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Sugars in clouds: Measurements and modelling investigation of their aqueous photodegradation

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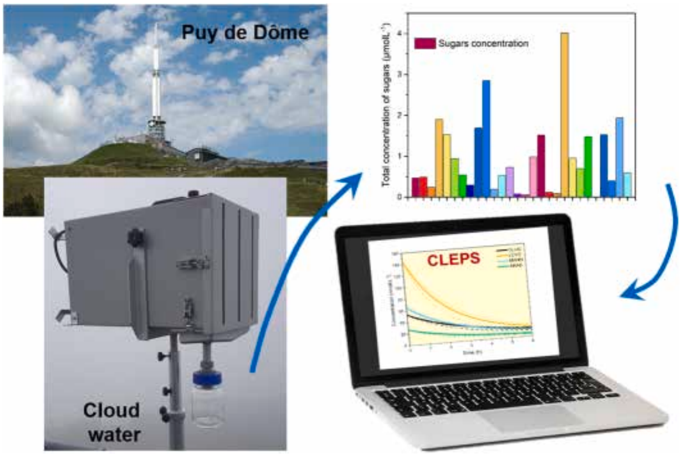
HIGHLIGHTS

- For the first time the concentration of 26 sugars is analyzed in 28 cloud samples by LC-MSMS.
- The total concentration is 0.98 ± 0.94 µmol L-1, levoglucosan is the most concentrated.
- Modelling results show that cloud chemical reactivity can transform efficiently some sugars.

GRAPHICAL ABSTRACT



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ABSTRACT

Currently, studies show that only 10–30% at best of the organic matter dissolved in cloud water is characterized and sugars are among the compounds still unexplored. Numerous studies on the atmospheric particulate matter (PM) demonstrate their ubiquity, and their incorporation into cloud phase is therefore expected in light of their solubility.

In this work, a large array of sugars are measured at low concentration levels with an innovative LC-MSMS technique in 28 cloud water samples collected at the puy de Dôme and their environmental variability is analyzed. The total sugar concentration reaches 4.0 µmol L^{-1}, with an average value of 0.98 ± 0.94 µmol L^{-1}, with no clear seasonal trend. This represents on average 1.2% of dissolved organic carbon but reaches up to 3.7%

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for one sample. The most abundant sugars is levoglucosan (average 247.2 nmol L^{-1}) followed by glucose (168.2 nmol L^{-1}), mannitol (136.5 nmol L^{-1}) and 2-methyl-tetrols (130.6 nmol L^{-1}). Reactivity in the aqueous phase is simulated with the cloud chemistry model CLEPS to gain insights in the half-life time of four selected compounds in different meteorological and chemical scenarios. Results show a fast degradation of sugars in the aqueous phase, especially during summer, that could question the use of these tracers for long range transport in the free troposphere.

1. Introduction

It is still difficult to quantify the effect on climate and global warming of the composition of organic carbon in aerosol particles (Calvin et al., 2023). Aerosols have both a direct effect on climate through their ability to reflect, disperse and absorb solar radiation, but also an indirect effect affecting cloud formation, which is influenced by aerosol hygroscopicity. This last property may be controlled by the presence of hydrophilic compounds, such as polysaccharides, that are structural components of plants, algae, fungi and bacteria, or that are linked to soil resuspension (Scaramboni et al., 2015). The presence of sugars has been highlighted in numerous works about the chemical composition of aerosols collected in various locations worldwide, as reported in (Marynowski and Simoneit, 2022). These soluble compounds can therefore be dissolved in the aqueous phase after aerosol activation into cloud droplets.

In recent years, studies of the chemical composition of cloud and fog water, and aqueous-phase reactions have been carried out in numerous regions of the world and at different altitudes: from seaside sites (Triesch et al., 2021), hill sites (Collett et al., 2008; van Pinxteren et al., 2005, 2016), mountain sites (Aleksic et al., 2009; Bauer et al., 2002; Deguillaume et al., 2014; Ghauri et al., 2001; Wei et al., 2017) to aircraft measurements (Boone et al., 2015). Specific attention has been given to characterize dissolved organic carbon present in comparable amounts as sulfate and nitrate in cloud and fog water (Collett et al., 2008; Herckes et al., 2013). Recent research focused on the non-targeted analysis of cloud water dissolved organic matter, with the aim of resolving its complex composition and orientate future research on specific compounds (Bianco et al., 2018; Zhao et al., 2013). These works report the presence of molecules with hydrogen to carbon ratio (H/C) and oxygen to carbon ratio (O/C) about 2 and 1, respectively, which defines saccharides. As reported in (Pailler et al., 2024), samples collected at puy de Dôme (Central Massif region, France) and on the slope of Mt. Maïdo (Reunion Island, France) and analyzed by high resolution mass spectrometry, contain the molecular formula $C_5H_{10}O_5$ and $C_6H_{12}O_6$, which correspond to pentose and hexose sugars. Measurements presented in (Dominutti et al., 2022) confirm the presence of saccharides in cloud water collected at the Reunion Island.

The presence of saccharides in cloud water is principally the result of the dissolution of aerosol particles after their activation into droplets. Three main categories of these biomolecules are currently identified in atmospheric PM. First, *sugar alcohols*, like arabitol (ARAB), erythritol, inositol, mannitol (MANN), threitol and 2-methyl-tetrols, are produced by fungi, lichens, detritus of mature leaves and soil microorganisms and are linked to soil resuspension (Medeiros et al., 2006) or to isoprene photooxidation pathway (Surratt et al., 2010). Second, *primary sugars*, like sucrose, glucose (GLUC) and fructose, derive from plant debris, microorganisms, animals and lichens and are considered as good tracers for primary biological aerosol particles (Fu et al., 2014). In particular, sucrose and fructose have been widely used as tracers of airborne pollen (Mampage et al., 2022). Finally, *anhydrosugars*, including for instance levoglucosan (LEVO), mannosan and galactosan, are produced by thermal degradation of cellulose or hemicellulose and are thus linked to biomass burning emissions (Bhattarai et al., 2019).

Saccharides are commonly considered as chemical tracers of primary biological aerosol particles (Zhu et al., 2015) because of their stability in atmospheric particles (Fraser, 2010). However, in the aqueous phase, the second order rate constants of certain of them such as pentose and hexose sugars with hydroxyl radical were estimated to be of the order of 10^{8-9} $M^{-1}s^{-1}$ (Bucknall et al., 1978; Buxton et al., 1988; Reuvers et al., 1973). This indicates an enhanced reactivity with photogenerated hydroxyl radicals ($^{\bullet}OH$) in cloud aqueous phase. In particular (Hoffmann et al., 2010), demonstrated through laboratory experiments and modelling that LEVO is not as stable as previously thought in the atmosphere, especially under high relative humidity conditions. Thus, saccharides concentrations could be influenced by some extent of chemical and photochemical reactivity in cloud droplets.

The aim of this study is to evaluate the concentration of sugars in cloud water collected at the puy de Dôme observatory (PUY). In contrast to aerosols and gases, clouds are sampled on event basis, and analyzed "offline". The volume needed for physicochemical and microbiological characterization is not always reached. For this reason a dataset of 28 samples, which is usually considered too small for aerosols and gases, is wide for cloud analysis. Moreover, for this work we used a strict sampling procedure, since collectors are unmounted, washed and autoclaved after sampling and mounted just before the sampling. Sterile conditions are strictly respected for parallel biological characterization of the samples. Only with this procedure we can measure low concentrations of sugars (nM). The correlations between the concentration of these compounds and the meteorological parameters and concentrations of inorganic ions are investigated. The reactivity in the aqueous phase is estimated with the cloud chemistry model CLEPS (Mouchel-Vallon et al., 2017; Pailler et al., 2023) to gain insights in the half-life time of four selected compounds in different seasonal scenarios.

2. Materials and methods

1. Sampling meteorological and physicochemical characterization

Cloud water collection was performed at the PUY observatory. This observatory belongs to the atmospheric survey networks EMEP (European Monitoring and Evaluation Program), GAW (Global Atmosphere Watch), and ACTRIS (Aerosols, Clouds, and Trace gases Research Infrastructure); it is part of the fully instrumented platform for atmospheric research Cezeaux-Opme-puy de Dôme (CO-PDD) (Baray et al., 2020).

Cloud water sampling is regularly performed at this site using the cloud collector BOOGIE (Vaitilingom et al., 2025) installed on the roof of the observatory (1465 m a.s.l.). This work focuses on 28 samples collected between 2018 and 2022 during 25 different cloud events (labelled from A to Y). To study the seasonal effect, 9 cloud events (10 samples) are collected during spring, 5 cloud events (7 samples) during summer, 8 in autumn and 3 during winter. Three cloud events are collected with two samplers in parallel and are reported as N1 and N2 (May 06, 2021), O1 and O2 (July 08, 2021), and P1 and P2 (July 16, 2021). The clouds collected are most of the time *stratus* or *cumulus*. The free troposphere or boundary layer conditions can be retrieved from the ^{222}Radon measurement performed at PUY: as reported in Farah et al. (2018), measurement below the threshold of $^{222}Rn = 0.5$ Bq m^{-3} correspond to free troposphere conditions. These are observed for all the samples except samples F and M, collected in the boundary layer (^{222}Rn measurements of 1.1 ± 0.2 and 0.6 ± 0.2 Bq m^{-3}, respectively). Samples B, D and W show intrusion of air masses from the boundary layer, since the ^{222}Rn measurements are 0.47 ± 0.14, 0.44 ± 0.16 and 0.45 ± 0.10 Bq m^{-3}, respectively.

During sampling, temperature varies between −0.3 °C and 12 °C, the liquid water content ranges between 0.1 and 0.7 g m^{-3}. Samples are collected during non-precipitating cloud events and negative temperatures are avoided to prevent ice formation on the collector, which has an impact on the collection efficiency and the composition of the sample itself. The aluminum impactor is cleaned and sterilized by autoclaving before each cloud collection. Cloud water is filtered using a 0.20 μm nylon filter within 1 h of its collection to eliminate microbial cells and residual particles. Sampling date and duration, and meteorological conditions during the collection of the samples are reported in Table S1. The table also reports the wind speed and direction, measured with a Vaisala anemometer, the liquid water content (LWC) and the average droplet radius (R_e), measured with a Gerber PVM 100. The QA/QC of these measurements is detailed in (Baray et al., 2020). pH is measured immediately after sampling with a Hanna pH meter HI-98103. Aliquots of each sample are frozen on site and stored at −20 °C for the chemical analyses. Various analytical methods are used to quantify oxidant concentrations (H_2O_2, NO_3^-, Fe(II) and Fe(III)), concentrations of inorganic and organic ions and of dissolved organic carbon (DOC) (Bianco et al., 2015).

The air mass origins for each cloud event are determined using a 72-h back-trajectory calculated with the CAT model (Renard et al., 2020) at an interception height of 1465 m a.s.l., corresponding to the PUY summit, and reported in Fig. S2. The statistical analysis of physicochemical composition and back-trajectories enables the classification of previous cloud samples in four categories: marine (low ion concentration, coming from the W/NW sectors), continental (moderate ions concentration), highly marine (with high concentration of Na^+ and Cl^-) and polluted (high concentration of NO_3^-, NH_4^+ and SO_4^{2-}) (Deguillaume et al., 2014; Renard et al., 2020). Samples presented in this dataset belong mostly to the marine category, with the exception of samples Q and Y, belonging to the continental category.

2. Analysis of sugars

The analysis of the soluble fraction of sugars, sugar alcohols, and anhydrosugars is carried out by an UHPLC method with tandem mass spectrometry detection (Exion LC30AD + AB Sciex 5500 Q-TRAP) with HILIC column (Luna Omega Sugar from Phenomenex) (Glojek et al., 2024). This analysis allows the quantification at low concentrations of saccharide anhydrides (LEVO or sedoheptulosan), a large series of polyols (xylitol, ARAB, sorbitol, MANN, glycerol, adonitol, galactitol, inositol, maltitol), sugars (GLUC, fructose, trehalose, erythrulose, rhamnose, ribose, xylose, mannose, galactose, sucrose, maltose, lactose, melezitose), and other species (2-methyl-tetrols). Most of the 26 species that can be quantified are species of primary or secondary biogenic origin. More details are reported in Paragraph S1. The limit of quantification for each compound is reported in Table S2. Galactosan and mannosan, as well as erythritol and threitol, are co-eluted and were therefore not quantified. The four isomers of the 2-methyl tetrols are not separated, but their calibration slopes are identical. They are quantified as the sum of the four species.

3. Cloud chemistry model

In this study, the cloud chemistry model CLEPS (Cloud Explicit Physico-chemical Scheme) is used. It is based on the Dynamically Simple Model for Atmospheric Chemical Complexity (DSMACC) (Emmerson and Evans, 2009) using the Kinetic PreProcessor (KPP). The gas phase reactivity is simulated by the Master Chemical Mechanism (MCM v3.3.1) (Jenkin et al., 2015) while the aqueous phase reactivity is described by the CLEPS mechanism (Mouchel-Vallon et al., 2017). Photolysis rates in the gaseous and aqueous phases are calculated with the TUV v4.5 model. The mass transfer of chemical compounds between the gas and the aqueous phases uses the Schwartz parametrization (Schwartz, 1986).

The aqueous phase mechanism CLEPS considers the detailed chemical reactions of H_xO_y, chlorine, carbonates, NO_y, sulfur, iron, manganese and copper in the aqueous phase; the mechanism describes the oxidation of organic compounds with 1–4 carbon atoms. In order to reach a stationary state, an 8-day long simulation (called "spin up") is performed considering the gas phase reactivity only (clear sky). The chemical scenarios used in this work are adapted from (Pailler et al., 2023) and are presented in Paragraph S2. The cloud appears on the 7th day at 10 a.m. and lasts 6 h. Four sugars, ARAB, GLUC, LEVO and MANN and their reactivity with hydroxyl radical (•OH) are added to the aqueous mechanism used in (Pailler et al., 2023b), as reported in Table 1. Two different scenarios (winter and summer) and six sensitivity tests are performed, initializing the simulations based on physicochemical and meteorological measurements as reported in Table S3. In all scenarios, pH is fixed at a constant value of 5. Temperature, LWC and droplet radius are kept constant during the simulations. Other parameters are kept identical to those described in Pailler et al. (2023).

3. Results and discussion

1. Saccharides in cloud water and analysis of the environmental variability

Fig. S1 reports the concentration of main inorganic ions for each cloud event presented. All the samples are classified as marine, with the exception of sample Q, collected on September 16, 2021, and sample Y, collected on April 25, 2022, belonging to the continental category. Samples collected in the boundary layer (F and M) or with intrusions of air masses from the boundary layer (B, D and W) show concentrations of ions similar to those collected in the free troposphere. The total concentration of sugars varies from <DL to 3.9 μmol L^{-1}, with an average value of 0.95 ± 0.91 μmol L^{-1}, without a clear seasonal trend, as reported in Fig. 1a. Unfortunately, the relatively limited dataset, the variable liquid water content that influences the concentration in the liquid phase, and the long range transport observed in free tropospheric conditions leading to transformations, could hide the seasonal trend commonly observed for aerosol samples collected in the boundary layer (Samaké et al., 2019b). It is worth noting that the highest concentration of sugars is reached for the continental sample Q, collected in late summer, while sample Y, also continental but collected during spring, show a concentration of sugars in line with the marine samples. Unfortunately, only two samples of continental origin are present in the dataset presented and it is difficult to draw conclusions regarding the influence of air mass origin. The average of the total concentration of sugars for each season is also not statistically different (*t*-test, $p>0.05$).

The sum of the carbon concentration of individual saccharides represents in average 1.2% of the dissolved organic carbon but reaches up to 3.7% for sample J (March 02, 2019, winter). Fig. 1b and Table S4 present the concentration of all the measured sugars, which varies from 0 to 1.5 μmol L^{-1}. The most abundant sugars are ARAB, GLUC, LEVO, MANN and 2-methyl-tetrols. For the further discussion, sugars with average concentration lower than 5 nmol L^{-1} are not considered, which

Table 1
Second order rate constants (M^{-1} s^{-1}) of ARAB, GLUC, LEVO and MANN with hydroxyl radical (•OH) implemented in CLEPS cloud chemistry model.

Id	Compound	Reaction	Rate constant ($M^{-1}s^{-1}$)	Reference
1)	Arabitol	ARAB + •OH → products	1.8×10^9	Moore et al. (1979)
2)	Glucose	GLUC + •OH → products	1.5×10^9	Buxton et al. (1988)
3)	Levoglucosan	LEVO + •OH → products	2.4×10^9	Hoffmann et al. (2010)
4)	Mannitol	MANN + •OH →products	1.9×10^9	Motohashi and Saito (1993)

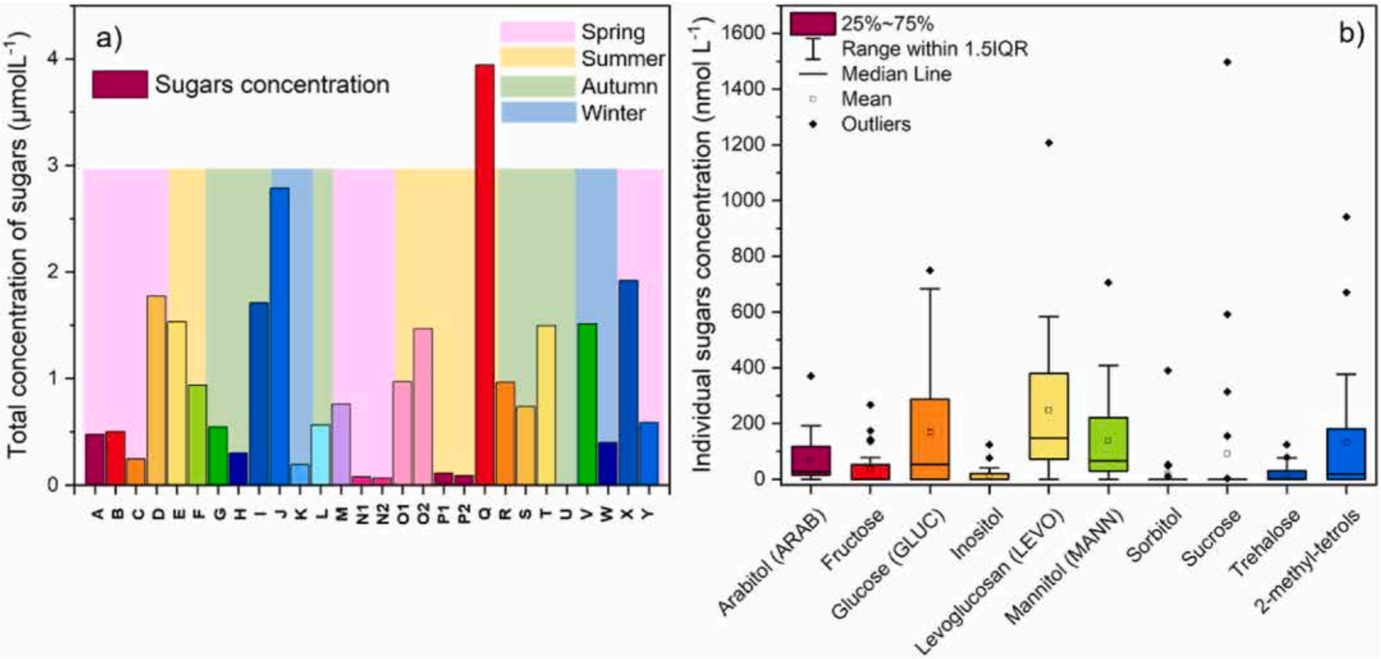


Fig. 1. a) Total concentration of sugars in cloud water samples (µmol L^{-1}); the background depicts the season, with spring in pink, summer in yellow, autumn in green and winter in blue. b) Concentrations (nmol L^{-1}) of all the saccharides measured in this work. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

leads to the exclusion of lactose, maltitol, maltose, melezitose, and xylose. Samples N1 and N2 and O1 and O2, collected in the same date with two different collectors in parallel, show concentrations not significantly different ($p>0.05$), as reported in Fig. S3. Samples P1 and P2, also collected in the same date, have different concentrations of sugars, although the profile is similar. This difference could be influenced by the lower LWC (0.2 g m^{-3}) observed for cloud collected on July 08, 2021 (samples O1 and O2) compared to the values measured for N1 and N2 (0.4 g m^{-3}) and P1 and P2 (0.7 g m^{-3}), which could lead to a less homogeneous dissolution of sugars present in the aerosol particles at lower LWC.

Fig. 2 presents the relative contribution of individual sugars to the total concentration for each season (spring, summer, autumn, and winter). On yearly average, LEVO is the most concentrated and represents from 6.8% (summer) to 51.0% (spring) of the total concentration. MANN and 2-methyl-tetrols account for 3.6%–21.5% and 2.6%–23.0%, respectively, while GLUC ranges from 5.7% to 22.9% and ARAB from 2.3% to 10.9%. Other sugars, like fructose and sucrose, present higher concentrations only in winter, of 10.9% and 41.1%, respectively. Isoprene oxidation products (2-methyl-tetrols) are found to be more abundant in summer and autumn (23.0% and 19.9%, respectively) than in winter (5.2%) and spring (2.6%).

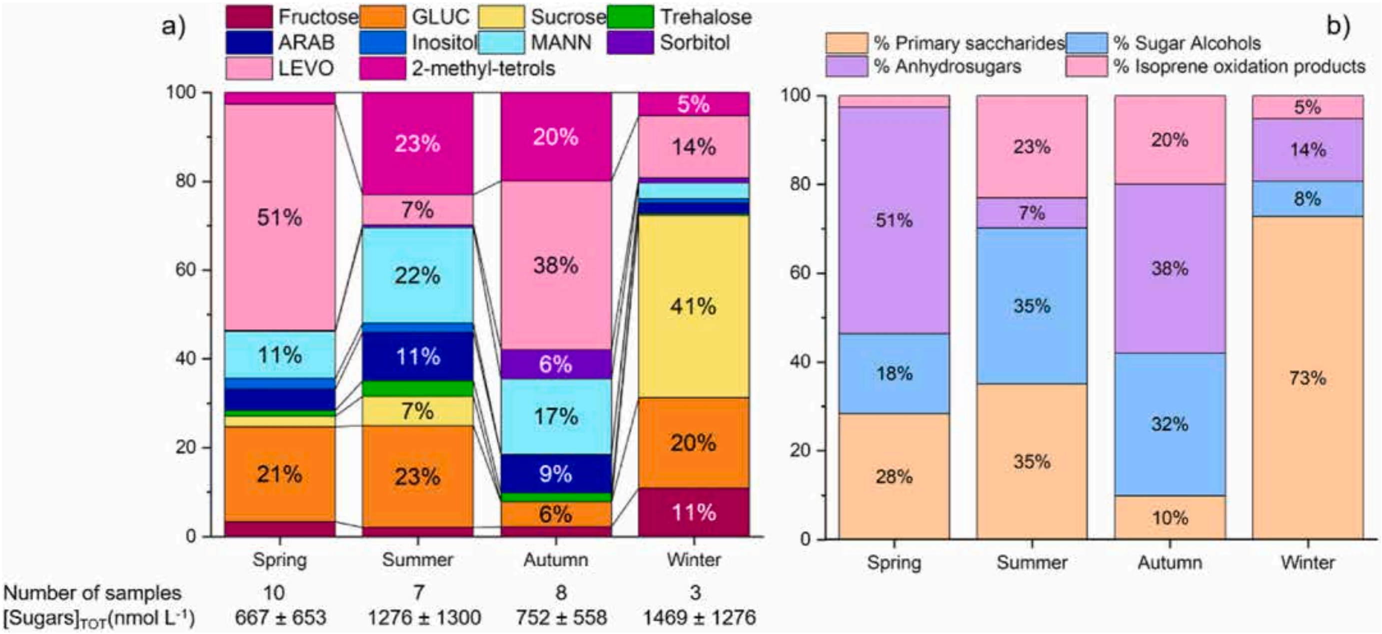


Fig. 2. a) relative contributions (%) of individual sugars for spring, summer, autumn, winter and for all the dataset (total) based on aqueous concentrations. b) Relative contributions of different classes for the four seasons and for the entire dataset.

3.1. Primary sugars

Primary saccharides are represented in this study by fructose, GLUC, sucrose and trehalose. Fructose and GLUC have broad biogenic sources from terrestrial plants, pollen, fruits and detritus (Speranza et al., 1997). GLUC is the most abundant carbohydrate in vascular plants (Zhu et al., 2015). Similarly, sucrose is the dominant component in airborne pollen grains, since it plays a key role in the plant flowering processes. Previous studies highlight their stability in the atmosphere, with stable concentrations up to 7 days (Samaké et al., 2019a). At PUY, they reach concentrations of 267 nmol L^{-1} (fructose), 749 nmol L^{-1} (GLUC), 1.497 μmol L^{-1} (sucrose) and 123 nmol L^{-1} (trehalose) (Fig. 1b), with seasonal variations: fructose and sucrose, present higher fractions in winter (10.9 and 41.1%, respectively; Fig. 2a). GLUC shows similar contributions in spring, summer and winter, while in autumn it only represents 5.7% of the total concentration of sugars.

The aqueous average concentrations of 102 ± 78, 262 ± 239 and 512 ± 592 nmol L^{-1} for fructose, GLUC and sucrose, respectively, corresponds to an atmospheric concentrations per volume of air of 5.6, 13.4 and 57.1 ng m^{-3}. This is calculated with Eq. (1), where C_{sugar} is the concentration of the sugar, either in [ng m^{-3}] or [nmol L^{-1}], MW is the molecular weight and LWC is the mean liquid water content in [g_{water} m_{air}^{-3}] measured during the sampling. When the LWC is not available, we used the value of 0.325 g m^{-3}, which is the average of the measurements for the samples presented in this study and representative of stratus and cumulus clouds (Renard et al., 2020).

$$C_{sugar}\ [\mathrm{ng\ m^{-3}}] = C_{sugar}\ [\mathrm{nmol\ L^{-1}}] \times MW\ [g_{sugar}\ \mathrm{mol^{-1}}] \times LWC\ [g_{water}\ m_{air}^{-3}] \times 10^{-3} \qquad \text{Eq. 1}$$

Fructose was detected in only 10 samples, GLUC in 18 and sucrose in 5, but, when present, these sugars show high concentrations. It is interesting to highlight that the aqueous concentration of these sugars is either below the limit of quantification, of 1.7, 11.7 and 20.1 nmol L^{-1}, respectively, either higher than 40 nmol L^{-1}.

The concentrations of GLUC in ng m^{-3} are comparable to the values reported by (Marynowski and Simoneit, 2022) for atmospheric aerosol collected in rural and urban sites, without distinction. Their concentrations are expected to be higher during summer due to the vegetation bloom and therefore lower during winter. At PUY, higher relative abundances of these primary saccharides are observed during winter (72.8%) and summer (35.1%), followed by spring (28.4%) and autumn (9.9%) (Fig. 2b). Fig. S4 reports the concentrations for each season. Only three samples belong to winter, and for two of them (J and V) the concentrations of the three sugars are higher than the values observed for the other seasons. Nevertheless, sample K, also collected during winter, shows low concentrations of fructose, GLUC, and sucrose, below the detection limits. It is difficult to find an explanation for this result: the concentrations observed are not correlated with particle number concentration, or with other meteorological parameters such as temperature. Moreover, for samples J, V and K, the microphysical cloud properties could also explain these variations in the aqueous concentrations but unfortunately those data were not available. More samples collected during winter are needed to draw conclusions.

Excluding the three winter samples, the concentration of GLUC in the samples is correlated with temperature ($R^2 = 0.48$, $p = 0.001$), suggesting the input of primary plant and spore particles as observed in aerosols (Medeiros et al., 2006; Yttri et al., 2007; Zhu et al., 2015). Nevertheless, fructose is not correlated ($R^2 = 0.09$, $p > 0.05$) with the temperature, suggesting different sources than GLUC (Simoneit et al., 2004). reported that GLUC and sucrose concentrations in aerosols were correlated with soil dust, desert silt and road dust, suggesting resuspension of soil as an important source. The correlation of these sugars with Ca^{2+} and Mg^{2+}, which are generally linked to dissolution of mineral dust in cloud water, is not statistically significant for this dataset ($p > 0.05$) except for sucrose and Mg^{2+} ($p = 0.0007$). This could be due to the fact that this dataset does not include identified strong dust events. Other works, presenting aerosol samples collected in the boundary layer (marine and ambient atmospheres, respectively) suggested that the biomass burning could be a source of GLUC and fructose in aerosol (Gonçalves et al., 2021; Scaramboni et al., 2015), but a statistically significant correlation between these sugars and LEVO is not found for this dataset ($p > 0.05$).

3.2. Sugar alcohols

Sugar alcohols are represented in this study by ARAB, inositol, MANN and sorbitol. The concentrations reached at PUY are, respectively, 370 nmol L^{-1}, 123.4 nmol L^{-1}, 706 nmol L^{-1} and 390 nmol L^{-1}, as reported in Fig. 1b. The relative abundance of these sugars is generally higher in summer (10.9%, 2%, 21.5% and 0.6% for ARAB, inositol, MANN and sorbitol, respectively), and lower in autumn and winter, except for sorbitol that shows a contribution of 6.5% in autumn (Fig. 2a).

The averaged concentrations found in cloud samples is 79 and 165 nmol L^{-1} for ARAB and MANN, respectively (Fig. 1), corresponding to atmospheric concentrations equal to 4.0 and 9.8 ng m^{-3}, calculated using Eq. (1). These values are lower than those reported for GLUC, fructose and sucrose, but the number of samples containing ARAB and MANN is higher: only 3 samples show concentrations below the limit of quantification, producing a quite homogeneous dataset. Fig. 3a reports the concentration of ARAB and MANN, together with other sugar alcohols such as inositol and 2-methyl-tetrols, measured in this work. Sugar alcohols are particularly abundant during summer and autumn (35.1% and 32.2%, respectively), and also significant in spring (18.0%) and winter (8.0%) (Fig. 2b). ARAB and MANN concentrations follow a clear seasonal trend, supported by a correlation between sugar concentrations and temperature, $R^2 > 0.3$ (Fig. 3b, $p = 0.001$ for ARAB and $p = 0.0009$ for MANN). ARAB and MANN are often measured in atmospheric aerosols and their high concentrations in spring-summer season (80–120 ng m^{-3}) could be the results of the emission of fungal spores, which are classified as coarse particles (PM10) (Samaké et al., 2019a, 2019b, 2020, 2021). These particles are subjected to sedimentation that may lead to low concentrations in the free troposphere.

Inositol is a minor component in remote marine aerosols, having similar sources and seasonal behavior as other sugar alcohols (Zhu et al., 2015). Even if clouds sampled at PUY have been shown to receive compounds from marine origin (Renard et al., 2022), the inositol concentration is below the detection limit for 15 samples and generally lower than those of ARAB and MANN.

2-methyl-tetrols are produced by plants, but can be also produced by photooxidation of isoprene. These compounds have been at first measured in aerosols (Decesari et al., 2006; Kourtchev et al., 2005; Nozière et al., 2011) and then the isoprene photooxidation pathway has been investigated through chamber experiments (Kroll et al., 2005; Surratt et al., 2006, 2010). In previous studies, the sum of their concentrations has been shown to follow a seasonal trend and varies between 0.5 and 50 ng m^{-3} between autumn and summer in the boreal forest (Finland) (Kourtchev et al., 2005) and 0.5–200 ng m^{-3} between wet and dry season in the Amazonian forest (Brazil) (Decesari et al., 2006). In cloud water samples collected at PUY, the concentration of 2-methyl-tetrols are between 0.1 and 41.6 ng m^{-3}. Although no obvious correlation between 2-methyl-tetrols concentration and temperature is observed ($R^2 = 0.288$), these compounds show a clear seasonal trend, with higher concentrations in summer and lower concentrations in spring (Fig. 3a). This indicates that vegetation emissions are plausible sources, as reported by Glojek et al. (2024).

3.3. Anhydro sugars

Levoglucosan (LEVO) is produced by the pyrolysis of carbohydrates, such as cellulose and starch, and it is commonly used as a tracer for

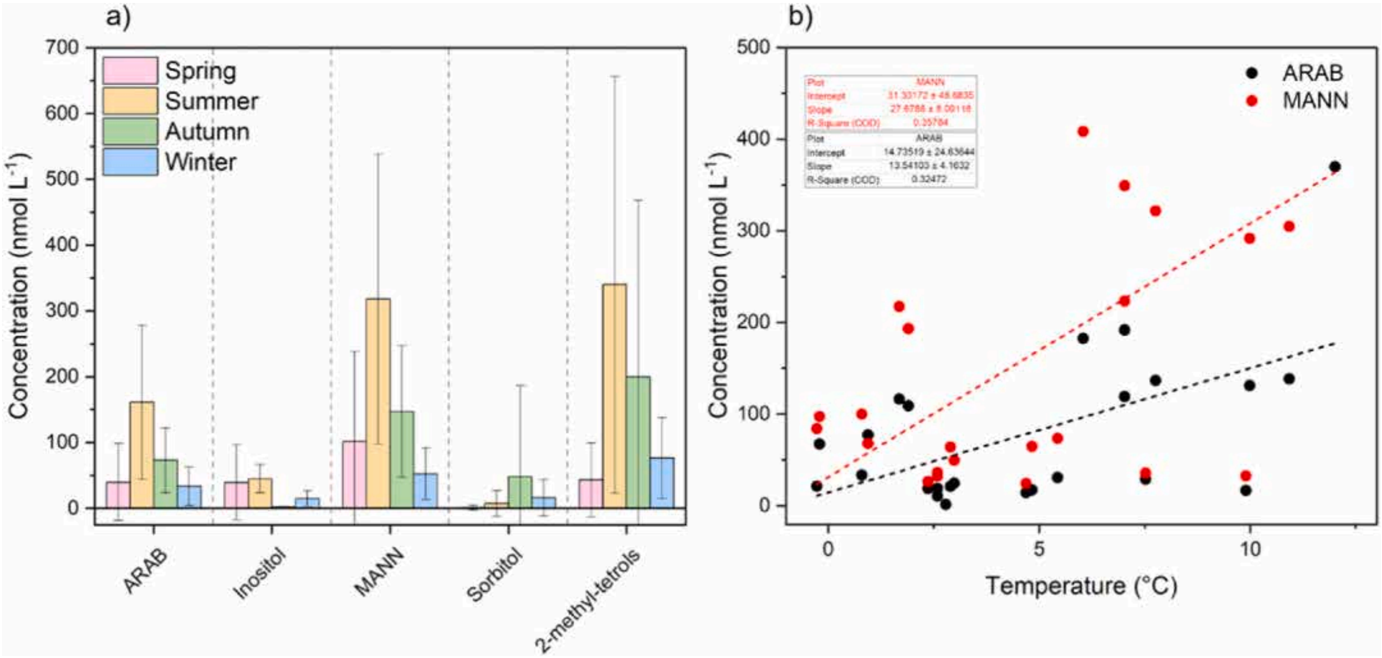


Fig. 3. a) concentration of sugar alcohols and isoprene derivatives in cloud water samples collected during spring, summer, autumn and winter. The error bars represent the standard deviation on the measurements (n = 10 for spring, 7 for summer, 8 for autumn and 3 for winter). b) correlations of ARAB and MANN with temperature during sampling. The correlation coefficient R^2 (Pearson) of the linear fit for MANN is 0.36 and for ARAB 0.32.

biomass burning contribution to aerosol. It can also be produced by coal burning (Wu et al., 2021). The concentration in cloud samples collected at PUY spans from 0 to 1.2 μmol L^{-1}, and LEVO is one of the most concentrated sugars, with relative contribution higher than 7% for all the seasons. The higher contribution is reached in spring (51.0%), followed by autumn (38.0%) and winter (14.1%) (Fig. 2a). This is in contrast with the seasonal trend commonly observed for atmospheric PM, which shows higher concentrations in winter, due to domestic biomass burning, and lower concentrations in spring and summer. The seasonal variability of atmospheric dynamics could give some hints on this difference: biomass burning emissions accumulate in the boundary layer during winter with possibly low turbulence and therefore a less efficient transport into the free troposphere where cloud forms; this could be an explanation of the low concentration observed in winter in our samples. During spring, the boundary layer height increases with the temperature rise and LEVO is probably more transported to the free troposphere. It's worth noting that in the free troposphere, LEVO concentration could also be drastically reduced by the aqueous reactivity (see Section 2).

The average aqueous concentration of 247.2 nmol L^{-1} corresponds to an atmospheric mass concentration of 13.0 ng m^{-3}. This value is in the range of values reported for rural sites (Barbaro et al., 2024; 2015; Borlaza et al., 2022; Fu et al., 2012; Gosselin et al., 2016; Medeiros et al., 2006; Schneider et al., 2011; Yttri et al., 2007; Zhu et al., 2015), but it is one order of magnitude lower than values reported for urban sites (Fu et al., 2012; Golly et al., 2019; Pietrogrande et al., 2014; Wan and Yu, 2007; Wang et al., 2011), attesting that concentrations of LEVO in clouds collected at PUY are representative of a background site, far from local emissions.

The correlations between the concentration of LEVO and meteorological parameters, such as wind speed, particle number concentration, temperature and LWC was investigated and no glaring correlation was found (R^2 always below 0.3, $p < 0.05$). The PUY summit can be located in the free troposphere, especially for meteorological conditions favoring cloud formation; therefore clouds are supposedly not influenced by local emissions. To better understand the influence of long-range transport on the concentration of LEVO, the back-trajectories of air masses computed by the CAT model and corresponding to samples A, B, I, J, L, R, S, W, X, and Y were analyzed in correspondence to potential sources by biomass combustion in wildfires. It is worth noting that in average 25 % of the wildfire emissions are injected into the free troposphere (FT) and 75 % into the planetary boundary layer (PBL) (Veira et al., 2015) and a direct correlation between the cloud event and the fire spot is difficult to find, since samples are collected in the free troposphere. The goal of the discussion is to highlight the periods influenced by wildfire emissions. In Northern Europe, particularly in Scandinavia and around the Baltic Sea, the annual levels of wildfire emissions were the highest on record in these years (European State of the Climate - *Wildfires*, *2018-2019-2020-2021*, n.d.), that could explain the concentrations of LEVO always higher than 100 nmol L^{-1} (corresponding to 5 ng m^{-3}), which is more than twice the concentration in samples collected in the first half of 2021. Samples R, S, W, X and Y also showed a high concentrations of LEVO (601 ± 348 nmol L^{-1}, 32 ± 18 ng m^{-3}), probably due to the exceptional intensity of wildfires starting in March 2022 in Albania, Austria, Bosnia Herzegovina, Bulgaria, Croatia and Germany (European Commission. Joint Research Centre., 2023).

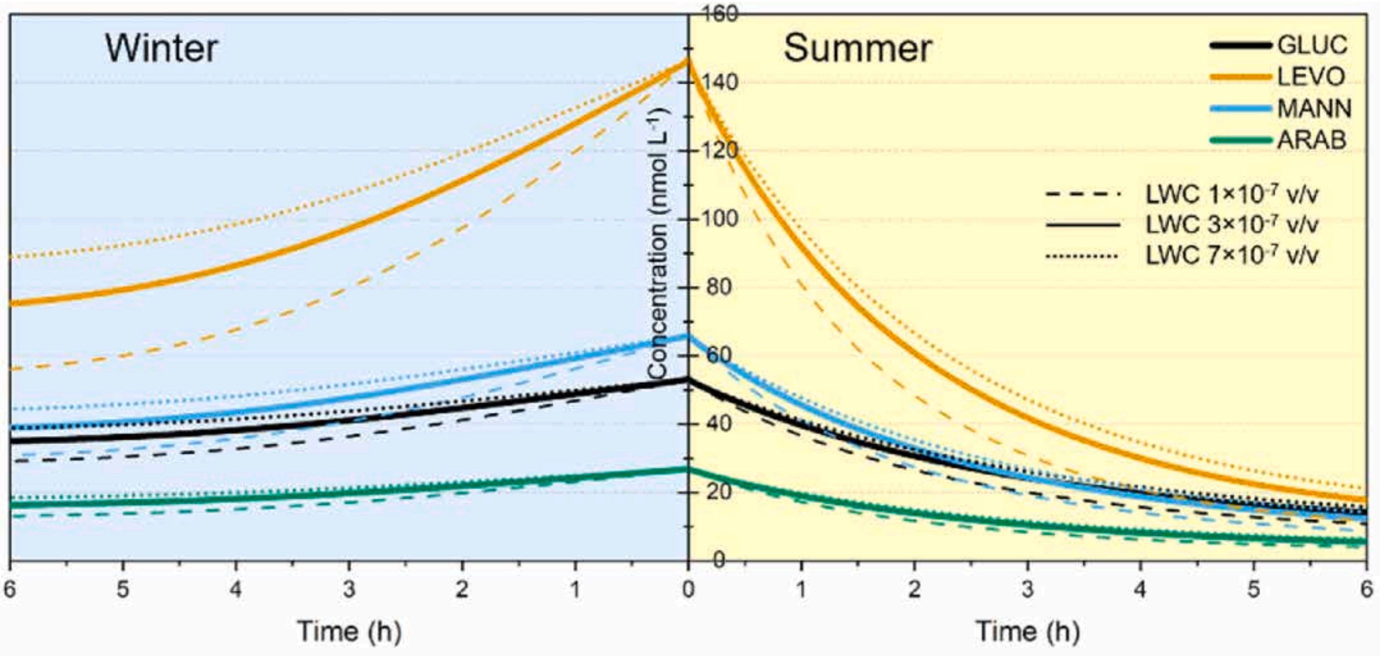
2. Modelled degradation rates of selected saccharides in cloud water

Saccharides are often used as chemical markers: in particular, LEVO is considered as a marker of biomass burning, while ARAB and MANN are markers of fungi emissions. Nevertheless, recent studies question the use of these molecules as tracers for long range transport. For instance (Hoffmann et al., 2010), demonstrated that LEVO can efficiently react with $^{\bullet}$OH, nitrate and sulfate radical anions in atmospheric hydrometeors and deliquescent particles. More recently, Fu et al. (2023) reported that biomass burning emissions might be underestimated, as LEVO can undergo degradation processes in the atmosphere. They argue that liquid phase process may dominate the aging process of levoglucosan during its long-range transport. The same effect could also be suspected on other saccharides that are possibly impacted by the atmospheric aqueous reactivity during their atmospheric transport.

The estimation of the reactivity in cloud water is problematic: cloud is a multiphasic environment with a complex equilibrium between gases, particles and water. This environment is difficult to be reproduced in chambers and by laboratory experiments. It is also arduous to estimate the residence time of compounds in cloud and the partitioning of saccharides between aerosols and clouds. Cloud chemistry models are able to provide the estimation of the reactivity in a multiphasic environments (Barth et al., 2021). In this frame, we aimed at estimating the photochemical degradation of four representative saccharides, namely arabitol (ARAB), glucose (GLUC), levoglucosan (LEVO) and mannitol (MANN), in samples collected at PUY. These compounds are chosen because they present the higher median concentrations in cloud samples presented in this work: 27.0 nmol L^{-1}, 53.2 nmol L^{-1}, 147.0 nmol L^{-1}, and 66.1 nmol L^{-1} for ARAB, GLUC, LEVO and MANN, respectively. Moreover, the four chosen saccharides represented primary sugars (GLUC), sugar alcohols (ARAB and MANN) and anhydro sugars (LEVO). For each sugar, second order rate constants with $^{\bullet}OH$ are retrieved from literature and reported in Table 1. The aqueous phase concentrations of the different sugars are initialized in the model as the median of all the samples presented in this dataset. The actinic flux was set either at winter solstice (December 21st) or at summer solstice (June 21st) to simulate the photodegradation under to contrasted seasonal scenarios (winter vs summer). Cloud appears in the model at noon, where the actinic flux is maximal, and lasts for 6 h, until 6 p.m. Cloud microphysical parameters (LWC and mean radius) have been chosen based on in situ measurements and kept constant during simulations, since they control cloud chemical reactivity. The standard simulation hereafter named LWC3 is performed using LWC of 3×10^{-7} v/v, corresponding to 0.3 g m^{-3}, and droplet radius of 10 μm. Two other sensitivity tests are performed to simulate clouds with small droplets and low LWC, setting LWC at 1×10^{-7} v/v and droplet radius at 3.5 μm (LWC1), and clouds with large droplets and high LWC, setting LWC at 7×10^{-7} v/v and droplet radius at 14 μm (LWC7).

The cloud chemistry model CLEPS is used as a diagnostic tool to describe the aqueous reactivity of these sugars with $^{\bullet}OH$ in a multiphasic environment for summer and winter conditions. Aqueous and gaseous photochemical production and mass transfer modulate the concentration of $^{\bullet}OH$ in cloud water. For the summer and winter simulations, diurnal aqueous $^{\bullet}OH$ concentrations are controlled by the aqueous phase production from the reaction O_3 and $HO_2^{\bullet}/O_2^{\bullet-}$ and to a lesser extent by the mass transfer of $^{\bullet}OH$ from the gaseous phase. We have chosen not to consider additional sources of $^{\bullet}OH$ through the photolysis of nitrate because this source has been shown to be negligible for the conditions encountered in the puy de Dôme (Bianco et al., 2015). The $^{\bullet}OH$ concentrations during the winter and summer simulations and the sensitivity tests are reported in Fig. S5 with values in the range of 10^{-14} M. As expected, since the photochemistry is reduced during winter, the $^{\bullet}OH$ concentration are reduced. For both simulations, $^{\bullet}OH$ concentration decreases during the simulation time since the photoproduction of $HO_2^{\bullet}/O_2^{\bullet-}$ radicals decreases with the decrease in actinic flux.

Fig. 4 presents the degradation of the four sugars for winter (light blue) and summer (yellow) as a function of cloud lifetime. At first



t ½ (h)	ARAB	GLUC	LEVO	MANN
Summer LWC1	1.62	2.00	1.17	1.52
Summer LWC3	2.10	2.58	1.52	1.97
Summer LWC10	2.38	2.92	1.72	2.23
t ¾ (h)				
Winter LWC 1	1.87	2.23	1.40	1.77
Winter LWC 3	2.77	3.83	2.07	2.62
Winter LWC 10	3.80	4.92	2.75	3.55

Fig. 4. Modelling evaluation of the degradation of ARAB (green), GLUC (black), LEVO (yellow) and MANN (light blue) over the cloud period that last 6h. In the model CLEPS, the cloud appears at noon (12PM) and lasts until 6 p.m. Solid lines present the results for the reference simulation (LWC3), with LWC of 3×10^{-7} v/v and droplet radius of 10 μm. Dashed lines represent the sensitivity test LWC1, with LWC of 1×10^{-7} v/v and droplet radius of 3.5 μm, and dotted line the sensitivity test LWC7, with LWC of 7×10^{-7} v/v and droplet radius of 14 μm. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

glance, LEVO is more reactive than MANN and ARAB, which present similar degradation; GLUC is the less reactive compound, according to the trend observed for the second order reactivity constants. Considering only LWC3, depicted by solid lines, the half life time of all the sugars considered is lower than 2h in summer conditions. Nevertheless, the degradation in winter is lower, and only LEVO reaches the 49% of degradation in 6h, while ARAB and MANN reach 40% and GLUC 34%. This result could possibly explain the higher concentrations of GLUC observed in winter in the samples collected at PUY. The dotted lines represent the sensitivity test LWC7, while the dashed ones the LWC1. As expected, modifying the LWC impacts the aqueous phase concentrations of the $^\bullet$OH: generally, the higher the LWC, the more diluted the droplets and *vice versa*, meaning that the chemical rates exhibited a global decrease at higher LWC values for a dilution effect, as already observed for carboxylic acids in (Pailler et al., 2023). The higher the concentration of $^\bullet$OH, the higher the degradation: since $^\bullet$OH are more concentrated in the summer than in winter scenarios, due to the actinic flux, the degradation is higher in the summer scenarios. Similarly, the degradation is higher for droplets with low LWC, since the concentration of $^\bullet$OH is higher. This could lead to the efficient degradation of sugars in cloud water, especially during summer and in thin cloud or fog.

In conclusion, the aqueous phase is an efficient environment for the transformation of saccharides, even in winter conditions, with lower actinic flux. Therefore, saccharides should be considered with caution as marker of fungal activity or biomass burning, especially for aged air masses that could undergo cloud cycles. In addition, these sugars can enter microbial metabolism and an additional microbial degradation may occur in cloud droplets, with a variation of their concentration.

4. Conclusion

Sugars have been detected on aerosol collected in different places of the world. They can dissolve in the cloud aqueous phase after their activation into cloud droplets. Among those biomolecules, different categories are identified: i) sugar alcohols, are produced by fungi, lichens, mature leaf detritus and soil microorganisms and are related to soil resuspension or photooxidation pathway of isoprene; (ii) primary sugars come from plant debris, microorganisms, animals and lichens and are considered as good tracers for primary biological aerosol particles; (iii) Anhydrosugars, such as levoglucosan, are produced by thermal degradation of cellulose or hemicellulose and are therefore related to biomass combustion.

28 samples collected in 2018–2022 at the puy de Dôme observatory have been carried out to analyze the environmental variability of sugar concentrations. The analysis is performed by an innovative UHPLC method with tandem mass spectrometry detection that allows low detection limits.

The total sugar concentration reaches 4.0 μmol L^{-1}, with an average value of 0.98 ± 0.94 μmol L^{-1}, with no clear seasonal trend. This represents on average 1.2% of dissolved organic carbon reaching up to 3.7% for one sample. The most abundant sugars are arabitol, glucose, levoglucosan, mannitol and 2-methyl-tetrols. The concentrations of sugars in clouds are quite different from those measured in aerosols: differences are observed for the absolute air concentrations, always lower than those reported in aerosols, but also for the seasonal variations. Multiple reasons can lead to this result: first, sugars may be emitted in the coarse modes (>2.5 μm) of aerosols and therefore hardly transported in the free troposphere. Second, sugars aqueous reactivity leads to additional transformation than what is observed in the aerosols phase (dry aerosol).

The concentration of glucose in the samples is well correlated with temperature, suggesting the intake of primary plant particles and spores already evidenced for aerosols particles. Concentration in ng m^{-3} are comparable to the reported values for atmospheric aerosols collected at rural and urban sites. Sugar alcohols are particularly represented in summer and autumn (35% and 32%, respectively), and to a lesser extend but still significant in spring (18%) and winter (8%). Arabitol and mannitol concentrations follow a seasonal trend, supported by a correlation between sugar concentrations and temperature. 2-methyl-tetrol isomers, which are produced by photooxidation of isoprene, show a seasonal trend, with higher concentrations in summer and lower concentrations in spring. The concentration of levoglucosan ranges from below the detection limit to 1.2 μmol L^{-1}, making it one of the most concentrated sugars for all seasons. The highest contribution is reached in spring (51%), followed by autumn (38%) and winter (14%). The yearly mean aqueous concentration of 247.2 nmol L^{-1} corresponds to an atmospheric mass concentration of 13.0 ng m^{-3}. This value is within the range of reported yearly mean values for rural sites.

The CLEPS cloud chemistry model is used to assess the reactivity of the 4 main sugars in the aqueous phase. Modeling results show that sugars are efficiently transformed, with a half-life of less than 2 h in the summer scenario for all sugars. Therefore, saccharides should be cautiously considered markers of fungal activity or biomass burning for air masses that undergo cloudy cycles during their atmospheric transport. These sugars may also undergo additional microbial degradation in cloud droplets, leading to changes in their concentrations.

CRediT authorship contribution statement

Angelica Bianco: Writing – review & editing, Writing – original draft, Visualization, Resources, Investigation, Formal analysis. **Lucas Pailler:** Writing – review & editing, Visualization, Software. **Muriel Joly:** Writing – review & editing, Formal analysis. **Anne-Marie Delort:** Supervision, Conceptualization. **Sophie Darfeuil:** Writing – review & editing, Formal analysis. **Jean-Luc Jaffrezo:** Writing – review & editing, Supervision, Resources, Formal analysis, Conceptualization. **Laurent Deguillaume:** Writing – review & editing, Supervision, Software, Funding acquisition, Conceptualization.

Data availability

Data are available in the Supplementary material, but further information can be obtained on request.

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Declaration of competing interest

The contact authors have declared that none of the authors has any competing interests.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2025.121167.

Data availability

Data will be made available on request.

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