Source apportionment of fine aerosol at a rural background site in Central Europe based on seasonal distributions of dicarboxylic acids, sugars and related compounds

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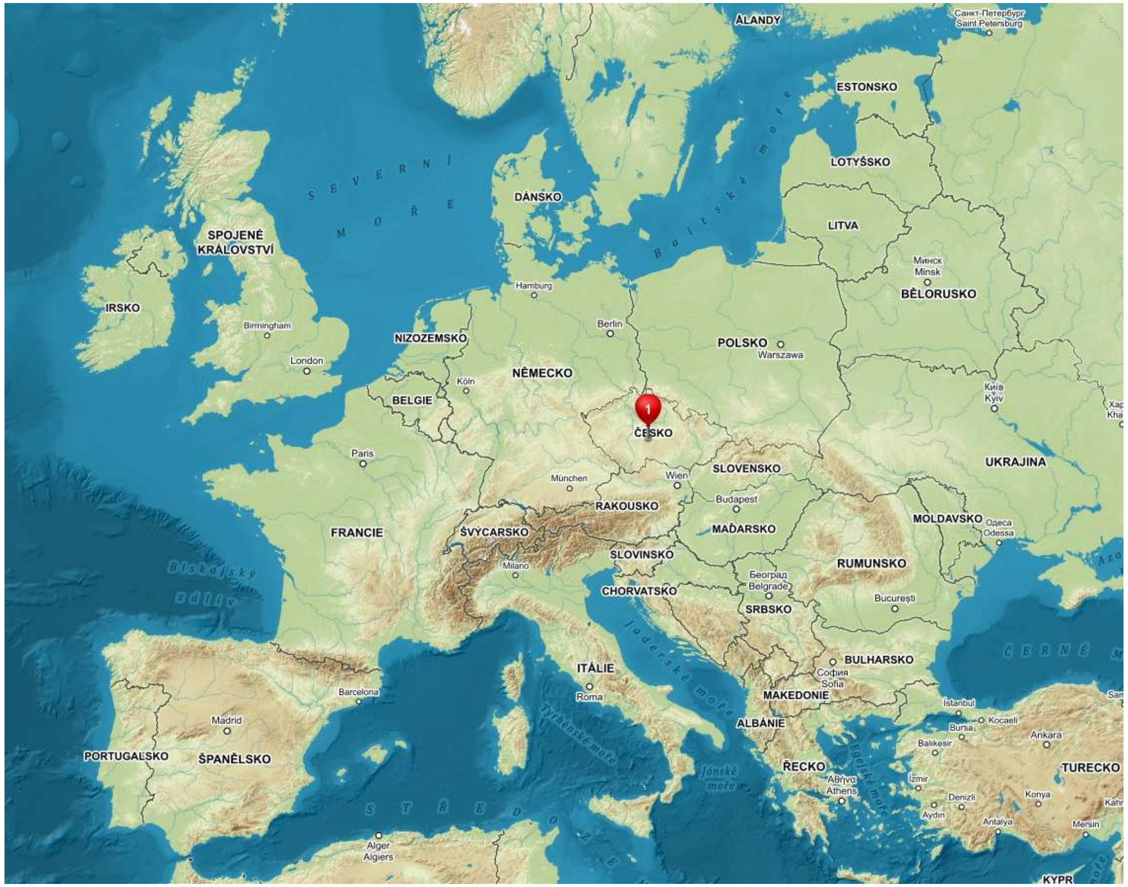
Site – Košetice Observatory

Central European rural background site
Characteristic: agricultural landscape and forests, out of range of major soureces of pollution
location: N: 49° 34' 24.13'' E: 14° 4' 49.67'' Altitude: 534 m ASL



Sampling

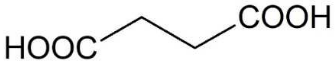
- PM1 aerosol fraction, quartz fiber filters
- Period: 27 Sep 2013 – 9 Aug 2014 (every 2nd day)
- 146 samples with 24-h time resolution + blanks

Analyses

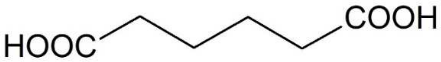
Normal-chain diacids


Oxalic, C_2

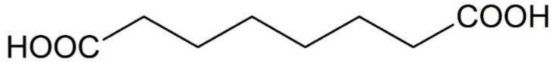

Malonic, C_3


Succinic, C_4


Glutaric, C_5


Adipic, C_6

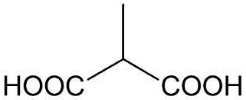

Pimelic, C_7

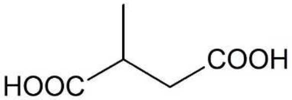

Suberic, C_8

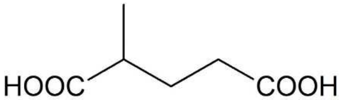

Azelaic, C_9


Undecanedioic, C_{11}

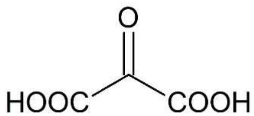
Branched-chain diacids

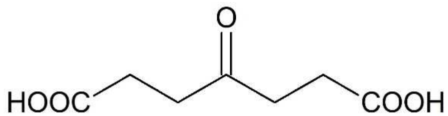

Methylmalonic, iC_4


Methylsuccinic, iC_5

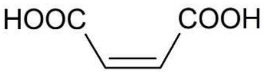

2-Methylglutaric, iC_6

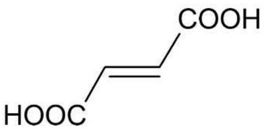
Ketodiacids

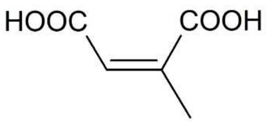

Ketomalonic, kC_3


4-Ketopimelic, kC_7

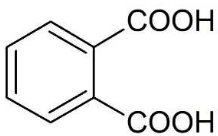
Unsaturated diacids

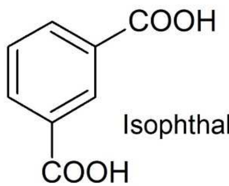

Maleic (cis), M

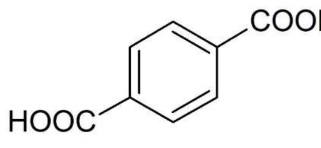

Fumaric (trans), F


Methylmaleic (Citraconic), mM

Aromatic diacids

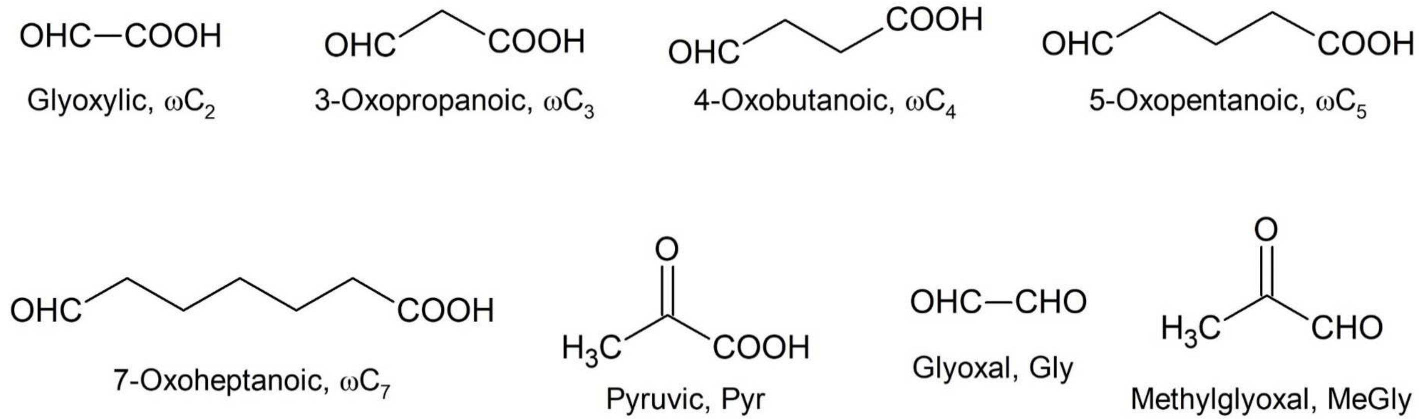

Phthalic, Ph


Isophthalic, iPh


Terephthalic, tPh

Analyses

Diacid's related compounds:



Saccharides:

- anhydrosugars (levoglucosan, mannosan, galactosan)
- sugar alcohols (arabitol, mannitol, erythritol)
- primary sugars (glucose, fructose, mannose, galactose, sucrose)

Total PM_1 mass and Carbon -> EC + OC

Water-soluble ions: SO_4^{2-}, NO_3^-, Cl^-, oxalate NH_4^+, K^+ → LWC calculation

Meteorology: Wind speed + direction, RH, Temperature, Global radiation

Overview

Year-round averages [%]:

OC/PM_1 = 25.1

ΣtDA-C/OC = 2.14

Avg. seasonal distribution

Autumn	Winter	Spring	Summer

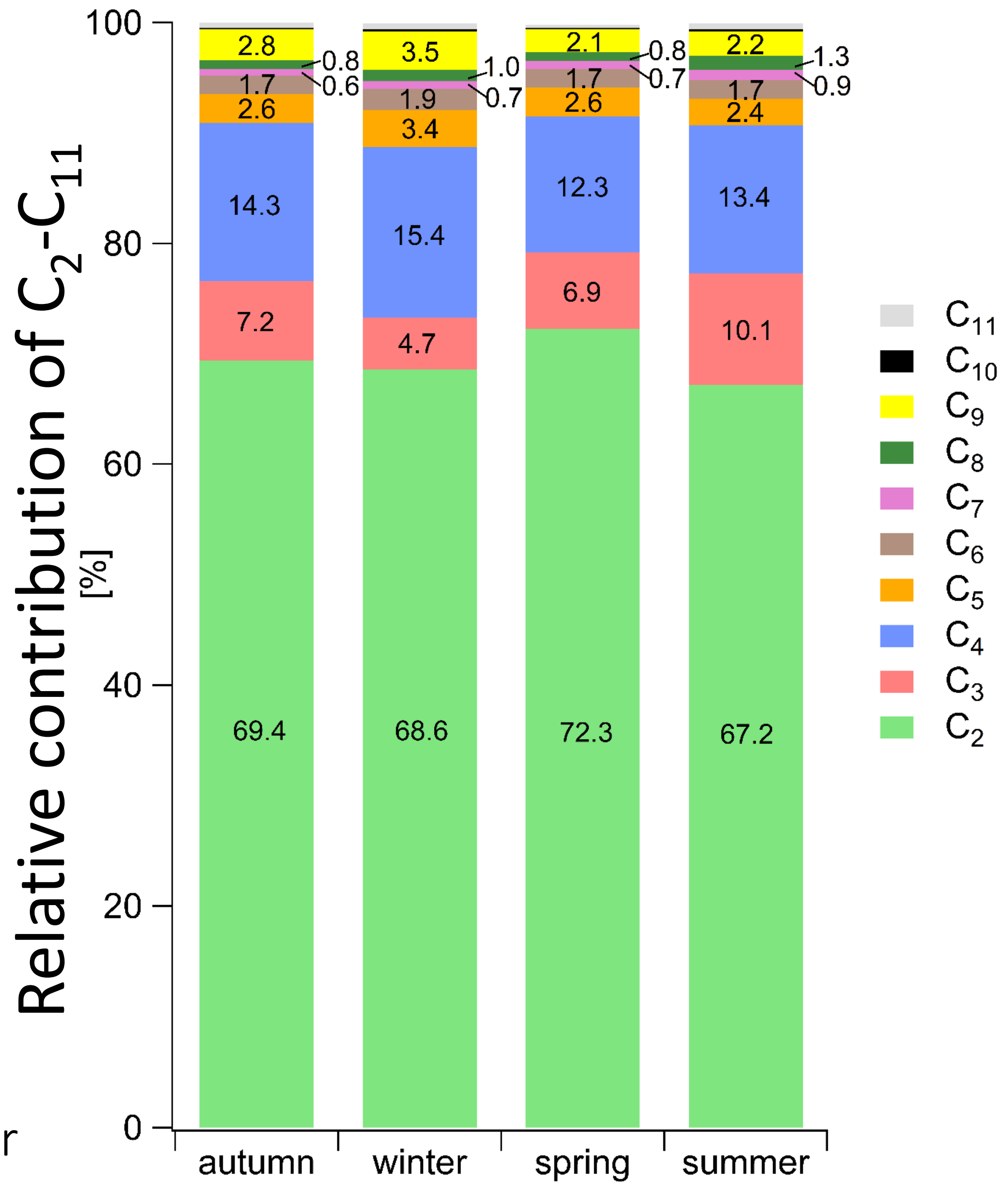
ΣtDA [ng/m^3]

Autumn	Winter	Spring	Summer
157	171	202	162

ΣtDA-C/OC [%]

Autumn	Winter	Spring	Summer
1.81	1.69	2.38	2.70

More intense SOA formation and aging in summer



Normal-chain diacids vs. LWC, T and O_3 correlations (r)		**Autumn**			**Winter**			**Spring**			**Summer**		
		LWC	**T**	**O_3**	**LWC**	**T**	**O_3**	**LWC**	**T**	**O_3**	**LWC**	**T**	**O_3**
Oxalic	**C_2**	**0.64**	0.22	0.03	**0.81**	-0.26	0.08	**0.65**	0.20	**0.41**	**0.53**	**0.59**	**0.53**
Malonic	**C_3**	**0.43**	**0.42**	0.20	**0.79**	-0.23	0.13	**0.51**	0.26	**0.42**	**0.51**	**0.56**	**0.54**
Succinic	**C_4**	**0.59**	0.21	-0.01	**0.76**	-0.28	0.09	**0.60**	0.10	0.25	**0.49**	**0.54**	**0.59**
Glutaric	**C_5**	**0.64**	0.06	-0.08	**0.65**	-0.19	0.14	**0.62**	-0.02	0.22	**0.53**	**0.55**	**0.65**
Adipic	**C_6**	**0.58**	0.10	0.03	**0.64**	-0.24	0.17	**0.54**	0.03	0.29	**0.44**	**0.65**	**0.59**
Pimelic	**C_7**	**0.63**	0.05	0.00	**0.63**	-0.18	0.14	**0.41**	0.06	0.20	**0.24**	**0.58**	**0.63**
Suberic	**C_8**	**0.47**	0.05	0.07	**0.42**	-0.14	0.04	0.29	0.26	**0.33**	0.11	**0.82**	**0.53**
Azelaic	**C_9**	**0.51**	-0.20	-0.08	**0.38**	-0.19	-0.08	**0.37**	0.04	0.15	0.09	**0.63**	**0.38**
Sebacic	**C_{10}**	-0.18	-0.21	-0.01	**0.48**	-0.32	-0.01	**0.54**	-0.37	0.04	0.11	**0.58**	**0.71**
Undecanedioic	**C_{11}**	0.28	0.30	0.13	**0.46**	-0.16	-0.09	0.20	**0.32**	**0.33**	0.20	**0.70**	**0.44**

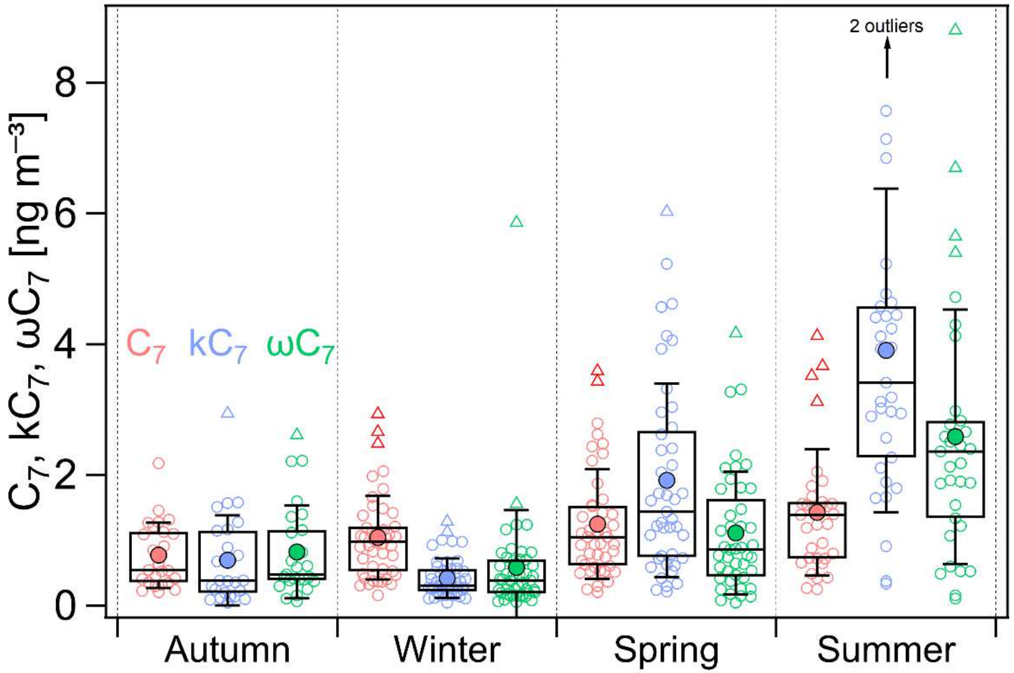
Correlation analyses (r)

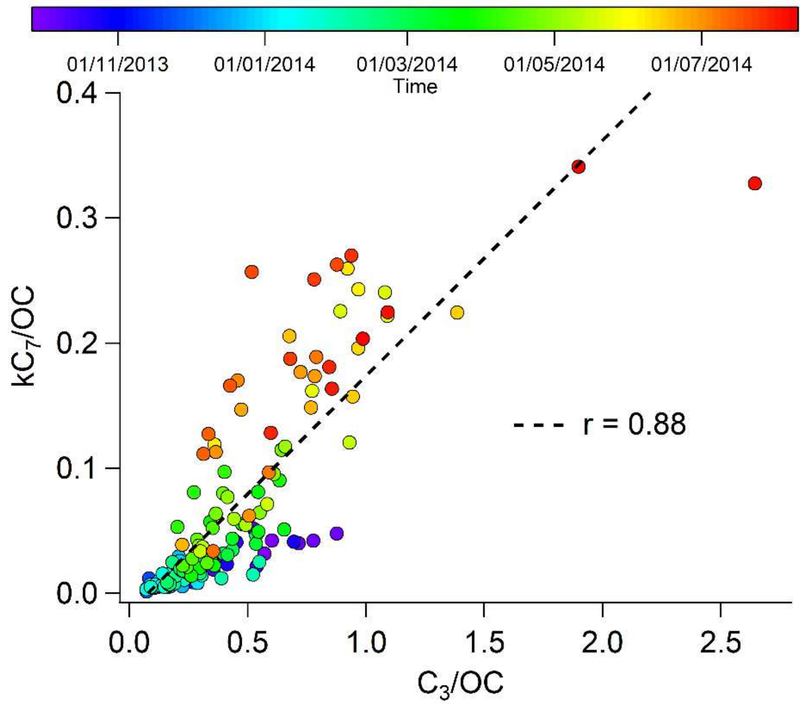
- Temp., GR … rough proxy of seasonal changes
- O3 … indicator of the strength of photooxidation
- RH, LWC … indication of aqueous phase reactions

	Year correlations	Temperature	Global radiation	RH	O_3	LWC
Malonic	C_3	**0.47**	**0.55**	**-0.41**	**0.49**	**0.34**
Methylmalonic	iC_4	**0.56**	**0.52**	**-0.39**	**0.43**	0.17
4-Ketopimelic	kC_7	**0.77**	**0.79**	**-0.61**	**0.69**	0.06
7-Oxoheptanoic	ωC_7	**0.59**	**0.57**	**-0.46**	**0.51**	0.12
Methylsuccinic	iC_5	**-0.64**	**-0.48**	**0.42**	**-0.43**	**0.65**
Maleic	M	**-0.72**	**-0.59**	**0.45**	**-0.50**	**0.55**
Methylmaleic	mM	**-0.72**	**-0.59**	**0.41**	**-0.48**	**0.52**
Levoglucosan	LVG	**-0.70**	**-0.54**	**0.42**	**-0.48**	**0.60**

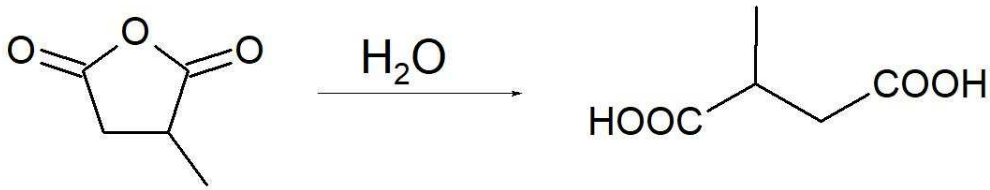
7-C acids

- formed probably by oxidation of (n-7) unsaturated fatty acids
- (n-7) fatty acids abundant in *Brassica napus* (Mukherjee & Kiewitt, 1980, Planta)
- markers of biogenic sources?

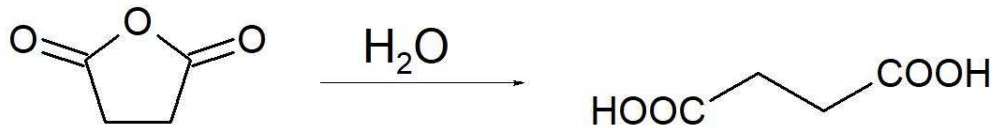




Hydrolylis of furandiones



Methylsuccinic, iC_5

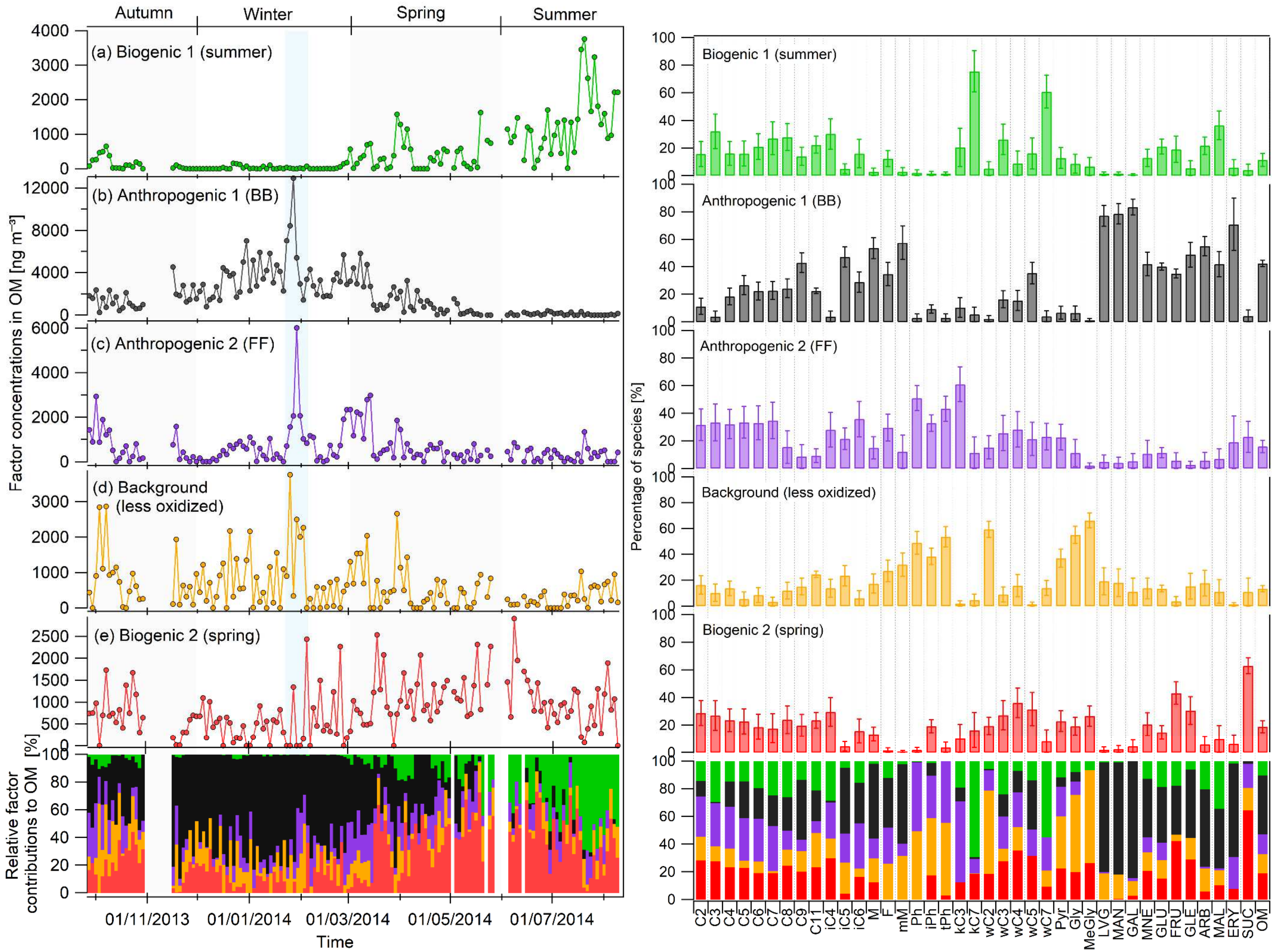


Succinic, C_4

Year correlations	Temperature	Global radiation	RH	O_3	LWC
iC_5	-0.64	-0.48	0.42	-0.43	0.65
M	-0.72	-0.59	0.45	-0.50	0.55
mM	-0.72	-0.59	0.41	-0.48	0.52
LVG	-0.70	-0.54	0.42	-0.48	0.60

Furandiones: products of photooxidation of anthropogenic VOC (Al-Naiema et al. 2017, Atmos. Environ.)

PMF



Biogenic

Anthrop. BB

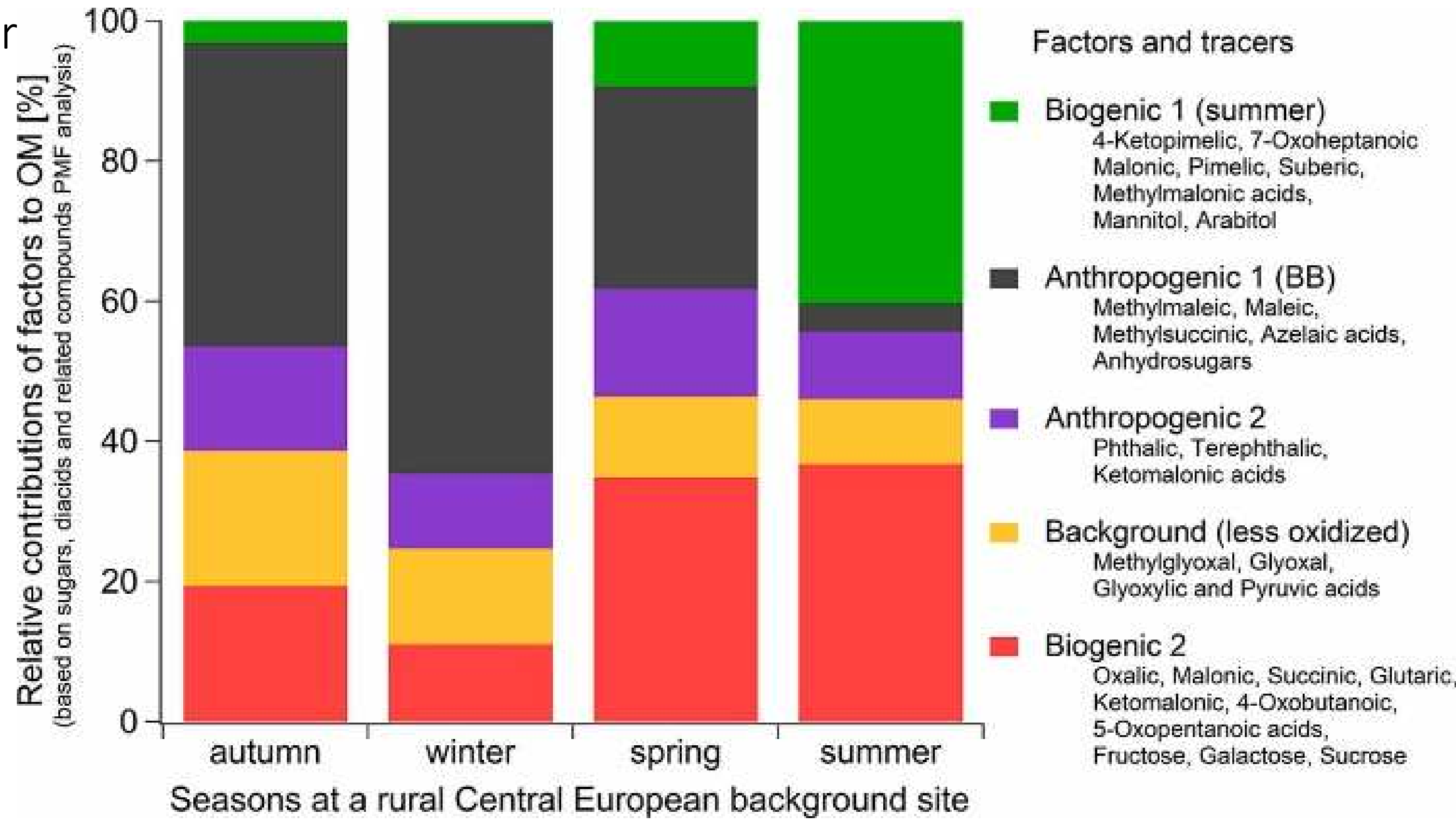
Anthrop. FF

Background

Biogenic 2

Conclusions

- Clear difference between winter and summer diacids composition in PM_1
- Biogenic, anthropogenic and background factors resolved by PMF analysis
- Methylsuccinic, aromatic and unsaturated aliphatic acids as typical anthropogenic tracers
- Organic acids with seven and three carbons determined as biogenic tracers
- Two mechanisms of SOA formation - preferred aqueous-phase in winter, while gaseous-phase in summer.



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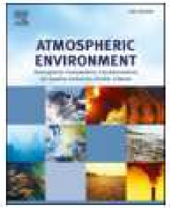

Anthropogenic and biogenic tracers in fine aerosol based on seasonal distributions of dicarboxylic acids, sugars and related compounds at a rural background site in Central Europe

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