

Levels of carbohydrates in PM₁ particulate matter emitted during wintertime

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Carbohydrates in the air



Anhydrosugars

Sugar alcohols

Primary saccharides

Sources of carbohydrates in the air

Anhydrosugars

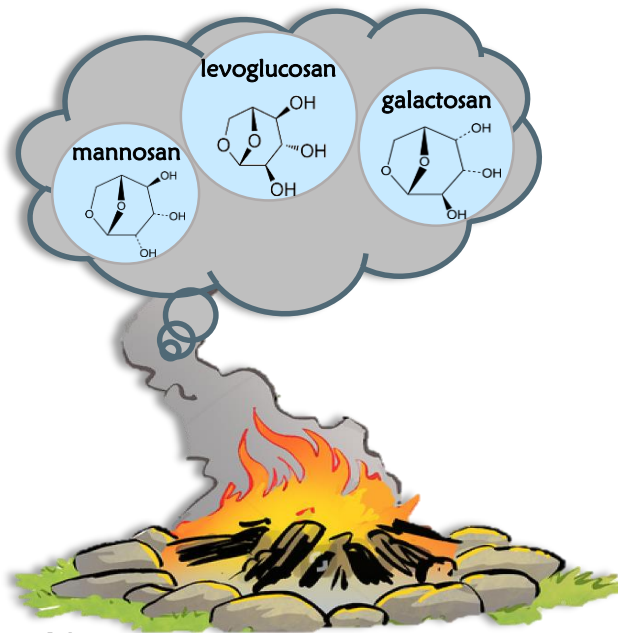
Levoglucosan (1,6-anhydro- β -D-glucopyranose)

Mannosan (1,6-anhydro- β -D-mannopyranose)

Galactosan (1,6-anhydro- β -D-galactopyranose)

- ❖ dehydrated derivatives of monosaccharides
- ❖ large quantities by anthropogenic activities

- ✓ agricultural waste burning
- ✓ residential wood combustion
- ✓ forest fires



Sources of carbohydrates in air

Sugar alcohols

- **Xylitol**
- **Erythritol**
- **Sorbitol**
- **Arabitol**
- **Mannitol**

- ❖ reduced sugars
- ❖ components of plants, spores, bacteria, lichens, and lower plants

- ✓ primary biological sources such as pollen, fungi, and bacteria
- ✓ breakdown products of polysaccharides
- ✓ direct volatilization of plant materials
- ✓ metabolic activity of various microorganisms
- ✓ thermal stripping of biomass burning



Sources of carbohydrates in air

Primary saccharides

- **Glucose**
- **Fructose**
- **Galactose**
- **Mannose**
- **Saccharose**

- ✓ continuous emissions from primary biological particles such as pollen, fungi, algae, growing leaves and decayed matter
- ✓ biomass burning (cellulose - glucose, hemicellulose - galactose, and mannose)
- ✓ biologically active soil dust



Aim of the study

- ✔ to investigate the levels of carbohydrates in PM₁ particulate matter collected during wintertime in Zagreb City, Croatia
- ✔ to compare results with the analysis of carbohydrates in PM₁₀ particulate matter
- ✔ to determine the plausible source of carbohydrates
- ✔ to statistically compare carbohydrates and polycyclic aromatic hydrocarbons (PAHs) (Spearman correlation, Factor analysis, Principal Component Analysis (PCA))

Experimental

Sample collection

- ⊙ fraction of PM₁ particulate matter
- ⊙ urban background station
- ⊙ sampling period: wintertime of 2020 (60 days)
- ⊙ National Measuring Station for Continuous Air Quality Monitoring



Experimental

SAMPLE COLLECTION

Quartz filters Tissuquartz 2500QAT-UP
(Pall Life Sciences)
($A = 1,5 \text{ cm}^2$)



LVS3 Sven Leckel
($55 \text{ m}^3/\text{day}$)



SAMPLE TREATMENT

GRAVIMETRY

Sample conditioning :

$t = 24 \text{ h}, 48 \text{ h}$

$\text{RH} = 50 \pm 5 \%$

$T = 20 \pm 1 \text{ }^\circ\text{C}$



SAMPLE PREPARATION

- ultrasonic extraction in ultra-pure water
- centrifugation

SAMPLE ANALYSIS

- **HIGH PERFORMANCE ANION-EXCHANGE CHROMATOGRAPHY WITH PULSED AMPEROMETRIC DETECTION**

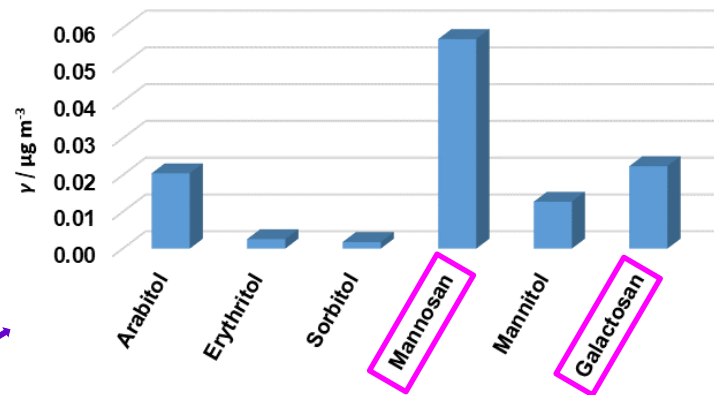
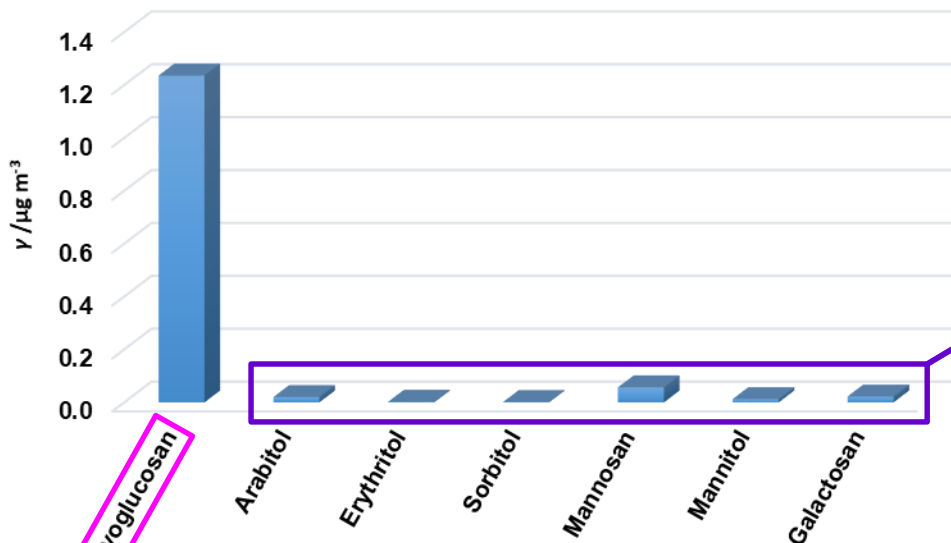


Eluent: NaOH, $0,4 \text{ ml/min}$

Separation column:
CarboPack MA1,
Thermo Fischer Scientific

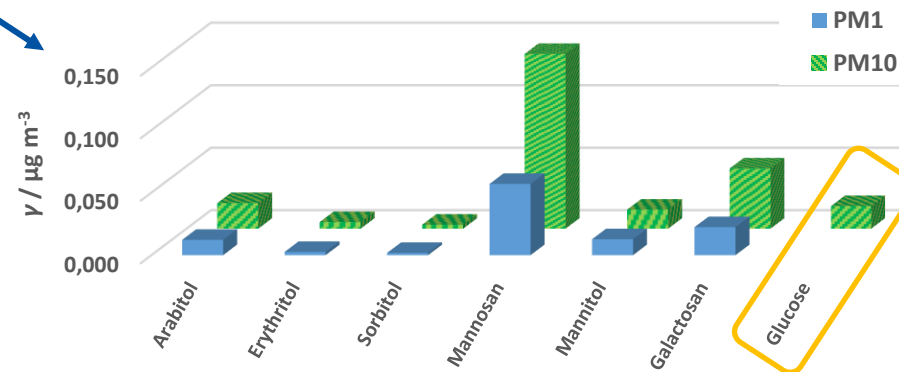
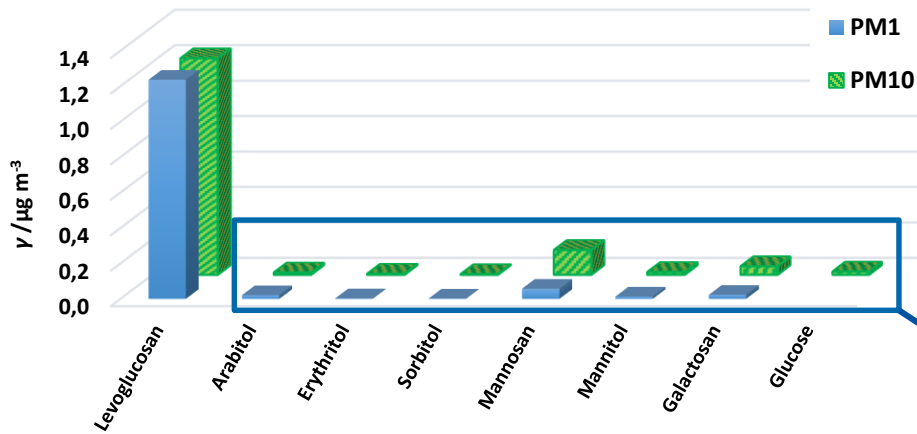
Results

Average mass concentrations of carbohydrates in PM₁ fraction



| $\gamma / \mu\text{g m}^{-3}$ | average | $\pm \delta$ | max | min |
|-------------------------------|---------|--------------|--------|--------|
| Levoglucosan | 1.2361 | 0.9974 | 4.5505 | 0.128 |
| Arabitol | 0.0205 | 0.0128 | 0.0576 | 0.0011 |
| Erythritol | 0.0026 | 0.0015 | 0.0089 | 0.0001 |
| Sorbitol | 0.0018 | 0.0037 | 0.0113 | 0.0001 |
| Mannosan | 0.057 | 0.037 | 0.1603 | 0.0072 |
| Mannitol | 0.0128 | 0.0096 | 0.0360 | 0.003 |
| Galactosan | 0.0224 | 0.0210 | 0.0824 | 0.0009 |

Comparison of mass concentration in PM₁ and PM₁₀ fraction

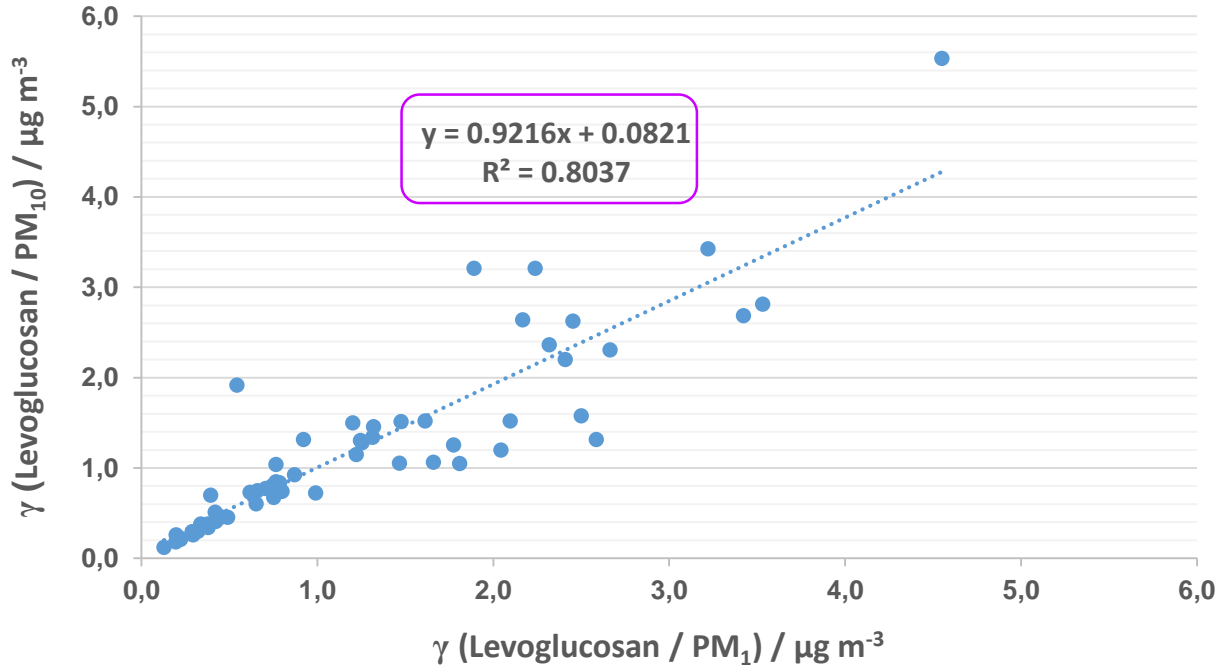
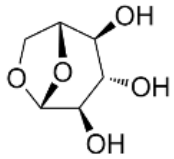


✓ similar mass concentration of levoglucosan in both fractions

✓ PM₁ < PM₁₀

✓ Glucose in PM₁₀

Correlation of levoglucosan in PM₁ and PM₁₀ fraction



➤ 92.2 % of levoglucosan in PM₁₀ fraction is bounded to PM₁ fraction

Spearman correlation between carbohydrates and polycyclic aromatic hydrocarbons in PM₁ fraction

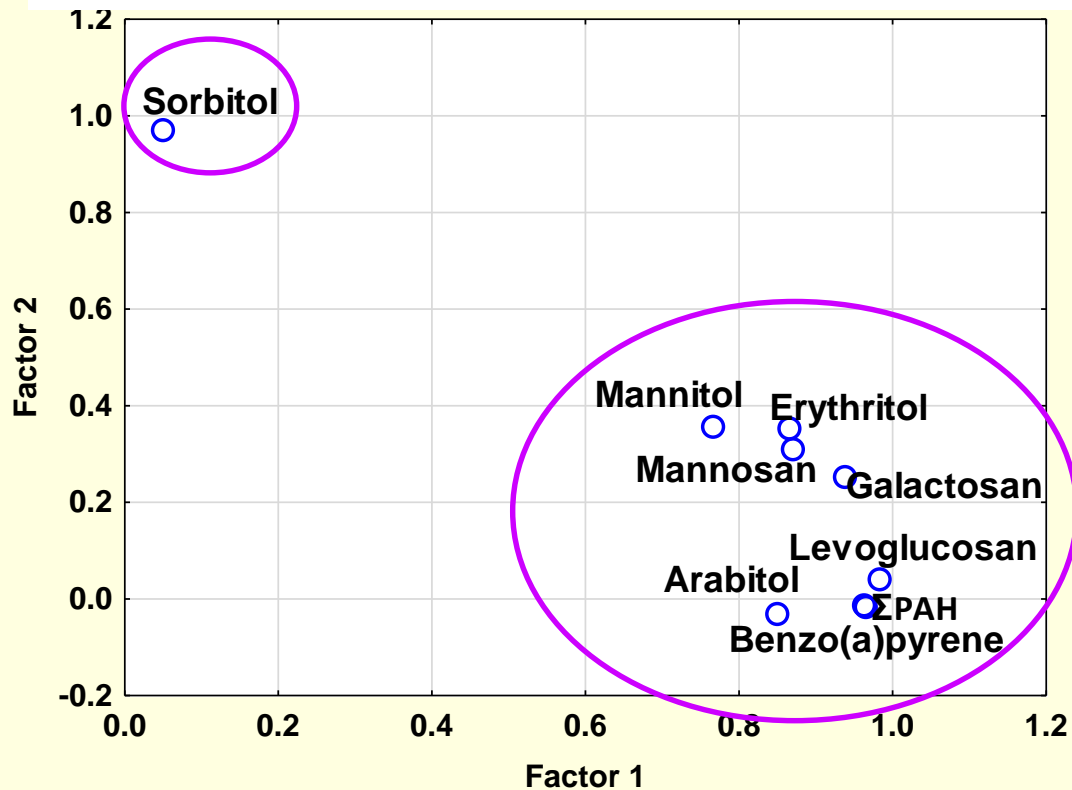
$p < 0.05$

| | Levoglucosan | Arabitol | Erythritol | Sorbitol | Mannosan | Mannitol |
|------------|--------------|----------|------------|----------|----------|----------|
| Arabitol | 0.94 | | | | | |
| Erythritol | 0.82 | 0.82 | | | | |
| Sorbitol | 0.09 | 0.13 | 0.31 | | | |
| Mannosan | 0.91 | 0.85 | 0.87 | 0.23 | | |
| Mannitol | 0.72 | 0.70 | 0.76 | 0.29 | 0.74 | |
| Galactosan | 0.91 | 0.86 | 0.88 | 0.25 | 0.94 | 0.82 |

| | Levoglucosan | Arabitol | Erythritol | Sorbitol | Mannosan | Mannitol | Galactosan |
|----------------|--------------|----------|------------|----------|----------|----------|------------|
| Benzo[a]pyrene | 0.96 | 0.87 | 0.76 | 0.05 | 0.86 | 0.70 | 0.89 |
| ΣPAH | 0.96 | 0.87 | 0.75 | 0.05 | 0.86 | 0.70 | 0.88 |

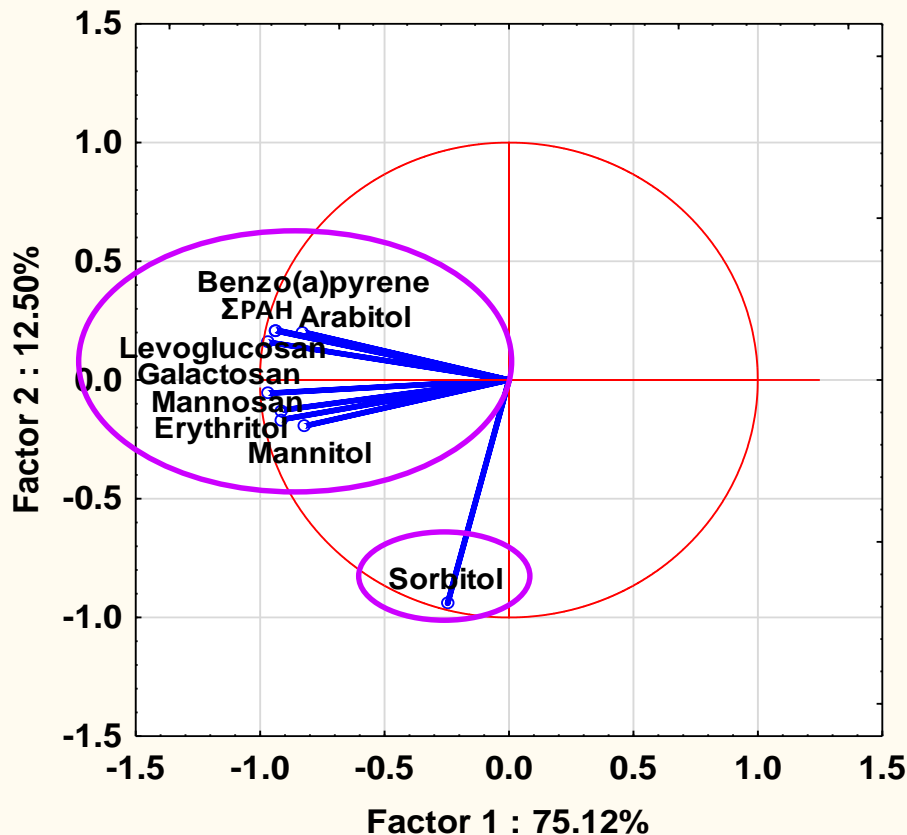
- ✓ **carbohydrates** : very strong ($\rho > 0.8$) and strong ($\rho > 0.6$) correlation → except for sorbitol
- ✓ **PAHs and carbohydrates**: very strong ($\rho > 0.8$) and strong ($\rho > 0.6$) correlation → except for sorbitol
- ✓ **sorbitol**: insignificant correlation → different source ??

Factor analysis between carbohydrates and polycyclic aromatic hydrocarbons in PM₁ fraction



- ✓ confirmation of Spearman correlation
- ✓ separates two factors that may indicate two different pollution sources
- ✓ **Factor 1.** includes anhydrosugars, sugar alcohols, and polycyclic aromatic hydrocarbons
- ✓ **Factor 2.** sorbitol

PCA analysis between carbohydrates and polycyclic aromatic hydrocarbons in PM₁ fraction



✓ Confirmation of factor analysis

✓ two possible pollution sources

✓ **1. source** related to biomass burning

anhydrosugars, sugar alcohols, and polycyclic aromatic hydrocarbons

- residential heating during wintertime

✓ **2.source** probably related to biogenic activity (fungal spores, microorganisms)

Conclusions

- ✓ During wintertime in PM₁ fraction of particulate matter sampled in the urban background station in Zagreb City, anhydrosugars and sugar alcohols are detected
- ✓ Most dominant compound in the PM₁ fraction of particulate matter was levoglucosan
- ✓ More than 90 % of levoglucosan in the PM₁₀ fraction is bound to the PM₁ fraction
- ✓ Spearman correlation showed a very strong and strong correlation among all of the detected carbohydrates and PAHs except for one sugar alcohol (sorbitol)
- ✓ Factor analysis confirmed the assumption of different sources of analyzed compounds; two factors were found
- ✓ PCA analysis confirmed the factor analysis; two pollution sources
 1. biomass burning from residential heating
 2. biogenic activity
- ✓ Further research will be focused on the seasonal variations and more input parameters (related analytes, meteorology) that would give more precise source identification of pollutants

The background of the slide is a light blue network diagram. It consists of numerous small circular nodes, some of which are highlighted with a darker blue or grey fill. These nodes are interconnected by a web of thin, light grey lines, creating a complex, interconnected pattern that resembles a social network or a data network.

Thank you for your attention!