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Origin and significance of saccharides during initial pedogenesis in a temperate climate region

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ABSTRACT

Saccharides are common constituents of soils, but their role and origin in the initial phases of pedogenesis remain unclear. Here we show the detailed composition of neutral sugars extracted from arenosols at different development stages, combined with additional lipids of diverse origins using gas chromatography-mass spectrometry (GC–MS). During the first stage (I) of development sucrose is the most abundant saccharide in the soil crust at up to 45,000 µg/g TOC. Sucrose is also the predominant compound in the second and third development stages, but its concentration decreased to the range of 1600 to 16,000 µg/g TOC. Stages II and III of soil development were characterized by a gradual increase in arabitol, mannitol and trehalose, compounds typical for fungi and lichen. Their abundances increased from several percent (compared to the major sucrose) to 10–32% for mannitol and 34–54% for trehalose. Moreover, in stage III there was a considerable increase in the contents of the saccharides: pinitol, *myo*-inositol, *scyllo*-inositol, arabinose, together with non-sugar compounds: dehydroabietic acid, *p*-hydroxybenzoic acid, gallic acid and sitosterol. All these latter compounds are higher plant markers, mainly derived from conifer detritus. The relationships between the ratios of trehalose/sucrose vs. (mannitol + arabitol)/sucrose and TOC vs. (mannitol + arabitol)/sucrose differentiated precisely the top soil layer of arenosols which are covered by different stages of biological soil crust. Our study shows that free sugars, supplemented by lipid biomarkers and total organic carbon contents, are good indicators of soil in the initial phase of pedogenesis.

1. Introduction

Carbohydrates (saccharides) are the most abundant class of organic compounds in the Earth's biosphere, and the most common compound groups that build living organisms (BeMiller, 1989; Huber et al., 2006). Their complex role includes storing energy and protection of membranes and macromolecules against different types of stress (Thevelein, 1984; Asiegbu, 2000; Elbein et al., 2003; Solomon et al., 2007).

Saccharides are frequent constituents of lake and marine sediments (Hernes et al., 1996; Sigleo, 1996; Amon and Benner, 2003), but these compounds occur even more often in peat bogs (Klok et al., 1984; Moers et al., 1990a,b; Comont et al., 2006; Disnar et al., 2008; Jia et al., 2008) and soils (Greenland and Oades, 1975; Oades, 1993; Amelung et al., 1996; Nierop et al., 2001; Kögel-Knabner, 2002; Simoneit et al., 2004; Rushdi et al., 2006; Gunina and Kuzyakov, 2015 and references therein). Free sugars are generally labile and unstable, but in favorable conditions these compounds can also be preserved in ancient sedimentary rocks (Moers et al., 1994; Fabbri et al., 2009; Marynowski et al., 2018, 2019).

In soils, carbohydrate C as a % of total C can even reach 20–30% (Lowe, 1978; Oades, 1993). However, their significance and development during soil formation are still not well understood. Particularly little is known about the composition and role of free sugars in biological soil crust, which covers the first millimeter of top soil during the initial phase of formation, i.e. pedogenesis (Fischer et al., 2010a). The highest concentrations of free saccharides are generally associated with temperate climate conditions where surface litter is abundant, but even there not all soils contain high concentrations of free sugars. The most plausible case is their rapid utilization by microorganisms (Greenland and Oades, 1975).

Most of the studies concerning the occurrence of sugars in soils have focused on the composition of monosaccharides, which are a combination of free, bound and extended saccharides released from soils using different hydrolysis methods (e.g. Trouve et al., 1996; Larre-

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Larrouy and Feller, 1997; Amelung et al., 1996, 1999; Debosz et al., 2002; Zhang et al., 2007). Hydrolysis yields high concentrations of monosaccharides, but breaks the glycosidic bonds between oligosaccharides and generates most of the monosaccharides from biopolymers such as hemicellulose and cellulose, thus obliterating the origin of particular saccharide monomers. An alternative often used method is pyrolysis-GC–MS, sometimes improved by derivatization of the resultant products (Kögel-Knabner, 2000; Nierop et al., 2001). Both methods can be useful in the calculation of the total carbohydrates in soil, but destroy primary mono- and oligosaccharides, and therefore blur the information about their origin.

Sugars are generally not distinctive for specific source types or biological species, but the co-occurrence of specific saccharides in sedimentary organic matter or ambient air with a comparison to lipids can provide information about their source. For example, the co-occurrence of such compounds as arabitol, mannitol and trehalose can be a good indicator of fungal metabolism, which was confirmed based on comparison to modern fungi (Marynowski et al., 2019; see also: Asiegbu, 2000; Simoneit et al., 2004; Medeiros et al., 2006; Solomon et al., 2007; Hybelbauerová et al., 2008). In turn, glucose is ubiquitous in all living organisms, but can be also a product of cellulose decomposition in soil (e.g. López-Mondéjar et al., 2016). Other compounds like D-*chiro*-inositol and D-pinitol are widely distributed in gymnosperm species (e.g. BeMiller, 1989; Duquesnoy et al., 2008) and are less common in angiosperms. Furthermore, *myo*-inositol is present in many plants where it is converted to D-glucuronic acid and subsequently into xylose, arabinose and other saccharides (BeMiller, 1989). Thus, identification of saccharides in soil can shed new light on the origin of the organic matter, especially during the first pedogenesis stages.

Thus far, little is known about the occurrence of neutral sugars in soils and their interconnections with living organisms colonizing soils in the early stages of pedogenesis. Numerous studies have focused on environmental topics showing trehalose as a main disaccharide occurring in soils and associated this compound genetically with fungi (e.g. Simoneit et al., 2004; Rushdi et al., 2006, 2016). Sucrose has rarely been identified as a dominating sugar (Zhou et al., 2009; Fu et al., 2012; Giri et al., 2013), but the reason for the distribution changes between these two disaccharides remains unclear. Even less is known about the occurrence and genesis of monosaccharides in soils, especially since they are not necessarily the same compounds reported using the hydrolysis method (e.g. Nierop et al., 2001).

Here we present the detailed determination of mono- and oligosaccharides from arenosols (sandy-textured soils that lack any significant development of a soil profile) in a temperate climate region to observe their subsequent development connected with successive colonization in pedogenesis. We suggest, that the composition and concentration of neutral sugars detected in arenosols are good indicators of soil development. For instance, the colonization of sand by cyanobacteria and algae in the first stage of pedogenesis can result in photosynthesis of specific mono- and disaccharides, which, in turn, can change together with the subsequent colonization of soil by other organisms. The main goal of the paper is the correlation between sugars, lipids and living organisms colonizing the soils and their mutual relationships.

2. Samples and methods

2.1. Samples

Soils were sampled from the Błędowska Desert (5 × 12 km; South Poland) during April and May 2010, the months with the highest humidity. In total 15 surface samples (not exceeding 5–10 cm deep) were collected, among which 13 were selected for analysis. Samples were collected in glass containers and dried in the laboratory on Petri dishes. All arenosol samples can be classified as sandy soils with a low to very low clay content. For more details about sampling and sample descriptions see Rahmonov et al. (2015). Soil stages (especially stages I and II vs. III) differ macroscopically. In stages I and II the crust is very thin and light (greenish during growth). In stage III the crust is dark and thicker. However, we have divided the collected soils into three groups based on differences in their TOC values (Table 1).

2.2. Total organic carbon content

The total carbon (TC) and total inorganic carbon (TIC) contents were determined by using an Eltra CS-500 IR-analyzer with a TIC module. The TC was determined by using an infrared cell detector for CO_2, which evolved from the combustion of organic matter under an oxygen atmosphere with the simultaneous thermal decomposition of carbonates. The TIC content was determined by an infrared detector for CO_2 that was derived from the carbonates by reaction with 15% warm hydrochloric acid. The total organic carbon (TOC) was calculated as the difference between the TC and TIC. The instrument was calibrated utilizing the Eltra standards.

2.3. Extraction and derivatization

Powdered samples (ca. 15 g) were extracted using a dichloromethane (DCM)/methanol mixture (1:1 v:v) with an ultrasonic bath. All spectroscopically pure solvents were of super dehydrated grade. Aliquots of the total extracts were converted to trimethylsilyl (TMS) derivatives by reaction with N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA), 1% trimethylchlorosilane, and pyridine as well as with N-methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA), 1% trimethylchlorosilane, and pyridine for 3 h at 70 °C. The excess reagent was then removed under blow-down with dry nitrogen and the sample mixture dissolved in an equivalent volume of *n*-hexane. Only derivatization using MSTFA gives almost complete TMS derivatization of soil sugars. A blank sample (silica gel) was analyzed using the same method. Trace amounts of phthalates, *n*-fatty acids (FAs) and *n*-alkanols were found. Saccharides were not detected in blank samples.

2.4. Gas chromatography – mass spectrometry

Gas chromatography – mass spectrometry (GC–MS) analyses were carried out with an Agilent Technologies 7890A gas chromatograph and Agilent 5975C Network mass spectrometer with Triple-Axis Detector (MSD) at the Faculty of Earth Sciences, Sosnowiec, Poland. Helium (6.0 Grade) was used as a carrier gas at a constant flow of 2.6 ml/min. Separation was obtained on J&W HP5-MS (60 m × 0.32 mm i.d., 0.25 μm film thickness) fused silica capillary column, coated with a chemically bonded phase (5% phenyl, 95% methylsiloxane), for which the GC oven temperature was programmed from 45 °C (1 min) to 100 °C at 20 °C/min, then to 300 °C (hold 60 min) at 3 °C/min, with a solvent delay of 10 min.

The GC column outlet was connected directly to the ion source of the MSD. The GC–MS interface was set at 280 °C, while the ion source and the quadrupole analyzer were set at 230 and 150 °C, respectively. Mass spectra were recorded from 45 to 550 da (0–40 min) and 50–700 da (> 40 min). The MS was operated in the electron impact mode, with an ionization energy of 70 eV.

2.5. Quantification and identification

An Agilent Technologies MSD ChemStation E.02.01.1177 and the Wiley Registry of Mass Spectral Data (9th edition) software were used for data collection and mass spectra processing. Mono- and disaccharides were identified based on comparison of mass spectra and retention times with those of standards and data published by Medeiros and Simoneit (2007). The following standards were used: D-(+)-xylose (Sigma-Aldrich), L-arabinose (Amresco), D-(+)-mannose (Acros Organics), D-(−)-fructose (Sigma-Aldrich), D-(−)-ribose (Acros

Table 1
Saccharide and non-saccharide composition and distribution in soils. Relative abundances in %, normalized to major peak = 100.

Sample	2_OR	4_OR	5_OR	6_OR	8_OR	7_OR	9_OR	10_OR	11_OR	12_OR	13_OR	14_OR	15_OR
Development stage	STAGE III					STAGE II			STAGE I				
TOC [%]	8.0	8.8	9.3	5.4	4.6	0.9	1.4	1.0	0.4	0.7	0.5	0.5	0.3
Organic compounds													
Saccharides													
Glycerol	5	25	22	18	9	1	0.4	0.3	0.3	0.1	0.2	0.4	0.1
Threitol	0.1	0.1	0.2	0.2	0.1	0.03	0.0	0.05	0.01	0	0.01	0	0
Erythritol	0.0	1	1	1	0.4	0.2	0.1	0.6	0.1	0.1	0.2	0.1	0
α-Arabinose	0.3	1	0.4	1	1	0.1	0.1	0.1	0.3	0.1	0.1	0.1	0.02
β-Arabinose	0.4	1	1	1	1	0.2	0.2	0.1	0.5	0.1	0.1	0.3	0.03
Levoglucosan	0.05	0.1	0.2	0.1	0.1	0.0	0.02	0.02	0.04	0.03	0.02	0.02	0
Arabitol	3	7	3	3	2	1	1	0.7	0.2	0.1	0.1	0.1	0.1
Adonitol	0.3	1	1	1	1	1	3	2	0.3	0.3	0.4	0.1	0.1
α-Fructose	0.3	1	0.3	2	1	1	0.4	0.6	0.6	0.2	0.4	0.3	0.2
β-Fructose	0.4	2	1	3	1	0.4	0.6	0.4	0.7	0.2	0.2	0.4	0.1
Pinitol	1	1	3	3	1	1	0.2	0.4	0.9	0.8	0.4	0.3	0.5
Glucofuranose?	0.1	1	2	1	0.3	1	0.0	0.1	0.1	0.1	0.1	0.1	0.03
α-Galactose	0.4	1	0.4	1	0.5	0.1	0.2	0.1	0.2	0.1	0.1	0.2	0.04
Gluconic acid-γ-lactone	1	1	1	1	1	1	0.5	0.6	0.7	0.1	0.2	0.5	0.1
α-Glucose	2	2	5	6	3	1	0.6	0.7	0.7	0.5	0.7	0.3	0.3
β-Mannose + β-Galactose	1	3	1	2	1	1	0.7	0.5	0.6	0.3	0.3	0.4	0.1
Mannitol	32	13	15	14	10	4	5	7	0.2	0.3	0.4	0.2	0.5
Sorbitol	3	4	5	3	3	3	1.4	2	0.5	0.3	0.4	0.8	0.3
Mannoic acid-γ-lactone	1	1	1	1	0.4	0.1	0.1	0.1	0.05	0.01	0.01	0.0	0
β-Glucose	1	5	11	7	4	0.4	0.5	0.5	0.7	0.5	0.7	0.4	0.3
Gluconic acid	1	2	1	1	2	0	0.1	0.1	0.1	0.04	0	0.1	0
scyllo-Inositol	0.2	0.4	0.2	0.2	0.2	0	0.0	0	0.02	0	0	0	0
myo-Inositol	3	8	13	12	9	0.3	0.4	0.3	1.2	0.2	0.2	1.5	0.5
Glyceryl glucopyranoside	6	6	19	14	8	1	1	6	1.2	0.6	0.9	1.5	0.2
Glyceryl galactopyranoside	1	1	2	2	1	3	0.3	2	0.2	1.4	2.1	0.1	0.5
Sucrose	100	100	100	100	100	100	100	100	100	100	100	100	100
Trehalose	54	52	36	35	34	8	7	6	2	5	5	2	2
Trisaccharides?	4	14	22	11	10	4	1	3	4	1	1	10	2
n-Fatty acids													
Octanoic acid	0.1	2	1	1	0.4	0.1	0.03	0.04	0.02	0.1	0.02	0.01	0
Nonanoic acid	0.4	2	1	2	1	0.1	0	0.04	0.02	0.1	0.02	0.02	0.1
Decanoic acid	0.1	0.2	0.2	0.2	0.1	0	0.5	0	0	0	0	0	0
Tetradecanoic acid	1	3	2	1	1	1	0.2	0.34	0.3	0.1	0.35	0.25	0
Hexadecanoic acid	8	16	11	7	7	9	4	6	5	5	6	3	2
9,12-Octadecadienoic acid	8	14	10	5	6	4	4	5	3	1	2	3	1
trans-9-Octadecenoic acid	14	30	23	10	19	11	10	7	3	3	5	2	1
trans-11-Octadecenoic acid	1	2	1	1	1	1	1	1	0.2	0.4	1	0.1	0.2
Octadecanoic acid	1	2	2	1	1	2	1	1	1	1	1	0.4	0.3
Dicarboxylic acids													
Succinic acid	0.2	1	1	1	0.2	1	0.3	0.42	0.18	1	0.25	0.16	1
Glutaric acid	0.1	1	0.2	0.3	0.2	0	0	0	0	0.0	0	0	0
Malic acid	1	1	2	2	1	0.1	0.2	0.04	0.02	0.1	0.01	0.03	0
Adipic acid	0.2	1	0.3	0.4	0.2	0.1	0.03	0	0.03	0	0	0	0
Pimelic acid	1	1	1	1	1	0	0	0	0	0	0	0	0
Suberic acid	1	2	1	1	1	0.5	0.2	0.13	0.34	0.3	0.20	0.11	0
Azelaic acid	1	4	2	3	2	2	0.5	0.48	0.43	0.5	0.46	0.25	0.1
Aromatic carboxylic acids													
Benzoic acid	0.03	0.04	0.02	0.05	0.02	0	0	0	0	0	0	0	0
p-Hydroxybenzoic acid	1	3	2	3	2	0.1	0.1	0.05	0.2	0.04	0.05	0.13	0.03
Gallic acid	1	2	4	3	2	0	0	0	0	0	0	0	0
Dehydroabietic acid	1	3	2	3	3	0	0	0	0	0	0	0	0
7-Oxodehydroabietic acid	0	1	1	1	1	0	0	0	0	0	0	0	0
Steroids													
Campesterol	1	1	1	1	1	0.5	0.44	0.27	0.1	0	0.09	0.1	0
Stigmasterol	1	1	0.4	0	0.3	0.4	0.13	0.15	0.2	0	0.12	0.1	0
Sitosterol	1	2	2	2	2	1	0.46	0.26	0.1	0	0.26	0.1	0
Stigmast-4-en-3-one	0.1	1	1	1	0.2	0	0.24	0	0	0	0	0	0

Organics), D-glucose (Sigma-Aldrich), D-(+)-galactose (Sigma-Aldrich), L-(−)-arabitol (Sigma-Aldrich), D-(+)-arabitol (Sigma-Aldrich), adonitol (Sigma-Aldrich), mannitol (Sigma-Aldrich), D-sorbitol (Sigma-Aldrich), xylitol (Sigma-Aldrich), erythritol (Sigma-Aldrich), threitol (Sigma-Aldrich), dulcitol (Sigma-Aldrich), *myo*-inositol (Sigma-Aldrich), D-pinitol (Sigma-Aldrich), 1,6-anhydro-β-D-glucose (levoglucosan; Sigma-Aldrich), D-glucuronic acid (Sigma-Aldrich), D-gluconic acid (Merck), sucrose (Sigma-Aldrich), gallic acid (Sigma-Aldrich), and trehalose (a.k.a. mycose, Fluka). Ethylvanillin ≥98% (Sigma-Aldrich) was used as internal standard (IS). Concentrations were measured based on comparison of the IS peak area with the peak area of particular saccharides using the total ion current mode.

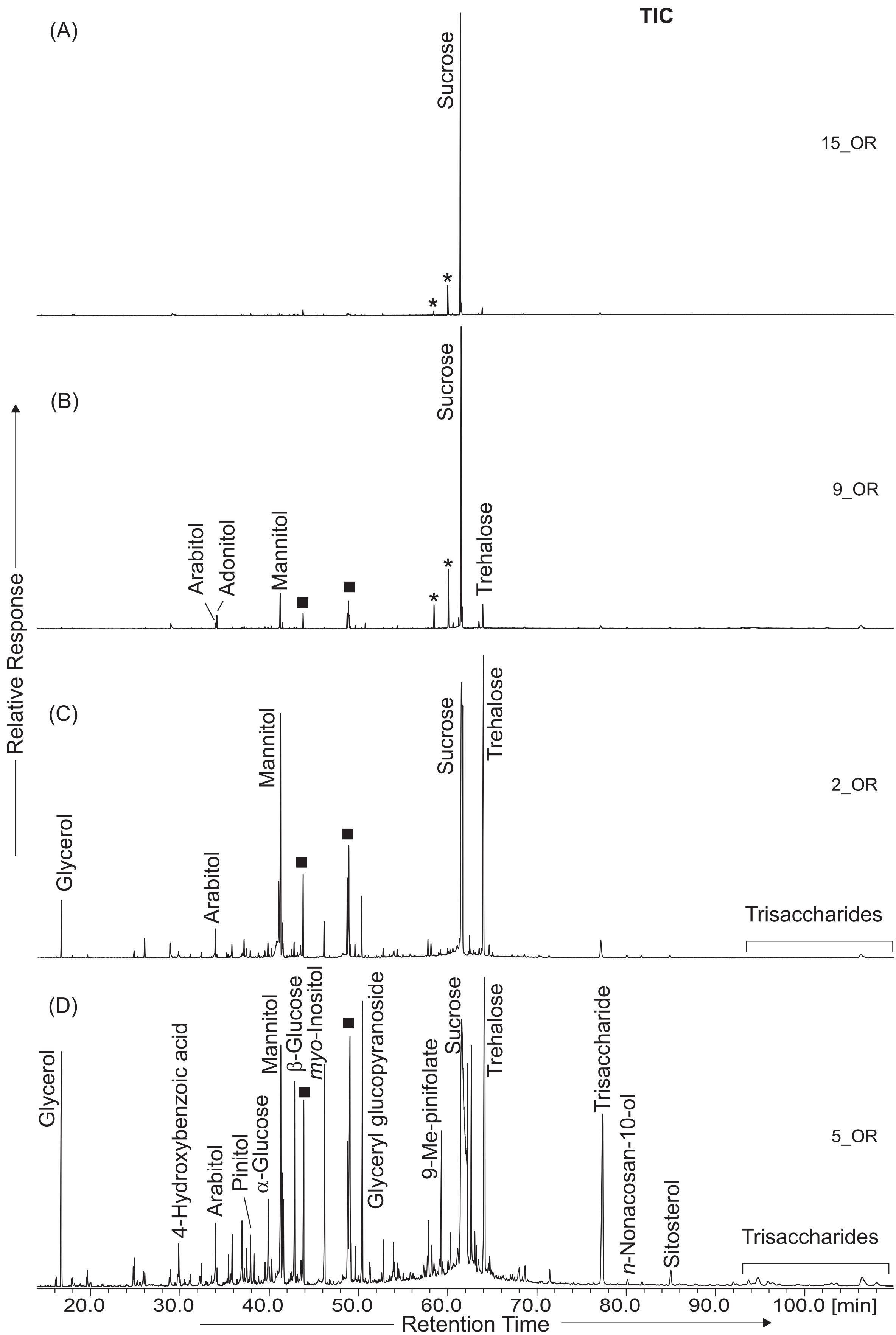

Fig. 1. GC–MS data for soil extracts (as TMS derivatives) showing differences in compound distributions. (A) Stage I of soil development, (B) stage II of soil development, (C) and (D) stage III of soil development. *n*-Fatty acids are denoted by squares. Asterisks denote not fully derivatized sucrose.

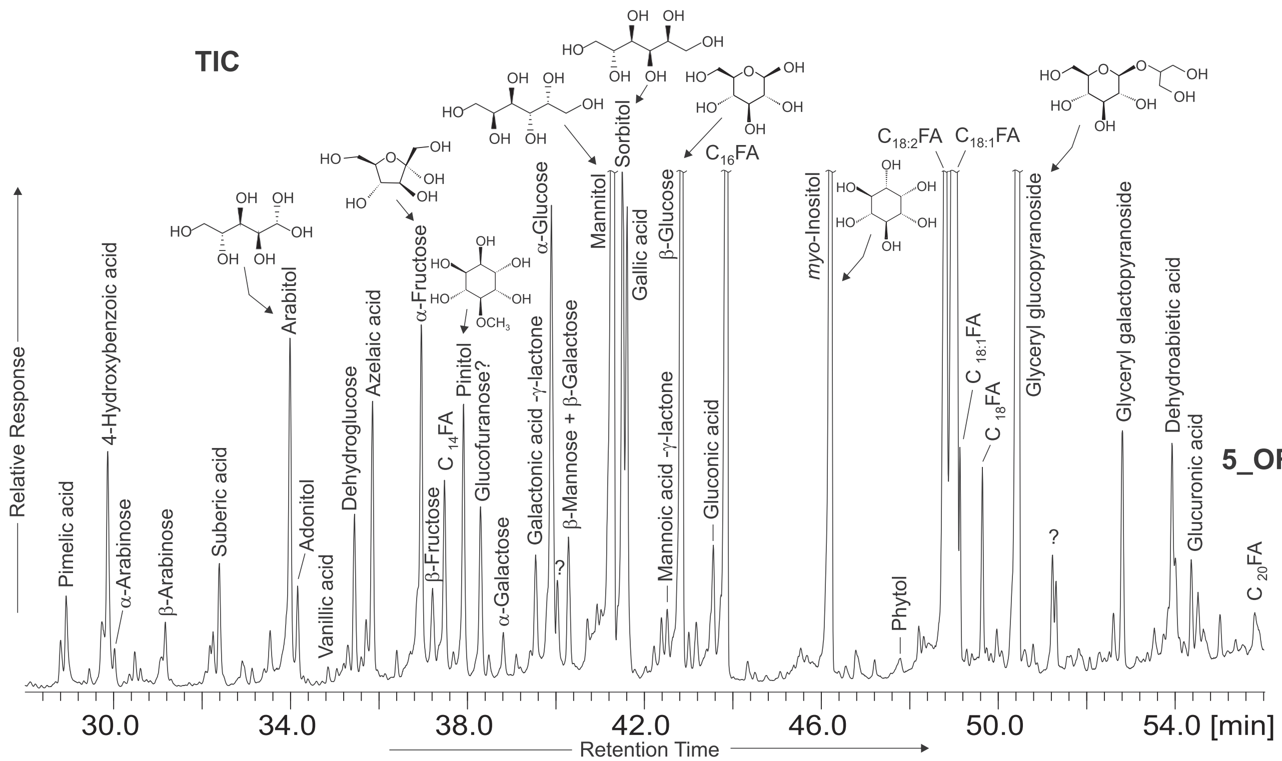

Fig. 2. GC–MS TIC trace of the polar fraction of a stage III soil showing diversity of monosaccharides and their predominance. The main compounds are off-scale to show the smaller peaks in the chromatogram.

3. Results

3.1. Total organic carbon data

The soil samples differed significantly in total organic carbon (TOC) content. Three groups of samples can be distinguished, i.e., organic rich soils with TOC > 4%, organic poor soils with TOC < 0.9, and intermediate samples with 0.9 < TOC < 1.5% (Table 1). TOC values defined the particular soil development stages. Organic-poor soils correspond to development stage I, organic matter rich soils are defined as stage III, and intermediate TOC values correspond to stage II (Table 1).

3.2. Composition of saccharides in arenosols

All identified sugar compounds are listed in Table 1. Sugars were definitely the most abundant compounds in all analyzed soil extracts (Figs. 1 and 2, Tables 1, S1). Mono- and disaccharides (including sugar alcohols) were identified at high relative contents in the soils, but their concentrations and distributions varied between samples. Trisaccharides were tentatively identified in some samples. The most abundant saccharide in all soils was sucrose. Its concentration ranged between 11,000 and 45,000 µg/g TOC in samples classified as stage I of soil development, from 3600 to 9600 µg/g TOC for samples classified as stage II, and from 1600 to 16,000 µg/g TOC for stage III (Tables 1, S1). Distinct concentration variations were also observed for other sugars (Table S1). Differences are particularly important when comparing samples from stages I and III and this applies to both sugars and non-sugar compounds. All sugar concentrations (excluding sucrose) increased when comparing soils classified in stages I and III. This is particularly distinct for arabinose, arabitol, mannitol, pinitol and *scyllo-* and *myo*-inositol (Table 1). Also, the ratios between selected sugars (and non-sugars) differed between samples (Table 2). However, the differences between samples from stages I and II were not as important as in the case of stages I and III (Tables 1 and 2).

3.3. Non-sugar compounds

The main group of compounds identified in the soils were *n*-alkanoic acids (including unsaturated C_{18} compounds), *n*-dicarboxylic acids, aromatic carboxylic acids as well as steroids (Table 1). The concentrations of these compounds increased with soil development (Table S1). The dicarboxylic acids and aromatic carboxylic acids were absent or present in trace amounts in stages I and II. Sterols were present in most samples (except samples 13_OR and 15_OR), but their concentrations increased notably during the development of soil crust. Some non-sugar compounds were used to discriminate particular soil crust stages (Table 3).

4. Discussion

4.1. Pioneer organisms of top soil layer of arenosol formation

In the initial phase of vegetation succession and soil development (stages I and II) biological soil crust is formed mainly by species of cyanobacteria (*Chroococcus minor*, *Ch. minutus*, *Ch. varius*, *Synechococcus aeruginosus*, *Gloeocapsa atrata*, *Merismopedia glauca* and not very common *Nostoc* sp.) and algae (*Cylindrocapsa* sp., *Klebsormidium crenulatum*, *Pinnularia borealis*, *Stichococcus chlorelloides*, *S. cf. fragilis*). Cyanobacteria species form small gelatinous colonies. *S. aeruginosus*, *P. borealis*, S. *chlorelloides* and *S. cf. fragilis* are unicellular forms. *Cylindrocapsa* sp., and *K. crenualtum* are filamentous taxa, which were found in the majority, especially the unidentified species of the *Cylindrocapsa* genus. *Cylindrocapsa* sp. formed characteristic woolly clusters of intertwined threads 0.5–1.0 cm thick on the sand surface. Further colonization (stage III) is associated with encroachment of unidentified fungi and lichens in the area previously occupied by cyanobacteria and algae. Lichens are represented mainly by species of the genus *Cladonia*, such as *Cladonia foliacea, C. glauca, C. furcata, C. cariosa, C. chlorophaea, C. pyxidata, C. floerkeania, C. fimbriata, C. gracilis, C. subulta* or as *Cladina mitis, C. arbuscula* and *Coelocaulon aculeata*. For

Table 2
Ratios of saccharides and other compounds showing differences in soil development. The ratios marked with an asterisk were multiplied by 1000. C8 + C9FA = sum of 8 and 9 carbon atoms *n*-fatty acids.

Sample	2_OR	4_OR	5_OR	6_OR	8_OR	7_OR	9_OR	10_OR	11_OR	12_OR	13_OR	14_OR	15_OR
Development stage	STAGE III					STAGE II			STAGE I				
Molecular proxies													
Trehalose/Sucrose*	536.4	516.2	356.6	353.9	342.6	75.0	70.2	62.4	18.7	49.9	45.1	22.6	24.4
(Mannitol + Arabitol)/Sucrose*	346	203	179	173	118	43	69	75	4	4	5	3	6
(Mannose + Galactose)/Arabinose	0.44	0.57	0.60	0.87	1.00	0.50	0.28	0.24	1.08	0.46	0.49	0.70	0.29
Arabitol/Adonitol	8.16	6.20	4.39	4.58	2.81	0.75	0.41	0.30	0.65	0.23	0.28	0.86	0.81
Mannitol/Sorbitol	10.53	3.63	3.00	4.08	3.59	1.32	3.77	3.36	0.44	1.07	0.88	0.29	1.86
(Pinitol + *scyllo*-Inositol)/Sucrose*	7.88	16.72	30.39	27.24	12.51	8.68	1.88	3.93	9.47	8.10	3.74	2.61	5.24
myo-Inositol/Sucrose*	34.78	78.19	133.0	120.8	93.71	2.93	3.80	3.47	11.76	2.45	2.49	14.57	4.53
p-Hydroxybenzoic acid/Sucrose*	6.72	27.19	24.14	26.69	17.57	1.13	0.62	0.48	2.37	0.35	0.46	1.28	0.26
(C8 + C9FA)/Sucrose*	5.00	39.93	21.06	24.87	1.11	10.46	0.54	0.77	0.39	1.07	0.40	0.29	1.03

* Indicates ratio multiplication by 1000.

more details see Cabała and Rahmonov (2004), Rahmonov and Oleś (2010) and Rahmonov et al. (2015).

4.2. Changes in saccharide distributions and their possible origin

Sucrose was the main free sugar among all samples analyzed, and dominated significantly over the other compounds (Table 1; Fig. 1). Because during stage I of soil crust development the dominant organisms are filamentous algae (mainly *Cylindrocapsa* genus) and cyanobacteria, the most plausible (but not necessarily the only) sources of sucrose seem to be these two groups of organisms. Miralles et al. (2013) showed that glucose and sucrose are the main sugars at an early stage of pedogenesis and sucrose is much more abundant in cyanobacteria-dominated soils. The sucrose concentration calculated in relation to TOC in samples from stage I reaching > 40,000 µg/g TOC (Table S1). All other saccharide amounts identified for stage I, when normalized to sucrose (as 100%), did not exceed 5% (Table 1). Fischer et al. (2010a,b) reported the minimum time for initial pedogenesis formation is 3 years. In such soils, the TOC content is ca. 0.4% (Fischer et al., 2010a,b), which generally corresponds to our stage I of soil crust development. Based on TOC content, we propose that soil crusts of stage I are relatively young, and formed over the last few years as a consequence of the gradual overgrowth of the Błędowska Desert. In fairly older soil crusts (stage II) the concentrations of arabitol, mannitol, and trehalose gradually increased compared to sucrose (Tables 1, 2 and S1; Figs. 1 and 3). All these compounds, although quite universal in living organisms, are remarkably common in fungi and lichen (da Silva et al., 1993; Marynowski et al., 2019 and references therein). The sugar distributions indicate that after pioneering colonization by cyanobacteria and algae the subsequent organisms inhabiting the arenosol are lichen and fungi. At stage III of pedogenesis, the compounds related to fungi and lichen increased significantly, reaching 10–32% in the case of mannitol and 34–54% in the case of trehalose (Table 1). Furthermore, compounds typical for coniferous higher plants are quite abundant in this type III soil, including such organic compounds as pinitol, *myo*-inositol, *scyllo*-inositol and arabinose (BeMiller, 1989). Also, the concentrations of other saccharides, not uniquely assigned to any specific group of organisms, increased (Tables 1, 3 and S1). These include typical decomposition or metabolite products like glucose, glycerol and fructose (Gunina and Kuzyakov, 2015). Fructose is present in many organisms, especially in flowering plants and pollen, but can also originate from sucrose hydrolysis (e.g. Simoneit et al., 2004; Miralles et al., 2013). Moreover, gluconic acid and trisaccharides were identified (Tables 1 and S1), both found in *Nostoc commune* cyanobacteria (Brüll et al., 2000). *Nostoc* is a genus of filamentous, nitrogen fixing cyanobacteria frequent in arid and semi-arid soil (Huang et al., 1998; Brüll et al., 2000), and was found in low amounts in our samples.

Levoglucosan, an anhydrosugar, which is an abundant product of biomass burning (Simoneit et al., 1999), was detected at very low concentrations in these soils (Tables 1 and S1). Its origin would be connected with minor pollution of the soil by fallout from regional fire emissions, but due to its occurrence in unburned fossil wood (Marynowski et al., 2018), a source connected with slow biomass oxidation/decomposition cannot be ruled out.

Soil particulate matter was identified as one of the main sources of sugars in ambient air (e.g. Simoneit et al., 2004). Deserts, including sandy coastal areas in a temperate climate region, can be considerable sources of saccharides from advected soil crust particles, especially during formation of stage I, when consolidation is weak. When sucrose dominates significantly over trehalose in ambient air, we suggest that sugars could advected by wind in particles from young arenosol. However, there are numerous other sucrose sources, e.g.: dust from agricultural tilling and harvesting, pollen, spores, etc. (e.g. Rogge et al., 2007; Fu et al., 2012; Marynowski et al., 2018), therefore more studies are needed to prove this suggestion.

4.3. Origin of non-sugar compounds in arenosol

The most abundant organic compounds, excluding sugars, are saturated and unsaturated *n*-alkanoic acids, with 9,12-octadecadienoic, *trans*-9-octadecenoic and *n*-hexadecanoic acid as dominant (Tables 1 and S1). These compounds are ubiquitous in plants and microorganisms, and irrelevant as particular source indicators, except for 9, 12-octadecadienoic acid which is most common in plants (Gurr et al., 2002). Short chain *n*-fatty acids (FA) were present from C_8 to C_{10}, and occur in many organisms (Gurr et al., 2002), but commonly most abundant in bacteria (Hollocher et al., 2001). Seven dicarboxylic acids

Table 3
Stages of extractable compound development in soil crusts and their possible sources.

Stages	Main compounds	Source
Stage I	Sucrose > 90%	cyanobacteria, filamentous algae
Stage II	sucrose, trehalose, mannitol, sorbitol, adonitol, *trans*-9-octadecenoic acid	cyanobacteria, filamentous algae, lichen, fungi
Stage III	all from stage II plus: fructose, pinitol, *myo*-inositol, glucose, dehydroabietic acid, gallic acid, dicarboxylic acids, sitosterol	filamentous algae, lichen, fungi, bacteria, higher plant detritus (mainly conifers)

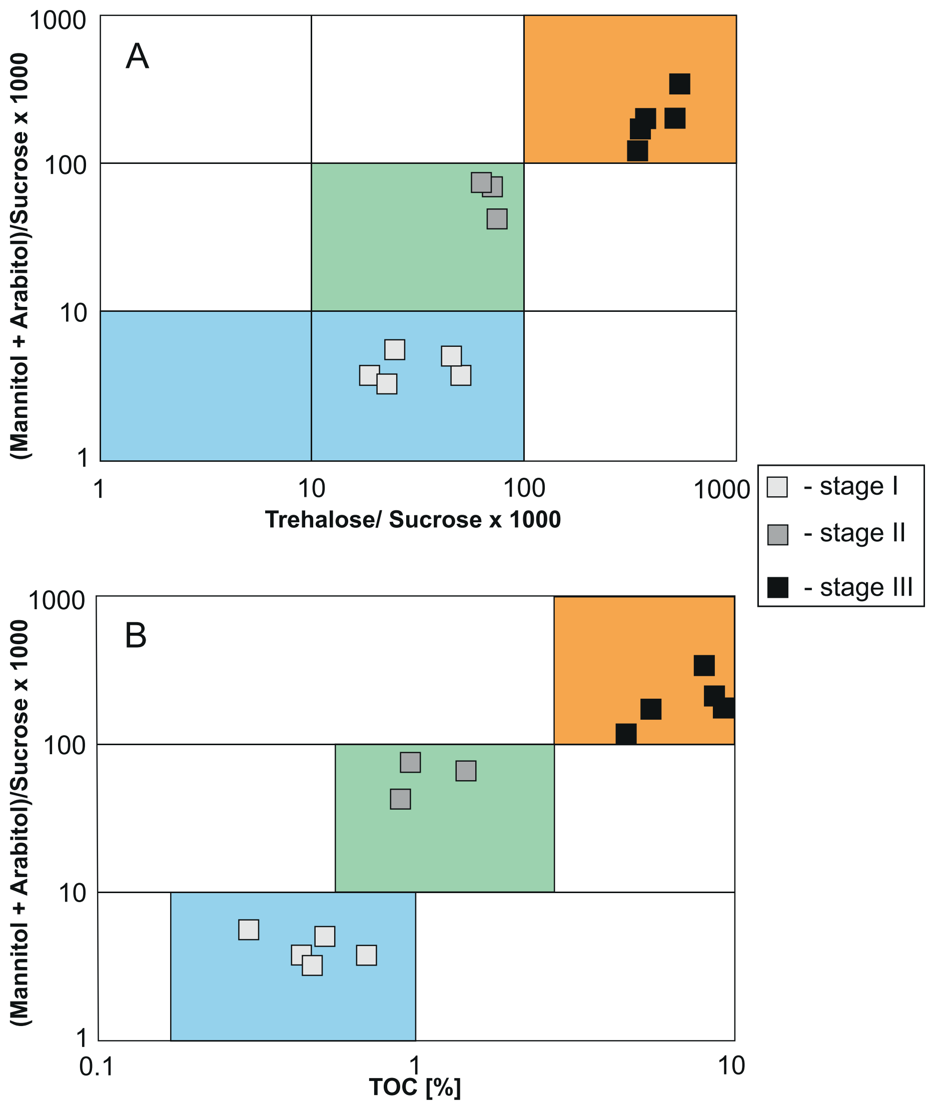

Fig. 3. Cross plots of TOC and saccharide ratios showing the differentiation between stages of soil crust development. Logarithmic scale was used. For particular ratios see Table 2. The blue fields correspond to stage I, green to stage II and orange to stage III of soil development. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

were identified, with azelaic acid as most abundant (Tables 1 and S1). Dicarboxylic acids are primary compounds of C3 plants (Narukawa et al., 1999), but can also originate from fossil fuel combustion or be produced via photooxidation of volatile organic compounds and unsaturated fatty acids (Kawamura and Bikkina, 2016). Moreover, malic acid is a product of fungal metabolism (West, 2015). Aromatic carboxylic acids like benzoic, *p*-hydroxybenzoic, and gallic acids were identified in these soils. They are common lignin decomposition products (e.g. Rybicki et al., 2016). Their low concentrations (Table S1) are in agreement with the generally low amounts of lignin in arenosols (Nierop et al., 2001). Dehydroabietic and 7-oxodehydroabietic acids as well as imbricatolic acid were identified only in stage III of soil development, and are typical resin acids derived from coniferous plants (e.g. Otto and Simoneit, 2001; Rybicki et al., 2016). Their occurrence is connected with the transport of conifer detritus to the soil. Sitosterol was the most abundant of the steroids (Table 1), and is the most common higher plant sterol (Otto and Simoneit, 2001).

4.4. Sugars as soil forming compounds

As is widely known, abundant neutral saccharides are important binding agents for soil grain aggregation and further colonization by succeeding organisms (e.g. Chenu, 1993). Moreover, some plant debris (e.g. pine needles, pollen, etc.) can easily anchor on the initial soil crust, supplying additional organic matter to the soil. Considering the high concentration of neutral sugars in the initial pedogenesis stage (Table S1), these compounds can be responsible for soil aggregation and gradual formation of crust. They also play a protective role in soil, creating a means of defense for the microorganisms, and their disappearance would lead to structural collapse of the crusts (Miralles et al., 2013; Dümig et al., 2014). In addition, sucrose and other sugars are the energy source utilized by microorganisms that colonize soil, even though more complex substrates are usually metabolized preferentially instead of simple sugars as glucose or sucrose (Miralles et al., 2013). Our study partially confirms the report by Miralles et al. (2013) that showed a predominance of sucrose in the initial stages of soil formation, but no evidence for a high concentration of glucose linked with algae, although they seem to be the most abundant organisms in the crust investigated (Cabała and Rahmonov, 2004). The glucose content becomes important only at stage III of soil development, but still not exceeding 15% compared to the major sucrose (Table 1).

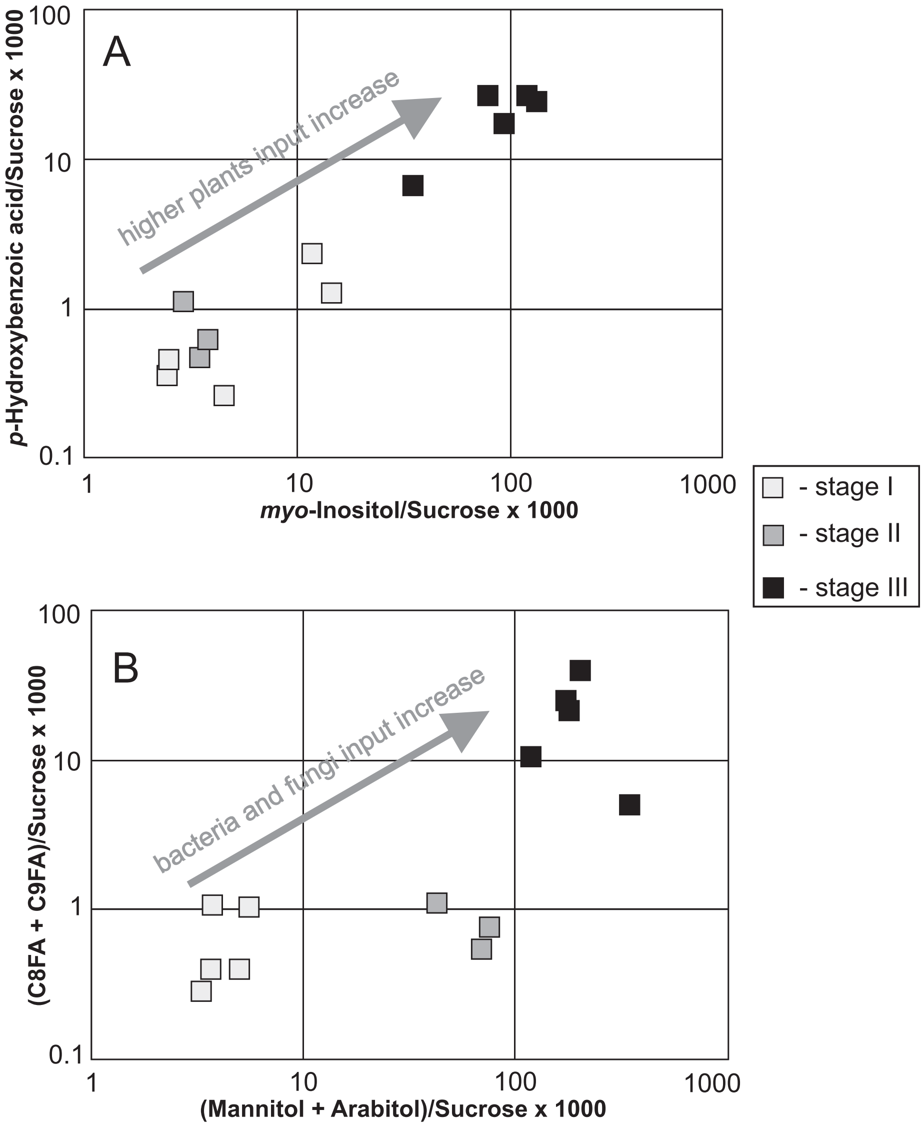

Fig. 4. Cross plots of: A). *p*-hydroxybenzoic acid/sucrose vs. *myo*-inositol/sucrose ratios showing the increased contribution of higher plants in the soils, and B). (C8FA + C9FA)/sucrose vs. (mannitol + arabitol)/sucrose ratios showing increased bacteria and fungi input with soil development. Logarithmic scale was used.

4.5. Differentiation of temperate climate soil crust

Among disaccharides sucrose and trehalose (mycose) were reported as significant compounds in tropical and temperate soils, however, between these two sugars trehalose was often reported as most abundant (Simoneit et al., 2004; Medeiros et al., 2006; Rogge et al., 2007; Rushdi et al., 2006, 2016). It seems these arenosols are the exception due to the genetic connection between sucrose and the dominating organisms including cyanobacteria as well as green, filamentous algae (Table 3). However, even during the initial phase of pedogenesis, the trehalose concentration increased concurrently with soil development.

Based on saccharide distributions and their comparison to TOC data, we have observed, that it is possible to differentiate the first stage of soil formation on sand in a temperate climate region using discrimination diagrams (Figs. 3 and 4; Table 3). Because some saccharides and non-saccharide compounds are clearly connected with certain living organisms (e.g. BeMiller, 1989; Otto and Simoneit, 2001; Simoneit et al., 2004; Duquesnoy et al., 2008; Marynowski et al., 2018, 2019), the application of discrimination diagrams can help in assignment of a young soil to its particular stage. The increase in the values of the (mannitol + arabitol)/sucrose vs. trehalose/sucrose ratios (R^2 = 0.89) reflected an increase of fungi and lichen in relation to algae and cyanobacteria in the soil crusts. Because the TOC values clearly increased from stages I to III, that is also a good parameter of soil development, which correlated well with the (mannitol + arabitol)/sucrose ratio (R^2 = 0.81). The correlation between the *p*-hydroxybenzoic acid/sucrose vs. *myo*-inositol/sucrose ratios (R^2 = 0.91) reflected the increased contribution of conifer plants in the soil, while the (C_8FA + C_9FA)/sucrose (where C_8FA and C_9FA = short chain fatty acids with 8 and 9 carbon atoms in the molecule) vs. (mannitol + arabitol)/sucrose ratios (R^2 = 0.6) revealed the gradual increase of bacteria and fungi + lichen activities (see Hollocher et al., 2001). The presence of conifers was confirmed by a gradual increase in the sitosterol and dehydroabietic acid concentrations (Table S1). Excellent correlations between the (pinitol + *scyllo*-inositol)/sucrose vs. *p*-hydroxybenzoic acid/sucrose and *myo*-inositol/sucrose ratios were observed (R^2 > 0.8), which indicated that the (pinitol + *scyllo*-inositol)/sucrose ratio is also a useful indicator for a conifer contribution (mainly as detritus) in arenosols. A good correlation was also noticeable between the arabitol/adonitol vs. mannitol/sorbitol ratios (R^2 = 0.77), showing a decreased contribution of adonitol and sorbitol vs. arabitol and mannitol during soil development, which can indicate that adonitol and sorbitol are genetically connected with algae and/or cyanobacteria while arabitol and mannitol are fungi/lichen derived compounds.

However, more data is needed for the determination of the origin of adonitol and sorbitol. The ratio of (mannose + galactose)/(arabinose + xylose) has been used to determinate the microbial vs. plant contribution to soils (Amelung et al., 1999; Gunina and Kuzyakov, 2015). In case of these arenosols there was no correlation between that and any other ratio values. However, in previous studies hydrolysis was the method used for the determination of these monosaccharides, thus skewing the data. This ratio seems useless for free sugars extracted from soil.

5. Conclusions

1. The study of free saccharides from soil crusts led to a more detailed characterization of soil development in the initial phase of pedogenesis in a temperate climate region.
2. Cyanobacteria and algae are the main living organisms which form the arenosol crust during stage I of development. Sucrose, most probably from cyanobacteria and dominant filamentous algae of the *Cylindrocapsa* genus, is the major compound reaching > 90% of all soluble organic compounds. The role of lichen and fungi gradually increases in stage II, even as these organisms are still not clearly observable in the samples. Growth is manifested by an increase of TOC as well as the rise of arabitol, mannitol and trehalose contents in the soil crust. Lichen and fungi, next to algae and cyanobacteria, are the most important organisms colonizing the soil during stage III of pedogenesis. The concentrations of arabitol, mannitol, and trehalose also increased significantly in this stage. Moreover, the concentrations of the higher plant sugars (pinitol, *myo*-inositol, *scyllo*-inositol, arabinose) and non-sugar compounds (dicarboxylic acids, dehydroabietic acid, gallic acid, sitosterol) progressively increased.
3. The relationships between the ratios of trehalose/sucrose vs. (mannitol + arabitol)/sucrose and TOC vs. (mannitol + arabitol)/sucrose differentiate exactly the three stages of soil crust development. These ratios can be used in future studies of arenosol development.
4. The metabolic products from cyanobacteria, algae, lichen and fungi, especially in the form of sugars (not exclusively), provide the basic nutrients for the massive development of other organisms, and thus accelerate the processes of humus horizon formation as part of pedogenesis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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