Supplement of Atmos. Chem. Phys., 22, 6021–6043, 2022
https://doi.org/10.5194/acp-22-6021-2022-supplement

Atmospheric Chemistry and Physics
Open Access
EGU

Supplement of

Cellulose in atmospheric particulate matter at rural and urban sites across France and Switzerland

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Supplementary Information

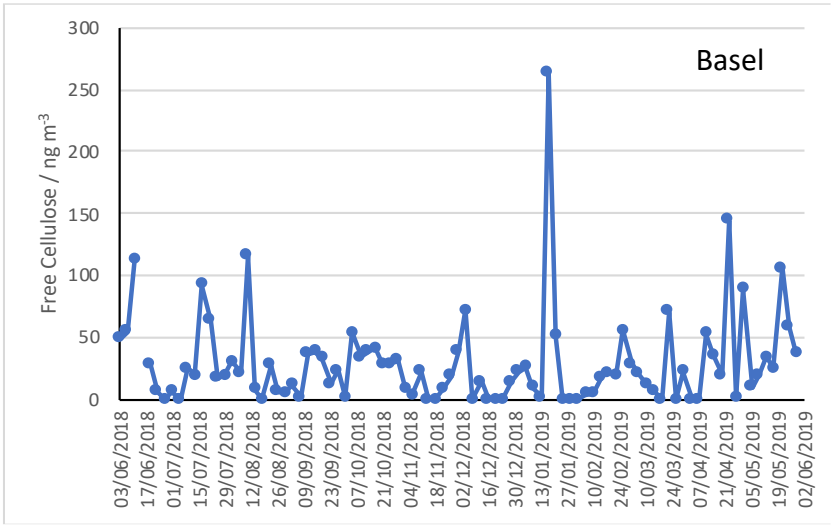
Cellulose method validation

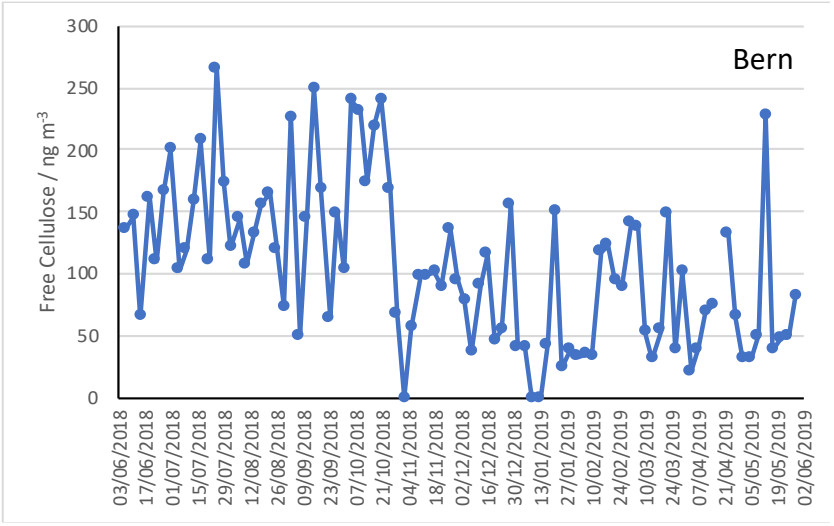
Thymol buffer
The pH 4.8 buffer was created in 1L batches, which was sufficient for approximately 300 samples, including cellulose hydrolysis standards. 0.5 g of thymol was added to a beaker with some Milli-Q ultrapure water, with 1.37 mL NaOH (50%). The dissolved thymol solution was transferred to a 1 L volumetric flask and filled halfway, before 2.682 mL acetic acid was added. After several inversions, the volumetric flask was filled up to the 1 L mark and the pH was measured. If the pH was approximately 4.8, then the buffer was left unmodified and transferred to a 1 L storage bottle. If the pH differed significantly from 4.8, the pH was adjusted using either acetic acid or NaOH 50% before transfer.

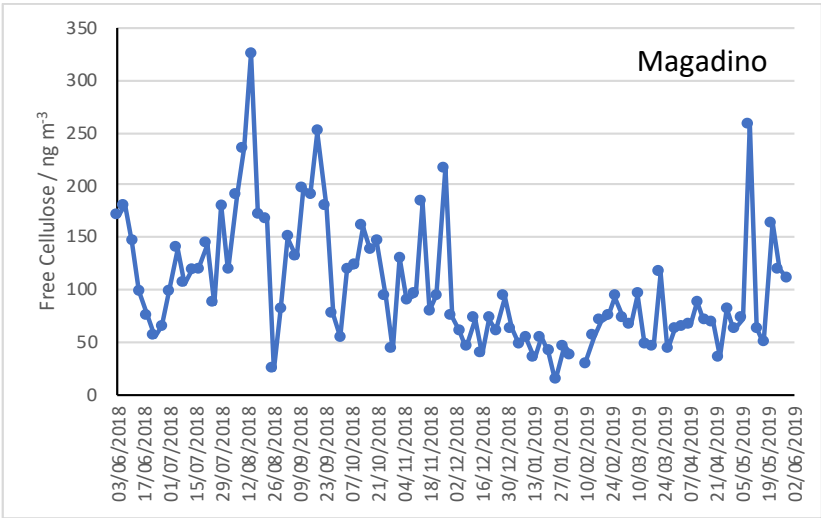
Standard solutions
Six glucose and six cellulose hydrolysis standard solutions are included in each analytical batch run on the HPLC-PAD. The glucose standards were diluted from a stock solution (1 g L^{-1}) using ultrapure water and the dynamic range covered concentrations from 0.1 – 9.99 µg cm^{-3} with a correlation coefficient (r) > 0.99 . Standard cellulose solutions were made to determine the cellulose-to-glucose hydrolysis efficiency for each batch. The standards were prepared alongside the samples, with the same enzyme quantities and buffered solution, and were subjected to the same incubation and centrifugation processes. The six standards were prepared using a cellulose mother solution (1 g L^{-1}), except for the blank solution in which no cellulose was added. The remaining five standards had cellulose concentrations of 0.096, 0.649, 1.944, 5.039 and 10.028 µg cm^{-3}. After incubation and cellulose hydrolysis, glucose concentrations within the standards were measured and subsequently multiplied by 0.9 to give measured cellulose concentrations. The cellulose-to-glucose hydrolysis efficiency was determined by a calibration curve of standard vs measured cellulose concentrations.

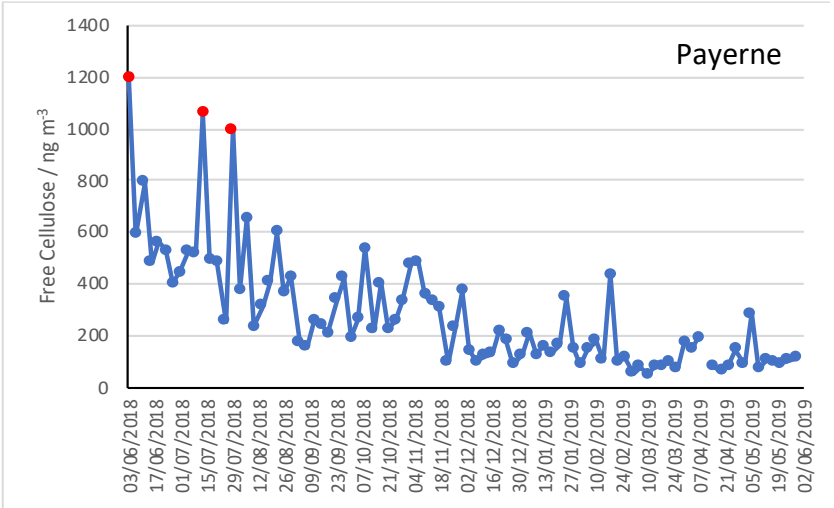
Method validation
A repeatability test was completed using the same sampling techniques as those completed for each sample across the individual monitoring sites. Briefly, a high-volume sampler (Digitel DA80, 30 $m^3 h^{-1}$) was used to deposit PM onto a pre fired quartz fibre filter (Tissu-quartz PALL QAT-UP 2500 diameter 150 mm) on the roof of the OSUG-B laboratory, Grenoble, and sampled a total of 615.1 m^3. Ten filter punches of 21 mm were then taken and subjected to the same procedure as for normal samples. Each filter punch was then analysed three times using the same HPLC-PAD method, to monitor repeatability in terms of both cellulose hydrolysis and glucose concentration detection. The glucose content of the ten filters was found. The repeatability (Relative Standard Deviation – RSD) was found to range from 0.7 – 5.7 % for the three repeats of the same filter sample. The RSD of the glucose content within the ten filter punches was calculated to be 9.9 %.

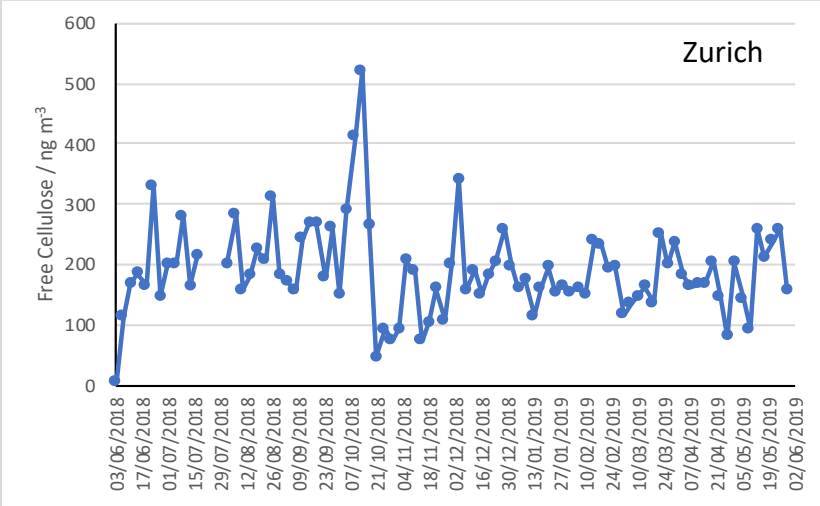
Evolution of Cellulose Concentrations










Zurich
Free Cellulose / ng m-3
600
500
400
300
200
100
0
03/06/2018
17/06/2018
01/07/2018
15/07/2018
29/07/2018
12/08/2018
26/08/2018
09/09/2018
23/09/2018
07/10/2018
21/10/2018
04/11/2018
18/11/2018
02/12/2018
16/12/2018
30/12/2018
13/01/2019
27/01/2019
10/02/2019
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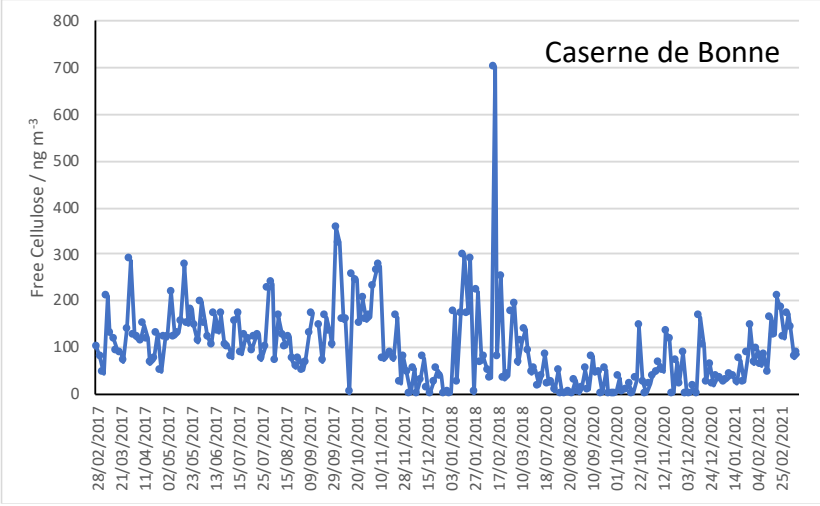
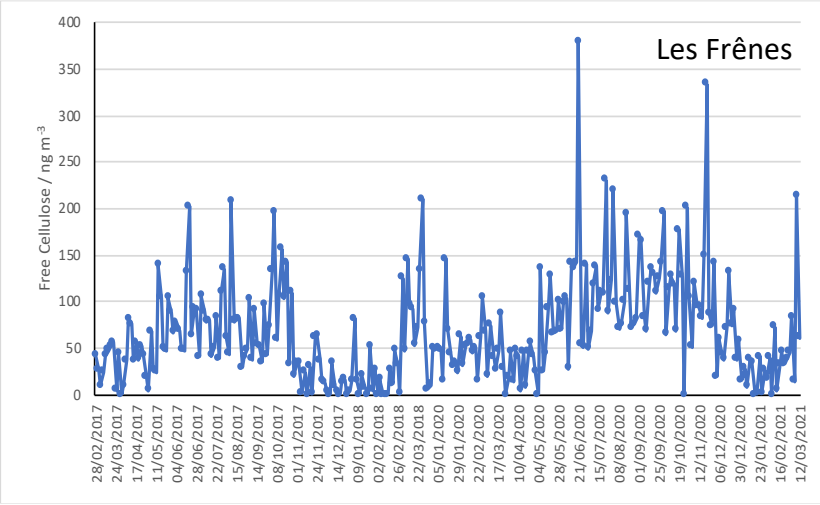
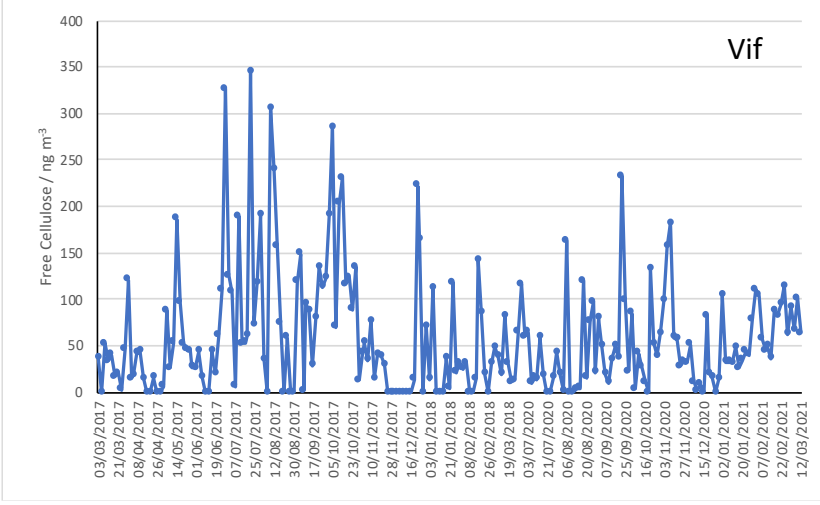
24/03/2019
07/04/2019
21/04/2019
05/05/2019
19/05/2019
02/06/2019


Caserne de Bonne
Free Cellulose / ng m-3
800
700
600
500
400
300
200
100
0
28/02/2017
21/03/2017
11/04/2017
02/05/2017
23/05/2017
13/06/2017
15/07/2017
25/07/2017
15/08/2017
09/09/2017
29/09/2017
20/10/2017
10/11/2017
28/11/2017
15/12/2017
03/01/2018
27/01/2018
17/02/2018
10/03/2018
18/07/2020
20/08/2020
10/09/2020
01/10/2020
22/10/2020
12/11/2020
03/12/2020
24/12/2020
14/01/2021
04/02/2021
25/02/2021


Les Frênes
Free Cellulose / ng m-3
400
350
300
250
200
150
100
50
0
28/02/2017
24/03/2017
17/04/2017
11/05/2017
04/06/2017
28/06/2017
22/07/2017
15/08/2017
14/09/2017
08/10/2017
01/11/2017
24/11/2017
14/12/2017
09/01/2018
02/02/2018
26/02/2018
22/03/2018
05/01/2020
29/01/2020
22/02/2020
17/03/2020
10/04/2020
04/05/2020
28/05/2020
21/06/2020
15/07/2020
08/08/2020
01/09/2020
25/09/2020
19/10/2020
12/11/2020
06/12/2020
30/12/2020
23/01/2021
16/02/2021
12/03/2021


Vif
Free Cellulose / ng m-3
400
350
300
250
200
150
100
50
0
03/03/2017
21/03/2017
08/04/2017
26/04/2017
14/05/2017
01/06/2017
19/06/2017
07/07/2017
25/07/2017
12/08/2017
30/08/2017
17/09/2017
05/10/2017
23/10/2017
10/11/2017
28/11/2017
16/12/2017
03/01/2018
21/01/2018
08/02/2018
26/02/2018
19/03/2018
03/07/2020
21/07/2020
06/08/2020
20/08/2020
07/09/2020
25/09/2020
16/10/2020
03/11/2020
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02/01/2021
20/01/2021
07/02/2021
22/02/2021
12/03/2021

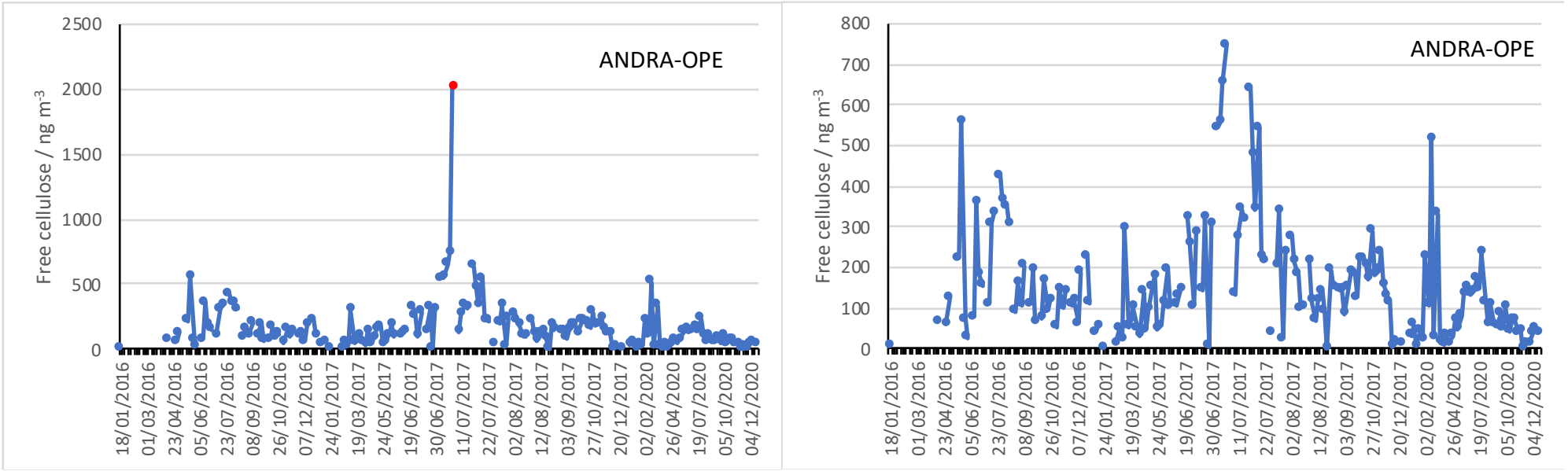

Figure S1: Overall evolution of PM_{10} cellulose concentrations (ng m^{-3}) across the nine sites. Names are indicated at the top of each graph. ***Note: The concentration evolutions for ANDRA-OPE are coded according to the sampling years. Additionally, two graphs of the overall cellulose concentrations for ANDRA-OPE are shown. The right graph has the episodic spike (indicated in red on the left graph) removed, to illustrate the concentration evolution over the total sampling period.***

Table S1: Literature comparison of seasonal and site variability of ambient cellulose concentrations.

LF = Les Frênes, CB = Caserne de Bonne. Grenoble metropole sites = LF, CB, VIF.

Cellulose (ng m-3)			**Annual**		**Winter**		**Spring**		**Summer**		**Autumn**		**Reference**
Site (Type)	*Particle Size (μm)*	# Samples	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	
LF (Urban background)	10	286	67 ± 55	(1 – 379)	34 ± 29	(1 – 146)	57 ± 44	(1 – 214)	98 ± 58	(29 – 379)	93 ± 60	(1 – 333)	This study
VIF (peri-urban)	10	218	59 ± 63	(0.0 – 344)	43 ± 47	(0.0 – 222)	44 ± 38	(3 – 186)	68 ± 87	(1 – 344)	77 ± 65	(1 – 286)	This study
CB (urban)	10	206	99 ± 85	(1 – 701)	85 ± 111	(1 – 701)	131 ± 56	(46 – 288)	94 ± 59	(3 - 238)	95 ± 85	(3 – 357)	This study
ANDRA-OPE (Rural)	10	174	169 ± 199	(3 – 2027)	90 ± 115	(3 – 518)	102 ± 116	(12 – 560)	247 ± 260	(7 – 2027)	90 ± 67	(13 – 290)	This study
ANDRA-OPE	2.5	51	16 ± 15	(0.3 – 41)	17 ± 21	(0.3 – 41)	< LD	< LD	15 ± 12	(6 – 32)	16 ± 18	(2 – 40)	This study
Basel (Suburban)	10	90	29 ± 38	(2 – 266)	27 ± 57	(2 – 266)	35 ± 37	(10 – 154)	32 ± 35	(11 – 179)	23 ± 16	(3 – 83)	This study
Bern (Urban-traffic)	10	89	124 ± 75	(25 – 318)	66 ± 45	(30 – 159)	76 ± 52	(25 – 241)	143 ± 45	(99 – 306)	138 ± 72	(78 – 318)	This study
Magadino (Rural)	10	90	117 ± 67	(16 – 348)	53 ± 23	(17 – 103)	84 ± 48	(43 – 282)	135 ± 65	(60 – 348)	131 ± 54	(48 – 279)	This study
Payerne (Rural)	10	90	284 ± 225	(53 – 1194)	163 ± 84	(90 – 437)	108 ± 54	(53 – 284)	553 ± 246	(235 – 1194)	300 ± 114	(96 – 538)	This study
Payerne	2.5	90	118 ± 77	(29 – 678)	105 ± 29	(71 – 201)	74 ± 33	(29 – 163)	161 ± 122	(75 – 678)	132 ± 52	(74 – 275)	This study
Zurich (Urban)	10	88	190 ± 75	(7 – 521)	189 ± 48	(116 – 342)	177 ± 51	(81 – 260)	197 ± 71	(7 – 330)	198 ± 112	(48 – 521)	This study
Zurich	2.5	89	57 ± 24	(11 – 163)	52 ± 16	(31 – 89)	52 ± 26	(13 – 199)	58 ± 20	(33 – 109)	64 ± 31	(11 – 163)	This study
AZO, Portugal (Maritime)	2.5	118	16.3	-	13.8	-	-	-	18.5	-	-	-	Sanchez-Ochoa 2007
AVE, Portugal (Maritime)	2.5	119	71	-	107	-	-	-	46.7	-	-	-	Sanchez-Ochoa 2007
KPZ, Hungary (Rural)	2	111	181	-	115	-	-	-	229	-	-	-	Sanchez-Ochoa 2007
SIL, Germany (Mountain)	10	116	122	-	39.3	-	-	-	162	-	-	-	Sanchez-Ochoa 2007
PDD, France (Mountain)	10	110	83	-	39.9	-	-	-	135	-	-	-	Sanchez-Ochoa 2007
SBO, Austria (Troposphere)	2.5	118	47	-	29.4	-	-	-	62.5	-	-	-	Sanchez-Ochoa 2007
BIR, Norway (Rural)	10	4	<LOD	-	-	-	-	-	-	-	-	-	Glasius 2018
	10	4	89 ± 20	-	-	-	-	-	-	-	-	-	Yttri 2011b
VAV, Denmark (Rural)	10	4	<LOD	-	-	-	-	-	-	-	-	-	Glasius 2018
	10	4	86 ± 16	-	-	-	-	-	-	-	-	-	Yttri 2011b
ROT, Netherlands (Urban)	10	4	24 - 43	-	-	-	-	-	-	-	-	-	Glasius 2018
Oslo, Norway (Urban)	10	33	80	-	30	-	-	-	130	-	-	-	Yttri 2011a
	1		5.8	-	6	-	-	-	5.5	-	-	-	
Hurdal, Norway (Rural)	10	33	54.5	-	43	-	-	-	66	-	-	-	Yttri 2011a
	1		12	-	12	-	-	-	-	-	-	-	
Lille Valby, Denmark (Rural)	10	4	172 ± 113	-	-	-	-	-	-	-	-	-	Yttri 2011b
Hyyttiälä, Norway (Rural)	10	4	133 ± 43	-	-	-	-	-	-	-	-	-	Yttri 2011b

Table S1 cont.: Literature comparison of seasonal and site variability of ambient cellulose concentrations.

Cellulose (ng m-3)			**Annual**		**Winter**		**Spring**		**Summer**		**Autumn**		**Reference**
Site (Type)	*Particle Size (µm)*	# Samples	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	
SCH, Vienna (Background)	10	365	90	(0 - 550)	126	-	79	-	85	-	83	-	Caseiro 2008
RIN, Vienna (Traffic)	10	365	140	(30 - 560)	143	-	133	-	150	-	120	-	Caseiro 2008
KEN, Vienna (Traffic)	10	365	130	(40 - 350)	128	-	137	-	139	-	98	-	Caseiro 2008
LOB, Vienna (Background)	10	365	90	(20 - 200)	75	-	88	-	107	-	79	-	Caseiro 2008
DB, Graz (Traffic)	10	365	130	(40 - 540)	116	-	159	-	141	-	114	-	Caseiro 2008
GS, Graz (Urban)	10	365	200	(0 - 830)	276	-	231	-	134	-	156	-	Caseiro 2008
BB, Graz (Background)	10	365	230	(110 - 720)	320	-	232	-	174	-	200	-	Caseiro 2008
RU, Salzburg (Traffic)	10	365	130	(50 - 440)	125	-	119	-	102	-	163	-	Caseiro 2008
LE, Salzburg (Urban)	10	365	110	(30 - 180)	87	-	135	-	99	-	90	-	Caseiro 2008
AN, Salzburg (Background)	10	365	80	(40 - 130)	54	-	72	-	101	-	74	-	Caseiro 2008

Cellulose concentrations in PM_{10} and $PM_{2.5}$

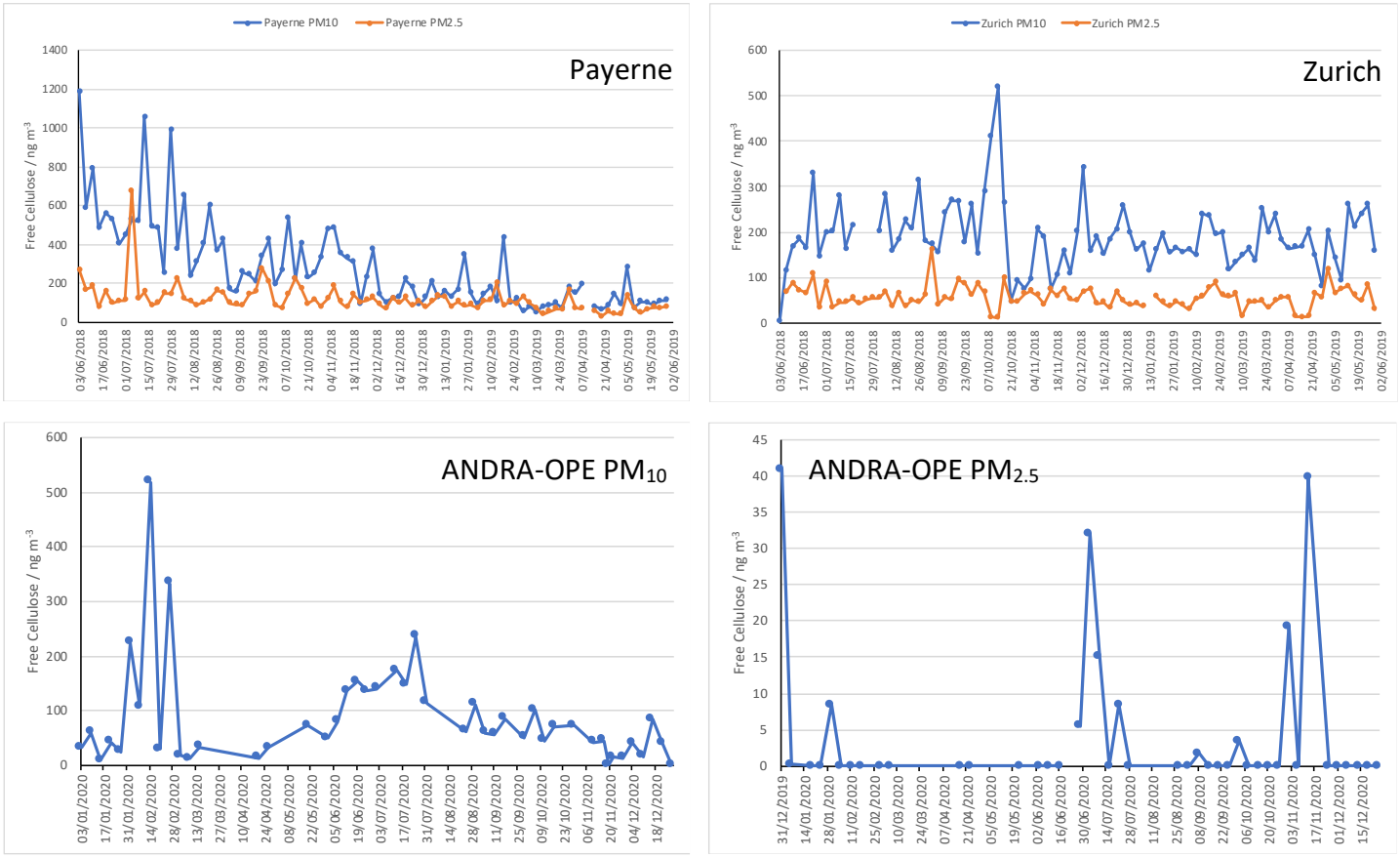

Figure S2: Total cellulose (ng m^{-3}) evolution within PM_{10} and $PM_{2.5}$ taken at Payerne, Zurich and ANDRA-OPE.

Table S2: Ratio of monthly mean cellulose concentrations within $PM_{2.5}$: PM_{10}.

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Payerne	0.57	0.67	0.99	0.45	0.62	0.24	0.32	0.32	0.59	0.41	0.37	0.71
Zurich	0.26	0.31	0.26	0.25	0.36	0.45	0.25	0.24	0.36	0.23	0.42	0.26
ANDRA-OPE	0.49					0.049	0.11		0.027	0.048	1.02	

Temporal Variations

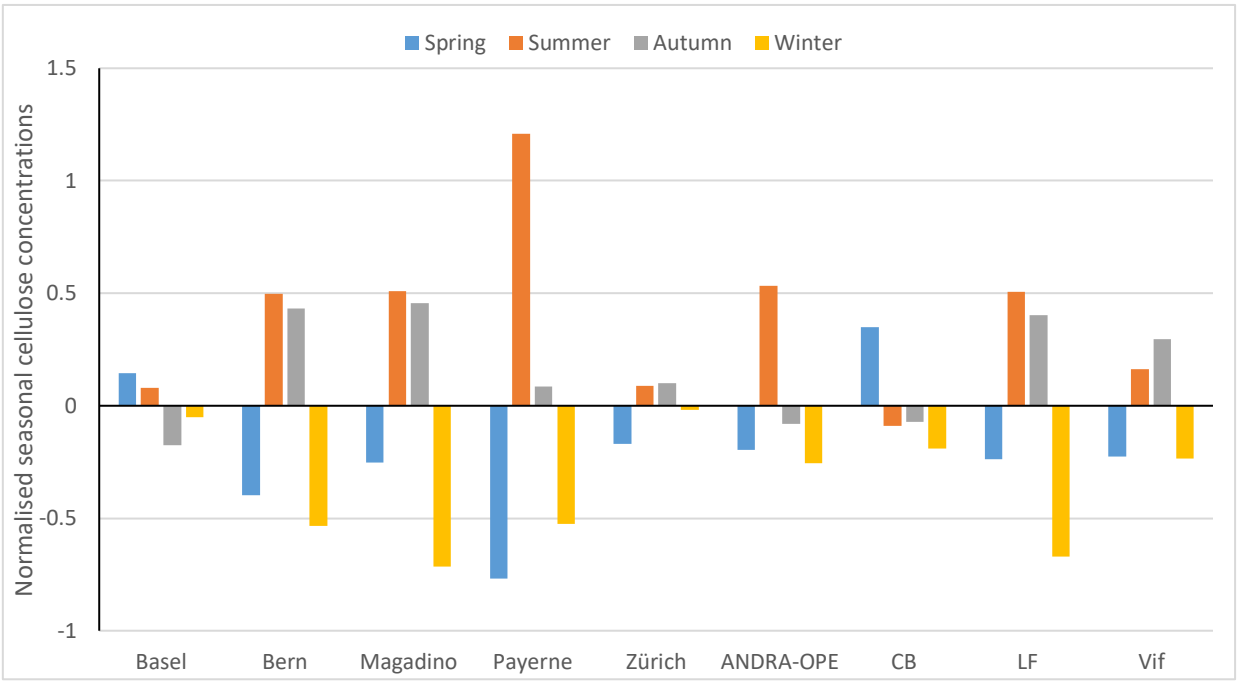

Figure S3: Normalised seasonal cellulose concentrations for the nine measured sites, using their individual annual average cellulose concentrations. A larger value here represents a more significant deviation from their annual mean concentration. LF = Les Frênes, CB = Caserne de Bonne. Grenoble metropole sites = LF, CB, VIF.

Relative Contribution of Cellulose-C to OC

Table S3: Contributions of cellulose-C to OC in percentages and the ratio of summer-to-winter contribution to OC. LF = Les Frênes, CB = Caserne de Bonne. Grenoble metropole sites = LF, CB, VIF.

Cellulose-C/OC, %	LF	VIF	CB	ANDRA - OPE	Basel	Bern	Magadino	Payerne	Zurich
Average	0.91 ± 0.79	0.94 ± 0.79	1.23 ± 0.98	3.19 ± 2.43	0.70 ± 1.03	1.26 ± 0.66	1.71 ± 1.27	5.88 ± 4.39	3.76 ± 2.87
Max	6.17	7.03	6.05	18.30	6.28	4.08	7.80	19.71	16.14
Spring	0.80 ± 0.59	0.76 ± 0.64	1.62 ± 0.57	2.72 ± 3.51	0.87 ± 0.57	1.23 ± 0.80	2.43 ± 1.81	4.36 ± 4.58	4.41 ± 3.09
Summer	1.45 ± 0.93	1.37 ± 1.61	1.51 ± 1.01	4.08 ± 2.14	0.77 ± 1.23	1.60 ± 0.46	1.89 ± 0.93	9.10 ± 3.95	3.18 ± 1.92
Autumn	1.12 ± 0.80	1.15 ± 1.03	1.13 ± 1.06	3.11 ± 1.97	0.34 ± 0.22	1.34 ± 0.65	1.60 ± 0.65	5.64 ± 4.19	2.41 ± 1.05
Winter	0.38 ± 0.34	0.47 ± 0.46	0.84 ± 0.95	1.45 ± 1.43	0.87 ± 1.64	0.78 ± 0.39	0.73 ± 0.82	4.12 ± 2.80	5.23 ± 3.94
Winter/Summer	0.26	0.34	0.55	0.36	1.14	0.49	0.39	0.45	1.64

*Tables S4: Contributions of **coarse mode** (particle size between 10 and 2.5 µm) cellulose-C to **coarse mode** OC for the three sites measuring both PM_{10} and $PM_{2.5}$ cellulose. Site classifications: ANDRA-OPE, Rural Background; Payerne, Rural; Zurich, Urban.*

Site	Average Coarse Mode Cellulose-C / ngC m-3	Average Coarse Mode OC / ngC m-3	Ratio / %
ANDRA-OPE	32.74	1037.50	3.16
Payerne	73.08	663.40	11.02
Zurich	59.57	456.70	13.04

Tracer Correlations

Table S5: Full table of correlations of cellulose with characteristic chemical tracers across the two sampling periods, complete with n and p values. Levoglucosan total and seasonal correlations are highlighted in blue

Spearman correlations	CB			LF			Vif			Basel			Bern		
	Rs	n	*p*	Rs	n	*p*	Rs	n	*p*	Rs	n	*p*	Rs	n	*p*
Mean Polyols	0.282	192	<0.0001	0.603	265	<0.00001	0.419	181	<0.00001	0.333	87	0.002	0.610	89	<0.0001
Mean Glucose	0.279	190	<0.0001	0.570	264	<0.00001	0.477	179	<0.00001	0.393	88	0.000	0.631	89	<0.0001
Mean Levo	-0.065	190	0.380	-0.384	265	<0.00001	-0.076	181	0.309	0.002	90	0.984	-0.069	89	0.521
Spring	-0.027	38	0.871	-0.195	72	0.101	0.011	34	0.949	0.224	23	0.304	0.317	23	0.139
Summer	0.095	40	0.559	-0.004	62	0.977	0.320	44	0.034	0.033	22	0.883	0.191	22	0.395
Autumn	0.106	55	0.441	-0.213	59	0.105	-0.159	55	0.246	-0.035	23	0.874	-0.105	23	0.634
Winter	0.132	57	0.328	0.181	72	0.128	0.046	48	0.757	0.237	22	0.289	0.488	22	0.021
Mean EC	0.194	192	0.070	-0.081	265	0.189	0.041	186	0.578	0.342	86	0.001	0.247	87	0.021
Mean Ca2+	0.139	192	0.543	0.279	265	<0.00001	0.115	181	0.123	0.370	90	<0.0001	0.447	89	<0.0001
Mean Ti	0.284	123	0.001	0.344	114	0.000	0.025	100	0.805	0.404	76	<0.0001	0.386	86	<0.0001

Spearman correlations	Magadino			Payerne			Zurich			ANDRA-OPE		
	Rs	n	*p*	Rs	n	*p*	Rs	n	*p*	Rs	n	*p*
Mean Polyols	0.784	90	<0.0001	0.678	90	<0.0001	0.432	88	<0.0001	0.656	162	<0.0001
Mean Glucose	0.657	89	<0.0001	0.706	89	<0.0001	0.426	84	<0.0001	0.580	162	<0.0001
Mean Levo	-0.374	85	0.000	-0.182	89	0.088	-0.029	87	0.791	-0.429	161	<0.0001
Spring	0.000	23	1.000	-0.053	22	0.817	0.136	23	0.536	-0.429	23	0.041
Summer	0.106	22	0.639	0.078	23	0.723	0.063	19	0.797	-0.056	73	0.637
Autumn	-0.144	19	0.556	0.305	22	0.167	0.006	23	0.979	-0.141	40	0.384
Winter	0.056	21	0.810	-0.134	22	0.552	0.032	22	0.887	-0.032	25	0.881
Mean EC	-0.030	86	0.786	0.069	88	0.523	0.254	85	0.019	0.108	166	0.165
Mean Ca2+	-0.121	90	0.255	0.213	90	0.044	0.289	88	0.006	0.328	160	<0.0001
Mean Ti	0.051	90	0.632	0.314	90	0.003	0.309	88	0.003	0.179	112	0.059

Local vs Regional Origin

Tables S6 and S7: Covariations (R^2) in polyol concentrations across the Swiss-based (top) and Grenoble-based (bottom) sites. R^2 values close to 1, shaded red, indicate a strong correlation between polyol concentrations at different sites. Note: polyols = sum of arabitol, mannitol and sorbitol. A colour key (right) shows the R^2 values and their corresponding colours.

R^2				
Bern	0.8889			
Magadino	0.6145	0.6265		
Payerne	0.8078	0.8551	0.4024	
Zurich	0.8446	0.9071	0.6008	0.6778
	Basel	Bern	Magadino	Payerne

R^2		
CB	0.977	
VIF	0.9548	0.965
	LF	CB

1
0.8
0.6
0.5
0.4
0.2
0

Interannual Variability

Table S8: Comparison of ambient free cellulose concentrations (ng m^{-3}), between Grenoble-based data sets: LF = Les Frênes (Urban background), CB = Caserne de Bonne (Urban), Vif (Peri-urban).

[Cellulose] / ng m^{-3}	Average	Max	Spring	Summer	Autumn	Winter
2017 - 2018						
LF	60.7 ± 45.8	210.3	61.8 ± 44.8	81.4 ± 42.6	64.2 ± 49.2	23.0 ± 20.0
Vif	78.1 ± 73.7	344.4	45.7 ± 38.2	113.6 ± 99.5	97.1 ± 69.6	62.5 ± 64.3
CB	130.1 ± 90.3	700.8	132.4 ± 57.0	127.6 ± 45.3	150.1 ± 86.7	108.5 ± 143.7
2020 - 2021						
LF	79.4 ± 59.7	379.0	54.6 ± 45.4	115.2 ± 67.7	122.0 ± 58.2	29.9 ± 42.8
Vif	54.9 ± 44.8	232.8	80.8 ± 18.4	36.3 ± 43.2	62.1 ± 55.7	49.0 ± 34.5
CB	64.4 ± 50.1	209.4	120.4 ± 45.6	36.5 ± 38.4	40.6 ± 39.3	70.9 ± 58.1

Table S9: Comparison of cellulose contribution to OC, between Grenoble-based data sets: LF = Les Frênes (Urban background), CB = Caserne de Bonne (Urban), Vif (Peri-urban).

Cellulose-C/OC, %	Average	Max	Spring	Summer	Autumn	Winter	Winter/Summer
2017 - 2018							
LF	0.81 ± 0.68	4.24	0.87 ± 0.66	1.22 ± 0.74	0.72 ± 0.55	0.23 ± 0.27	0.19
Vif	1.16	7.02	0.73 ± 0.66	1.91 ± 1.87	1.50 ± 1.11	0.43 ± 0.43	0.22
CB	1.54 ± 1.03	6.05	1.59 ± 0.55	1.96 ± 0.87	1.63 ± 1.14	0.97 ± 1.25	0.50
2020 - 2021							
LF	0.99 ± 0.87	6.17	0.72 ± 0.47	1.69 ± 1.05	1.50 ± 0.83	0.44 ± 0.35	0.26
Vif	0.65 ± 0.68	3.32	1.05 ± 0.81	0.64 ± 0.30	0.79 ± 0.75	0.49 ± 0.49	0.77
CB	0.66 ± 0.56	2.58	1.84 ± 0.81	0.59 ± 0.54	0.47 ± 0.37	0.69 ± 0.46	1.18

Table S10: Full table of correlations of cellulose with characteristic chemical tracers across the two sampling periods within the Grenoble metropole, complete with n and p values. Levoglucosan total and seasonal correlations are highlighted in blue.

Spearman Correlations	2017 - 2018									2020 - 2021								
	CB			LF			Vif			CB			LF			Vif		
	Rs	n	*p*	Rs	n	*p*	Rs	n	*p*	Rs	n	*p*	Rs	n	*p*	Rs	n	*p*
Mean Polyols	0.465	123	< 0.00001	0.626	121	< 0.00001	0.585	101	< 0.00001	-0.092	69	0.462	0.683	144	< 0.00001	0.220	80	0.499
Mean Glucose	0.472	123	< 0.00001	0.618	121	< 0.00001	0.661	100	< 0.00001	-0.075	67	0.545	0.564	143	< 0.00001	0.238	80	0.335
Mean Levo	-0.073	123	0.424	-0.478	121	< 0.00001	-0.213	101	0.032	0.253	69	0.360	-0.385	144	< 0.00001	0.100	80	0.378
Spring	-0.077	34	0.665	-0.177	40	0.275	-0.195	30	0.302	0.400	4	0.600	-0.185	32	0.311	0.400	4	0.600
Summer	0.054	29	0.780	-0.166	31	0.375	0.429	25	0.032	-0.253	14	0.383	-0.026	31	0.890	0.258	19	0.286
Autumn	0.161	31	0.387	-0.388	29	0.037	-0.361	28	0.060	0.274	24	0.195	-0.104	30	0.584	0.041	27	0.839
Winter	0.335	29	0.076	0.057	21	0.806	0.348	18	0.154	-0.120	27	0.551	0.188	50	0.190	-0.119	30	0.531
Mean EC	0.152	123	0.093	-0.108	121	0.238	-0.065	106	0.508	0.181	69	0.135	0.007	144	0.931	0.157	80	0.164
Mean Ca2+	0.142	123	0.117	0.222	121	0.014	0.000	101	0.999	0.307	69	0.010	0.322	144	0.000	0.324	80	0.034

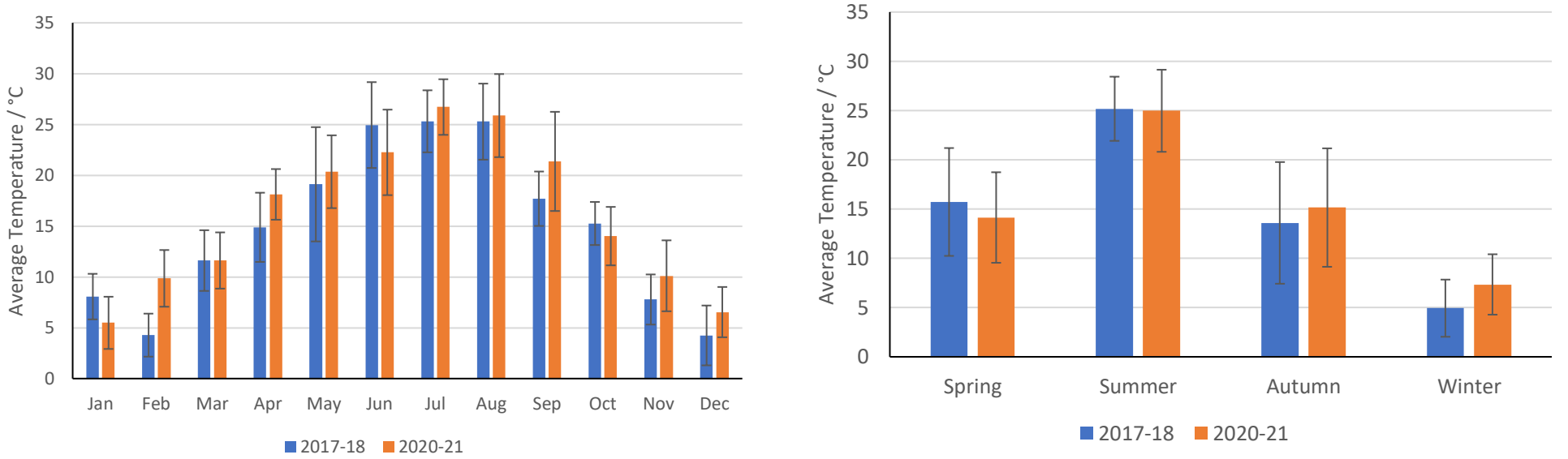

Figure S4: Mean averages temperatures for the Grenoble metropole by month (left) and by season (right). Blue bars represent temperature averages across 2017-2018, with orange equivalents representing 2020-2021 averages. Black error bars represent one standard deviation of the seasonal and monthly averages.

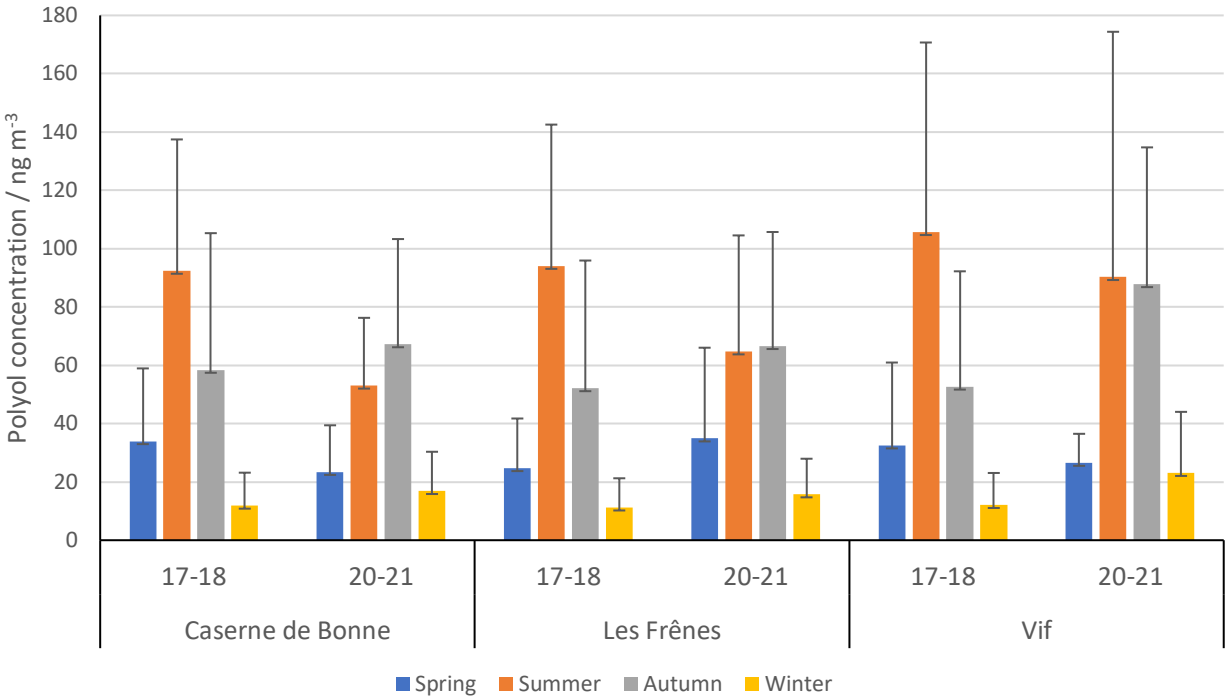

Figure S5: Seasonal mean averages of polyol (sum of arabitol, sorbitol and mannitol) concentrations (ng m^{-3}) of the three sites within the Grenoble metropole across the two separate sampling periods: 2017-18 and 2020-21. Black error bars represent one standard deviation of the seasonal means. Only positive error bars are shown to aid clarity. Seasons are defined as: Dec-Feb (winter), Mar-May (spring), Jun-Aug (summer), Sep-Nov (autumn). Site classifications are as follows: Caserne de Bonne – urban; Les Frênes – urban background; Vif – peri-urban.

Table S11: Comparison of ambient free cellulose concentrations (ng m^{-3}), between ANDRA-OPE data sets.

[Cellulose] / ng m^{-3}	Average	Max	Spring	Summer	Autumn	Winter
ANDRA-OPE						
2016	170.0 ± 121.3	560.7	185.6 ± 193.6	233.4 ± 130.6	121.4 ± 45.6	119.9 ± 80.0
2017	208.5 ± 249.4	2027.0	96.6 ± 75.2	216.8 ± 172.9	183.1 ± 50.4	35.4 ± 36.4
2020	89.5 ± 94.6	518.2	30.2 ± 23.0	128.3 ± 50.6	54.8 ± 26.0	111.5 ± 148.3

Table S12: Comparison of cellulose contribution to OC, between ANDRA-OPE data sets.

Cellulose-C/OC, %	Average	Max	Spring	Summer	Autumn	Winter	Winter/Summer
ANDRA-OPE							
2016	3.64 ± 3.14	18.30	5.10 ± 6.65	4.34 ± 2.15	2.88 ± 1.57	2.36 ± 2.62	0.54
2017	3.72 ± 2.26	9.59	2.03 ± 1.01	4.07 ± 2.70	4.54 ± 1.87	1.05 ± 1.16	0.26
2020	1.76 ± 1.18	5.19	1.84 ± 1.84	2.43 ± 1.11	1.58 ± 1.17	1.32 ± 0.65	0.54

Table S13: Full table of correlations of cellulose with characteristic chemical tracers across the three sampling periods at ANDRA-OPE, complete with n and p values.

Spearman Correlations	ANDRA-OPE								
	2016			2017			2020		
	Rs	n	*p*	Rs	n	*p*	Rs	n	*p*
Mean Polyols	0.440	40	0.004496	0.523	52	0.00007	0.630	38	0.000023
Mean Glucose	0.210	40	0.193396	0.573	51	< 0.00001	0.409	38	0.010784
Mean Levo	-0.306	40	0.055	-0.296	52	0.033122	-0.684	38	< 0.00001
Mean EC	-0.121	40	0.457	0.034	52	0.811	0.085	39	0.612
Mean Ca2+	0.225	40	0.163	0.110	52	0.438	0.618	34	0.000