Influence of Rain on the Abundance and Size Distribution of Bioaerosols

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Abstract. Assessing the environmental, health and climate impacts of bioaerosols requires knowledge of their size and abundance. These two properties were assessed through daily measurements of chemical tracers for pollens (sucrose, fructose, and glucose), fungal spores (mannitol and glucans) and Gram-negative bacterial endotoxins in fine particulate matter ($PM_{2.5}$), coarse PM ($PM_{10-2.5}$) and PM_{10} (as the combination of $PM_{2.5}$ and $PM_{10-2.5}$) during the spring tree pollen season (mid-April to early-May) and late summer ragweed season (late-August to early-September) in the Midwestern US in 2013. Under dry conditions, pollen and fungal spore tracers were primarily in coarse PM (>75%), as expected for particles greater than 2.5 µm. Rainfall on May 2 corresponded to maximum atmospheric pollen tracer levels and a redistribution of pollen tracers to the fine PM fraction (>80%). Both changes were attributed to the osmotic rupture of pollen grains that led to the suspension of fine-sized pollen fragments. Fungal spore tracers peaked in concentration following spring rain events and decreased in particle size, but to a lesser extent than pollens. A short, heavy thunderstorm in late summer corresponded to an increase in endotoxin and glucose levels, with a simultaneous shift to smaller particle sizes. Simultaneous increases in bioaerosol levels and decrease in their size has significant implications for population exposures to bioaerosols, particularly during rain events. Chemical mass balance (CMB) source apportionment modelling and regionally-specific pollen profiles were used to apportion PM mass to pollens and fungal spores. Springtime pollen contributions to PM_{10} mass ranged from 0.04–0.8 µg m^{-3} (0.2-38%, averaging 4%), with maxima occurring on rainy days. Fungal spore contributions to PM_{10} mass ranged from 0.1–1.5 µg m^{-3} (0.8–17%, averaging 5%), with maxima occurring after rain. Overall, this study defines changes to size distributions and concentrations of pollens, fungal spores, and endotoxins in response to rain in the Midwestern United States and advances the ability to apportion PM mass to pollens.

1 Introduction

Inhalable bioaerosols (<100μm) act as aeroallergens, triggering mild to severe allergic respiratory diseases (D'Amato et al., 2007a; Dales et al., 2003). Types of bioaerosols include viruses (<0.3 μm), bacteria (0.25-8 μm), fungal spores (1-30 μm), and plant pollens (~5-100 μm) (Jones and Harrison, 2004; Matthias-Maser and Jaenicke, 1995). Once
5 inhaled, bioaerosols reach different regions of the respiratory system based on their size (Oberdörster et al., 2005; Brown et al., 2013), which is dependent on the route of breathing, age, gender, and activity level (Brown et al., 2013). In general, particles of 3 μm and 5 μm for adults and children, respectively, travel beyond the larynx (Brown et al., 2013). Human immune system produces antibodies against inhaled aeroallergens that initiate airway symptoms (e.g., cough and runny nose), and exacerbate diseases like asthma and allergic rhinitis. Allergic respiratory diseases are estimated to affect 334
10 million people worldwide, particularly children (GAN, 2014).These respiratory illnesses are predicted to increase in response to global trends of increasing carbon dioxide concentrations (Singer et al., 2005; Ziska and Caulfield, 2000) and temperatures (Beggs, 2004) that enhance the allergenicity (Singer et al., 2005) and quantity (Ziska and Caulfield, 2000) of pollens, and duration of pollen seasons (Beggs, 2004; Beggs and Bambrick, 2006). The protection of sensitive populations from bioaerosols requires understanding environmental exposures to bioaerosols as a function of their type, size, and
15 temporal variation.

Ambient levels of pollens vary seasonally with growing cycles (Galán et al., 1995; Targonski et al., 1995). Springtime in the Midwestern United States is generally characterized by high levels of tree pollens (Targonski et al., 1995), such as oak (Wallner et al., 2009), birch (Emberlin et al., 2002), alder, and hazel (Niederberger et al., 1998). Summertime has elevated concentrations of grass pollens (e.g., Timothy and Rye grass) and weed pollens, especially ragweed (Targonski
20 et al., 1995). Daily pollen levels are affected by temperature, with warmer conditions favouring pollen development, maturation, and active release (van Vliet et al., 2002). Rainfall promotes the passive release of intact pollens by agitation (Taylor and Jonsson, 2004). In rainy conditions, pollen grains absorb water, osmotically rupture, and release cytoplasmic starch granules (D'Amato et al., 2007b). Microscopy studies have shown that intact birch pollens of 22 μm in size can rupture and release around 400 starch granules (Staff et al., 1999) ranging from 0.03 - 4 μm (D'Amato et al., 2007b).
25 Consequently, human exposures to pollens in the atmosphere are highly dependent on pollen type, season, and local meteorology.

Fungal growth and spore release is also promoted by elevated temperatures (Corden and Millington, 2001) and wet conditions (Pasanen et al., 2000). Fungi discharge spores via splash-induced emission, as is the case for *Cladosporium*, a prominent fungal genus (Troutt and Levetin, 2001; Oliveira et al., 2009) that releases spores by mechanical shock and fast
30 air currents produced by rain drops (Elbert et al., 2007; Allitt, 2000). Fungi that belong to the division Ascomycetes disperse spores in moist conditions (Jones and Harrison, 2004) leading to elevated spore levels several hours after rain (Allitt, 2000; Packe and Ayres, 1985). The release of bioaerosols during and after rain events can trigger significant changes to ambient bioaerosol numbers (Knox, 1993; Huffman et al., 2013) and mass concentrations (Marks et al., 2001).

Bacteria in the atmosphere are typically settled on soil or vegetative surfaces and are found in cell agglomerates (Jones and Harrison, 2004). Taxonomic analysis has revealed that soil and plant surfaces serve as sources of bacteria in the Midwestern US (Bowers et al., 2011). Ambient bacterial levels increase with temperature (Carty et al., 2003) due to conditions that favour vegetation and bacterial habitat (DeLucca and Palmgren, 1986; Romantschuk, 1992). In vegetation-covered areas, atmospheric bacterial concentrations peaked after approximately 1 h of rain relative to areas with bare soil (Robertson and Alexander, 1994). This response to precipitation has been attributed to rain moving plants and aerosolizing bacteria (Jones and Harrison, 2004). With strong dependences on local meteorology, bacteria, are likely to exhibit high temporal variability.

Once released, bioaerosols in the atmosphere promote cloud and ice nucleation (Pope, 2010; Sun and Ariya, 2006; Franc and Demott, 1998). Intact birch, walnut and willow pollens have been demonstrated to be cloud condensations nuclei (CCN) (Pope, 2010), with cytoplasmic pollens granules ranging 0.05-0.3 µm being the most CCN active, due to their hygroscopicity and longer residence time (Steiner et al., 2015). Bacteria also are CCN, at relatively low supersaturations (Sun and Ariya, 2006; Franc and Demott, 1998). Because of their ordered structures, bioaerosols are effective ice nuclei (IN) forming ice crystals at sub-cooled temperatures, including intact pollens (Diehl et al., 2001; Diehl et al., 2002), pollen extracts (Augustin et al., 2013), fungal spores (Murray et al., 2015), and bacteria (Sun and Ariya, 2006; Pouleur et al., 1992). Their ability to act as CCN and IN affects the earth's climate through changes to cloud albedo and precipitation cycles (Diehl et al., 2001; Sun and Ariya, 2006).

Atmospheric levels of bioaerosols can be assessed through measurements of specific chemical and biological tracers. Glucose, fructose and sucrose are main energy storage material in plants, major contributors to pollen mass (Speranza et al., 1997; Fu et al., 2012) and have been used as pollen tracers in China and the United States (Fu et al., 2012; Jia et al., 2010a; Jia et al., 2010b) Although not unique to pollens, these three sugars also comprise a minor fraction of suspended soil (Rogge et al., 2007), road dust (Simoneit et al., 2004) and biomass burning (Medeiros and Simoneit, 2008). Mannitol and arabitol are sugar alcohols that serve as energy storage materials in fungi and are used to identify the presence of airborne fungal spores and to quantify their contributions to PM mass (Bauer et al., 2008; Zhang et al., 2010). 1,3-β-D-glucans are immune-active polysaccharides in fungal cell walls (Thorn et al., 2001; Bonlokke et al., 2006) that are also tracers of fungal spores that have been used to assess exposure levels in indoor and outdoor environments (Madsen, 2006; Crawford et al., 2009). Endotoxins are lipopolysaccharides in Gram-negative bacterial membranes that induce respiratory inflammations (Douwes et al., 2003; Thorne et al., 2015). Ambient levels of endotoxins have been measured in outdoor (Pavilonis et al., 2013) and occupational settings (Thorne et al., 2009). Measurement of these bioaerosol tracers allows for the evaluation of the atmospheric concentrations and size distributions of pollens, fungal spores, and Gram-negative bacteria.

Given the important role of bioaerosols in the health of sensitive populations and in atmospheric processes, a robust understanding of bioaerosol types and their response to changing meteorological conditions is needed. Our central objectives were *i)* to assess temporal variations in pollens, fungal spores and endotoxin concentrations and size distributions, *ii)* evaluate environmental conditions that lead to high levels and decreases in bioaerosol sizes across fine ($PM_{2.5}$) and coarse

($PM_{10-2.5}$) modes, *iii*) chemically profile regionally-important pollen types (red oak, pin oak, cotton ragweed, giant ragweed and corn) for use in source apportionment, and *iv*) estimate pollen and fungal spore contributions to PM mass by way of chemical mass balance (CMB) modelling. The outcomes of this study include an improved understanding of changes in ambient concentrations and PM size distributions of bioaerosols in response to rain events and their contributions to PM

5   mass.

2 Methods

2.1 Sample collection

Daily (24 h) PM samples in spring and late summer were collected from 17 April–9 May, and 15 August–04

10   September, respectively, in 2013, at the University of Iowa air monitoring site in Iowa City, Iowa, US (+41.6647, – 91.5845). $PM_{2.5}$ and $PM_{10-2.5}$ were collected on 37-mm Teflon filters (Pall Corp.) using an Andersen dichotomous sampler (Series 241), with a total flow rate of 16.67 L min^{-1}, and a coarse flow rate of 1.667 L min^{-1}. PM_{10} was determined as the sum of $PM_{2.5}$ and $PM_{10-2.5}$ measurements. An additional set of $PM_{2.5}$ samples were collected on to 90-mm quartz fiber filters (Pall Life Sciences) using a medium-volume sampler (URG Corp.), with a Teflon-coated aluminium cyclone operating at a flow

15   rate of 90 L min^{-1}. All flowrates were measured using a rotameter at the beginning and the end of each sampling period; average flowrates were used to calculate air volumes. Filters were changed at 08:00 local time. One field blank was collected for every 5 samples. Filters were stored at -20 ˚C in the dark until analysis.

To assess the representativeness of 2013 PM levels to typical conditions in Iowa, $PM_{2.5}$ and PM_{10} mass measurements were compared to measurements from 2010-2015 downloaded from the Technology Transfer Network (TTN)

20   Air Quality System (AQS) Data Mart (USEPA, 2013). The federal reference method (FRM) site for Johnson County, Iowa is located at Hoover Elementary School, (+41.6572, – 91.5035), 6.3 km east of the University of Iowa air monitoring site. $PM_{2.5}$ concentrations were compared to average levels over the sampling period calculated from hourly measurements while PM_{10} data were compared to filter measurements collected from midnight to midnight every three days.

25   ### 2.2 PM mass measurement

PM mass was determined by the difference of pre- and post-sampling Teflon filter weights. Filter measurements made in a temperature (21.9 °C) and humidity controlled (25±5%) room using an analytical microbalance (Mettler Toledo XP26) after conditioning 48 hours. Standard deviations of triplicate measurements were used as the error associated with the mass measurement.

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2.3 Analysis of carbohydrates and inorganic ions

All glassware was prebaked at 500˚C for 5 hours, while plastic vials used were pre-rinsed with ultrapure (UP) water (resistivity >18.2 MΩ cm^{-1}) (Barnstead EasyPure II, 7401). Teflon filters (containing $PM_{10-2.5}$ samples) were cut in half using ceramic scissors on a clean, guided glass surface. Prior to extraction, Teflon filters were pre-wet with 100 µL of acetone

(Sigma Aldrich). Subsamples of Teflon and quartz fiber filters (containing $PM_{2.5}$) were extracted into 4.00 mL of UP water by rotary shaking for 10 min at 125 rpm, ultra-sonication for 30 min at 60 Hz (Branson 5510, Danbury, CT, US), and then rotary shaking for 10 additional min. The extract was then filtered through a 0.45 μm polypropylene syringe filter (GE Healthcare, UK).

5   Carbohydrate concentrations were determined by high performance anion exchange chromatography (HPAEC) with pulsed amperometric detection (PAD, Dionex ICS 5000, Thermo Fisher, Sunnyvale, CA, USA). The HPAEC-PAD instrument consisted of an eluent organizer, dual pump, degasser, column compartment, electrochemical detector (ED50), AS-DV autosampler, CarboPac PA20 analytical column (3 X 150 mm, Dionex), guard column (3 X 30 mm), and a 10 μL injection loop. An isocratic separation of carbohydrates (erythritol, arabitol, fucose, trehalose [Alfa Aesar], glucose, fructose,

10   arabinose, xylitol, xylose [Sigma Aldrich], rhamnose, mannose, ribose [Acros], sucrose and mannitol [Fisher Scientific]) was achieved with 10 mM sodium hydroxide (NaOH, Fisher Scientific) that was stored under N_2 (Praxair). The detector cell contained a gold disposable working electrode, to which quadruple waveform A was applied relative to a pH-Ag/AgCl reference electrode (Rocklin et al., 1998; Jensen and Johnson, 1997). Chromeleon 7 software was used for instrumental control, data acquisition and analysis. Carbohydrates were quantified against seven-point calibration curves ranging from

15   0.0100–2.50 ppm. Each analysis batch consisted of eight PM samples, two field blanks, one lab blank and one spike recovery sample. Summarized in Table S1 are carbohydrate extraction efficiencies (94-103%), instrument detection limits, and method detection limits.

      Inorganic ion concentrations were determined using ion exchange chromatography with suppressed conductivity detection (ICS-5000, described above) following Jayarathne et al. (2014). Briefly, anions were separated on an Ionpac AS22

20   analytical column (4 X 250 mm, Dionex) preceded by a guard column and followed by a suppresser (Dionex AERS 500). Cations were separated on an Ionpac CS12A analytical column (3 X 150 mm, Dionex) preceded by a guard column, and followed by suppresser (Dionex CERS 500). Seven-point calibration curves were prepared from Seven Anion Standard and Six Cation-II Standard (Dionex) over the range of 0.010–10.0 ppm. Method performance metrics are summarized elsewhere (Jayarathne et al. 2014).

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2.4 Analysis of biomarkers

      Biomaers were analyzed in extracts from the remaining halves of Teflon filters containing coarse PM and entire Teflon filters containing fine PM. Filters were extracted via shaking into 2 mL of sterile pyrogen-free (PF) water for 1 h at 22˚C. Extracts were then centrifuged (5 min at 600g at 4 ˚C).

30   For analysis of fungal glucans, one aliquot of the supernatant was transferred into a PF borosilicate tube, mixed with 10x PF phosphate buffered Saline containing 0.05% Tween-20 (a surfactant), shaken for 1 h, autoclaved for 1 h, shaken for 20 min shaking, and then centrifuged for (600g at 4˚C) 20min. Glucans were quantified by enzyme immunoassay as previously described by Blanc et al. (2005). A 12-point calibration curve prepared from (1-3, 1-6)-β-D-glucan

(*scleroglucan*) ranged from 3-5000 ng mL $^{-1}$. The solution absorbance was measured at 450 nm (SpectraMax Plus 384; Molecular Devices, Sunnyvale, CA, USA).

For analysis of endotoxins, a second aliquot of the supernatant was subjected to the kinetic chromogenic *Limulus* amebocyte lysate assay (LAL) (Lonza, Inc., Walkersville, MD) as described in Thorne (2000). The 12-point calibration
5   curve was generated utilizing endotoxin standard (*Escherichia coli* 055:B5) at concentrations ranging from 0.024-50 Endotoxin Units (EU) mL^{-1}. The solution absorbance was measured at 405 nm (SpectraMax M5, Molecular Devices).

2.5 Collection and analysis of pollens

Oak pollens were harvested from pin and red oak trees in park areas surrounding Iowa City during the spring of
10   2013 into pre-cleaned aluminium foil lined bags. Cotton and giant ragweed pollens were collected in late-summer of 2015 from bushes near roadways in residential areas of Iowa City. Cotton ragweed and corn pollens were purchased (Polysciences Inc., Warrington, PA). Pollen images were taken using a Zeiss LSM 710 fluorescence microscope (Carl Zeiss Microscopy GmbH, 07745 Jena, Germany) following Pöhlker et al. (2012), and IX-81 inverted microscope (Olympus Corporation, Tokyo, Japan). Prior to extraction and chemical analysis, pollens were desiccated overnight and weighed (Mettler Toledo
15   XS204 and XP26 balances). Pollens (~0.005–0.015 g) were extracted and analysed following the methods described in section 2.3.

2.6 Chemical Mass Balance (CMB) modeling

PM mass was apportioned to fungal spores and pollens using EPA-CMB model (version 8.2). $PM_{2.5}$ and PM_{10} mass (from the sum of $PM_{2.5}$ and $PM_{10-2.5}$) was apportioned to bioaerosols using sucrose, glucose, fructose, and mannitol as fitting
20   species. Input source profiles included one pollen profile selected from red oak, pin oak (this study), white birch, Chinese willow, or Peking willow (Fu et al., 2012) and one fungal spore profile (Bauer et al., 2008). Sensitivity tests were conducted to assess the fit of different pollen profiles to ambient measurements, focusing on sampling days from 26 April–9 May when pollen tracer levels were highest.

2.7 Statistical analysis

Prior to statistical analysis, data points below detection limits were substituted with the limit of detection (LOD)/ $\sqrt{2}$ (Hewett and Ganser, 2007). Concentration measurements were tested for normality and log-normality using the Anderson-Darling test in Minitab (version 16). Species concentration measurements were not normally distributed, thus Spearman's rank order correlation was employed for non-parametric comparisons (r_s) in SPSS (Statistical Package for the Social
30   Sciences–21). PM measurements were normally distributed thus t-tests comparing PM means from dry and rainy periods was conducted in Minitab (version 16). Significance was assessed at the 95% confidence interval ($p \leq 0.05$).

3 Results and discussion

3.1 Characterization of pollens common to the Midwestern US

Red oak, pin oak, corn, cotton ragweed and giant ragweed pollen ranged in average diameter from 20 - 90 μm (Figure 1, Table 1). Together, glucose, fructose and sucrose accounted for an average of 5–14 % of pollen mass, while erythritol, arabinose, mannitol and rhamnose were detected in trace amounts (Table 1). Due to the relatively high mass fraction of glucose, fructose, and sucrose in pollens in the present and in prior studies (Fu et al., 2012; Speranza et al., 1997) these carbohydrates are the best candidates for assessing pollen contributions to ambient PM. Notably, the carbohydrate distributions in corn pollens differ from those previously reported (Speranza et al., 1997), with differences likely resulting from genetics (Speranza et al., 1997) and environmental factors (e.g. temperature, availability of water, and CO_2 levels) that are known to affect the synthesis and storage of carbohydrates (Aloni et al., 2001; Yoshida et al., 1998; Vesprini et al., 2002). Across different pollen types, the relative abundances of glucose, fructose and sucrose varied. For instance, the most abundant carbohydrate was sucrose for red oak, pin oak, and Polysciences cotton ragweed, fructose for corn pollen, and glucose for local cotton and giant ragweed. Sucrose to fructose ratios across different pollen types may serve to identify pollen types in ambient PM, in cases when a single pollen type is dominant (as discussed in section 3.6.1).

3.2 Fine and coarse PM concentrations

3.2.1 Spring

From 17 April to 9 May, 2013, daily PM_{10} levels in Iowa City ranged from 2–32 μg m^{-3} (with an average of 15±8.9 μg m^{-3}), and fine PM ranged from 2–13 μg m^{-3} (with an average of 7.1±3.0 μg m^{-3}). Comparison to PM levels at a nearby FRM site (located 6.3 km to the east) from 2010-2015 (Table S2), demonstrated that spring 2013 PM levels were typical for the surrounding years.

On 15 of the 23 spring sampling days, conditions were dry and no rain occurred (Figure 2a). On the remaining 8 days, daily rainfall totalled 0.3–85 mm. Rainfall corresponding to low PM with average fine PM levels decreasing from 8.3±2.6 μg m^{-3} on dry days to 4.7±2.2 μg m^{-3} on rainy days and coarse PM levels decreasing from 10±5.6 μg m^{-3} to 1.9±1.5 μg m^{-3} (Figure 2b). The PM reduction on rainy days was statistically significant (p<0.01) and was driven by wet deposition of PM in both size modes. Rain also affected the distribution of particles between the fine and coarse modes, with 48±11 % of PM_{10} was less than 2.5 μm on rainy days compared to 80±13 % on dry days. The shift in the PM size distribution of PM reflects that rain was more effective at scavenging and/or suppressing the release of coarse particles compared to fine particles.

3.2.2 Late summer

Only one brief rain occurred during the three-week campaign, on August 22 when a thunderstorm brought 1.0 mm between 10–11 am (Figure 3a). From 15 August to 4 September, 2013, Iowa City daily PM_{10} levels are shown in Figure 3b, ranged from 21–50 μg m^{-3} (averaging 33±8 μg m^{-3}) and fine PM levels ranged from 3–17 μg m^{-3} (averaging 12±4 μg m^{-3}). On average, fine PM accounted for 39±12 % of PM_{10}. Compared to adjacent years (2010-2015), the late-summer of 2013

exhibited higher PM levels (Table S3). This is attributed to unusually dry conditions that reduce soil moisture leading to increase soil resuspension, and lack of wet deposition.

3.3 Pollen tracers

3.3.1 Spring

The temporal variations of pollens were assessed utilizing the combination of glucose, fructose and sucrose as chemical tracers. Ambient concentrations of these pollen tracers were relatively low from 17–25 April when lower temperatures (averaging 7 ˚C) and rainy conditions prevailed. Pollen tracers levels were relatively higher from 26 April–9 May, coinciding with warmer temperatures (averaging 15 ˚C) that marked the transition from winter to spring (Figure 2c-e, Table S4). Temperature and coarse mode glucose and sucrose were significantly correlated ($r_s \geq 0.8$, $p<0.001$), reflecting that warmer temperatures promote the development, maturation, and release of pollens.

After the onset of spring, rain events increased pollen levels. For instance, maximum fructose and sucrose levels occurred on 2 May and maximum glucose on 9 May; rain occurred on both of these days, following a dry period with relatively high temperatures. Remarkably, rain events substantially altered the size distribution of pollen tracers. On a typical dry day, more than 80% of pollen tracers were present in coarse PM, which is expected for pollen particles that have geometric diameters in the range of 5-100 μm (Huffman et al., 2010). However, when pollen markers peaked on 2 May, mass fractions of glucose, fructose and sucrose in the fine mode reached 83%, 91% and 93%, respectively (Figure 2c–e, right axis). With continued rainfall on 3–4 May, pollen markers remained elevated in the fine mode relative to coarse PM. After the rain stopped, coarse mode pollens increased in concentration and resumed the typical size distribution by 5 May. Light rainfall on 9 May coincided with increases in glucose in both size modes, with only 14% of these tracers in the fine mode. Together, these data indicate the release of pollen fragments less than 2.5 μm during some rain events (2–4 May) and the passive release of larger pollen particles ranging 2.5–10 μm during others (9 May). Notably, this is the first observation of the release of fine particle pollen fragments to the atmosphere using chemical tracers. Most field measurements include analysis of either $PM_{2.5}$ or PM_{10}, while measurements in both size modes are required to capture this phenomenon.

The likely explanation for the increase in airborne pollens and simultaneous decrease in their size on May 2 is the rupturing of pollen walls as a result of the osmotic pressure that builds up inside the pollen due to absorbed moisture during rain (Taylor et al., 2004; Taylor et al., 2002). Osmotic shock has been previously demonstrated to cause rupturing of grass and birch pollens that releases cytoplasm (Taylor et al., 2004; Taylor et al., 2002; Suphioglu et al., 1992). Gusty winds can loft pollen fragments (Wallis et al., 1996) and strong winds on 2 May are likely to have contributed to the elevated fine pollen levels.

Differences in the size distributions of pollen tracers during the rain events on 2 May (mostly fine PM) and 9 May (mostly coarse PM) are expected to result from different pollen types predominating as evidenced by differing ratios of carbohydrates. On 2 May, the relative ratios of glucose and sucrose (normalized to fructose) in fine PM were 1.4 and 2.5,

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respectively, close to the ratios of red oak (1.2 and 2.1, respectively). Meanwhile, the respective carbohydrate ratios on 9 May (18 and 0.7, respectively) did not match any of the local or literature available pollen profiles. These data suggest that certain pollen types undergo osmotic rupturing and release fine particles, while others do not. Further studies are needed to identify the types of pollens that rupture and conditions under which osmotic rupturing occurs.

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3.3.2 Late summer

From mid-August to early-September, average temperature was moderately correlated with coarse mode glucose, fructose and sucrose ($r_s > 0.5$, $p < 0.02$). In the fine mode, glucose was frequently detected, while fructose and sucrose not (Figure 3c-e); this is likely due to the predominant pollen type having higher glucose concentrations relative to fructose and sucrose, as is the case for ragweed pollens (Table 1). The potential of glucose deriving from soil (Rogge et al., 2007; Simoneit et al., 2004) suspended in the air by splashing (Joung and Buie, 2015) was eliminated because there was no corresponding change in calcium, a well-established soil-tracer. Consequently, glucose is considered to be a tracer for pollens even in the absence of the other two pollen tracers, and the discussion of pollen size distribution relies solely on glucose for this time period. On average, 83% of glucose mass concentration was found in coarse mode (Figure 3c), consistent with typical size range of intact pollens (Huffman et al., 2010). The single late-summer rain event on 22 August coincided with an increase in fine mode glucose concentration and shift in glucose size distribution to 34% in the fine mode, compared to 16% on dry days. The late summer single rain event indicated passive release of pollen fragments in response to rain that was similar to spring (section 3.3.1). However, with only one rain event occurring in the late summer study in 2013, additional studies are needed to validate these trends and identify the responsible pollen types.

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3.4 Fungal spore tracers

3.4.1 Spring

Daily concentrations of coarse mode concentrations of two fungal spore tracers—fungal sugar mannitol and the fungal cell wall component glucan—were significantly correlated with daily average temperature ($r_s > 0.4$, $p < 0.05$). From 17–21 and 23-25 April, cooler temperatures prevailed (averaging 6 and 7 ˚C, respectively) and PM_{10} mannitol and glucan concentrations were relatively low (Figure 4a and b). An exceptionally high PM_{10} glucan level occurred (Figure 4b) on April 22, when temperature increased to a local maximum of 14 ˚C. From 26 April, temperatures warmed to an average of 15 ˚C, concurrent with an increase fungal spore tracer levels. The correlation of temperature with fungal spore tracers is consistent with warmer temperatures favouring fungal growth (Corden and Millington, 2001; Rodriguez Rajo et al., 2005).The two tracers were moderately correlated with one another ($r_s = 0.5$, $p < 0.02$), signifying their origin from the same source.

Rain influenced ambient concentrations and the size distributions of fungal spore tracers, by triggering passive and active release mechanisms. Maximum mannitol and glucan levels occurred on 5 May, which followed three days with rain (Figure 4a-b). The wet conditions that follow rain are favourable for active release of fungal spores (Rodriguez Rajo et al., 2005; Van Osdol et al., 2004). Known for releasing spores after rain are some Ascospores (Troutt and Levetin, 2001; Elbert

et al., 2007) which are abundant in the US (Shelton et al., 2002). Fungal spore tracer levels dropped on days when rain fell (e.g. 23 April, 2 May), due to particle removal by wet deposition. The size distributions of fungal spores, which typically have intact diameters in the range of 1–30 μm (Jones and Harrison, 2004), also were influenced by rain. During dry days, 13% of fungal spore tracers were in the fine PM fraction. On rainy days, the fraction of fungal spore tracers in the fine mode reached local maxima at 41% (23 April), 36% (24 April), and 54% (2 May) for mannitol and 38% for glucans (23 April; Figure 4a-b, right axis). The relative decrease in the size of fungal spores is attributed to a combination of the passive release of fungal spores less than 2.5 μm via rain splash and mechanical agitation of vegetative surfaces by rain drops (Allitt, 2000; Elbert et al., 2007; Huffman et al., 2013), and the removal of coarse fungal spore particles by droplet scavenging. Compared to pollens (section 3.3.1), rain events impacted the size distribution of fungal spores to a much lesser extent.

3.4.2 Late summer

From mid-August to early-September atmospheric concentrations of mannitol correlated with temperature (r_s= 0.5, p=0.01), consistent with increased fungal growth with elevated temperatures (section 3.4.1). Fine mode mannitol reached a maximum on 22 August when rain fell during a one hour period (Figure 5a), likely due to fungal spore release via rain splash and mechanical agitation (section 3.4.1). Coarse mode mannitol also increased on 22 August, most likely due to release of fungal spores after rain subsided in response to wet conditions. Mannitol in fine PM accounted for an average of 9±4 % of the total PM_{10} concentration and was not substantially different on 22 August (14%).

Coarse mode glucan concentrations in late summer were neither correlated with temperature (r_s=0.01, p=1), nor mannitol (r_s=0.2, p=0.3), which suggests an alternative, non-fungal source of glucans. Pollens is a likely source, due to the correlation of glucans with sucrose (r_s=0.5, p=0.04) and prior demonstration of glucans in ragweed pollens (Foto et al., 2004), which is a prevalent pollen in Iowa during the late summer. Alternatively glucans may have derived from bacteria, as suggested by the moderate, but not statistically significant correlation of coarse mode glucans with bacterial endotoxins (r_s=0.4, p=0.1), and prior observations that pathogenic bacteria that grow on crops (i.e. *Agrobacterium spp.*, and *Rhizobium spp.*) contain glucans in their structure (McIntosh et al., 2005). Agricultural crops are abundant in Iowa during the growing season and the mechanical agitation of plant surfaces by wind can aerosolize surface bacteria. Although glucans appear to have been influenced by bacterial and pollen levels in addition to fungi, the assessment of their ambient concentrations remains important, because they are immunostimulants that negatively impact human health (Thorn, 2001; Bonlokke et al., 2006).

3.5 Bacterial endotoxins
3.5.1 Spring

Coarse mode bacterial endotoxins, measured in endotoxin units (EU) against an *Escherichia coli* (055:B5) standard, were significantly correlated with daily average temperature (r_s=0.7, p<0.001). Lower temperatures averaging 7 °C from 17-25 April, led to low endotoxin levels compared to a warmer period averaging 11-23 °C from 26 April-1 May. The correlation

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of endotoxins with temperature agrees with prior ambient studies (Carty et al., 2003; Guan et al., 2014; Degobbi et al., 2011; Rathnayake et al., 2016) and is attributed to warmer temperatures increasing vegetative surfaces that serve as substrates for bacterial growth (Romantschuk, 1992; DeLucca and Palmgren, 1986; Carty et al., 2003). Heavy rain on 2 and 3 May led to a drop in PM_{10} endotoxin concentrations, due to wet deposition and suppression of soil dust particles upon which bacteria

5 settle. On average, 92 ± 5 % of PM_{10} endotoxins were in the coarse mode (Figure 4c). The distribution of bacterial endotoxins towards larger particles has been observed previously (Nilsson et al., 2011; Madsen, 2006), reflecting the association of bacteria plant parts, animal parts, soil, spores or pollen surfaces by settling and agglomeration (Jones and Harrison, 2004). Coarse mode endotoxins demonstrated a moderate positive correlation with calcium, the crustal element ($r_s=0.7$, $p<0.001$), which suggests soil resuspension as a source of endotoxins in Iowa City, which has been demonstrated previously in the

10 Midwestern US (Bowers et al., 2011; Rathnayake et al., 2016).

3.5.2 Late summer

In late summer ambient endotoxin concentrations had a positive moderate correlation with coarse mode endotoxins ($r_s=0.5$, $p=0.02$) similar to springtime (section 3.5.1). On 22 August, the only late summer day with rain, fine mode

15 endotoxin concentration reached a maximum (Figure 5c). Meanwhile, the endotoxin fraction in the fine mode increased to 36% relative to an average of 5 % on dry days. The release of endotoxin to fine PM is expected to be caused by the dissemination of Gram-negative bacteria due to agitation of plant parts from rain drops (Jones and Harrison, 2004; Constantinidou et al., 1990) and/or aerosolization of Gram-negative bacteria settled on to fine sized fungal spores by splashing rainwater (Jones and Harrison, 2004). Soil resuspension was suggested as an important source of bacterial

20 endotoxins in spring (section 3.5.1), however coarse mode endotoxins were not significantly correlated with calcium in late summer ($r_s=0.2$, $p=0.33$). Consequently, non-soil sources of bacteria were likely present, such as plant surfaces (Romantschuk, 1992; Jeter and Matthysse, 2005), particularly crops (Lindemann et al., 1982), which are highly relevant to the agricultural state of Iowa. This link could be further explored by examining the co-occurrence of bacterial endotoxins with markers of plant waxes (i.e. odd-numbered n-alkanes), but is beyond the scope of the present study. Consequently, the

25 sources of bacterial endotoxins appear to be differ across seasons in Iowa (Rathnayake et al., 2016).

3.6 Contributions of pollens and fungal spores to PM mass

CMB source apportionment modelling was applied to estimate mass contributions of pollens and fungal spores to PM_{10} and $PM_{2.5}$. This work extends the application of fungal spores tracer-to-mass ratios to estimate their contributions to

30 PM mass (Di Filippo et al., 2013; Zhang et al., 2010) to pollens for the first time. The CMB model requires representative source profiles for sources, which were drawn from the literature in the case of fungal spores (Bauer et al., 2008), birch, and willow pollens (Fu et al., 2012), and from this study (section 3.1).

3.6.1 Source apportionment in spring

The pollen profiles that explained the greatest fraction of the variance in the springtime measurements (assessed by the CMB R^2 value) were pin oak and red oak (Figure S1). The resultant R^2 value further increased when fungal spores were added to the model (Figure S1). Birch and willow profiles, which showed an excess of sucrose (Fu et al., 2012) explained a substantially lower fraction of the variance in ambient data, where glucose and fructose concentrations outweighed sucrose.

5　Hence, birch and willow pollen profiles were not considered further. Model results from using pin oak or red oak profiles in concert with the fungal spore profile produced consistent source contributions that were strongly correlated (Figure S2). Because red oak and pin oak fit ambient data to a comparable extent and both are sources of atmospheric pollens in Iowa, the best estimate of pollen contributions was calculated as the average contribution from red oak and pin oak.

Pollen and fungal spore contributions to PM_{10} and $PM_{2.5}$ estimated by the CMB model are shown in Figure 6 (and

10　Table S6). Overall, contributions to fine PM after onset of spring, from 26 April-09 May ranged from 0.01–0.7 µg m^{-3} for pollens and 0.03 – 0.1 µg m^{-3} for fungal spores, while contributions to PM_{10} were consistently higher at 0.04–0.8 µg m^{-3} for pollens and 0.13–1.5 µg m^{-3} for fungal spores. On dry days, pollens contributed an average of 0.7% of $PM_{2.5}$ and 3.3% of PM_{10}. On rainy days, pollen contributions to fine PM averaged 11% and reached a maximum of 42% on May 2. Fungal spore contributions to fine PM averaged 0.5% on dry days and 1.7% on days with rain. Meanwhile, fungal spores had the

15　greater contributions to PM_{10} mass on days following rain, reaching 8.7% on May 5. These source apportionment results demonstrate that bioaerosol contributions to PM_{10} mass in spring are typically low with averages of 4% and 5% for pollens and fungal spores, respectively), but can be significantly greater on days with rain, when bioaerosols are released and PM is removed by wet deposition. The distribution of bioaerosols in fine and coarse PM during spring is shown in Figure 7. For dry conditions, ~11% of pollens and fungal spores were observed in fine PM. However, during rainy days, 62% of pollen

20　mass and 20% of fungal spore mass were observed in fine PM. These results indicate the importance of rain in shifting the size distribution of bioaerosols by affecting release mechanisms (i.e. passive release by splashing and mechanical agitation, or osmotic rupture of pollens).

Bioaerosol contributions to PM in this study were relatively in good agreement with prior studies. The average fungal spore contribution to PM_{10} in spring (5%) was 1.6 times higher than suburban site of Vienna, Austria, and 1.6 times

25　lower than a tropical rainforest in China (Zhang et al., 2010), which were measured during springtime. Collectively, contributions from pollens (3.3%) and fungal spores (0.9%) to fine PM was ~2 times lower than contributions reported in US which determined in summertime (Coz et al., 2010). The slight variations of contributions could be attributed to the differences in ambient bioaerosol levels and geographical differences.

30　**3.6.2 Source apportionment in late-summer**

PM mass could not be apportioned to pollens in late summer, because of poor agreement between ambient data and source profiles. Fewer than 10% of the ambient PM samples had relative ratios of sucrose, fructose, and glucose in the range ragweed pollen profiles, which is a dominant pollen type in the Midwest. This lack of agreement could result from mixtures

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of pollen in the atmosphere that are not represented when utilizing a chemical profile for a single pollen type, and/or other dominant pollen types during late summer (e.g. Timothy grass and rye grass).

Fungal spore contributions to PM were estimated using the average mannitol conversion factor of 1.7 pg mannitol spore^{-1} (range from 1.2-2.4 pg mannitol spore^{-1}) and a spore mass of 33 pg from Bauer et al. (2008). Resultant fungal spore

5   mass contributions to $PM_{2.5}$ and $PM_{10-2.5}$ ranged from 0.04-0.31 µg m^{-3} and 0.45-3.44 µg m^{-3}, respectively, (Table S7). The contribution of fungal spores to $PM_{2.5}$ averaged 1% on dry days, and 3% on 22 August when it rained. Meanwhile, fungal spore contributions to $PM_{10-2.5}$ averaged 6% and reached to 16% on 22 August. The maximum fungal spore contributions to PM on 22 August is likely due to fungal spores released during rain by passive mechanisms and after rain by active mechanisms (section 3.4.1). This leads to an increase in fine sized fungal spores when raining, and coarse sized spores post-

10   rain (Huffman et al., 2013; Hjelmroos, 1993).

3.7 Implications of the release of fine bioaerosols surrounding rain events

The release of fine sized bioaerosols can influence cloud formation, by acting as CCN and IN. Pollen fragments are effective CCN and IN (Pope, 2010; Diehl et al., 2001; Diehl et al., 2002).When ruptured, one pollen granule produces

15   hundreds of fine-sized pollen particles (D'Amato et al., 2007b)significantly increasing the number of CCN and IN active particles in the atmosphere. Fungal spores and bacteria also active IN and CCN (Murray et al., 2015; Haga et al., 2014; Iannone et al., 2011; Bauer et al., 2003; Lindemann et al., 1982) When decreased in size (< 2.5 µm), these bioaerosols are more effective IN (Murray et al., 2015; Huffman et al., 2013). Because smaller particles have longer atmospheric lifetimes, fine bioaerosols will be transported longer distances before deposition, and thus may have effects in areas downwind of their

20   release.

The release of pollens, fungal spores, and Gram negative bacteria in fine particles during rain events, as observed surrounding spring and late-summer rain events in Iowa, has the potential to influence human health. Elevating ambient fungal spore levels, particularly from species like Ascospores and *Cladosporium,* trigger allergenic respiratory diseases like allergic rhinitis and asthma (Rivera-Mariani et al., 2011; Knutsen et al., 2012) and high environmental exposures may lead to

25   asthma exacerbations (Dales et al., 2003). Likewise, endotoxins induce inflammations in the respiratory tract (Dales et al., 2006; Liebers et al., 2008; Thorne et al., 2015). When pollen levels increase in concentration and decrease in size (as observed on May 2, May 9, and August 22), likely due to pollen rupturing, cytoplasmic pollen allergens (Suphioglu et al., 1992; Grote et al., 2001) will be released, leading to more direct exposure of humans to aeroallergens through inhalation. In the form of smaller particles, aeroallergens penetrate deeper into the respiratory tract where they may trigger more severe

30   allergenic responses (Taylor et al., 2002; Wilson et al., 1973). Acute asthma epidemics have been associated with rain events have been documented in Australia, Europe, Mexico and the US (D'Amato et al., 2007b; Dales et al., 2003; Grundstein et al., 2008) earning the name "thunderstorm asthma." Such epidemics typically occur during pollen seasons (D'Amato et al., 2007a; D'Amato et al., 2007b) and have been associated with ambient pollen counts (Marks et al., 2001). While lightning is

associated with tropospheric ozone formation (Griffing, 1977; GAN, 2014) lightning alone (in the absence of rain) has not caused asthma epidemics (Grundstein et al., 2008), suggesting that rainfall plays an important role in thunderstorm asthma.

Pollen forecasting models currently do not include mechanisms for the release of pollen in response to rain and instead assume that rain serves only as a sink of pollens, by means of droplet scavenging and wet deposition (Zhang et al., 2013). This erroneous assumption leads to predictions of low atmospheric pollen levels on days with rain (e.g. May 2), when pollen tracer levels are highest and primarily in the form of fine particles. A more accurate representation of airborne pollen levels is needed to support an early-warning system to sensitive populations, but must go beyond simply the co-occurrence of elevated pollen levels and thunderstorms, which are suggested to cause too many false alarms (Newson et al., 1998). For accurate model parameterizations, a mechanistic and species-level understanding of pollen bursting is needed and should include definitions of the pollen types, seasonality, and meteorological conditions that promote the release of fine pollen particles to the atmosphere. In the meantime, persons suffering from pollen allergies should follow the recommendations of D'Amato et al. (2007b): "when asthmatic patients realize that a thunderstorm is approaching, the best thing for thing for them to do is to stay indoors, with windows closed."

4. Conclusions

Daily concentrations of PM mass and bioaerosol tracers (including fructose, glucose, and sucrose for pollens, mannitol and glucans for fungal spores, and endotoxins from Gram-negative bacteria) demonstrated high day-to-day variability and influences from meteorology, particular rain. Warmer temperatures promoted pollen, fungal and bacterial growth leading to higher ambient levels of these bioaerosols during both spring and late summer periods. Rain events of spring triggered the release of pollens, with maximum levels of pollen tracers occurring on May 2 and May 9, when rain occurred following a period of elevated temperatures in spring. Airborne fungal spore tracers, however, were suppressed by spring rain and increased in concentration following rain events. Source apportionment by CMB modelling in concert with Midwestern pollen profiles indicated significant contributions from bioaerosols to PM mass on rainy days during springtime. Importantly, the size distribution of endotoxins and pollen and fungal spore tracers shifted towards fine particles (<2.5 µm) during periods of rain. The fragmentation of pollens due to osmotic rupture, shown previously only through microscopy methods, is demonstrated in this study for the first time by way of chemical tracers. The release of finer-sized bioaerosols during rain events has important implications for human exposures, because finer particles may penetrate more deeply into the lung and be transported over longer distances.

A detailed level of understanding of pollen release mechanisms, particular as pollen fragments, is needed to improve the accuracy of allergen prediction models that erroneously forecast low airborne allergen levels during periods of rain. Future research should focus on a more precise determination of the duration of heightened pollen levels during rain events with higher time resolution measurements. Similarly, measurements with higher PM size resolution should be employed to determine the specific size range of pollen fragments during these events. Additional efforts are needed to characterize the fungal and floral species that release fine-sized bioaerosols to the atmosphere and the mechanisms that

trigger such release, to allow for their accurate representation in atmospheric models to support accurate representations of environmental conditions and forewarn susceptible populations of conditions that may lead to high bioaerosol exposures.

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Table 1: Pollen diameter and mass fractions of carbohydrates and ions with standard errors. The carbohydrates arabitol, xylitol, trehalose, fucose, mannose, xylose and ribose were below detection limits.

	Red Oak			Pin Oak			Corn			Cotton ragweed[a]			Cotton ragweed[b]			Giant ragweed[b]		
n	5			5			5			5			3			3		
Diameter (µm)[c]	30			30			80			20			35			35		
Carbohydrates (µg mg^{-1})																		
Glucose	41.1	±	4.1	40.2	±	3.5	15.2	±	0.9	15.9	±	1.6	43.3	±	2.0	39.2	±	2.8
Fructose	33.0	±	1.8	33.9	±	2.9	25.0	±	1.1	13.5	±	0.6	24.4	±	1.1	22.9	±	1.5
Sucrose	68.3	±	4.5	55.2	±	3.2	13.4	±	1.7	59.4	±	3.3	28.0	±	1.4	27.9	±	1.3
Erythritol	8.1	±	3.1	8.7	±	3.4	28.7	±	3.2	NQ[d]			NQ[d]			NQ[d]		
Mannitol	0.1	±	0.01	0.2	±	0.01	<0.001			<0.001			0.2	±	0.01	0.8	±	0.1
Rhamnose	0.1	±	0.01	0.1	±	0.01	<0.001			<0.001			<0.001			<0.001		
Arabinose	0.3	±	0.03	0.5	±	0.1	0.9	±	0.2	0.3	±	0.03	1.2	±	0.1	2.3	±	0.2
Inorganic ions (µg mg^{-1})																		
Sodium	0.25	±	0.20	0.23	±	0.01	0.30	±	0.10	0.03	±	0.002						
Ammonium	1.36	±	0.11	1.11	±	0.90	0.89	±	0.16	1.33	±	0.13						
Potassium	7.56	±	0.81	6.43	±	0.51	11.97	±	0.16	5.22	±	0.48						
Magnesium	0.03	±	0.00	0.05	±	0.01	0.88	±	0.01	0.74	±	0.06	NA[e]					
Calcium	0.07	±	0.02	0.12	±	0.01	0.37	±	0.03	1.85	±	0.12						
Chloride	0.40	±	0.08	0.42	±	0.05	2.10	±	0.11	1.64	±	0.18						
Nitrate	0.19	±	0.04	0.31	±	0.11	<0.019			<0.019								
Phosphate	3.94	±	0.39	1.65	±	0.41	10.5	±	0.88	8.99	±	0.87						
Sulfate	0.79	±	0.29	0.46	±	0.02	0.94	±	0.12	0.25	±	0.03						

[a] Purchased from Ploysciences

[c] Approximate diameters

[e] Not analyzed (NA)

[b] Collected locally from Iowa City during late summer 2015

[d] Not quantified (NQ) due to chromatographic interferences

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Figure captions

Figure 1: Microscope images of pollens from (a) red oak, (b) pin oak, (c) corn, (d) cotton ragweed (Polysciences), (e) cotton ragweed (locally collected), and (f) giant ragweed. Images in colour were captured by fluorescence microscope, while black and white images were captured by an inverted microscope

Figure 2: Temporal variation in precipitation and average temperature (a) in Iowa City, IA in the spring of 2013. Ambient concentrations of PM mass (b), glucose (c), fructose (d) and sucrose (e) in coarse and fine size fractions. The percent of PM and bioaerosol tracer mass in fine particles is shown on the right-axis for samples in which the analyte was detected in both size modes. During rain on 2 May, PM is suppressed, while pollen tracers in the fine mode substantially increased.

Figure 3: Temporal variation in precipitation and average temperature (a) in Iowa City, IA in the late summer of 2013. Ambient concentrations of PM mass (b), glucose (c), fructose (d) and sucrose (e) in coarse and fine size fractions. The percent of PM and bioaerosol tracer mass in fine particles is shown on the right-axis for samples in which the analyte was detected in both size modes. Fungal spore tracers increased significantly in the fine mode during the 2 May rain event.

Figure 4: Ambient concentrations of mannitol (a), glucans (b), and endotoxins (c) in coarse and fine size fractions in Iowa City, IA during spring of 2013. The percent of PM and bioaerosol tracer mass in fine particles is shown on the right-axis for samples in which the analyte was detected in both size modes. Fungal spore tracers increased significantly on 5 May, following a rainy period.

Figure 5: Ambient concentrations of mannitol (a), glucans (b), and endotoxins (c) in coarse and fine size fractions in Iowa City, IA during late summer of 2013. The percent of PM and bioaerosol tracer mass in fine particles is shown on the right-axis for samples in which the analyte was detected in both size modes Mannitol, the chemical tracer for fungal spores, and endotoxins from Gram-negative bacteria in fine mode increased on 22 August when it rained.

Figure 6: Apportionment of PM_{10} mass (a) and $PM_{2.5}$ mass (b) during the spring of 2013 to pollens and fungal spores using CMB modeling.

Figure 7: Distribution of pollen and fungal spore mass (apportioned by the CMB model) across fine and coarse PM during dry and rainy conditions. The size distributions of pollens and fungal spores shifted towards fine particles during rain, with a more pronounced effect for pollens compared to fungal spores.

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Figure 1

Figure 2

Spring

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Figure 3

Late summer

Figure 4
Spring

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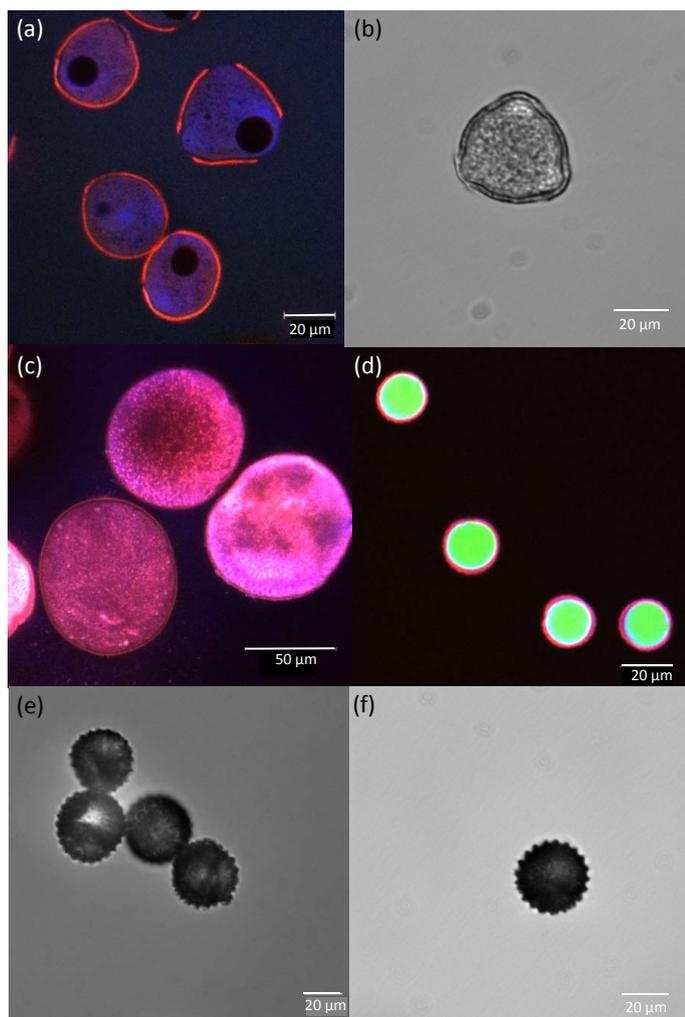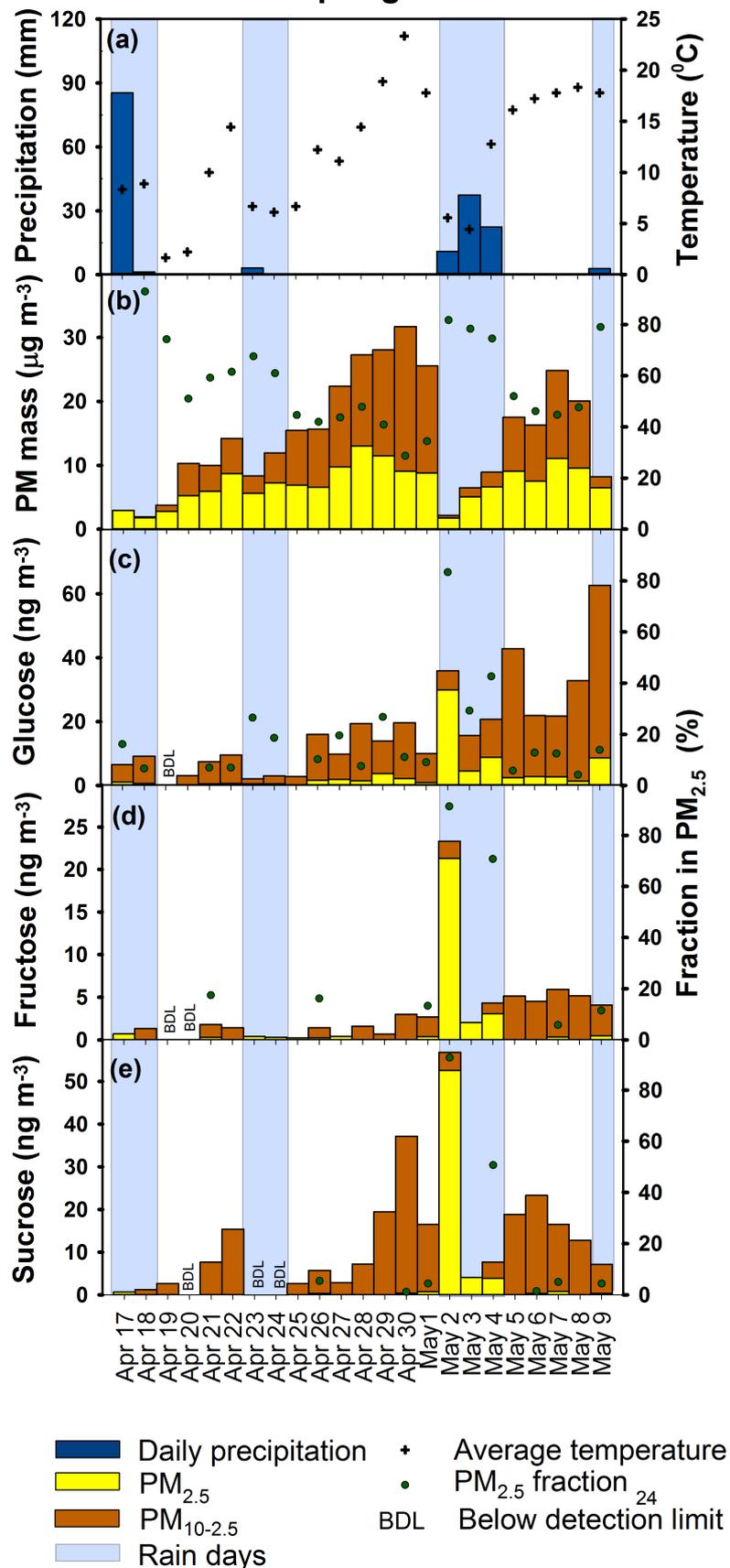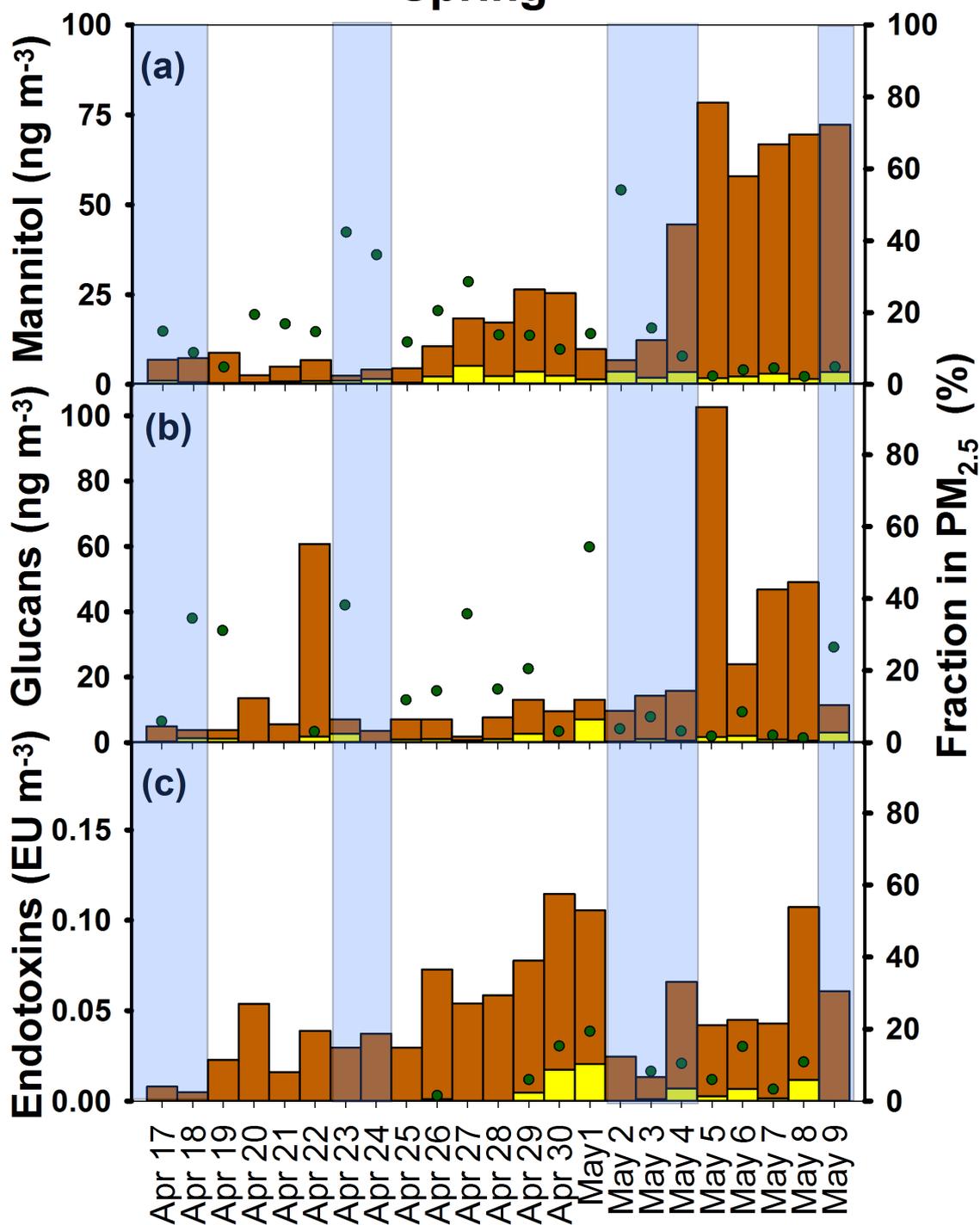
Figure 5

Late summer
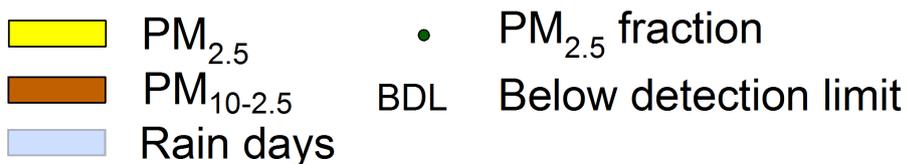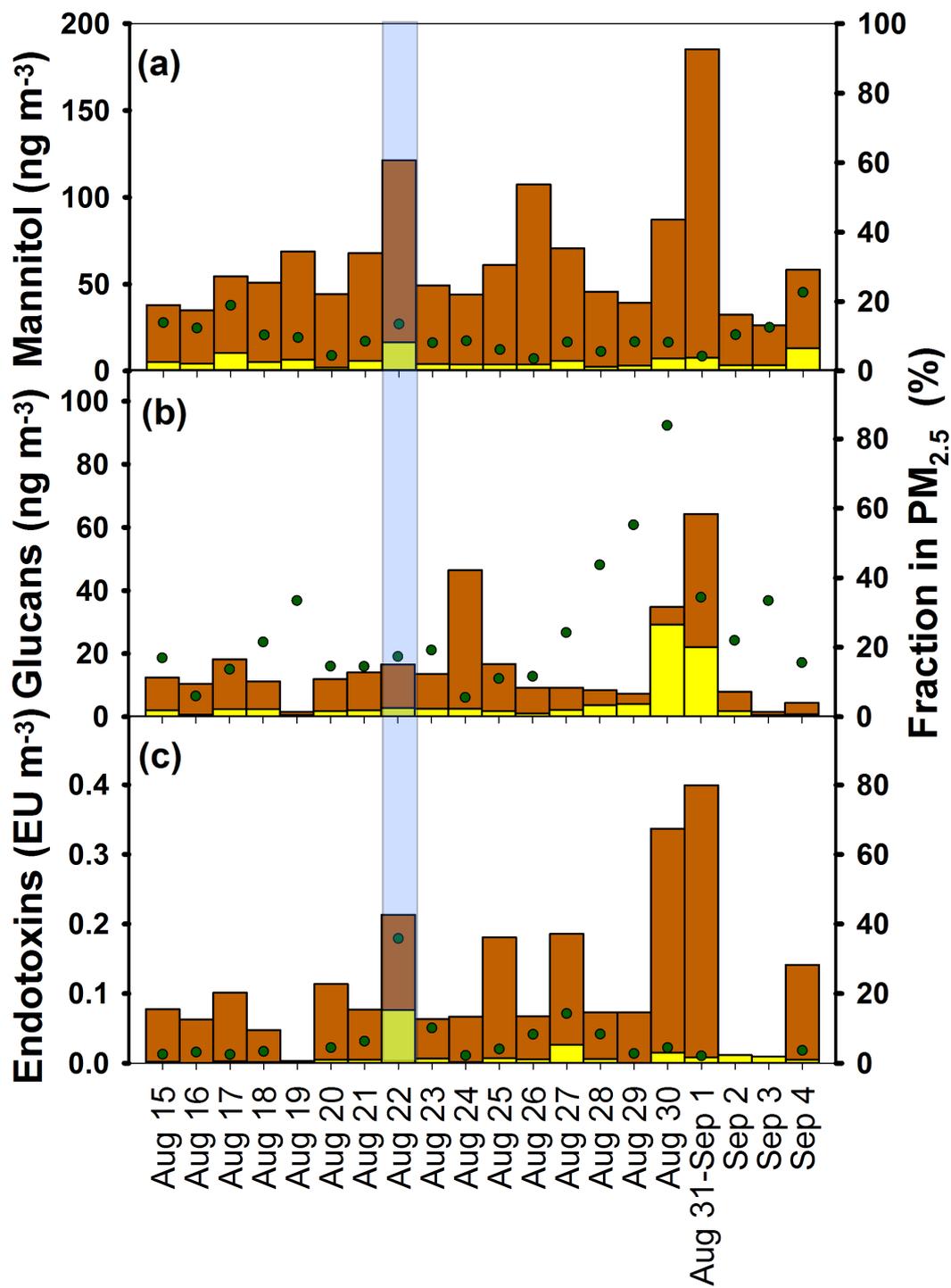
Figure 6
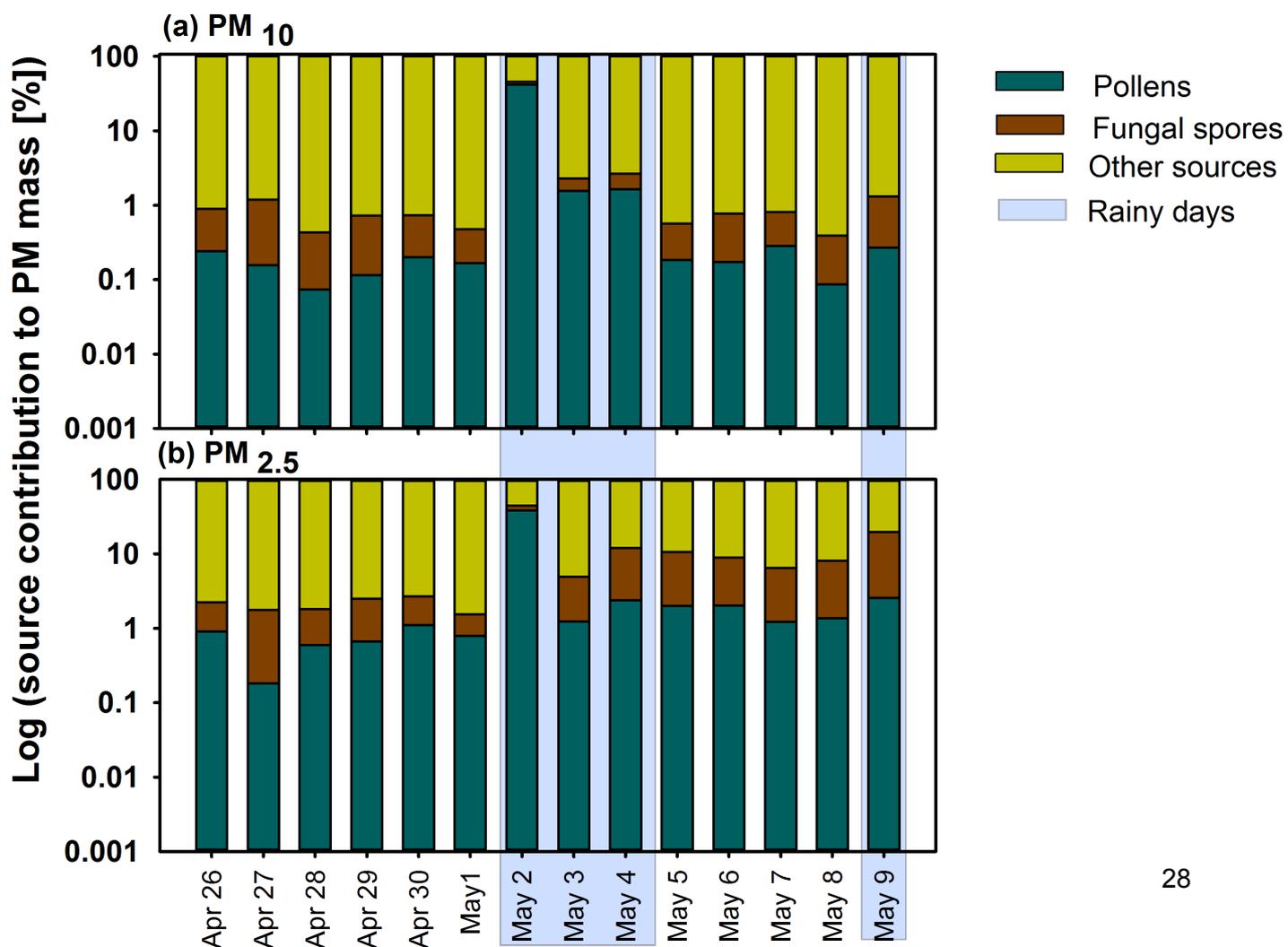
Figure 7

Pollens **Fungal spores**

(a) Dry conditions

(b) Rainy days

Fine (<2.5 μm)

Coarse (2.5-10 μm)