

Using Levoglucosan as a Molecular Marker for the Long-Range Transport of Biomass Combustion Aerosols

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Samples of ambient particulate matter (PM10) collected during a regional haze episode are analyzed for the molecular marker levoglucosan (1,6-anhydro- β -D-glucopyranose) to track biomass-combustion generated aerosol. The particle samples were collected as part of an increased monitoring effort to measure the effect of emissions from biomass fires in Mexico and Central America on ambient particle concentrations in Texas. Atmospheric concentrations of levoglucosan quantified from PM10 samples collected at 9 sites in Texas vary from 0.2 to 1.2 $\mu\text{g m}^{-3}$. Levoglucosan concentrations are highest at border and coastal locations, where it represents between 1.1 and 1.3% of the total PM10 mass concentrations measured. To be used as a tracer for the long-range transport of biomass aerosol, levoglucosan must be conserved in transport from source to receptor and not be subject to atmospheric reactions that would selectively remove the marker. One possible reaction specific to levoglucosan, acid-catalyzed hydrolysis, is studied under conditions simulating the aqueous chemistry of atmospheric droplets. Results show no degradation of levoglucosan over a period of 10 days. This stability is incorporated into the long-range transport analysis of biomass combustion during the haze episode to determine the relative impact of long-range transport of combustion aerosol and local sources on PM10 levels on inland locations.

Introduction

Widespread biomass burning in the tropics has been identified as a major source of trace gases and particulate matter to the atmosphere (1–3). Investigations of the effect of biomass combustion have shown the effects of biomass combustion emissions on elevated ozone levels (4), in cloud formation and reflectivity (5), and on global budgets of trace gases important to the radiative balance of the Earth (1–3). The impact from biomass combustion has been shown to affect atmospheric chemistry after transport periods of several days and thousands of kilometers (6), meaning that the effect of biomass combustion can be seen great distances from the source region.

Many methods exist to determine the contribution of biomass combustion to ambient air quality. Using optical properties of the atmosphere determined from satellite imagery (7, 8), determining the atmospheric composition of

trace gases (9–11), and measuring the chemical composition of atmospheric particles (12, 13) have all been used to quantify the contribution of biomass burning emissions on ambient air quality.

To track emissions from biomass combustion across Texas during a recent regional haze episode linked to biomass burning in Southern Mexico and Central America, the molecular marker for biomass combustion, levoglucosan (1,6-anhydro- β -D-glucopyranose), is quantified in samples of ambient particulate matter. Levoglucosan is produced in large quantities from the combustion and pyrolysis of cellulose (14–16) and has been identified in particulate matter produced from the combustion of many different types of organic material that contain cellulose (17).

This molecular tracer technique has successfully quantified the contribution of primary particle emission sources on ambient particulate matter concentrations in urban airsheds (14, 18). However, in order for molecular markers to be used in tracking the long-range transport of primary emissions, the compound must be emitted in large quantities, so that once diluted and mixed with particulate matter from other primary sources, the molecular marker is recognizable and quantifiable. Molecular markers must not undergo any selective reactions that would preferentially remove the tracers above deposition of the primary particulate matter. Further, the emissions of these molecular markers must be unique to specific emission sources and conserved in atmospheric transport (neither formed nor destroyed by atmospheric chemical reactions). In this application, the suitability for levoglucosan to track the long-range transport emissions from biomass combustion is evaluated in the transport of particulate matter from Southern Mexico and Central America across Texas.

Experimental Methods

Ambient Aerosol Analysis. Atmospheric particulate matter samples from nine routine monitoring locations across Texas were collected on May 14, 1998 (see Figure 1). Satellite images from this date show a major influx of smoke from biomass combustion sources in southern Mexico and Central America being transported from the south to the north and across Texas (19).

The samples of ambient particulate matter (PM10) were collected as part of an increased monitoring effort to quantify the effect of emissions from biomass combustion on particle concentrations in Texas. The samples were collected on quartz fiber filters as part of three separate monitoring operations by the Texas Natural Resource Conservation Commission (TNRCC), the City of Houston, and the City of Dallas. These monitoring organizations also provided the gravimetrically determined PM10 mass concentrations of the samples analyzed. Blank filters from the filter lots used to collect each of the samples were obtained and analyzed according to the same analytical techniques used for sample analysis.

A portion of each PM10 filter was analyzed to determine the chemical composition of ambient particulate matter collected. Organic and elemental carbon concentrations were determined by the thermal-optical method of Birch and Cary (20). The concentrations of ionic species were determined by ion chromatography, atomic absorption spectroscopy, and colorimetric procedures (see ref 21 and references therein).

A filter area of 52 cm^2 was cut from each of the PM10 samples and blanks and analyzed for individual organic compounds. This filter portion was spiked with a known

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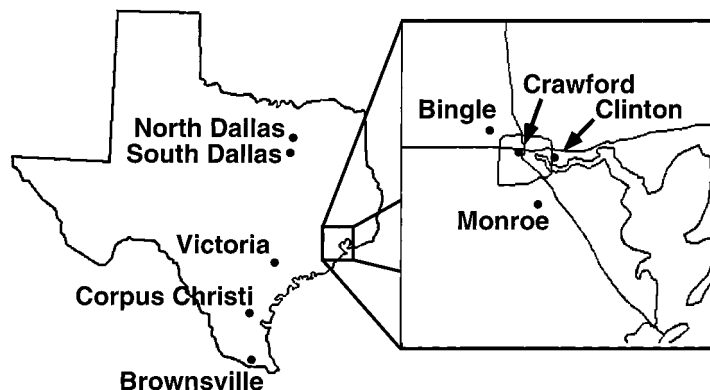


FIGURE 1. Map of Texas, showing sampling locations.

quantity of perdeuterated tetracosane ($n\text{-C}_{24}\text{D}_{50}$) to monitor extraction efficiency and blow down losses. The filter portion was extracted sequentially in high purity solvents including two aliquots of hexane and three aliquots of 2:1 benzene: 2-propanol. From each sample, the extracts were filtered over glass wool and combined into a boiling flask. The volume of the extracts from each sample was reduced to 3–5 mL by rotary evaporation, transferred into a conical vial, and further reduced to 300–500 μL under a gentle stream of prepurified nitrogen. The volume of each extract was determined using a 500 μL syringe.

Individual organic compounds were analyzed by gas chromatography–mass spectrometry (GC-MS) using a Hewlett-Packard 5973 Mass Sensitive Detector attached to a 5890 Gas Chromatograph without derivitization. The chromatographic separation was obtained using a 30-meter HP-5 capillary column with an internal diameter of 0.25 mm. A calibration standard made from levoglucosan (available from Sigma-Aldrich) was used to determine GC-MS response and a co-injection standard used to monitor the relative instrument response between analysis runs (22). The levoglucosan calibration standard was analyzed repeatedly showing a relative standard deviation of 27% between quantifications of a known amount. The quantification of the known quantity of $n\text{-C}_{24}\text{D}_{50}$ spiked onto the 11 filters (9 samples plus 2 blanks) as a recovery standard showed the recovery of $n\text{-C}_{24}\text{D}_{50}$ to range between 62% and 98% with a mean recovery of 85% and a standard deviation of 11% between extractions. The recovery efficiency of a variety of organic compounds of varying volatility and chemical composition has been shown to be well modeled by the extraction recovery efficiency of $n\text{-C}_{24}\text{D}_{50}$ spiked on filtered particulate matter (22). For that reason, the ambient concentrations of levoglucosan were corrected for the extraction and blow down losses by the fractional recovery of spiked $n\text{-C}_{24}\text{D}_{50}$.

Laboratory Tests of Levoglucosan Stability. In order for a molecular marker to be useful in tracing long-range transport from source region to receptor locations, the compounds must be conserved in transport. Previous work has shown that levoglucosan does not undergo decomposition reactions when exposed to ambient levels of gaseous photochemical oxidants such as ozone or nitrogen dioxide (14). However, upon reviewing the chemistry of levoglucosan, one reaction pathway that might selectively remove levoglucosan above and beyond the possible reactions of other molecular markers is the acid-catalyzed hydrolysis of levoglucosan to form $\beta\text{-D-glucose}$.

The compound levoglucosan has been studied as an intermediate in the conversion of biomass material into an alternative source of energy (23–25). Typical applications include pyrolysis of a cellulosic material, such as wood or newsprint, to produce levoglucosan. These industrial ap-

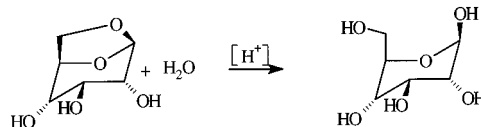


FIGURE 2. The acid-catalyzed hydrolysis of levoglucosan yielding $\beta\text{-D-glucose}$ as a possible reaction that could selectively remove levoglucosan, but not other molecular markers, from atmospheric particles.

plications have reported levoglucosan yields of between 25% and 50% (23). The tar produced containing the levoglucosan is hydrolyzed by acid catalysis to produce $\beta\text{-D-glucose}$. Additionally, levoglucosan has been studied as a feedstock in the production of polymers by using an acid-catalyzed ring-opening initiation reaction (26, 27). In both industrial applications, acid-catalyzed reactions are used to decompose levoglucosan to form $\beta\text{-D-glucose}$.

If levoglucosan undergoes an acid-catalyzed hydrolysis reaction in atmospheric aqueous droplets, as shown in Figure 2, it would not prove a useful tracer compound as the pH of atmospheric droplets is often acidic (28). The acidity of atmospheric droplets is commonly caused by sulfuric acid which is formed in gas-phase oxidation of sulfur dioxide and in numerous heterogeneous pathways (29). During the episode studied, significant concentrations of sulfuric acid are measured, with sulfate levels measured to be in excess of the buffering capacity of particle bound cations (see Results below).

The aqueous chemistry of aerosol droplets was simulated under two separate conditions. High-purity reagents used in this experiment included levoglucosan (Sigma-Aldrich, 98+% pure), ammonium sulfate (Sigma-Aldrich, 99.999% pure), 4-methoxyphenol (Sigma-Aldrich, 99% pure), and sulfuric acid (Fisher, 0.1 N). The simulations were all performed in deionized/distilled water and included a combination of ammonium sulfate, levoglucosan, and methoxyphenol (scenario 1) or a combination of sulfuric acid, ammonium sulfate, levoglucosan, and methoxyphenol (scenario 2). The second scenario simulated the chemistry of an acidic droplet with a pH of ~ 2 . This value was verified using pH paper.

Table 1 lists the concentrations of reagents in each scenario. These aqueous concentrations were used to approximate the concentrations of important solutes in aqueous aerosol droplets given the atmospheric concentrations derived from analysis of PM10 filters from this episode and the assumption of an atmospheric liquid water content of $5 \times 10^{-9} \text{ m}^3(\text{water}) \text{ m}^{-3}(\text{air})$ (30). Methoxyphenol was used as a surrogate for organic carbon concentrations measured during the episode as this and other alkyl derivatives of phenol that have been shown to be formed from the pyrolysis of lignin in wood combustion.

The concentrations of levoglucosan and $\beta\text{-D-glucose}$ (the product of the acid-catalyzed hydrolysis of levoglucosan)

TABLE 1. Solute Concentrations in the Experiment on Levoglucosan Stability

	solute	concn (g/L)
scenario 1:	4-methoxyphenol	8.00
	levoglucosan	0.50
	ammonium sulfate	4.00
scenario 2:	4-methoxyphenol	8.00
	levoglucosan	0.50
	ammonium sulfate	4.00
	sulfuric acid	0.50

were measured in aqueous solution by high-pressure liquid chromatography (HPLC) coupled to a refractive index (RI) detector. The analytical conditions were based on methods for carbohydrate analysis (31) and used a Hewlett-Packard HPXP 300 × 7.8 mm Bio-Rad column held at 80 °C. Water was used as the mobile phase with a flow rate of 0.7 mL/min. Concentrations of levoglucosan and β-D-glucose were quantified by calibrating the HPLC-RI detector with authentic standards available from Sigma-Aldrich. The standard mixture was run immediately before samples were analyzed, with a standard deviation between analyses of the authentic standard of ±11%.

Results

Ambient concentrations of levoglucosan measured from PM10 samples collected during the haze episode ranged from 0.2 ± 0.1 to $1.2 \pm 0.6 \mu\text{g m}^{-3}$ (95% confidence interval taken as two sigma). These concentrations represent between 0.2 and 1.3% of the total PM10 mass concentrations measured gravimetrically, as summarized in Table 2.

Additionally, the measured sulfate, organic and elemental carbon, and total cation and anion concentration (in $\mu\text{equivalents m}^{-3}$) are reported in Table 2. Other individual organic compounds used as source tracers, such as polycyclic aromatic hydrocarbons and petroleum biomarkers (18), were present in trace levels below quantification limits in some, but not all, of the samples.

From Table 2, the highest concentrations of the wood smoke molecular marker levoglucosan are observed in the border and coastal monitoring sites in Brownsville, Corpus Christi, and Victoria. The concentrations are lower in metropolitan Houston, ranging from 0.2 to $0.4 \mu\text{g m}^{-3}$, and in Dallas at $0.5 \mu\text{g m}^{-3}$. While the lower levoglucosan concentrations in Houston are also accompanied by lower total PM10 concentrations (ranging from 54 to $107 \mu\text{g m}^{-3}$), the PM10 concentrations in Dallas, exceeding $120 \mu\text{g m}^{-3}$, are higher than observed the locations with the highest levoglucosan levels. The PM10 levels in Houston are lowest at the southeastern monitoring location ($54 \mu\text{g m}^{-3}$) and highest adjacent to the industrial complex in the Houston Ship Channel ($107 \mu\text{g m}^{-3}$). This is consistent with overall transport from the south to the north and a superposition of local emission sources of coarse particulate material ($d_p > 2.5 \mu\text{m}$) on top of a regional concentration of fine particulate material ($d_p < 2.5 \mu\text{m}$) from the biomass combustion sources in Mexico and Central America. The fraction of PM10 concentrations that are observed in the molecular marker levoglucosan in southeast Houston (0.8%) is lower than observed at Brownsville (1.2%), Corpus Christi (1.1%), and Victoria (1.3%). This suggests that PM10 concentrations at this location include a lower total mass concentration of biomass combustion particulate matter plus a small additional contribution from local sources. In other parts of Houston, this additional contribution from local sources is highest in the industrial locations (adjacent to the Houston Ship Channel) where levoglucosan represents only 0.2% of the total PM10 mass measured. At the other two monitoring

locations in central and northwest Houston, levoglucosan represents 0.4% of the total PM10 concentrations. This is consistent with atmospheric transport from the south to the north that results in local emissions impacting locations in the central and northern region of the city greater than at the southeastern location.

The ambient concentrations of organic carbon measured from PM10 samples also show high levels at Brownsville, Corpus Christi, and Victoria. In addition, high organic carbon concentrations are measured in Dallas at the two monitoring locations that are not associated with high levoglucosan levels. In addition to the high concentrations of organic carbon expected with emissions from biomass combustion, high particulate sulfate concentrations are measured. While particulate sulfate is not a major chemical component present in the primary emissions from wood combustion (32, 33), high sulfate concentrations are measured in the border and coastal locations (13.4 to $14.6 \mu\text{g m}^{-3}$) and at the two locations in Dallas (20.3 to $21.4 \mu\text{g m}^{-3}$). It is expected that emissions of sulfur dioxide from biomass combustion would lead to secondary sulfate formation on transport from source locations to receptor measurement locations (2). Sulfate concentrations in Houston show a wider variation between 8.7 and $15.9 \mu\text{g m}^{-3}$, with highest concentrations at the Ship Channel monitoring location. This also suggests that local emissions in Houston are superimposed over a regional signature caused by long-range transport of fine particulate matter.

Except at the Houston Ship Channel and in Dallas, the charge balance for PM10 ionic species shows that cation (ammonium, magnesium, potassium, and sodium) and anion (chloride, nitrate, and sulfate) concentrations are roughly equivalent, with a mean cation-to-anion ratio of 1.03 ± 0.09 . In the Ship Channel and Dallas monitoring locations, measured anions exceed cations, indicating an acidic aerosol. This acidic aerosol solutions could affect the stability of the molecular marker, as levoglucosan undergoes acid-catalyzed hydrolysis to form glucose (23).

Atmospheric Stability of Levoglucosan. The two simulations of the atmospheric chemistry of levoglucosan in aqueous solutions shown in Table 1 were monitored for levoglucosan and β-D-glucose concentrations over a period of 10 days. The simulations were designed to simulate the possible composition of atmospheric liquid droplets that could catalyze the hydrolysis of levoglucosan to produce β-D-glucose. The time period of 10 days far exceeds the 48–72 h transport time from source region to receptor locations during the episode (19). The solute mixtures were blended and analyzed by HPLC-RI once every 3 h for 24 h and at the end of 10 days. Figure 3 shows the concentration of levoglucosan (relative to the initial concentration of levoglucosan) in the two simulations over the 10-day length of the experiment. From Figure 3, it is clear that the two scenarios showed no preferential degradation of the levoglucosan due to acid-catalyzed hydrolysis and suggests that levoglucosan does not undergo acid-catalyzed hydrolysis over the transport times of several days. This analysis is consistent with the observation of levoglucosan in ancient sediment deposits (34).

The impact of biomass combustion aerosol at inland sites can be calculated by source/receptor relationships using conserved molecular tracers only if source characterizations are available (18). Since levoglucosan formation from cellulose combustion is a function of the combustion temperature (16), source characterization need to be specific to the combustion conditions. Without proper source characterization, only estimations can be made. By assuming that particulate matter measured at the coastal location are representative of source emissions and using these measurements as source characterization, the impact of biomass

TABLE 2. Summary of Levoglucosan, PM10, Organic and Elemental Carbon, Sulfate, and Total Ions Measured in the Samples Analyzed

	levoglucosan ± 95% CI ($\mu\text{g}/\text{m}^3$)	PM10 ($\mu\text{g}/\text{m}^3$)	organic carbon ($\mu\text{g C}/\text{m}^3$)	elemental carbon ($\mu\text{g C}/\text{m}^3$)	sulfate ($\mu\text{g}/\text{m}^3$)	cations ($\mu\text{eq}/\text{m}^3$)	anions ($\mu\text{eq}/\text{m}^3$)
Border							
Brownsville	1.1 ± 0.6	94	32.7	0.2	13.4	0.30	0.32
Coastal							
Corpus Christi	1.0 ± 0.5	97	32.6	0.4	14.6	0.39	0.38
Victoria	1.2 ± 0.6	94	29.9	0.2	14.0	0.37	0.37
Dallas							
S. Dallas	0.5 + 0.3	124	30.4	0.5	21.4	0.38	0.46
N. Dallas	0.5 ± 0.3	119	32.3	0.4	20.3	0.39	0.44
Houston							
Bingle (NW Houston)	0.3 ± 0.2	70	15.2	<0.1	10.6	0.26	0.24
Clinton (Ship Channel)	0.2 ± 0.1	107	15.7	0.7	15.9	0.24	0.45
Monroe (SE Houston)	0.4 ± 0.2	54	10.3	<0.1	8.7	0.25	0.21
Crawford (Central Houston)	0.2 ± 0.1	66	14.1	0.1	11.4	0.27	0.27

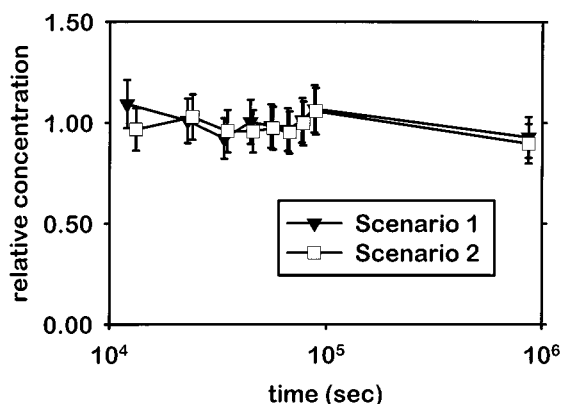


FIGURE 3. Results from the stability test of levoglucosan over a period of 10 days. Concentration is relative to initial concentration.

combustion on air quality at inland locations can be estimated. If PM10 levels at the coastal locations includes local emissions in addition to transport of biomass combustion aerosols from the source region, this analysis will **overestimate** the impact of biomass aerosols on inland locations. Using this analysis, 39–49 $\mu\text{g m}^{-3}$ of the observed 120–124 $\mu\text{g m}^{-3}$ observed in Dallas can be directly attributed to biomass combustion aerosol. Most likely this analysis will overestimate the impact of long-range transport to the inland locations, as the monitoring sites along the coast can be expected to measure some local emissions.

An improvement can be made on this analysis using available source composition information. Since levoglucosan formation is a function of combustion temperature, available source emission rates for levoglucosan cannot be used (14, 17). Assuming that the coastal locations include both primary biomass combustion aerosol and also localized PM10 emissions (such as sea salt) and knowing the fraction of wood combustion particulate matter that is organic carbon (0.48 for both soft and hardwood combustion (32)), we assume all organic carbon measured at the coastal locations is attributed to biomass combustion aerosol. This analysis predicts that 32–42 $\mu\text{g m}^{-3}$ of the observed 120–124 $\mu\text{g m}^{-3}$ can be directly attributed to biomass combustion aerosol at the two Dallas monitoring locations.

With the presented stability analysis showing that levoglucosan is conserved in transport from source to receptor, the question remains why PM10 concentrations of organic carbon are elevated in the two samples analyzed from Dallas that have significantly lower concentrations for the molecular marker for biomass combustion. Other molecular markers

for primary carbon particles were investigated but were present at only trace levels. According to the theory for secondary organic aerosol proposed by Odum et al. (35), aerosol yield will increase with increasing organic carbon particle concentrations. Using a typical background continental organic carbon particle concentration of 3.5 $\mu\text{g(C)} \text{ m}^{-3}$ (30), the particulate carbon concentrations measured along the coast during this haze episode of 30 $\mu\text{g(C)} \text{ m}^{-3}$, and parameters describing the secondary organic particle partition between the vapor and particle phases (36, 37), it is estimated that the additional primary organic carbon present during this haze episode would increase secondary organic aerosol yield from 1.2% to 5.1% for toluene and from 1.9% to 6.7% for the biogenic hydrocarbon α -pinene. This increase in particle yield via the absorption of semivolatile reaction products from oxidation of gas-phase hydrocarbons is due to the increased sites for physical absorption according to the theory proposed by Pankow (38, 39). In addition to increased yield of secondary organic aerosol, the oxidation of S(IV) to S(VI) has been observed on the surface of carbonaceous particles (40–42). These two mechanisms, one a physical explanation (sorption for secondary organic aerosol) and one a chemical explanation (formation of sulfate due to heterogeneous chemistry) may be responsible for the high observed particle levels in Dallas that cannot be attributed to direct particle emissions from biomass combustion sources.

In summary, direct emissions tracked to biomass combustion are shown to contribute between 26% and 41% of the PM10 concentrations at the two Dallas locations using the levoglucosan concentrations measured. However, it is possible that the primary carbonaceous particles emitted from the biomass combustion lead to the high PM10 levels either by a physical process (increased sorption of secondary organics) or by a chemical process (formation of sulfate by heterogeneous chemistry).

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