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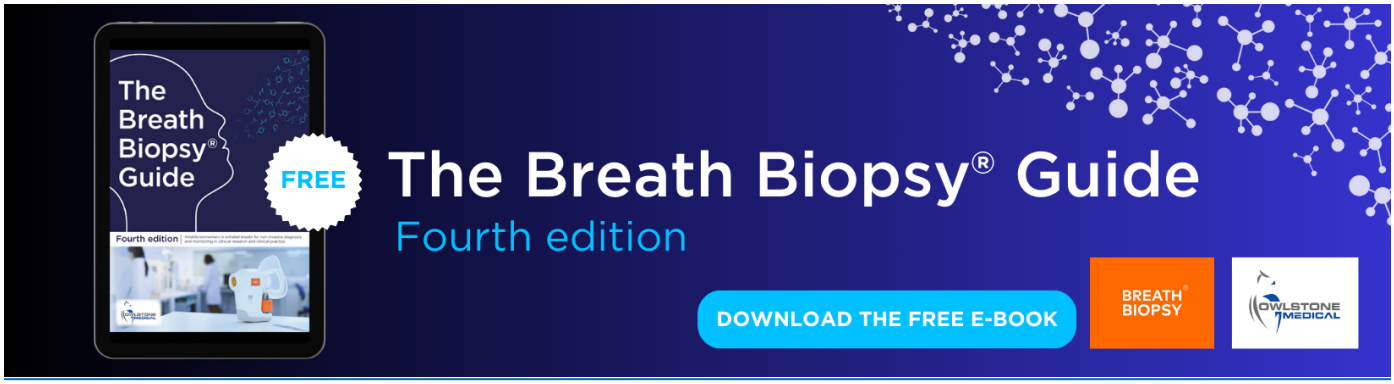

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Contribution of fungal spores to particulate matter in a tropical rainforest

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Abstract
The polyols arabitol and mannitol, recently proposed as source tracers for fungal spores, were used in this study to estimate fungal contributions to atmospheric aerosol. Airborne particulate matter ($PM_{2.5}$ and PM_{10}) was collected at Jianfengling Mountain, a tropical rainforest on Hainan Island situated off the south China coast, during spring and analyzed for arabitol and mannitol by high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD). The average concentrations of arabitol and mannitol exhibited high values with averages of 7.0 and 16.0 ng m^{-3} respectively in $PM_{2.5}$ and 44.0 and 71.0 ng m^{-3} in PM_{10}. The two tracers correlated well with each other, especially in the coarse mode aerosol ($PM_{2.5-10}$), indicating they were mainly associated with coarse aerosol particles and had common sources. Arabitol and mannitol in PM_{10} showed significant positive correlations with relative humidity, as well as positive correlations with average temperature, suggesting a wet emissions mechanism of biogenic aerosol in the form of fungal spores. We made estimations of the contribution of fungal spores to ambient PM mass and to organic carbon, based on the observed ambient concentrations of these two tracers. The relative contributions of fungal spores to the PM_{10} mass were estimated to range from 1.6 to 18.2%, with a rather high mean value of 7.9%, and the contribution of fungal spores to organic carbon in PM_{10} ranged from 4.64 to 26.1%, with a mean value of 12.1%, implying that biological processes are important sources of atmospheric aerosol.

Keywords: primary biogenic aerosol particles, molecular tracers, source contribution, PM_{10}, polyols, HPAEC

1. Introduction

Primary biological aerosol particles (PBAPs) in ambient air are formed by the suspension of particles of biological origin. There are various kinds of PBAPs, such as fungi, mosses, fern spores, viruses, bacteria, pollen, algae and plant as well as animal debris (Simoneit and Mazurek 1982, Després *et al* 2007, Burrows *et al* 2009). Recent estimates have shown contributions of PBAPs to the aerosol budget to be significant on a global scale (Heald and Spracklen 2009, Wiedinmyer *et al* 2009, Winiwarter *et al* 2009). Besides their adverse health effects, PBAPs may play an important role

in atmospheric processes, such as acting as ice nuclei (IN) or cloud condensation nuclei (CCN) (Dingle 1966, Schnell and Vali 1972, Jaenicke 2005, Bowers *et al* 2009, Pratt *et al* 2009) and thus exert important effects on climate forcing. As PBAPs act as outdoor allergens, airborne fungal spores, for example, have been associated with respiratory diseases, such as asthma and allergic rhinitis (e.g., Kurup *et al* 2000, Cakmak *et al* 2002). Fungal spores in particular have provoked an ongoing discussion because of their ubiquitous nature in the environment (Burge and Rogers 2000). While PBAPs may comprise a large fraction of the unidentified organic aerosol mass in the atmosphere, there are few studies reporting their contribution to ambient aerosol (Jaenicke *et al* 2007). Consequently, the need for quantifying the contribution of PBAPs to organic aerosol mass has been highlighted in recent studies. Fungal spores are produced during the life cycle of fungi, and often constitute the dominant biological component of ambient aerosols in the size range of 2–10 μm (Glikson *et al* 1995), as they have abundant sources, such as plants, animals, soil and human activities. It was estimated by Kendrick (1990) that there are over 100 000 fungal species whose spores may become airborne.

Sugar alcohols (aka polyols) are a common energy reserve material in fungi, and are produced in large amounts by many fungi. Thus, sugar alcohols, especially arabitol and mannitol, may constitute an important fraction of the dry weight of fungi (Carlile and Watkinson 1994). While four sugar alcohols (arabitol, mannitol, erythritol, and glycerol) are commonly found in fungi, arabitol and mannitol are particularly widespread (Carlile and Watkinson 1994). Although other sources of sugar alcohols in airborne particulate matter (PM) cannot be excluded, such as plants and algae, arabitol and mannitol have been mostly associated with fungal spores (Lewis and Smith 1967, Bieleski 1982, Graham *et al* 2003, Carvalho *et al* 2003, Ion *et al* 2005). Mannitol is the most widely distributed sugar alcohol in nature, and was proposed as a molecular tracer for actively wet discharged basidiospores by Elbert *et al* (2007). In addition to mannitol, arabitol has also recently been proposed as a suitable marker for fungal spores (Bauer *et al* 2008a). Moreover, Bauer and co-workers have determined a conversion factor that can be used to estimate the contributions of fungal spores to PM_{10} mass (Bauer *et al* 2008b).

Although ambient concentrations of sugar alcohols, including arabitol and mannitol, had previously been measured as part of several studies at various locations throughout the world, they were not recognized as molecular source tracers and, therefore, no estimations of fungal spore source contributions were made prior to the study by Bauer *et al* (2008a, 2008b). The polar nature of these species imposes analytical challenges, requiring chemical derivatization prior to the analysis by gas chromatography with mass spectrometric detection (GC-MS), which is the default analytical method for organic aerosol constituents. For the current study an alternative analysis method, high-performance anion exchange chromatography (HPAEC) with electrochemical detection, was used for the first time to measure sugar alcohols in ambient air. Moreover, to our knowledge, this is the first report of fungal spore contributions to atmospheric aerosol in a tropical region of Asia. Here we report the concentrations of arabitol and mannitol in ambient aerosol collected in a tropical rainforest in south China. Ambient characteristics of these tracer species were investigated through their mutual correlations in coarse and fine mode aerosol and in relation to meteorological parameters, and ambient concentrations were compared with those reported for other sites around the world. Furthermore, a preliminary estimate was made of the contribution of fungal spores to aerosol mass and organic carbon (OC).

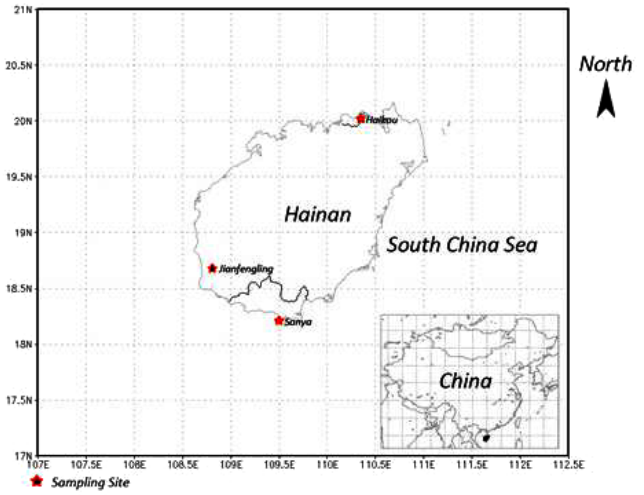

Figure 1. The geographic location of Jianfengling Mountain.

2. Experimental details

2.1. Site description and field sampling

Airborne particulate matter was collected at four background and rural sites in south China during the spring of 2004 as part of the 'Transport of Air Pollutant and Tropospheric Ozone over China' field campaign (Chan *et al* 2006, Engling *et al* 2010). The samples utilized in this report were collected at Jianfengling Mountain (18.67 °N, 108.81 °E, 820 m asl), situated in the southwest of Hainan Island, the southernmost province of China. The mountain is located about 120 km northwest of Sanya, the second largest city of Hainan province, facing the South China Sea. The sampling site was located within the Jianfengling National Forest Park, comprising a total area of 475 km^2 covered by rainforest. The nearest town is located at the foot of the mountain approximately 10 km away from the sampling site. Figure 1 shows the geographic location of Jianfengling Mountain. Additional information about this site can be found in Tang *et al* (2007). Aerosol sampling was conducted on top of a two-story building from 7 April to 18 May 2004. Mini-volume (Airmetrics, Eugene, OR, USA) samplers, equipped with $PM_{2.5}$ and PM_{10} size-selective inlets, were operated at a flow rate of 5.0 (±0.5) L min^{-1} for approximately 48 h. Samples were collected on pre-baked (500 °C) quartz fiber filters. Quality control procedures included collection of field blanks, which were obtained by mounting the filters in the sampler for 10 min without air

flow. In total, twelve field blanks were collected during the sampling period. After sampling, all sample filters were stored in sealed Petri dishes in a refrigerator at ∼4 °C for four years. As both compounds have very low vapor pressure, a loss due to volatilization during storage can be excluded. Moreover, the two polyols are believed to be quite stable in terms of potential oxidation by oxidants present in ambient air. Thus, storage losses are expected to be minimal, although this cannot be verified, since no internal standards were spiked onto the samples prior to storage. Recovery rates from sample preparation (extraction) were assumed to be 100% based on previous tests of spiked filter samples. These species are completely soluble in water, rendering aqueous extraction an ideal sample preparation method. The PM mass of each sample was determined gravimetrically using an electronic microbalance with 1.0 μg precision (Mettler M3, Mettler Instruments AG, Zurich, Switzerland) upon conditioning the sample filters at constant temperature and humidity for 24 h. In addition, daily meteorological data, including relative humidity and average temperature, measured on a meteorological tower located approximately 800 m away from the sampling site, were also used for analysis.

2.2. Chemical analysis

The chemical analysis of the filter samples was performed using the method outlined by Iinuma *et al* (2009). In brief, a portion of each filter (2.1 cm^2) was extracted with 2.0 mL of de-ionized water (>18.2 MΩ resistivity) under ultrasonic agitation for 60 min. The extracts were passed through a syringe filter (PTFE, 0.45 μm pore size) to remove insoluble material. All sample extracts were stored at 4 °C until sample analysis. Sample aliquots were injected (100 μL sample loop) without concentration or chemical derivatization into the ion chromatograph. The HPAEC-PAD system utilized here was a Dionex ICS-3000 series ion chromatograph, equipped with SP (quaternary pump and degasser), DC (column compartment), and ED (electrochemical detector and gold electrode) units (Dionex, Sunnyvale, CA, USA), as well as a SpectraSYSTEM AS3500 autosampler (Thermo Scientific, Waltham, MA, USA). The waveform used for pulsed amperometric detection was the standard quadruple potential for carbohydrate analysis (Dionex Technical Note 21). The separation was carried out on a Dionex CarboPac MA1 column (4 mm × 250 mm) with a CarboPac MA1 guard column (4 mm × 50 mm) with an aqueous sodium hydroxide (NaOH, 400 mM) eluent at a flow rate of 0.4 mL min^{-1}. Authentic standards were used for identification and obtaining the response factors of arabitol and mannitol. The bulk carbonaceous content of the aerosol samples, including OC and elemental carbon (EC), was determined with a semi-continuous carbon analyzer in offline mode (Sunset Laboratory, Tigard, OR, USA), using a modified NIOSH thermo-optical transmittance (TOT) method for charring correction (Birch and Cary 1996).

3. Results and discussion

The average $PM_{2.5}$ and PM_{10} mass concentrations at Jianfengling were 13.0 ± 4.2 and 18.1 ± 3.3 $\mu g\,m^{-3}$, respectively. The $PM_{2.5}$ (in PM_{10}) mass fraction was 70.9% on average, ranging from 55.8 to 92.7%, indicating that at Jianfengling atmospheric particulate matter was primarily present in the fine mode, with an average $PM_{2.5}$ to PM_{coarse} (PM_{10} minus $PM_{2.5}$) ratio of 3.4. Figure 2 shows the temporal variability of arabitol and mannitol concentrations in $PM_{2.5}$ and PM_{10} during the experimental period. Arabitol concentrations in $PM_{2.5}$ ranged between 4.0 and 10.4 ng m^{-3} (average of 7.0 ng m^{-3}), while the respective mannitol concentrations ranged from 10.6 to 27.5 ng m^{-3} (with an average of 16.0 ng m^{-3}). In PM_{10}, the maximum values of airborne arabitol and mannitol were 96.0 and 160.0 ng m^{-3}, respectively. The ratios of measured mannitol to arabitol in PM_{10} and $PM_{2.5}$ were 1.02–2.66 (average of 1.70) and 1.72–4.05 (average of 2.47), respectively. The contributions of arabitol to $PM_{2.5}$ and PM_{10} concentrations were 0.03–0.18% (average of 0.07%) and 0.06–0.51% (average of 0.26%), respectively, while those of mannitol were 0.06–0.36% (average of 0.16%) and 0.12–0.94% (average of 0.41%), respectively.

In this study, arabitol and mannitol showed poor correlation with levoglucosan, a molecular tracer for biomass burning (data not shown), demonstrating that these species are not directly generated through the combustion of biomass, although microbial and other biological species (including fungal spores) in contact with the plant material may be incorporated unaltered into the smoke particles during the burning process. Fungal spores were found in a previous study to be present in smoke from biomass burning, despite the high temperatures encountered in the fire (Mims and Mims 2004). The relationship between the concentrations of the two sugar alcohols in the coarse PM fraction and in PM_{10} is shown in figure 3. The strong correlations (R^2 = 0.997 and 0.986 for arabitol and mannitol, respectively) suggest that the sugar alcohols were mostly present in coarse particles, which is in good agreement with most findings reported in the literature for other locations (Graham *et al* 2003, Pio *et al* 2008, Kourtchev *et al* 2009). In contrast, at a boreal forest site (Hyytiälä, Finland) arabitol and mannitol were found to be mainly associated with fine mode aerosols (Carvalho *et al* 2003). Likewise, in a study by Lau *et al* (2006), ergosterol was used as a biomarker for the quantification of fungal spores and was predominantly associated with $PM_{2.5}$. A possible reason for these observations may be the fact that different assemblages of fungal communities (with differing particle size characteristics) are dominant at different sites. Other studies, however, have shown ambient fungal spores to be present predominantly in particles with aerodynamic diameters of 2–10 μm (Burge 2002), and specifically in size ranges of 2.5–3.0 μm for *Aspergillus fumigatus*, 3.5–5.0 μm for *Aspergillus niger*, 3.0–4.5 μm for *Penicillium brevicompactum*, and 7–17 μm by 5–8 μm for *Cladosporium macrocarpum* (Samson *et al* 1995).

We found that in both $PM_{2.5}$ and PM_{10}, the average arabitol and mannitol concentrations in May were higher than those in April. Active release of wet discharged ascospores and basidiospores occurs in most ascomycetes and in hymenomycetes (the largest order of basidiomycetes)

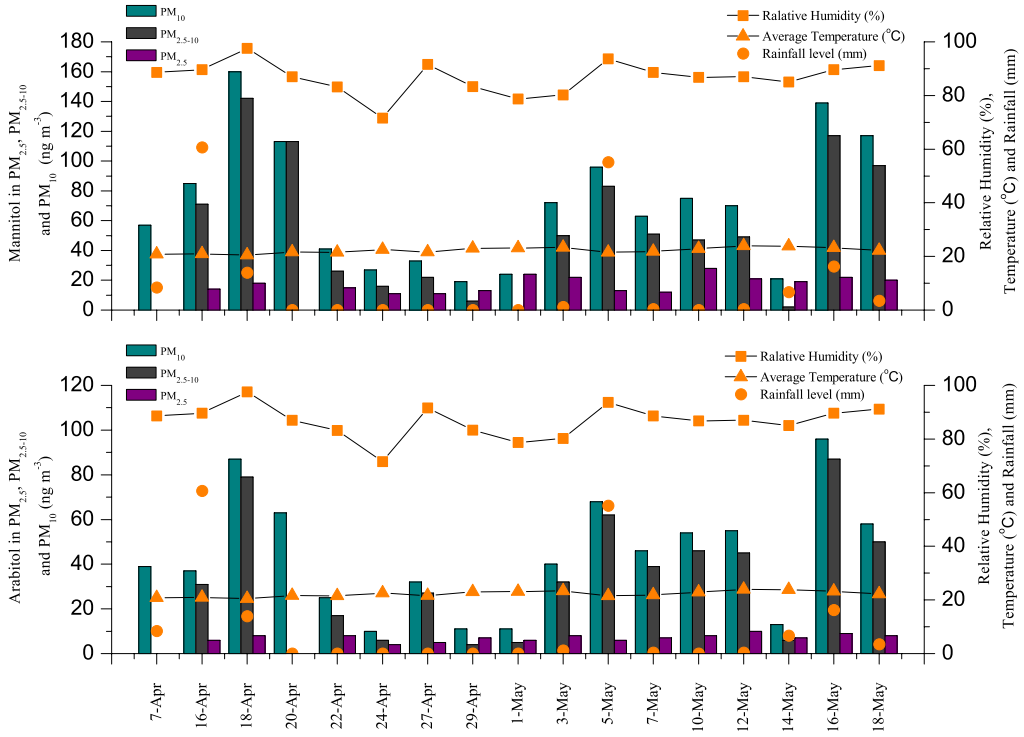

Figure 2. Timelines of arabitol and mannitol concentrations in $PM_{2.5}$, $PM_{2.5-10}$ and PM_{10}, as well as relative humidity, average temperature and rainfall level throughout the sampling period.

(Ingold 1984), which is influenced by ambient humidity and rainfall. Actively wet discharged ascospore concentrations have been found to increase during and after rainstorms. The release and resulting airborne concentrations of actively wet discharged basidiospores, on the other hand, appear to be more directly correlated with relative humidity rather than precipitation (Gregory and Hirst 1957, Hirst *et al* 1967, Burch and Levetin 2002, Elbert *et al* 2007). In contrast, dry discharged spores are preferentially emitted under dry and warm conditions. We correlated the concentrations of arabitol and mannitol with meteorological data at Jianfengling observed during the study period. In PM_{10}, mannitol showed a significant positive correlation ($R^2 = 0.442$; $p < 0.01$) with relative humidity (figure 3(d)). Arabitol also had significant positive correlation with relative humidity ($R^2 = 0.509$; $p < 0.01$) (figure 2). Elevated PM_{10} concentrations of arabitol and mannitol were usually observed after rain events. We thus conclude that fungal spores are mainly released through active wet discharge at Jianfengling. In addition, we found that arabitol and mannitol exhibited positive correlations with average temperature in PM_{10}, which was reported for several other studies as well (Ho *et al* 2005, Adhikari *et al* 2006, Sousa *et al* 2008).

The correlation between arabitol and mannitol ($R^2 = 0.886$, $p < 0.01$) in PM_{10}, was significant, as shown in figure 3(c), while that in $PM_{2.5}$ ($R^2 = 0.362$, $p < 0.05$) was poor. In contrast, good correlation between arabitol and mannitol in $PM_{2.5}$ was observed by Kourtchev *et al* (2009) at K-puszta, Hungary, a temperate location in Europe. Our observations indicate that in the coarse PM fraction the two sugar alcohols were mainly derived from the same sources, that is to say, fungal spores. In fine aerosol, the poor correlation was most likely due to the existence of additional contributing sources, such as small fungal fragments which have been identified in the sub-micron size range (Górny *et al* 2002), lichens, plant debris and other biogenic sources.

Quantitative estimates of fungal spore contributions to ambient PM mass, based on available source profile data and ambient tracer concentrations, are associated with a high degree of uncertainty due to the limited source data available to date. The conversion factors suggested by Bauer *et al* (2008a) (1.2 pg arabitol spore^{-1}; 1.7 pg mannitol spore^{-1}), Bauer *et al* (2008b) (33 pg fresh mass spore^{-1}) and Bauer *et al* (2002) (13 pg C spore^{-1}) were adopted in our study to obtain rough estimates of the contribution of fungal spores to the PM_{10} mass and to OC in PM_{10}. Using the published conversion factor for mannitol, the numbers of fungal spores in PM_{10} during this study ranged from 11 180 to 94 120 spores m^{-3}, with a mean value of 41 940 spores m^{-3}. These values were comparable to the fungal spore counts when using the arabitol conversion factor (1.2 pg arabitol spore^{-1}), ranging from 8330 to 72 500 spores m^{-3}. For better comparison with results from other studies, we used the mannitol conversion factor to estimate the contribution of fungal spores to ambient PM and OC mass at Jianfengling.

After obtaining the spore concentrations from the ambient mannitol concentrations by using the mannitol conversion factor (1.7 pg mannitol spore^{-1}), the estimated fungal mass in PM_{10} and OC_{10} can be calculated by using further conversion factors (33 pg fresh mass spore^{-1}; 13 pg C spore^{-1}). The relative contribution of fungal spores to PM_{10} mass was estimated to range from 2.33 to 18.2%, with a mean value

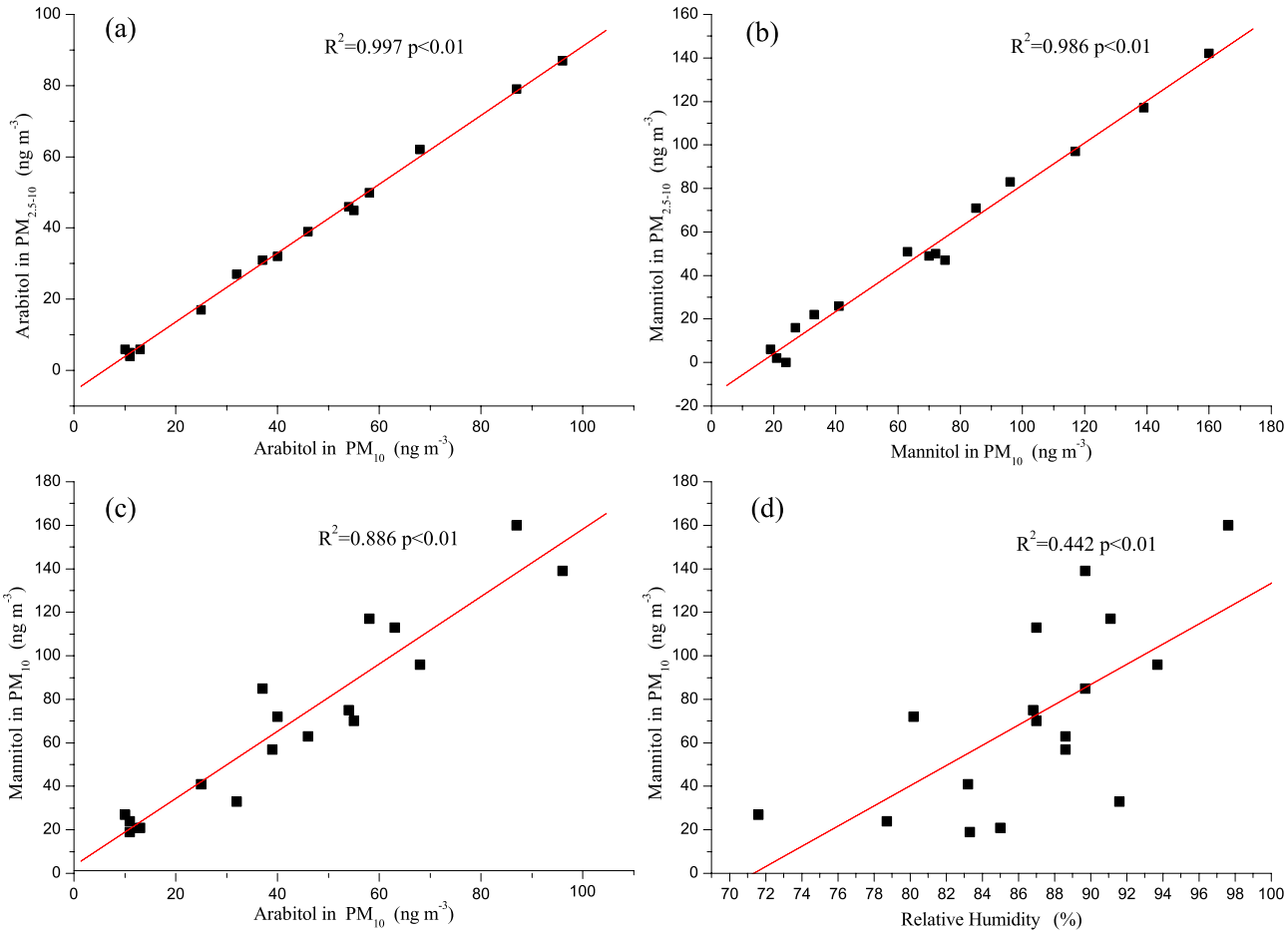

Figure 3. Correlations between (a) arabitol concentrations in $PM_{2.5-10}$ and PM_{10}, (b) mannitol concentrations in $PM_{2.5-10}$ and PM_{10}, (c) arabitol and mannitol concentrations in PM_{10}, and (d) between relative humidity and mannitol in PM_{10}.

of 7.92%. Fungal spore OC in PM_{10} ranged from 145.3 to 1223.5 ng m^{-3} (equivalent relative contributions were 4.64% to 26.1%, with a mean value of 12.1%). Bauer *et al* (2008b) reported mean contributions of fungal spores to PM_{10} and to OC_{10}, amounting to 4.8% and 2.3% for PM_{10} mass and 10% and 4.3% for OC_{10} at a suburban and urban site, respectively, which was comparable to our estimations. Using the same conversion factors, Kourtchev *et al* (2009) attributed 1.7% of $OC_{2.5}$ to fungal spores. These lower values are likely due to the fact that only fine mode PM measurements were performed. In contrast, Cheng *et al* (2009) used ergosterol as a biomarker for fungal spores, providing substantially lower (0.2%) mean fungal contributions to OC in PM_{10} in Hong Kong.

In fact, some uncertainties may be associated with our estimates, using the conversion factors suggested by Bauer *et al* (2002, 2008a, 2008b), because of the different ambient conditions at the two sites. The study by Bauer *et al* (2008b) was conducted in Vienna, Austria, from the end of March–July 2005, at a suburban and urban site, which were located in a park-like residential area and a mixed residential/industrial area, respectively. Consequently, the ambient temperatures and relative humidity, as well as the land cover (tropical rain forest) of this study, differ substantially from those of the study by Bauer *et al* (2008b). The fungal species and even the isolates of the same species may be significantly different at dissimilar locations. The conversion factors established for Vienna, Austria (i.e., a location in the moderate climate zone), may thus not be completely applicable for our study location (a tropical area), because certain characteristics of the fungi and their spores, including the concentrations of arabitol and mannitol, are not the same in different assemblages of fungal communities.

In order to characterize ambient aerosol and possible source contributions, it is important to quantify the total organic matter (OM) content in the sampled aerosol. A range of conversion factors for the computation of OM from measured OC values has been reported in the literature and used in various studies (Turpin and Lim 2001, Russell 2003, Chen and Yu 2007, Gilardoni *et al* 2009). Because forest areas are likely to have higher biogenic PM contributions and more intense secondary organic aerosol formation (due to the release of a multitude of reactive biogenic gaseous species, besides higher temperatures at this tropical location), an OM to OC ratio of 2.5 was adopted in our study, as suggested by Aiken *et al* (2008). The calculated contributions of OM to the total aerosol mass (PM_{10}) ranged from 49.5% to 97.4%, with a mean value of 68.8%, which is a rather high, yet reasonable estimate for a remote site such as Jianfengling.

In tropical regions, both physicochemical processes in the atmosphere and biological activity at the Earth's surface

Table 1. Overview of arabitol and mannitol concentrations reported in the literature and those measured at JFL.

Sampling sites	Sampling season	Particle size	Arabitol (mean) (ng m^{-3})	Mannitol (mean) (ng m^{-3})	References
JFL (China)	Spring	$PM_{2.5}$	7.0	16.0	This study
		PM_{10}	44.0	71.0	
Balbina (Brazil)	July	$PM_{2.5}$	13.84	15.17	Graham *et al* (2003)
		$PM_{2.5-10}$	41.74	53.30	
Rondônia (Brazil)	October (pasture)	$PM_{2.5}$	19.5	26.3	Graham *et al* (2002)
	October (forest)	$PM_{2.5}$	19.0	22.3	
Rondônia (Brazil)	Dry period	$PM_{2.5}$	16.7	21.9	Decesari *et al* (2006)
	Transition	$PM_{2.5}$	9.9	20.2	
	Wet period	$PM_{2.5}$	8.9	18.0	
Jülich (Germany)	July	$PM_{2.5}$	15.2	13.5	Kourtchev *et al* (2008)
Ghent (Belgium)	Summer	PM_{10}	105	97	Pashynska *et al* (2002)
	Winter	PM_{10}	26	26	
K-puszta (Hungary)	Summer	$PM_{2.5}$	4.8	5.3	Ion *et al* (2005)
California (USA)	September	PM_{10}	7.6	8.8	Cahill *et al* (2006)
Maine (USA)	May–October	$>1\ \mu m$	0.7–6.6	0.9–10.2	Medeiros *et al* (2006)
Averio (Portugal)	Summer	$PM_{2.5}$	5.20	7.82	Pio *et al* (2008)
		$PM_{2.5-10}$	16.73	12.01	
Helsfyr (Norway)	Fall	$PM_{2.5}$	1.7	2.0	Yttri *et al* (2007)
		PM_{10}	18	20	
Oslo (Norway)	Fall	$PM_{2.5}$	1.0	1.6	
		PM_{10}	5.3	8.1	
Birkenes (Norway)	Annual	$PM_{2.5}$	0.42	0.27	
		PM_{10}	6.0	4.3	
Elverum (Norway)	Winter	$PM_{2.5}$	4.3	2.8	
		PM_{10}	5.3	4.2	
	Summer	$PM_{2.5}$	2.0	2.0	
		PM_{10}	20	18	
Melpitz (Germany)	April–May	PM_{10}	4.2–35	1.6–23	Carvalho *et al* (2003)
Hyytiälä (Finland)	August	PM_{10}	1.4–241	<0.5–88	
Lobau (Austria)	Autumn	PM_{10}	7.0–63	8.9–83	Bauer *et al* (2008a)
	Summer	PM_{10}	28	42	
Schafberg (Austria)	Summer	PM_{10}	22	34	
Yuen Long (China)	Summer	$PM_{2.5}$	0.23–4.09	0.02–1.77	Hu *et al* (2008)
Mt. Tai (China)	Summer (daytime)	TSP	52.5	77.8	Fu *et al* (2008)
	Summer (nighttime)		56.4	83.9	
Jianfengling (China)	November	$PM_{2.5}$	15	16	Wang *et al* (2008)

are particularly intense, and consequently the abundance of fungal spores and other biogenic chemical species is typically higher than those in extra-tropical regions. The Jianfengling sampling site was situated within a tropical rainforest with high average temperatures of 21.0 and 22.9 °C in April and May of 2004, respectively. The average relative humidity during that period was high (>87%) at Jianfengling as well. Therefore, the mannitol peak concentrations (in PM_{10}) of 160 ng m^{-3} at Jianfengling were higher than observations at most locations around the world (table 1). The composition and abundance of airborne fungal spores are expected to depend on vegetation characteristics, seasonal and meteorological conditions, geographical location and human activities (Lacey 1981). Positive correlations between relative humidity or temperature and fungal spores have been reported in several studies (Ho *et al* 2005, Adhikari *et al* 2006, Sousa *et al* 2008). The concentrations of arabitol and mannitol (and hence of fungal spores) at Jianfengling are likely to be even higher in July (compared to our study period, April–May), because of the higher relative humidity and ambient temperatures during the summer months. Similar tracer concentrations to our observations in spring were measured in $PM_{2.5}$ at Jianfengling in autumn, as shown in table 1 (Wang *et al* 2008).

Arabitol and mannitol concentrations have also been reported for other forest sites (Graham *et al* 2002, 2003, Carvalho *et al* 2003, Ion *et al* 2005, Medeiros *et al* 2006, Fu *et al* 2008, Kourtchev *et al* 2008) and pasture sites (Graham *et al* 2002, Decesari *et al* 2006) (table 1). For instance, fine and coarse mode concentrations of arabitol and mannitol at Balbina, Amazonia in July 2001, a tropical rainforest and natural background site as well, were measured by Graham *et al* (2003), as shown in table 1. The fungi tracer levels observed in our study were comparable to the levels at the Amazonian background site, despite the difference in the sampling seasons. Compared with measurements conducted in two temperate coniferous forests in North America (Cahill *et al* 2006, Medeiros *et al* 2006), our study revealed substantially higher concentrations of arabitol and mannitol. It should be noted that most of the studies cited in table 1 utilized GC-MS analysis, except that by Yttri *et al* (2007), which used HPLC/HRMS-TOF analysis, and that by Bauer *et al* (2008a) using GC-FID analysis. The method (HPAEC-PAD) applied in this study is relatively new in its application to atmospheric

aerosols. Engling *et al* (2006) compared this method with two independent analytical techniques (HPLC-MS, GC-MS) and found good agreement between the different methods. Although there may be some influence on the results due to different analytical methods applied in the individual studies, it can be clearly seen from table 1 that higher arabitol and mannitol concentrations were usually associated with greater land cover, while also being dependent on the sampling season. Higher concentrations of the sugar alcohols were typically observed at inland locations (in contrast to coastal sites) and during the warmer or wet seasons.

Ambient levels of arabitol and mannitol have been reported for urban areas as well (Suzuki *et al* 2001, Pashynska *et al* 2002, Wang and Kawamura 2005, Yttri *et al* 2007). Suzuki *et al* (2001), for example, reported atmospheric concentrations of mannitol ranging between 3 and 66 ng m^{-3} in the urban area near Osaka Bay. At an urban site in Hong Kong, concentrations of mannitol in $PM_{2.5}$ were in the range of values below analytical detection limits up to 21.0 ng m^{-3}, with a mean value of 6.71 ng m^{-3} (Wan and Yu 2007). Urbanization could change patterns of vegetation, which is the primary fungal source, and therefore alter the concentrations and composition of fungal spores (Burge 2002). Generally, fungal levels at forest or rural sites are higher than in urban areas because of the broader vegetation coverage, although rather high ambient concentrations of fungal spore tracers have been observed at urban sites as well (Pashynska *et al* 2002). Abundance and variability of fungal aerosols in urban areas could be related to many factors, such as vegetation, vehicle traffic (and airflow dynamics in the streets), amount of suspended dust, and density of people carrying fungi (Giorgio *et al* 1996).

As shown from the (limited) literature data, arabitol and mannitol or other biogenic aerosol tracers are subject to strong geographical and seasonal variability. Therefore, additional research efforts are needed to better characterize the abundance, spatiotemporal variability, source processes and contributions of biological species to aerosol mass concentrations.

4. Conclusions

Biological aerosol particles constitute an important fraction of ambient aerosol loadings and may have significant influence on the global radiation budget via the indirect or direct aerosol effects. Conversely, few studies have reported contributions of bioaerosol to atmospheric aerosol mass, especially for tropical regions. Fungal spores often constitute the dominant biological component of airborne coarse particles. Measurements of the fungal tracers arabitol and mannitol in South China, using a new analytical method, HPAEC-PAD, revealed rather high concentrations of these polyols in ambient air, specifically in PM_{10}. Arabitol and mannitol correlated well with each other, particularly in coarse mode aerosol ($PM_{2.5-10}$), indicating common sources and predominant presence of these species in coarse particles. Correlation analysis of mannitol concentrations in PM_{10} with meteorological parameters revealed a dependence of the ambient tracer levels on relative humidity and temperature. Our results seem to imply that wet emission of fungal spores was the predominant source process for these biological species. Relative contributions of fungal spores to ambient PM_{10} mass were as high as 18.2% and 26.1% to the organic carbon in PM_{10}, based on estimates using the measured tracer concentrations. To our knowledge, these are the first published estimates of fungal spore contributions in a tropical region, indicating the significance of bioaerosol species as atmospheric aerosol constituents.

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