Supplement of Atmos. Chem. Phys., 22, 14019–14036, 2022
https://doi.org/10.5194/acp-22-14019-2022-supplement

Atmospheric Chemistry and Physics
Open Access

Supplement of

Measurement report: Characterization of sugars and amino acids in atmospheric fine particulates and their relationship to local primary sources

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Analysis of FAAs and CAAs concentrations

FAA were extracted using a method described by our previous study (Zhu et al., 2020). Briefly, a quarter of each filter sample (~300 m^3 of air) was cut and transferred into a Nalgene tube. After adding as internal reference (α-aminobutyric acid), the filter was ultrasonically extracted with Milli-Q water (18.2 MΩ cm) in an ice bath. Then, the extract was ultrasonic vibration, shaken, centrifuged and filtered through a 0.22-μm cellulose acetate membrane. The filtrate was lyophilized and resuspended in 1mL of HCl 0.1N (v/v). Later, the samples were purified by the cation exchange column (Dowex 50W X $8H^+$, 200–400 mesh; Sigma-Aldrich, St Louis, MO, USA). Enriched FAAs were eluted and collected.

A hydrolysis method was used to convert all of the total hydrolysis water soluble amino acids to FAAs. The concentrations of CAAs were calculated by subtracting the amounts of FAAs from the total hydrolysis water soluble amino acids (Zhu et al., 2020). In brief, one-sixteenth of each filter sample (~80 m^3 of air) was ultrasonically extracted twice for 30 min with Milli-Q water (18.2 MΩ cm). α-aminobutyric acid was added to act as an internal reference. After shaken and filtered, the extract was transferred to a glass hydrolysis tube and lyophilized. Subsequently, 10 ml 6 M HCl was added. Glass hydrolysis tube was flushed with N_2 for 3 min both below and above the liquid level and 25 μl ascorbic acid (20 μg $μl^{-1}$) was added to each extract to avoid oxidation of amino acids. The sample was hydrolyzed for 24 hr at 110 °C. After hydrolyzed and cooling at room temperature, the samples were redissolved in Milli-Q water and purified following the same procedure for FAAs. Each purified FAA and CAA was lyophilized to complete dryness. 150 μg anhydrous Na_2SO_4, 50μL pyridine, and 50μL N-methyl-N-(tert-butyldimethylsilyl) trifluoroacetamide were added in that order. Finally, the sample was heated at 70℃ for 1 hr to achieve the chemical derivatization of amino acids and then the derivatives were analyzed by gas chromatograph-mass spectrometer (Thermo Scientific, Bremen, Germany).

Detail quality assurance and control (recoveries, linearity, detection limits, quantitation limits, and corresponding effective limits in the aerosol samples of AAs, are available in our previous study (Zhu et al., 2020).

Analytical characteristics for sugar compounds

In total sixteen sugar compounds, including three anhydrosugars (levoglucosan, galactosan, mannosan), nine primary sugars (sucrose, glucose, fructose, ribose, trehalose, galactose, turanose, lactulose and maltose), and four sugar alcohols (arabitol, mannitol, pinitol and inositol), were detected in the Nanchang aerosols. The detailed method validation was provided in Table S2. Recoveries for sugars were better than 89% as obtained for the standards spiked onto the precombusted blank filters and treated as a real sample. The reproducibility of the analytical procedure was assessed through the relative standard deviation (RSD) of the replicate measurements. The RSD values ranged from 1.7 to 11.6%. The detection limits of sugars correspond to ambient concentrations of 0.2-0.9 ng $μL^{-1}$, which corresponds to ambient concentrations of 0.2-1.1 ng m^{-3} under a typical sampling volume of 1320m^3.

Analytical characteristics for water-soluble ions

Standard solutions of water-soluble ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-}) were used for making the external standard curve before the analysis of $PM_{2.5}$ samples. The correlation coefficients of the calibration curves were greater than 0.999. The detection limit of Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-} were 0.001 μg L^{-1}, 1.21 μg L^{-1}, 1.77 μg L^{-1}, 2.47 μg L^{-1}, 0.09 μg L^{-1}, 5.1μg L^{-1}, 21.6 μg L^{-1} and 11.5 μg L^{-1}, respectively. The relative standard deviation of the reproducibility test was less than 5%.

Table S1. The Characteristics of sampling sites.

Sampling sites	characteristics
Urban	an area characterized by high traffic volumes (1,042 vehicles h^{-1}), high population density (8,399 people km^{-2}) and low vegetation coverage (29%).
Rural	open area influenced by agricultural activities
Forest	~20 km from the city center, characterized by low traffic volumes (24 vehicles h^{-1}), low population density (315 people km^{-2}), and high vegetation coverage (71.2%).

Table S2. Calibration curves parameters, limits of detection (LOD), relative standard deviation (RSD), recoveries and of the sugar standards.

Compounds	Compound class	Concentration range (ng μL^{-1})	Slope	Intercept	r^2	LOD(ng μL^{-1})	LOD(ng m^{-3})	RSD(%)	Recovery(%)
Levoglucosan	Anhydrosaccharides	1.6-162.1	0.0156	-0.0252	0.999	0.8	1.0	3.2	106.5±3.4
Mannosan	Anhydrosaccharides	1.6-81.1	0.0193	-0.0114	0.993	0.6	0.7	8.8	102.6±9.1
Galactosan	Anhydrosaccharides	1.6-81.1	0.0392	-0.0351	0.992	0.8	1.0	3.5	89.4±3.1
Galactose	Monosaccharides	1.8-180.2	0.0320	-0.0195	0.995	0.9	1.1	3.1	107.9±3.3
Ribose	Monosaccharides	1.5-150.1	0.0340	-0.0278	0.991	0.4	0.5	6.0	90.4±5.4
Fructose	Monosaccharides	1.8-180.2	0.0178	-0.0246	0.991	0.5	0.6	5.3	104.2±5.5
Glucose	Monosaccharides	9-180.2	0.0126	-0.0654	0.975	0.9	1.1	7.0	107.7±7.6
Sucrose	Disaccharides	3.4-342.3	0.0286	-0.0261	0.990	0.7	0.8	1.7	104.4±1.8
Maltose	Disaccharides	3.6-180.2	0.0129	-0.0173	0.994	0.8	1.0	5.5	97.9±5.4
Turanose	Disaccharides	3.4-171.2	0.0194	-0.0381	0.993	0.9	1.1	3.2	95.0±3.0
Lactulose	Disaccharides	3.4-171.2	0.0208	-0.0243	0.993	0.8	1.0	4.4	108.0±4.8
Trehalose	Disaccharides	3.8-189.2	0.0271	-0.0195	0.991	0.6	0.7	2.7	91.4±2.5
Arabitol	Sugar alcohols	1.5-152.2	0.0268	-0.0392	0.999	0.4	0.5	10.8	91.8±9.0
Mannitol	Sugar alcohols	36.4-182.2	0.0052	-0.1391	0.996	0.2	0.2	8.4	93.5±7.9
Pinitol	Sugar alcohols	1.9-194.2	0.0262	-0.0213	0.992	0.4	0.5	10.2	94.8±9.6
inositol	Sugar alcohols	1.8-90.1	0.0278	-0.0124	0.995	0.6	0.7	11.6	108.8±12.6

Table S3. Statistical summary of correlations between levoglucosan and Nss-K^+ in aerosol samples.

Sampling sites	Linear regression	Correlation coefficient	p value	Significance of correlation at p value < 0.05	Reference
Urban, Nanchang, China	Lev = 0.07 K^++37.7	r=0.6	<0.05	Significant	this study
Rural, Nanchang, China		r=0.3	>0.05	Not significant	this study
Forest, Nanchang, China		r=-0.2	>0.05	Not significant	this study
rural region of São Paulo State, Brazil	Lev = 0.086 K^++0.032	r=0.62	<0.01	Significant	Urban et al., 2012
Kunmin, China	Lev = 107.72 K^++209.91	r=0.33	<0.05	Significant	Wang et al., 2021
Beijing, China, Summer	Lev = 0.05 K^++0.07	R^2=0.34	<0.05	Significant	Cheng et al., 2013
Beijing, China, Winter	Lev = 0.50 K^++0.03	R^2=0.82	<0.05	Significant	Cheng et al., 2013
Western North Pacific Rim		r=0.38	<0.01	Significant	Kawamura and Kunwar, 2015

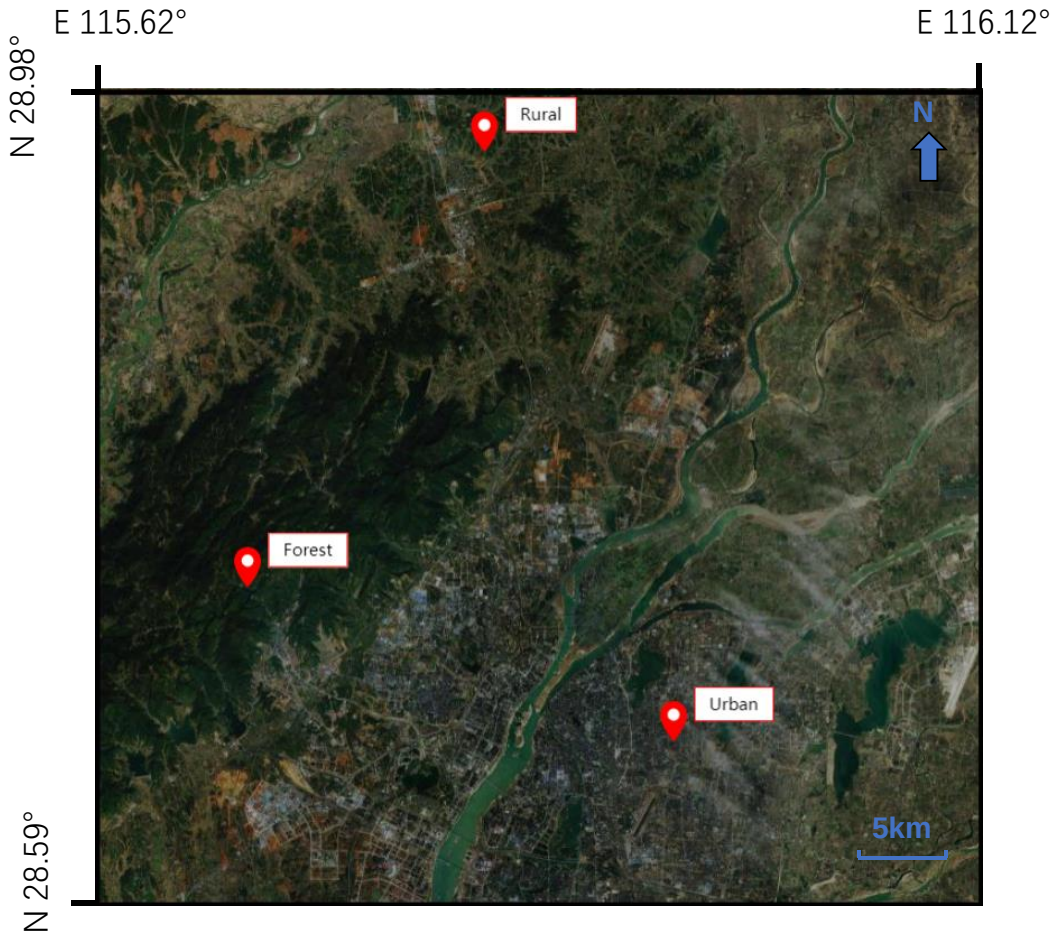

Figure S1. Map showing the locations of the sampling stations. The locational map was modified from MAPWORLD (https://map.tianditu.gov.cn/).

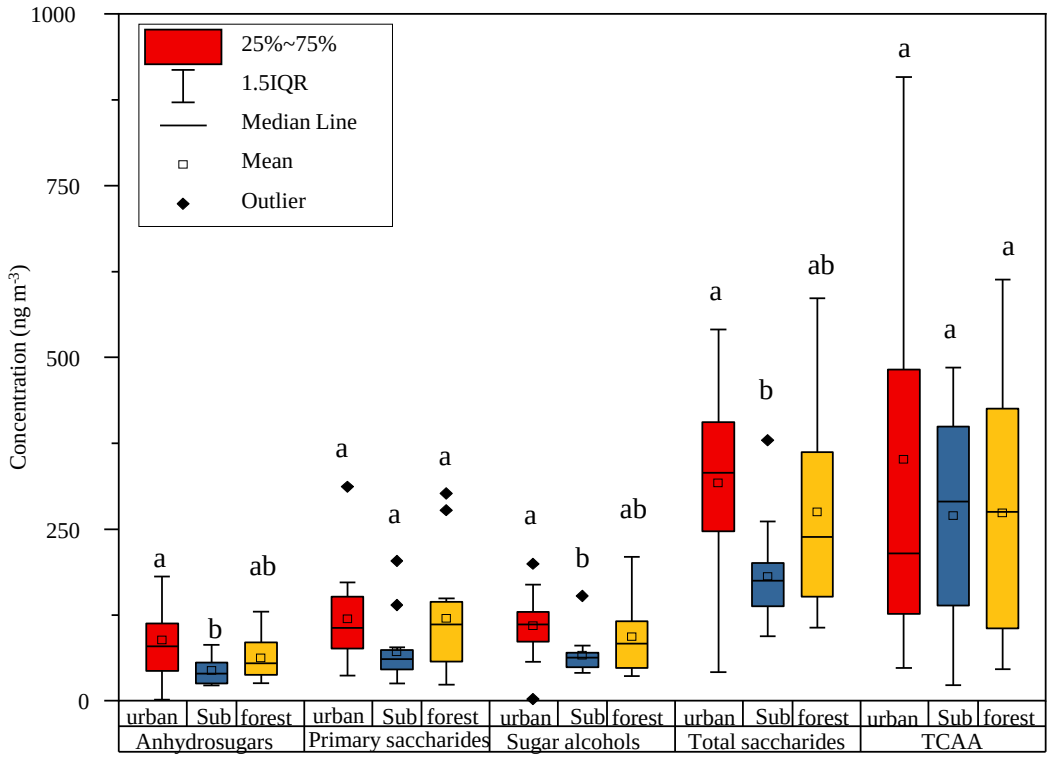

Figure S2. Concentrations of anhydrosugars, primary saccharides, sugar alcohols, total saccharides and TCAA in PM2.5 sampled from urban, rural and forest sites. The box encloses 50% of the data, the whisker is 1.5 interquartile range of the data, the horizontal bar is the median, hollow square is mean and solid diamond are outliers. Different lower case letters denote means found to be statistically different between sites (one-way ANOVA, $p < 0.05$).

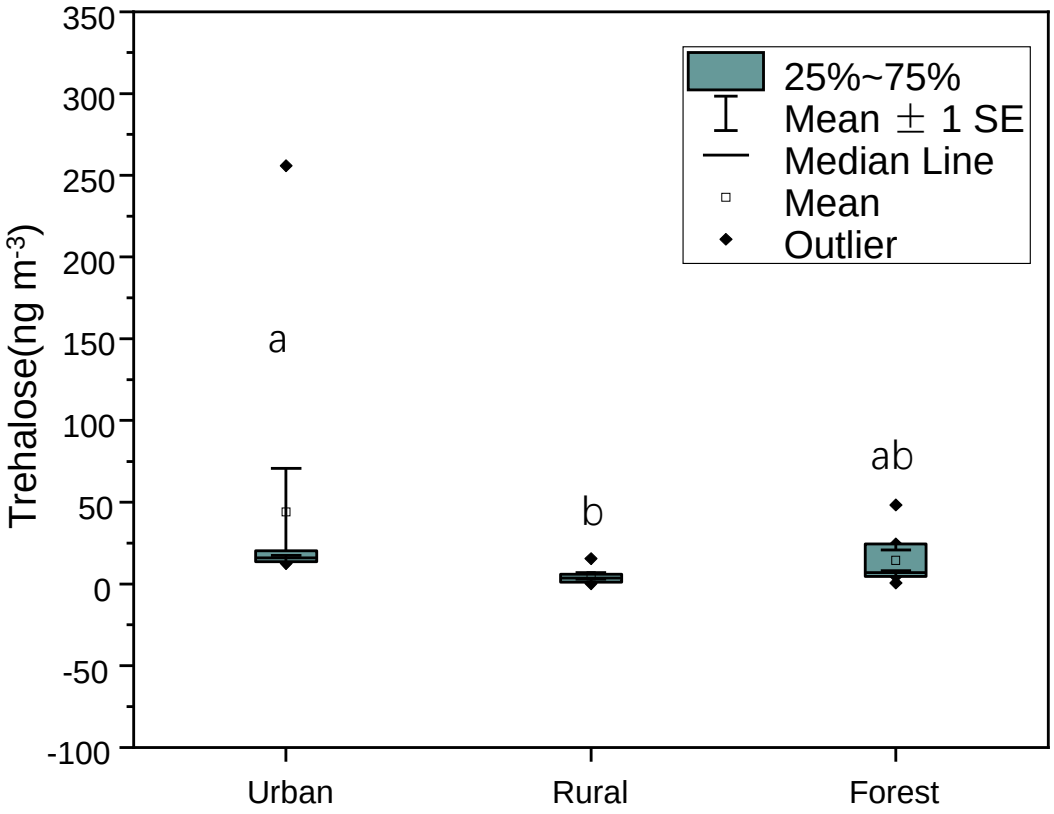

Figure S3. Concentrations of trehalose in PM2.5 sampled from urban, rural and forest sites. The box encloses 50% of the data, the whisker is standard error of the data, the horizontal bar is the median, hollow square is mean and solid diamond are outliers. Different lower case letters denote means found to be statistically different between sites (one-way ANOVA, $p < 0.05$).

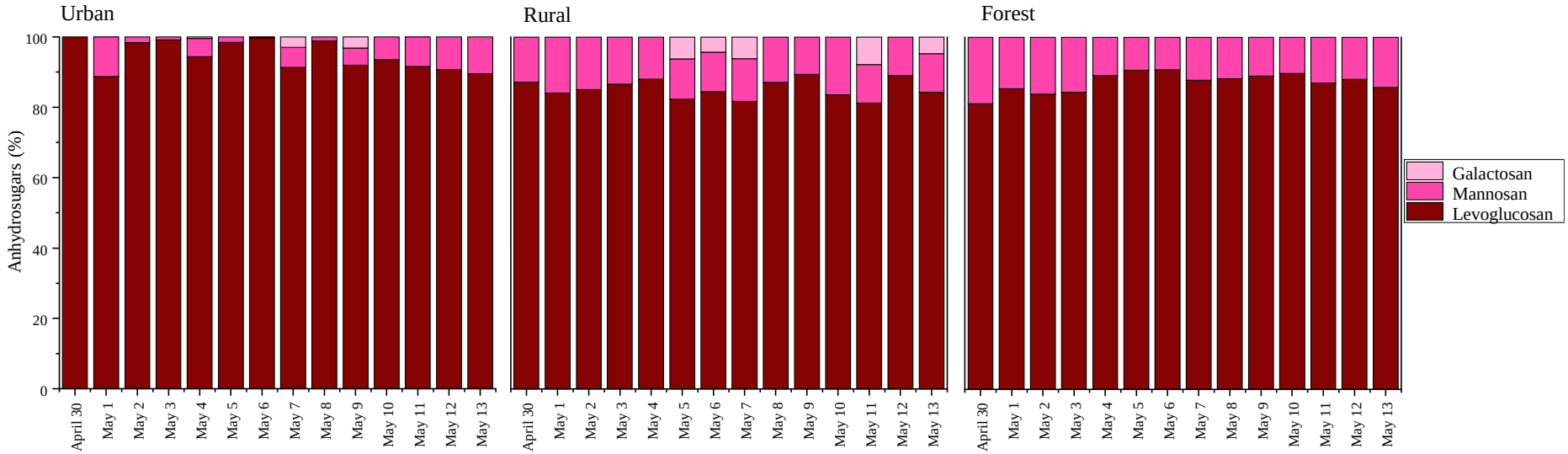

Figure S4. The percent distributions of each individual anhydrosugars (% of total anhydrosugars) in PM2.5 sampled in urban, rural and forest sites.

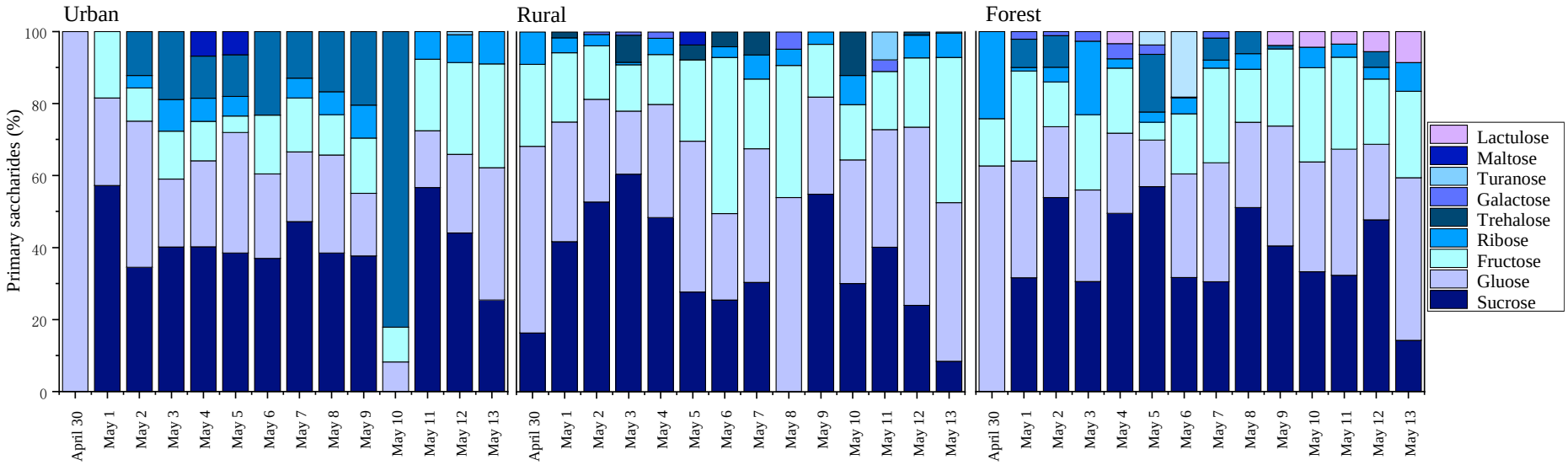

Figure S5. The percent distributions of each individual primary saccharides (% of total primary saccharides) in PM2.5 sampled in urban, rural and forest sites.

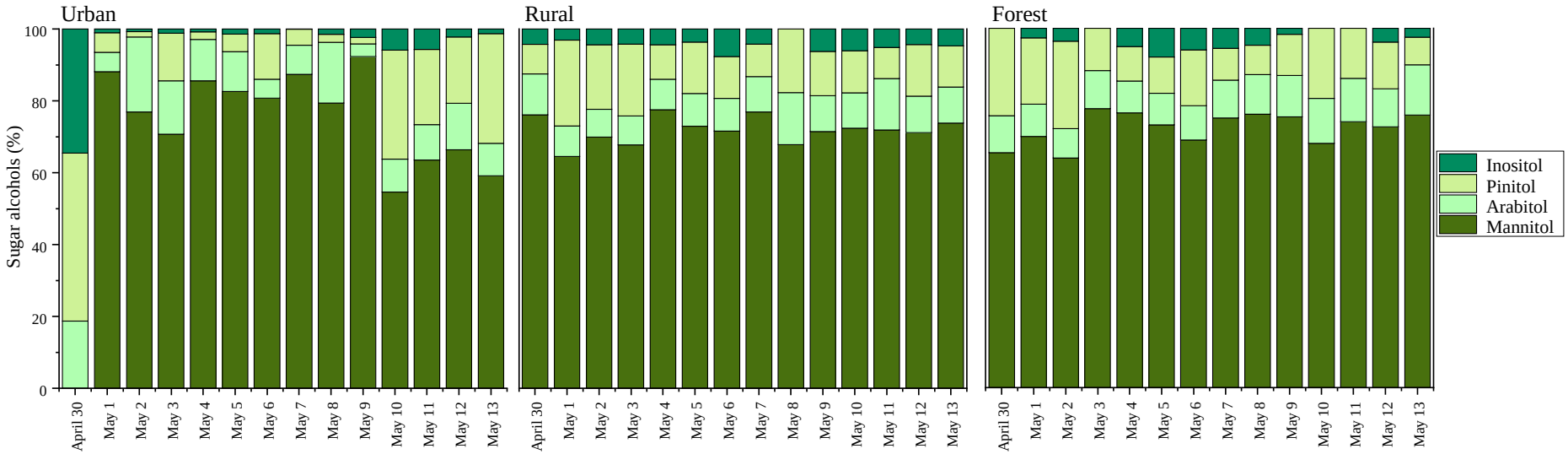

Figure S6. The percent distributions of each individual sugar alcohols (% of total sugar alcohols) in PM2.5 sampled in urban, rural and forest sites.

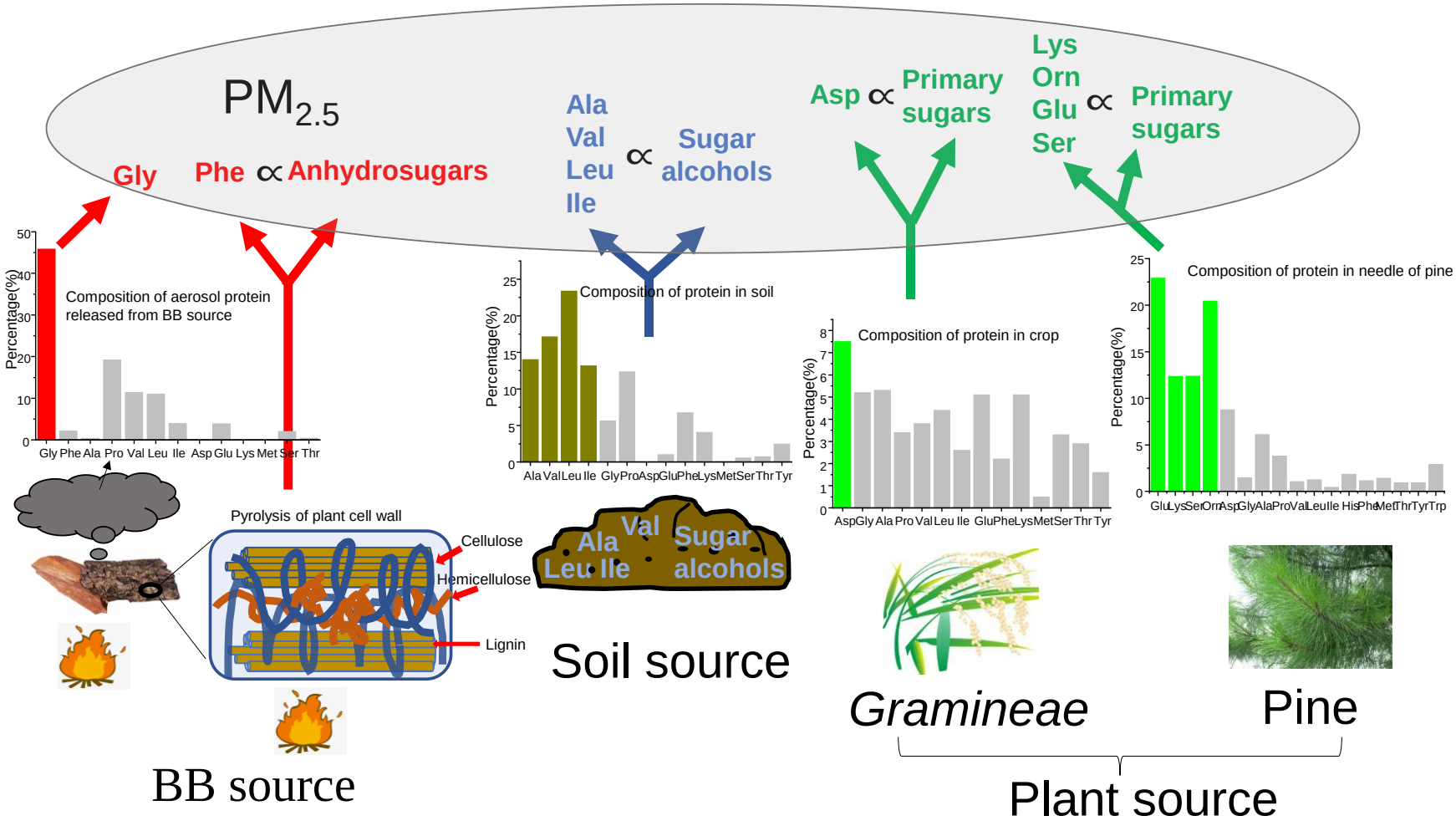

Figure S7. Grouping principles for CAAs.

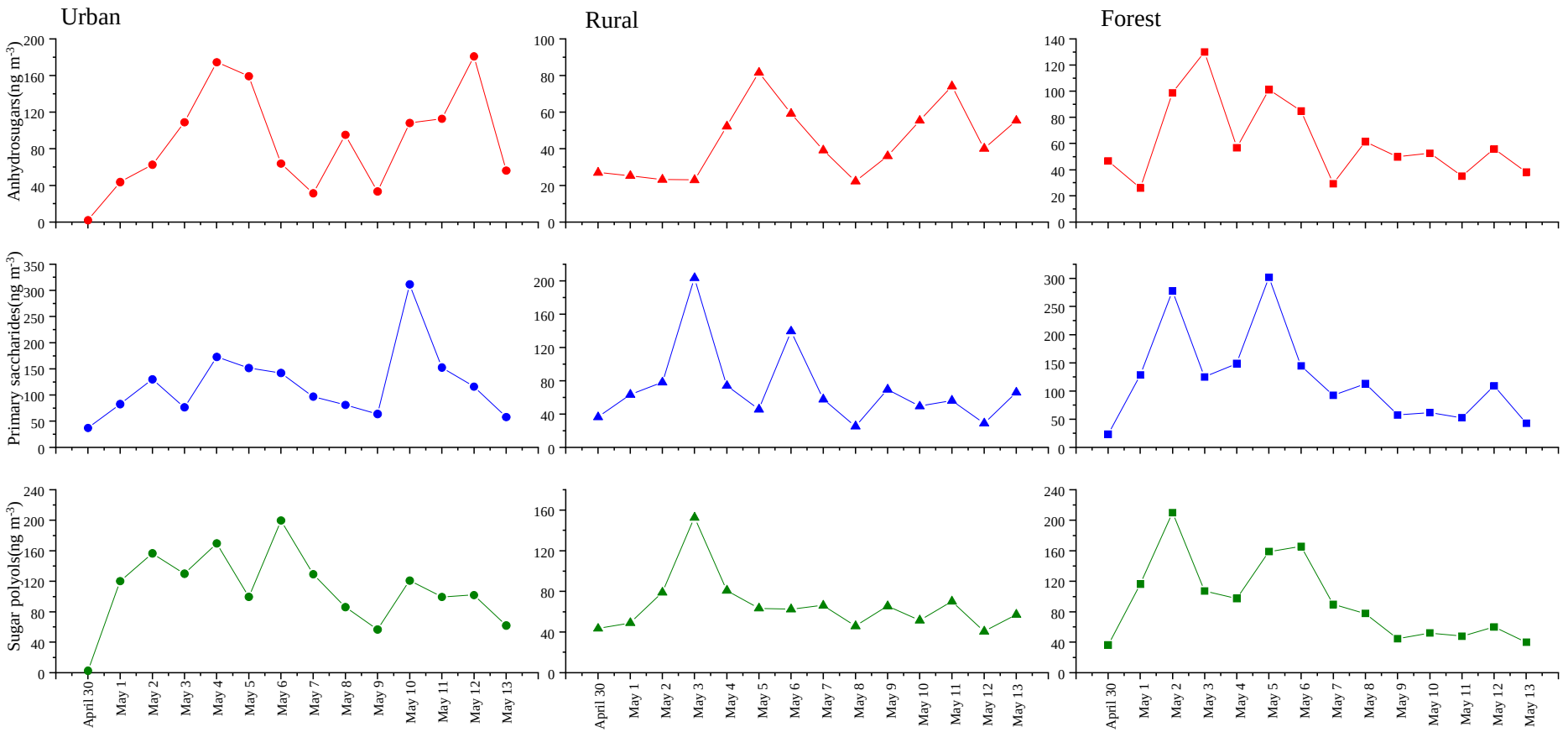

Figure S8. Temporal variations in the concentrations of anhydrosugars, primary saccharides and sugar alcohols detected in PM2.5 at urban, rural and forest sites.

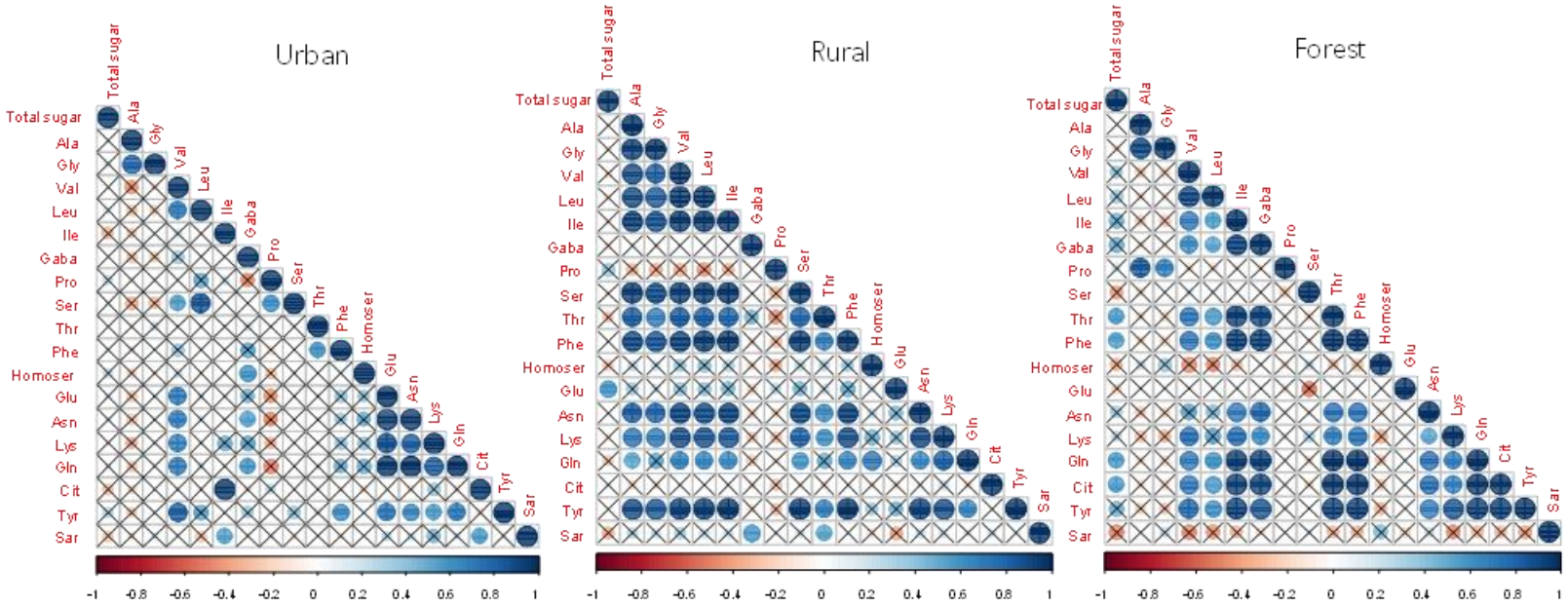

Figure S9. Pearson correlations between Σsugar concentrations and individual FAA species in PM2.5 collected in urban, rural and forest sites. The cross indicates a *p*-value higher than 0.05. The ball indicates a *p*-value less than 0.05. The larger a ball is, the more significant the correlation is