maximum in concentration of most compounds was observed in early autumn, during the period of leaf senescence and decay.

The monosaccharide glucose was the major compound found in the aerosols over the entire sampling period, with concentrations ranging from approximately 3.1 to 50 ng m<sup>-3</sup> (Fig. 2). Galactose, mannose, fructose and arabinose were also present in the aerosols in lower concentrations. The concentrations of galactose and mannose strongly covaried and showed a maximum in the smoke impacted samples. In contrast, fructose concentrations were maximal in early spring (4-5 ng m<sup>-3</sup>, Fig. 3a) and decreased to < 1 ng m<sup>-3</sup> by mid-summer (Table 1, Fig. 2). Concentrations of the polyols, mannitol and arabitol, also strongly covaried, with mannitol being approximately twice as prevalent as arabitol, with

maximum values observed in early autumn (Table 1, Fig. 2) during the leaf senescence period.

Myose (aka trehalose) was by far the most abundant disaccharide found in the aerosol samples. It was observed in all samples collected throughout the growing period, varying from approximately 1.5 to 18 ng m<sup>-3</sup>. Myose is present in bacteria, yeast, a wide variety of fungi, algae, a few plants, and invertebrates (Elbein, 1974). As observed for the sugar polyols, higher concentrations were found in early autumn (Fig. 2). The prevalence of myose in autumn is consistent with the observations of Hackl et al. (2000), who found higher amounts of myose in autumn than in spring in soil samples from a natural forest in Austria. Myose and saccharide polyols have been documented as useful tracers for soil input to atmospheric particles in regions impacted by erosion or agricultural activities (Simoneit et al., 2004a). The other disaccharides, sucrose and maltose, were detected in only a few samples (Table 1). Maltose, a microbial degradation product of starch, was observed during the beginning and end of the growing season. Sucrose was significant only in the spring, similar to fructose (Fig. 3a). This disaccharide is the predominant sugar in the phloem of plants and is particularly important in developing flower buds (Bielecki, 1995).

### 3.3. Smoke plume

The anhydrosugar levoglucosan increased by an order of magnitude in the aerosol samples collected between 25 June and 23 July (Table 1, Fig. 2), when a smoke plume from the Quebec wildfires passed over the study area (Figs. 1, 3b). Levoglucosan with minor mannosan and galactosan have previously been identified as major components of

organic particulate matter in areas impacted by wood smoke (Simoneit et al., 1999; Simoneit and Elias, 2000). The monosaccharides glucose, arabinose, galactose and mannose were also strongly enriched (by factors of 2-5) in the smoke-affected samples (Figs. 2, 3b), indicating that wildfires also enhance emissions of uncombusted saccharides. Glucose, arabinose, galactose and mannose occur as such and are found in hemicellulose polysaccharides (Pigman and Horton, 1970). Glucose, in particular, is commonly present at higher levels in vascular plants (Cowie and Hedges, 1984), while nonwoody tissues, such as leaves and needles, are typically richer in pectin, a polysaccharide containing arabinose and galactose as predominant sugars (Sjöström, 1981). This may explain the enrichment of those sugars in the smoke-impacted samples. In contrast, no significant concentration enrichments were observed for fructose, reduced sugars and disaccharides (Table 1, Figs. 2, 3b). The lack of any observed influence of the smoke plume on the concentrations of reduced sugars and disaccharides is consistent with the observations of Graham et al. (2002), who found no correlations between arabitol, mannitol, sorbitol, mycose and the combustion indicators, BC (black carbon), OC (organic carbon) and K (potassium) in smoke samples taken from an Amazonia Forest site.

#### 3.4. Seasonal variations in monosaccharide composition

The sugar composition of the aerosols varied systematically as the growing season progressed. The seasonal change in monosaccharide composition, as the percentage contribution of each compound, is shown in Figure 4. Since the concentrations of levoglucosan and other anhydrosaccharide products of biomass burning are independent

of the seasonal cycle, they were excluded from the calculations. In order to remove the influence of the smoke plume, the concentrations used for computing the relative sugar compositions for the periods from 25 June-9 July and 9-23 July were estimated by linear interpolation of the measured concentrations for the adjacent periods.

Glucose dominated the aerosol monosaccharides throughout the growing season, comprising about 40 to 75% of total monosaccharide composition (Fig. 4). In early spring, glucose was by far the most abundant monosaccharide, but sharply declined in relative composition as the growing season progressed. Galactose, mannose, arabinose comprised < 5%, respectively, of the total monosaccharides during the spring and increased to 10-20% of the total by mid-summer (Fig. 4). These changes in sugar composition in the aerosol samples appear to reflect the sugar production in the ecosystem, with major synthesis of primary sugars early in the growing season. In contrast, the relative concentrations of the sugar polyols mannitol and arabitol increased from < 5% in early spring to 15-20% of the total by early autumn. Mannitol, and to a lesser degree, arabitol are major fungal polyols in many green-algal lichens (Dahlman et al., 2003), and are well-known constituents of bacteria, fungi, and lower plants (Bielecki, 1982). The enhanced abundance of the reduced sugars in early autumn relative to those of primary monosaccharides synthesized by plants appears to reflect an increase in contributions from microbially degraded materials during the period of leaf senescence and decay. This conclusion is supported by the concurrent increase in the concentration of the disaccharide mycose during this period (Figs. 2, 3). In contrast, fructose comprised a significant component of the monosaccharide relative concentrations only in spring (Fig. 4) as its concentration declined by a factor of 4 during the growing season.

Therefore, the dominant sources of sugars above the Howland Forest are the natural background of aerosol particles emitted by the terrestrial biomass (plant detritus, airborne microbes comprised of bacteria, spores of lichens and fungi, and small algae), and their seasonal composition changes closely reflect the seasonality of sugar production and utilization by the ecosystem.

### 3.5. Comparison of sugar with plant wax and dehydroabietic acid distributions

In addition to sugars, plant epicuticular waxes comprised a major component of the higher molecular weight fraction of the aerosols at the Howland Forest. Table 1 shows the concentrations of the major wax classes ( $> C_{20}$  *n*-alkanoic acids, *n*-alkanols and *n*-alkanes). The *n*-alkanoic acids were the major wax class and comprised 32–56% of the total waxes (average 44%). The *n*-alkanols were the second most abundant class and comprised 30–52% of the total waxes (average 38%). Nonacosan-10-ol, a  $C_{29}$  secondary alcohol synthesized mainly by gymnosperms (Tulloch, 1976), was also detected and comprised 0.3–7% of the wax. The *n*-alkanes were the least abundant major wax class found and comprised from 9–17% of the total (average 14%). The predominance of *n*-alkanoic acids and high relative proportion of nonacosan-10-ol from leaf wax in the aerosols is consistent with the large component of coniferous vegetation in the northeastern United States and Canada.

The total wax concentration (sum of the major wax classes) in the aerosol samples increased by roughly a factor of 2 during the growing season, from  $\sim 10 \text{ ng m}^{-3}$  to  $\sim 25\text{--}30 \text{ ng m}^{-3}$ , and then declined again in the end of September to  $\sim 10 \text{ ng m}^{-3}$  (Table 1). Extreme increases in wax concentration, in particular the *n*-alkanoic acids, were observed during

the period when the smoke plume from the Quebec wildfires passed over the site. The factor of 3-5 increase in wax concentration mirrored that observed for the primary monosaccharides (Table 1) and indicated that biomass burning greatly enhances the emissions of waxes into the atmosphere, presumably by volatilization (steam stripping) during the initial stages of combustion (Standley and Simoneit, 1987; Elias et al., 1999; Simoneit, 2002). An increase in wax concentrations in aerosol samples affected by wildfire plumes has been observed previously by Abas et al. (1995), Conte and Weber (2002) and Kawamura et al. (2003).

As the growing season progressed, the concentrations of plant waxes relative to the primary sugars in the aerosols systematically decreased to a minimum in late summer, before rising again in early autumn when leaf senescence commenced (Fig. 5). At the start of the growing season (30 April-16 May), the ratio of primary monosaccharides (i.e., the sum of glucose, fructose, mannose, arabinose and galactose) to total wax, was about 5 and rapidly decreased to near unity by the end of June, when plant growth and leaf expansion are complete. This trend primarily reflects the decrease in glucose (and fructose) concentrations (Fig. 4), coupled with the increase in wax contents (Table 1). The concentration ratio of primary monosaccharides relative to plant waxes increased abruptly in the last three samples collected (17 September-1 October to 15-29 October). This increase coincided with the increase in sugars in the early autumn, and in particular that observed for the sugar polyols mannitol and arabitol and the disaccharide mycose. Thus, sugar emissions appear to increase as leaf senescence commences but wax emissions do not, suggesting a larger degradative/microbial component contributing to saccharide emissions at the end of the growing season. Interestingly, the primary

monosaccharides/total waxes ratio in the samples affected by the smoke plumes (25 June-9 July and 9-23 July) was nearly the same ratio observed in samples that were not influenced by biomass combustion, despite the very significant increases in concentrations in those samples (Fig. 5).

The diterpenoid dehydroabietic acid, an oxidation product of resin acids (Simoneit, 1977, 1986) and a molecular tracer for coniferous wood combustion (Standley and Simoneit, 1994), was observed in samples impacted by the wildfire plume and also in samples collected at the end of the growing season, i.e., autumn (Table 1, Fig. 3c). However, at that time (5-17 September onward) no smoke plume was evident at the sampling site. In addition, the increase in dehydroabietic acid amounts by the end of the growing season was not accompanied by corresponding high levoglucosan concentrations (Table 1, Fig. 2), suggesting that other emission sources of this compound are also significant. The higher emission concentrations of dehydroabietic acid found in the end of the growing season (autumn) may be related to the larger degradative/microbial component observed at this time. Yet, anthropogenic emissions by pulp mill industries located in Canada are also potential sources of dehydroabietic acid to the Howland aerosol samples (Laplante and Rilstone, 1995). Other biomarkers, such as sterols, triterpenoids and PAHs, were not detected in the total extract analyses of the aerosols. These compounds may be completely overwhelmed by the high sugar contents.



#### 4. Conclusions

Sugars and plant waxes were major components of the aerosols present in the boundary layer air masses collected above the Howland Experimental Forest, Maine, USA. The total sugar concentrations ranged from about 10 to 180 ng m<sup>-3</sup>, with maximum concentrations observed in samples affected by the smoke plume from upwind wildfires. The monosaccharide glucose was the most common sugar found, comprising approximately 40-75% of the total relative monosaccharide abundances throughout the sampling period. The other monosaccharides found (mannose, arabinose, fructose, galactose, mannitol and arabitol), despite their lower concentrations, exhibited a strong seasonal trend. Mannose, arabinose, galactose and fructose had greater relative contributions to the total sugar composition from spring to mid-summer, whereas the relative abundances of the polyols mannitol and arabitol increased throughout the growing season to a maximum in early autumn. The changes in the sugar composition in the aerosol samples reflect the seasonality of sugar production and utilization by the ecosystem, with major synthesis of simple sugars early in the growing season, and greater contributions of metabolites from microbial degradation of primary saccharides during early autumn, the period of leaf senescence and decay. A similar trend was observed for the disaccharides sucrose and mycose. Sucrose was significant only in spring, whereas mycose, a fungal metabolite, was prevalent in early autumn. Plant waxes increased in concentration during the growing season, with a strong enhancement during the smoke period, then decreased into autumn.

Smoke plumes from wildfires in Quebec passed over the Howland site in early July 2002. Levoglucosan increased by an order of magnitude in the aerosol samples collected during that time. Primary monosaccharides and plant waxes increased in concentrations by factors of 2-5 in the smoke-impacted samples, indicating that wildfires also enhance emissions and long-range transport of non-combusted organic compounds. In contrast, concentrations of fructose, reduced sugars mannitol and arabitol and the disaccharides sucrose, maltose and mycose were not significantly higher in the samples impacted by smoke, indicating that biomass burning was not a significant source of those compounds in aerosols.

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## Figure captions

Figure 1. (A) Smoke plume from Quebec wildfires over the northeastern USA and Atlantic Ocean on 8 July, 2002. MODIS satellite image courtesy of the Land Rapid Response Team, NASA/GSFC; (B) Four-day back-trajectories of air parcels ending at the Howland Experimental Forest, ME from the HYSPLIT model. The trajectory end times are shown in the legend, and the end height is 30 m above ground level. Black dot indicates Howland Forest location and parallelogram delineates area of high forest fire activity.

Figure 2. Examples of individual concentrations of monosaccharides (black bars), sugar polyol (gray bars), anhydrosugar (hachured bars) and disaccharide (white bars) found in aerosol samples collected above the Howland Forest canopy from May to October 2002. The sample collection periods affected by the passage of the smoke plume are indicated by an asterisk.

Figure 3. GC-MS total ion current (TIC) traces for total extracts (as TMS) of Howland Forest aerosol samples: (a) early growing season (16-28 May), (b) passage of plume from Quebec wildfires (25 June-9 July), and (c) late season (1-15 October). Symbols:  $\Delta$  = *n*-alkanoic acids,  $\circ$  = *n*-alkanols, DHA = dehydroabietic acid, X = contamination.

Figure 4. Seasonal change in monosaccharide composition (in percentages) of aerosols collected above the Howland Forest canopy. The anhydrosugars levoglucosan, mannosan and galactosan have been excluded from the calculations and the sugar compositions in the samples affected by the smoke plumes have been interpolated (see text).

Figure 5. Concentration ratios of the total primary monosaccharides (glucose, galactose, mannose, arabinose and fructose) relative to the total plant waxes in the aerosol samples.

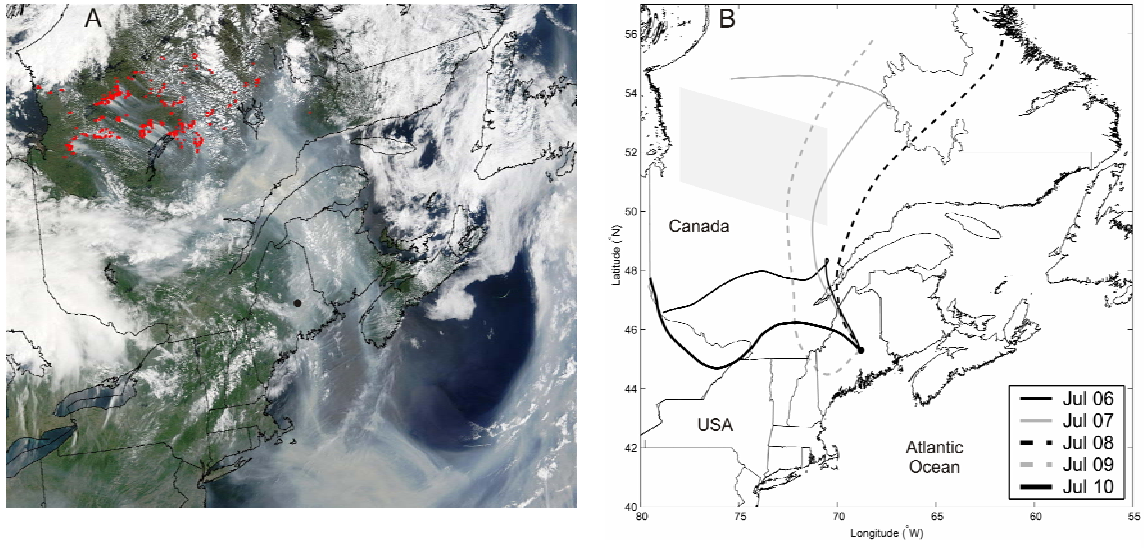


Figure 1

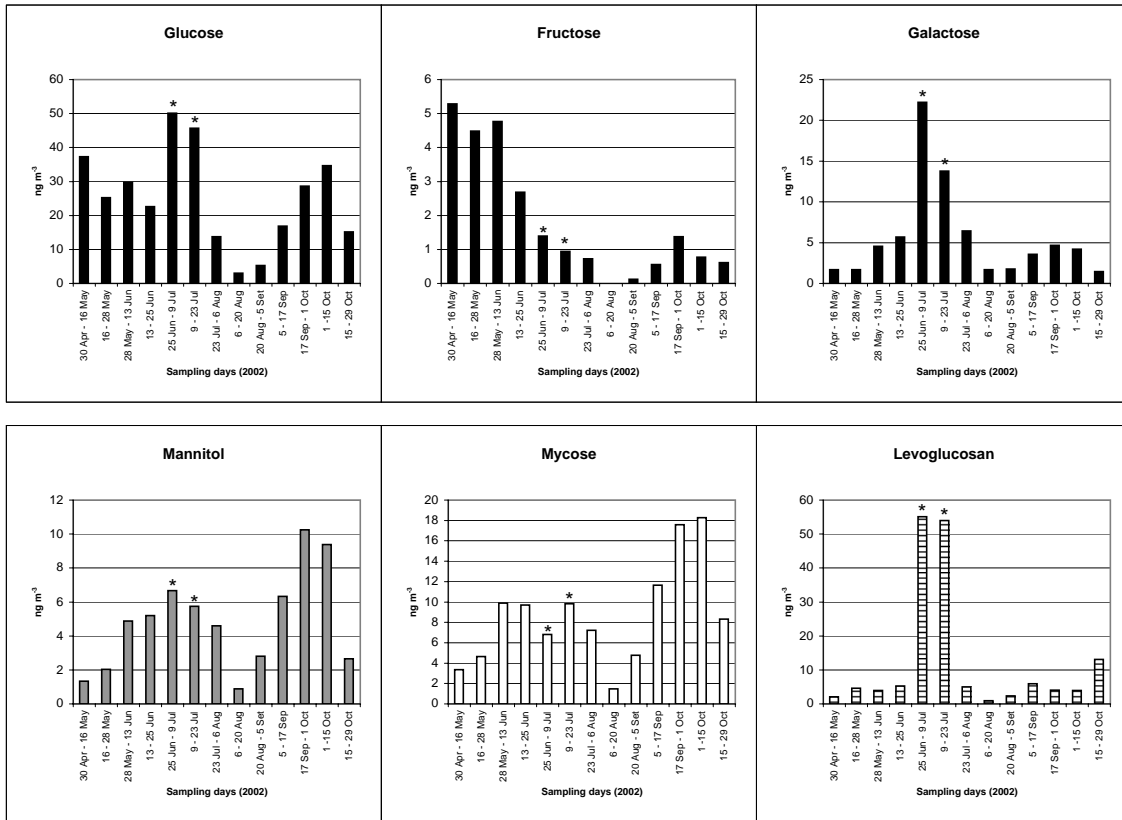


Figure 2

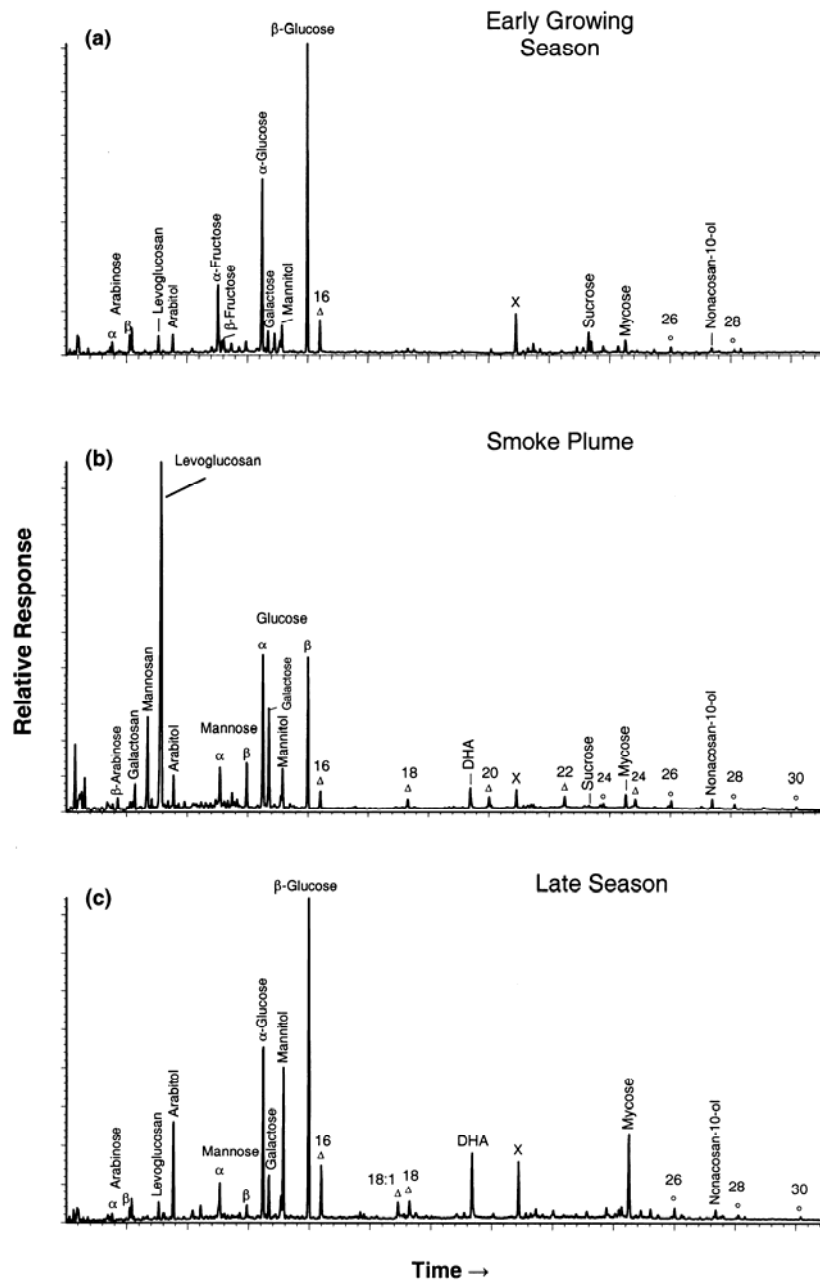


Figure 3

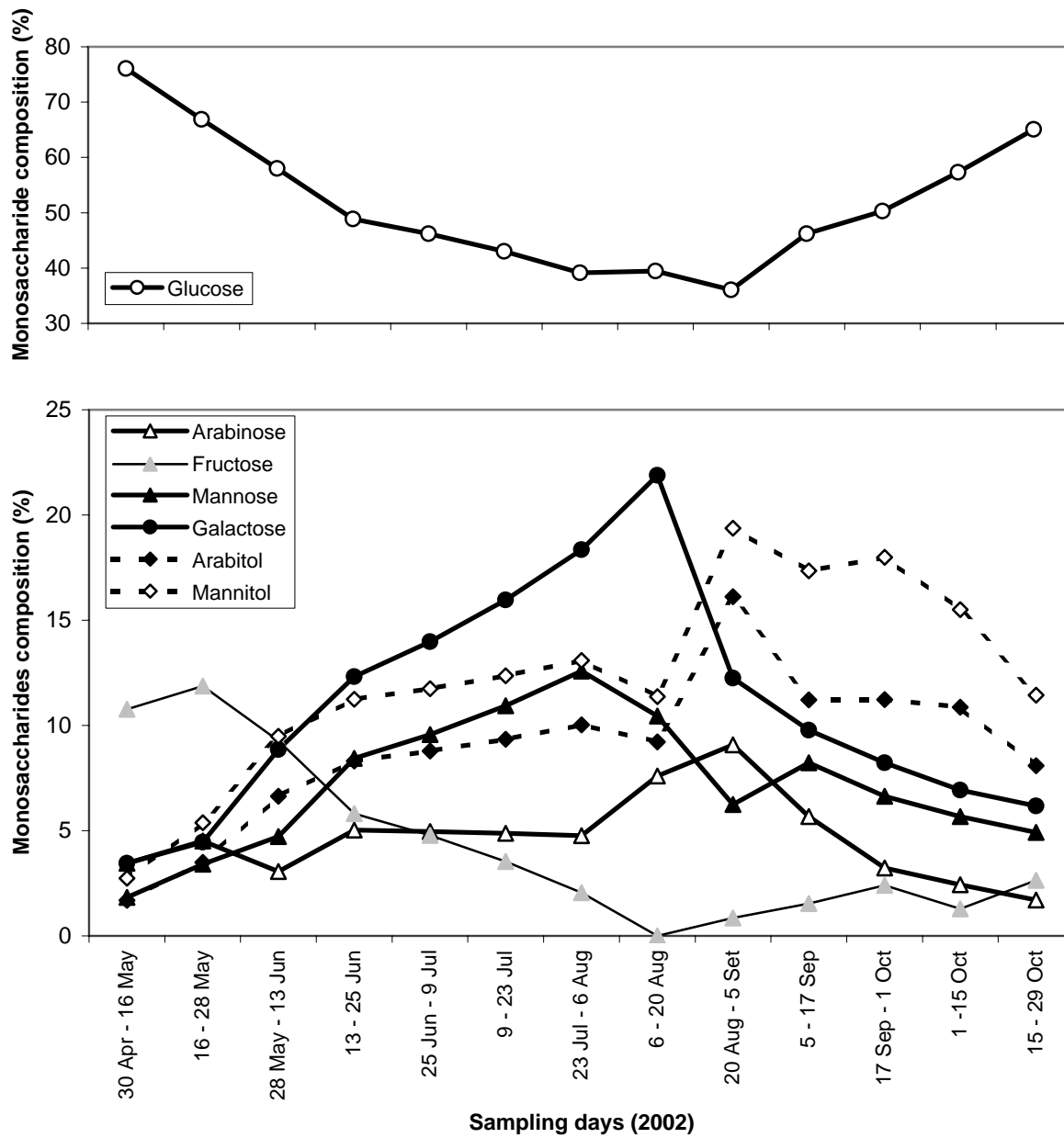


Figure 4

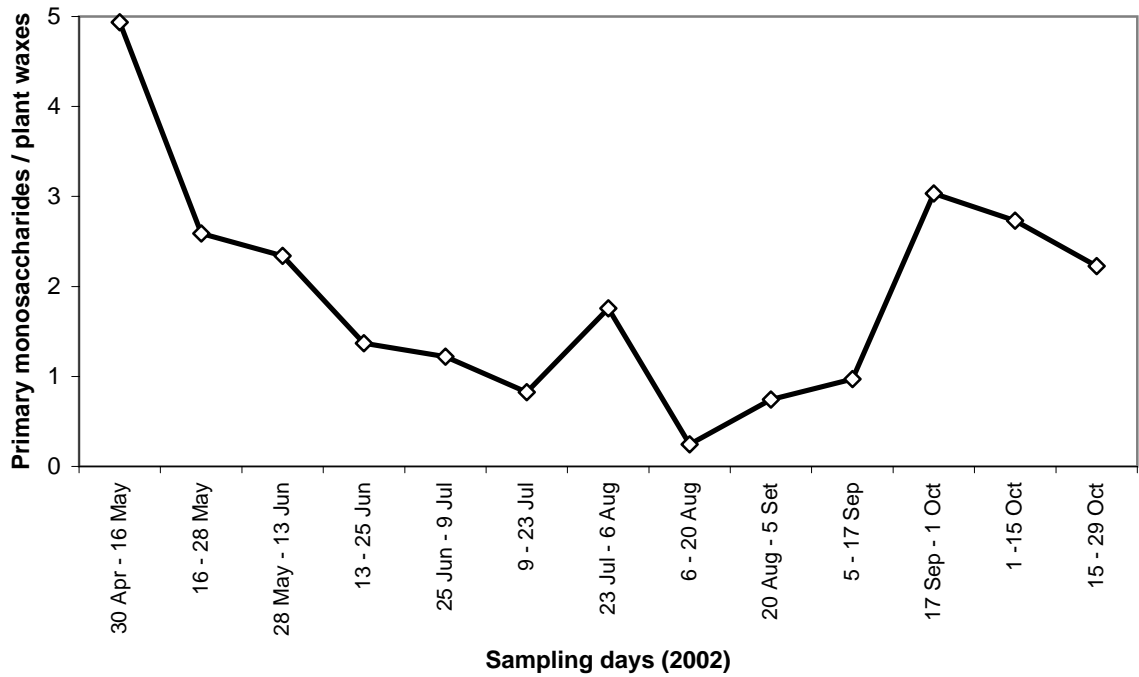


Figure 5



**Table 1. Concentrations (in ng m<sup>-3</sup>) of individual sugars, plant wax classes and dehydroabietic acid in above canopy aerosols collected at the Howland Experimental Forest, Maine.**

Compounds	Sampling period (2002)												
	30 April- 16 May	16-28 May	28 May- 13 June	13-25 June	25 June- 9 July *	9-23 July *	23 July- 6 Aug	6-20 Aug	20 Aug- 5 Sept	5-17 Sept	17 Sept- 1 Oct	1-15 Oct	15-29 Oct
<b>Sugars</b>													
<i>Monosaccharides</i>													
$\alpha$ - + $\beta$ -Arabinose	1.7	1.7	1.6	2.3	3.7	2.4	1.7	0.6	1.3	2.1	1.8	1.5	0.4
$\alpha$ - + $\beta$ -Glucose	37.3	25.3	29.8	22.6	50.1	45.7	13.8	3.1	5.2	16.9	28.7	34.7	15.1
$\alpha$ - + $\beta$ -Fructose	5.3	4.5	4.8	2.7	1.4	0.9	0.7	nd	0.1	0.6	1.4	0.8	0.6
$\alpha$ - + $\beta$ -Mannose	0.9	1.3	2.4	3.9	14.1	9.9	4.4	0.8	0.9	3.0	3.8	3.4	1.1
Galactose	1.7	1.7	4.5	5.7	22.2	13.8	6.5	1.7	1.8	3.6	4.7	4.2	1.4
Arabitol	0.8	1.3	3.4	3.8	5.4	5.0	3.5	0.7	2.3	4.1	6.4	6.6	1.9
Mannitol	1.3	2.0	4.9	5.2	6.7	5.8	4.6	0.9	2.8	6.3	10.2	9.4	2.7
Levoglucofan	2.1	4.6	4.0	5.3	55.1	54.0	5.0	1.0	2.4	5.9	4.1	3.9	13.1
Mannosan	nd	nd	nd	nd	10.4	7.6	nd	nd	nd	nd	nd	nd	1.8
Galactosan	nd	nd	nd	nd	2.6	1.1	nd	nd	nd	nd	nd	nd	1.0
<i>Disaccharides</i>													
Sucrose	4.1	5.6	nd	nd	1.5	nd	nd	nd	0.7	nd	nd	nd	nd
Maltose	4.1	1.3	nd	nd	nd	nd	nd	nd	nd	nd	nd	5.3	nd
Mycose	3.3	4.6	9.9	9.7	6.8	9.8	7.2	1.5	4.8	11.6	17.6	18.3	8.3
<b>Total</b>	<b>62.7</b>	<b>54.1</b>	<b>65.2</b>	<b>61.2</b>	<b>180.0</b>	<b>156.0</b>	<b>47.4</b>	<b>10.2</b>	<b>22.4</b>	<b>54.0</b>	<b>78.6</b>	<b>88.0</b>	<b>47.6</b>
<b>Plant wax classes</b>													
$\Sigma C_{23-35}$ <i>n</i> -alkanes	1.3	2.0	2.0	3.8	7.5	9.2	2.4	4.2	1.8	4.2	2.2	2.7	1.4
$\Sigma C_{20-34}$ <i>n</i> -alkanols	4.0	5.5	10.1	11.8	23.3	27.7	5.9	9.9	5.1	9.9	5.6	5.7	3.3
$\Sigma C_{20-34}$ <i>n</i> -alkanoic acids	4.2	5.8	6.3	11.5	44.2	51.2	7.1	10.9	5.7	12.7	5.5	7.9	3.7
Nonacosan-10-ol	0.8	0.7	0.9	1.8	3.0	2.7	0.9	1.4	0.8	1.1	0.1	0.1	0.7
<b>Total</b>	<b>10.3</b>	<b>14.0</b>	<b>19.3</b>	<b>29.0</b>	<b>78.0</b>	<b>90.8</b>	<b>16.3</b>	<b>26.4</b>	<b>13.4</b>	<b>27.9</b>	<b>13.4</b>	<b>16.4</b>	<b>9.1</b>
<b>Resin acid</b>													
Dehydroabietic acid	nd	nd	0.4	nd	3.5	2.4	3.3	nd	nd	3.0	2.9	3.6	2.8

nd: not detected.

\*Sampling period influenced by the passage of smoke plumes from Quebec wildfires.