

Supplementary material



Figure S1. Map with the sampling sites, ceilometer location, air quality stations, meteorological stations and Harbour location. Source: © Google Earth Pro.

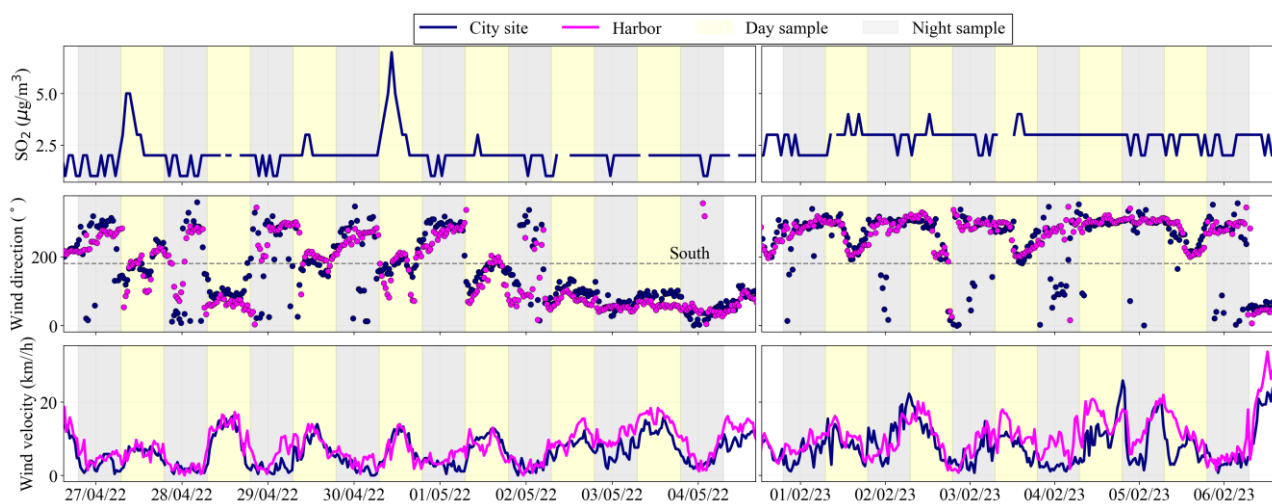


Figure S2. SO_2 , mean wind direction and velocity at the city site and harbour meteorological station.

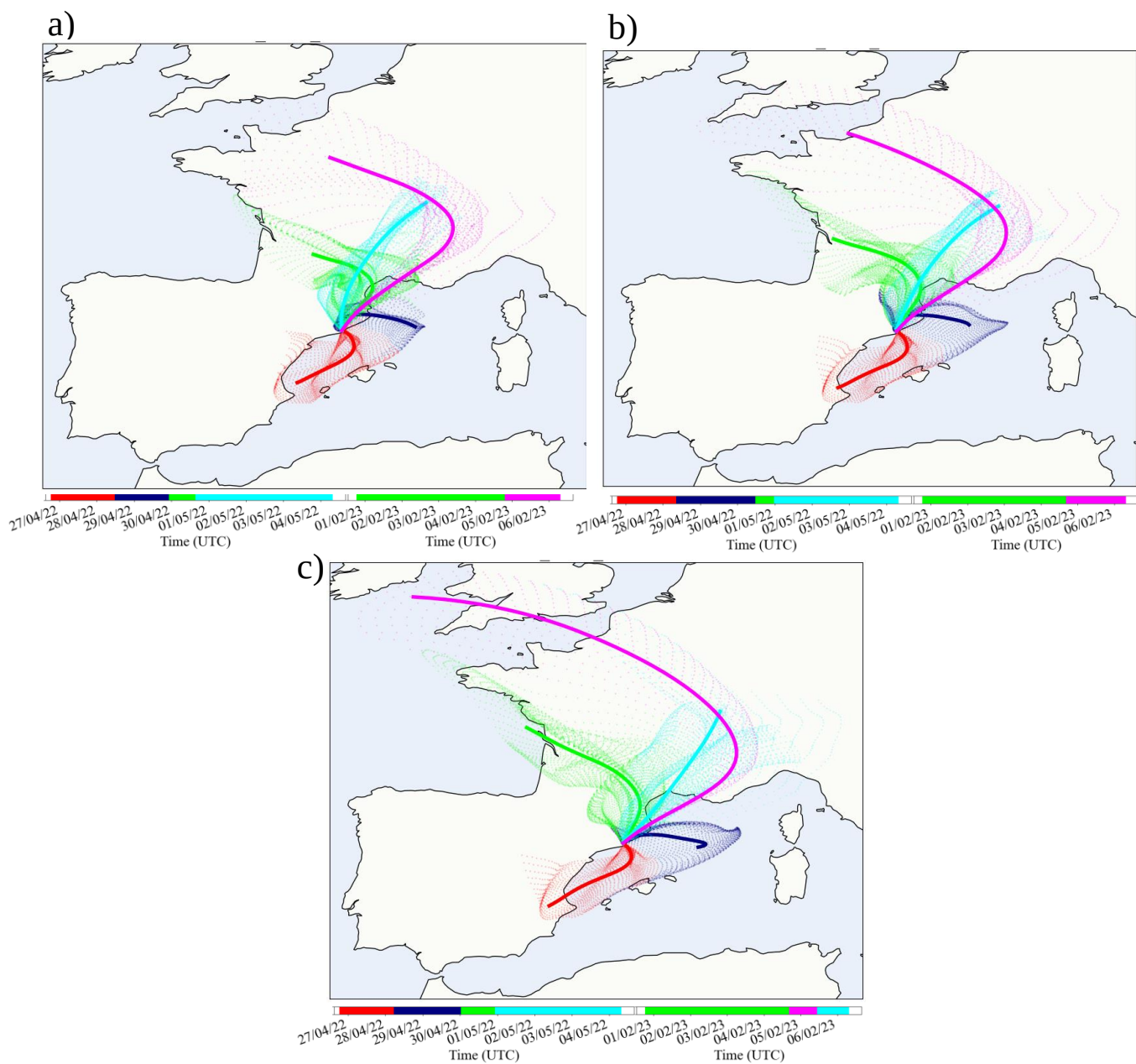


Figure S3. Mean trajectory of each 48h cluster (solid line) with all trajectory endpoints of that cluster (dots). The color legend shows the date of the cluster each trajectory belongs to for the two sampling campaigns. The three subfigures show the cluster analysis with trajectories computed at the city site at 100 m agl (a), middle site at 200 m agl (b) and the elevated site at 400 m agl(c).

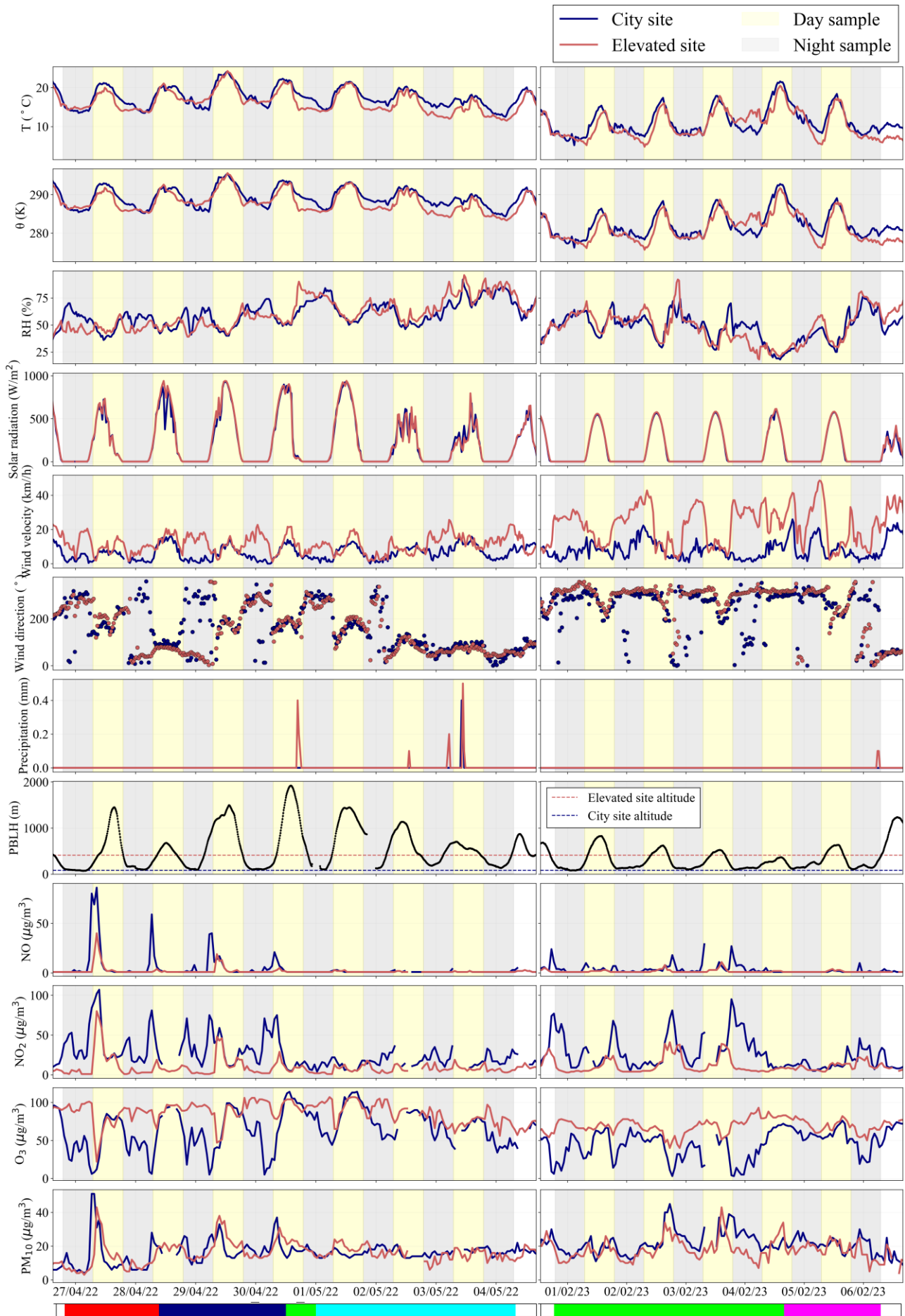


Figure S4. Meteorological and air quality variables during all sampling campaigns with the air trajectory cluster for each period in the x axis.

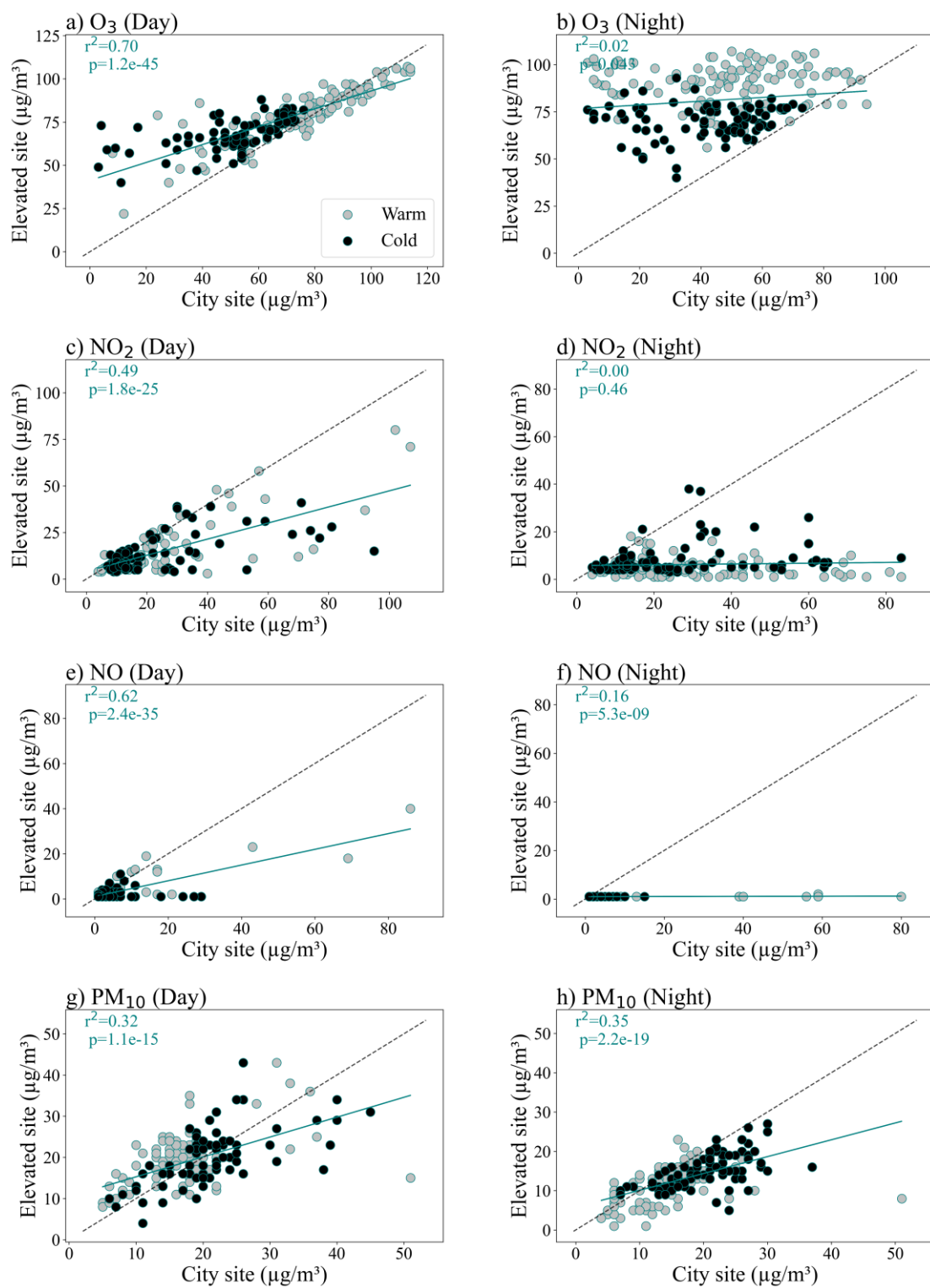


Figure S5. Correlation of air quality automatic data at both background sites during day and night periods.

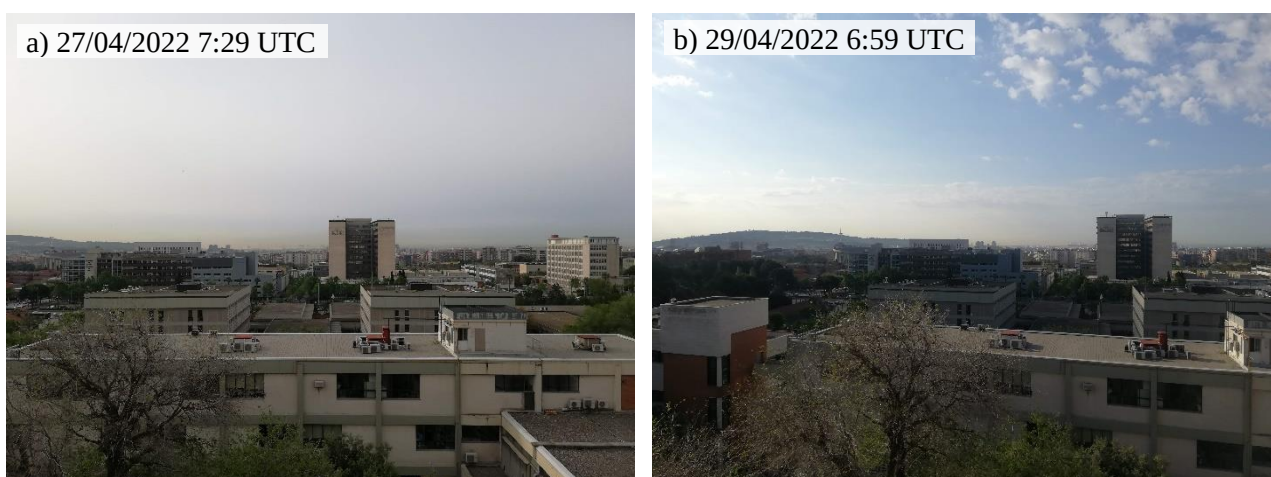


Figure S6. Photos taken from the city site to the city harbour during the sampling campaign.

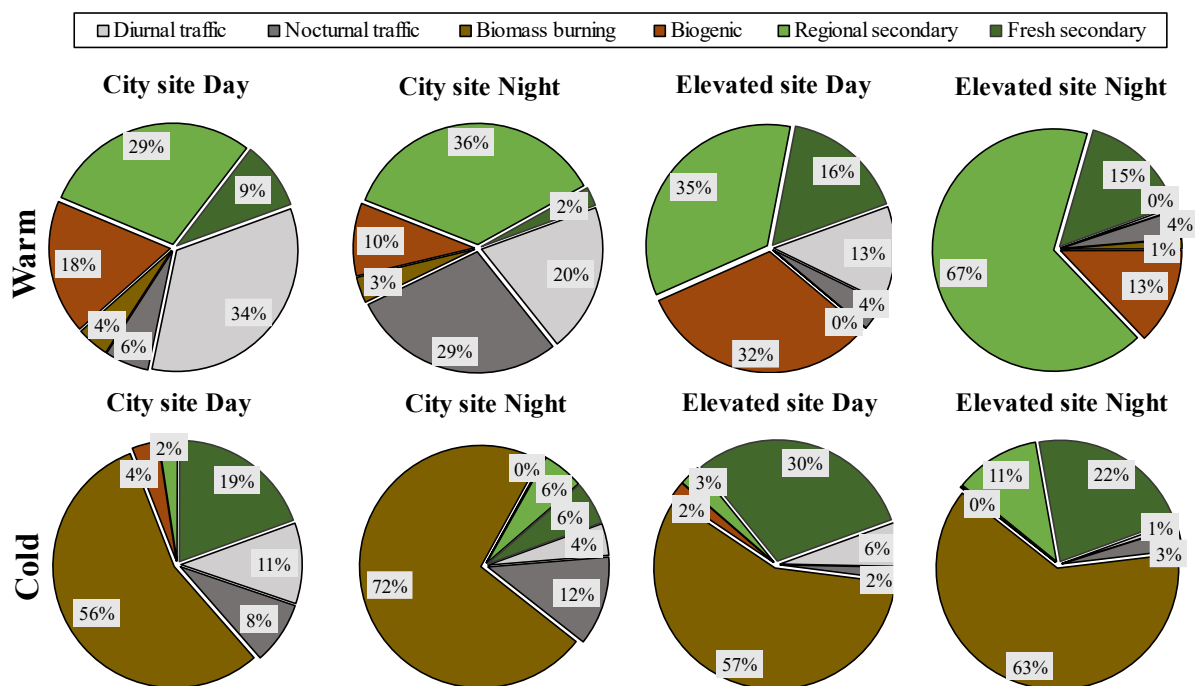


Figure S7. Pie charts the MCR-ALS scores separated by season, site and period of the day.

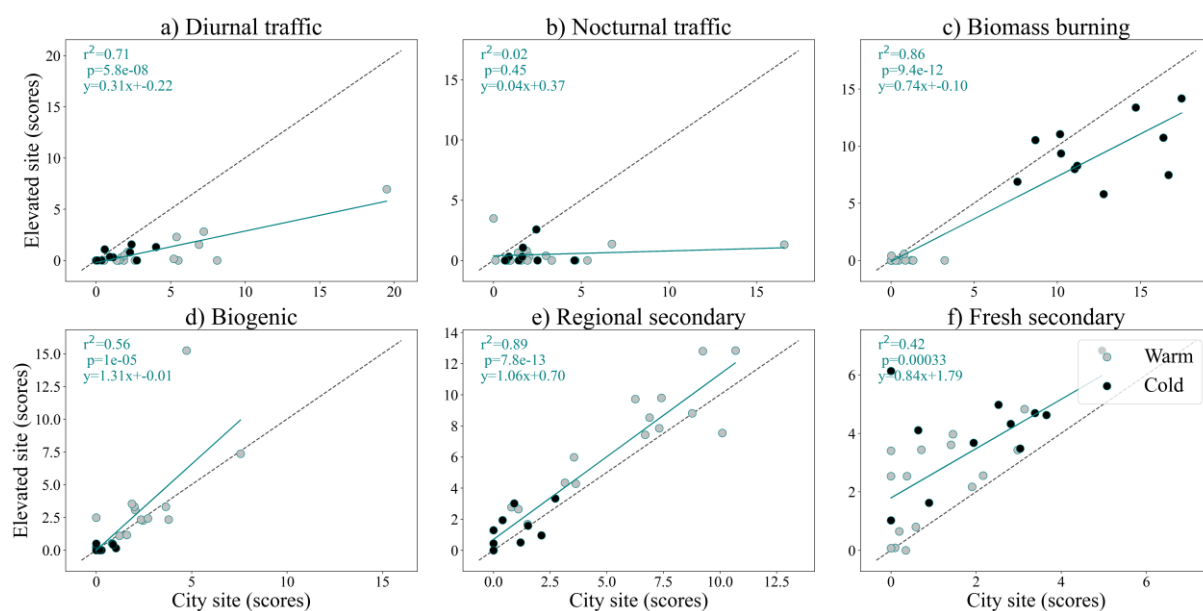


Figure S8. Correlation between MCR-ALS scores at both sites for the 6 components.

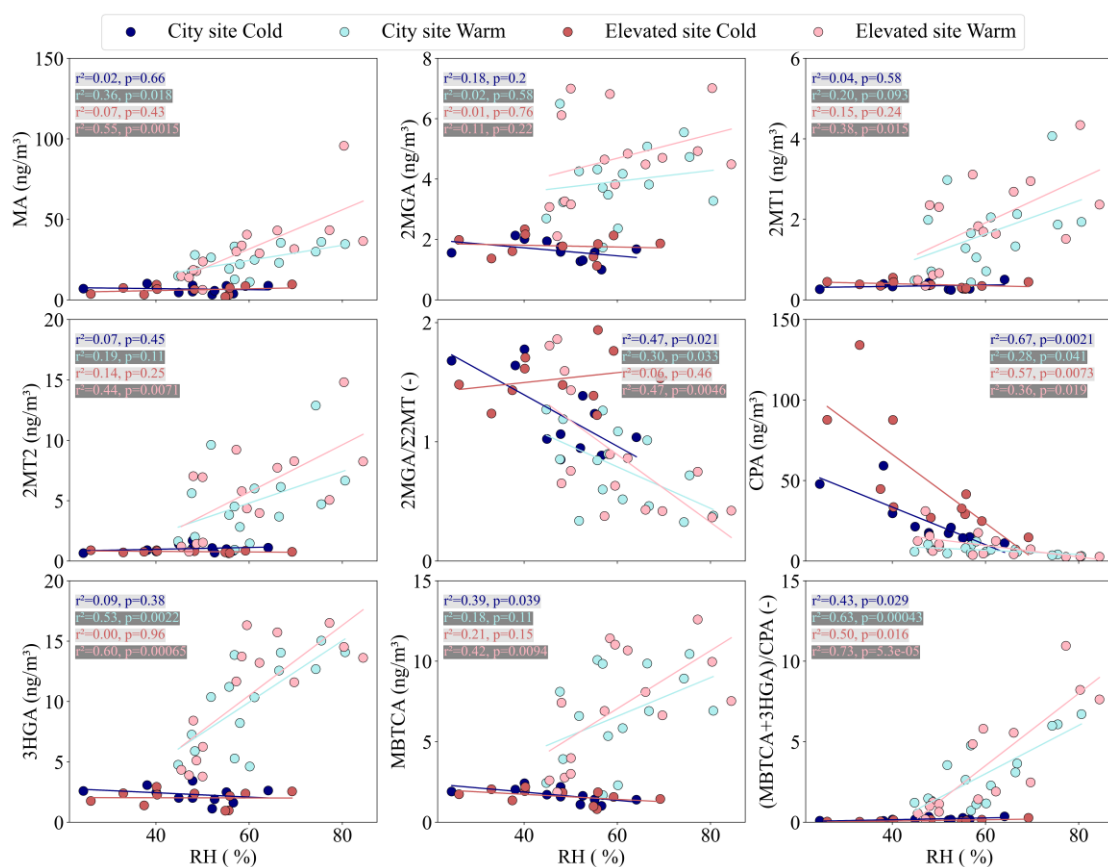


Figure S9. Concentration of Biogenic SOA compounds and ratios between them against Relative Humidity (RH) at the different sites and campaigns. Abbreviations are defined in Table 1.

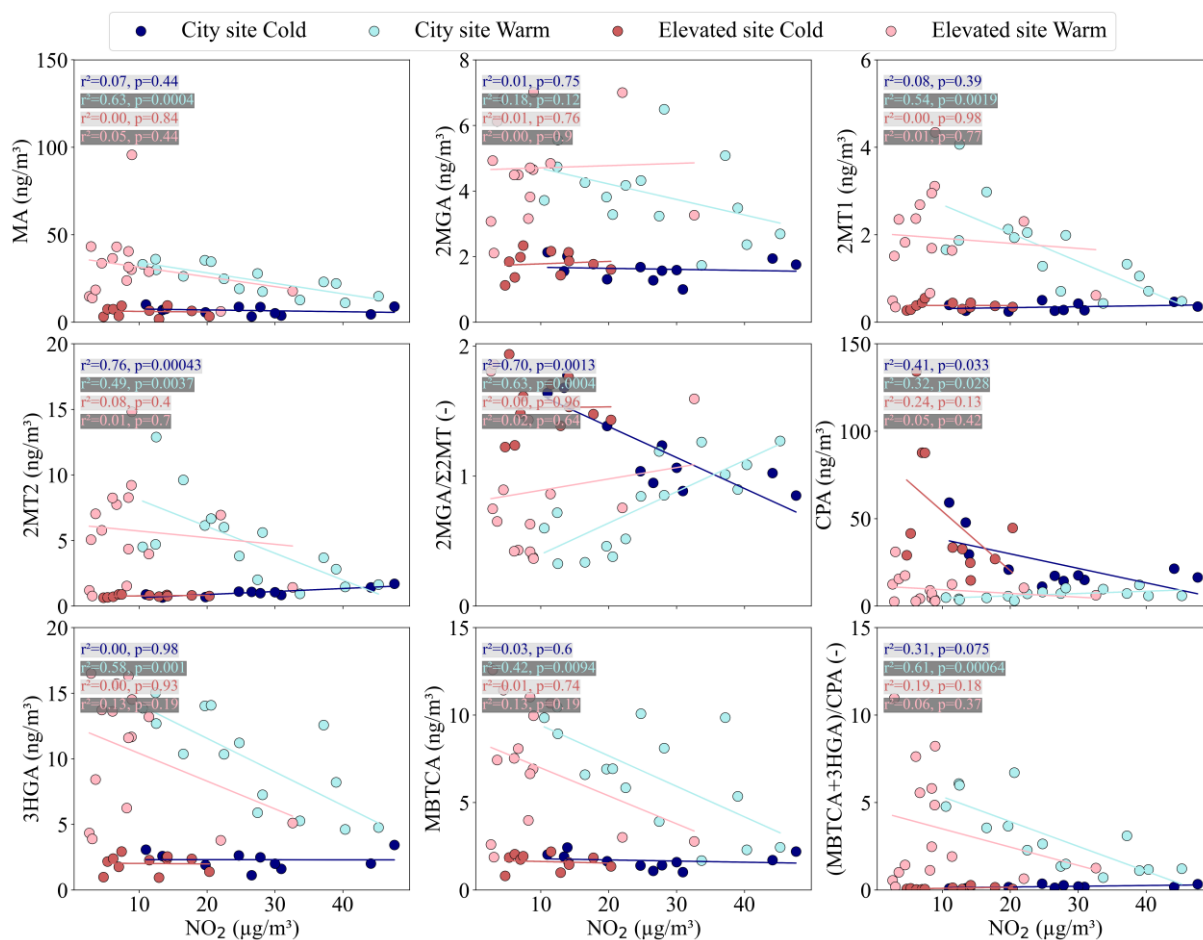


Figure S10. Concentration of Biogenic SOA compounds and ratios between them against NO_2 at the different sites and campaigns. Abbreviations are defined in Table 1.

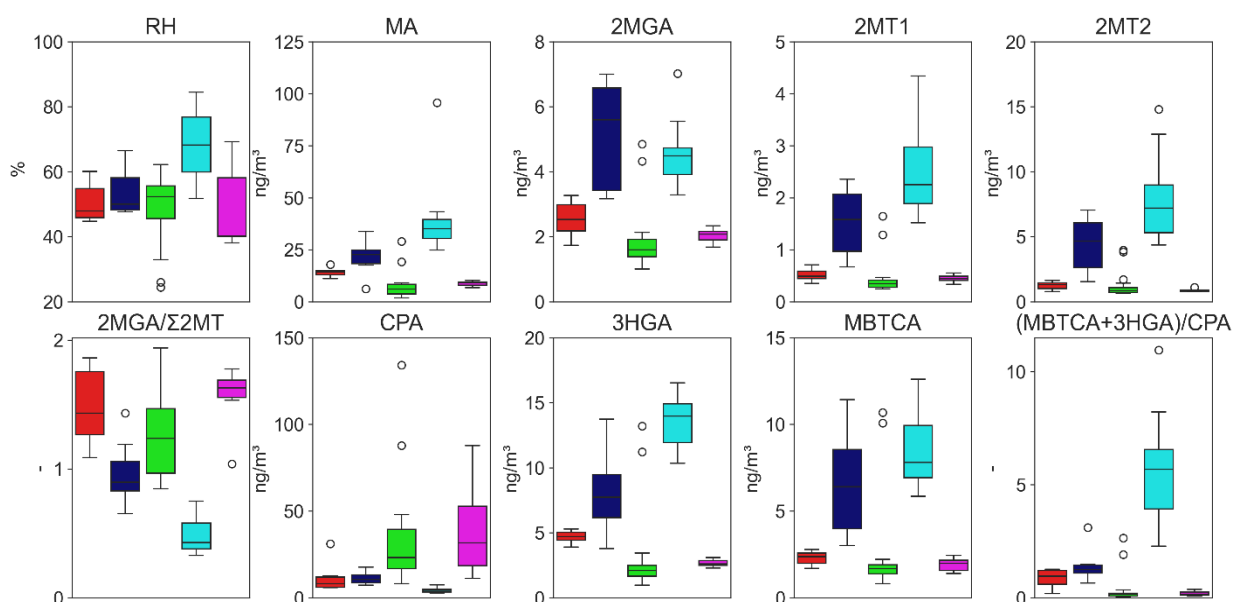


Figure S11. Concentration of Biogenic SOA compounds and ratios between them under different air mass origins. Colours of boxes correspond to the backward trajectory clusters of Figure S3 b; red: northward Mediterranean, blue: southward Mediterranean, green: southward Atlantic, light blue: southward continental, pink: Atlantic-continent. Abbreviations are defined in Table 1.

Table S1.. Average concentrations and standard deviations of day and night samples during warm and cold campaigns at both sites. Abbreviations are defined in Table 1..

	Warm								Cold							
	City site				Elevated site				City site				Elevated site			
	Day		Night		Day		Night		Day		Night		Day		Night	
	Avg	sd	Avg	sd	Avg	sd	Avg	sd	Avg	sd	Avg	sd	Avg	sd	Avg	sd
	pg/m ³															
PHE	33	16	41	17	24	13	8	4	82	17	92	19	87	17	70	13
ANT	3	2	5	4	2	2	ND	ND	12	2	15	2	13	2	12	4
FL	48	18	128	189	34	13	19	6	169	36	216	41	180	35	148	32
PYR	67	34	96	43	44	22	20	5	199	47	266	50	199	39	177	36
BAA	17	10	28	32	12	9	5	2	80	19	105	18	71	14	68	23
C+T	50	24	64	47	35	22	16	7	198	37	262	52	177	34	168	49
BBJKFL	94	60	94	74	52	24	24	9	310	46	502	81	299	54	319	107
BEP	58	33	57	34	33	17	13	5	165	24	262	42	147	32	170	54
BAP	24	14	36	35	17	9	7	2	138	27	218	43	135	31	147	50
PYL	4	2	7	5	3	2	1	0.3	29	8	41	11	23	6	28	14
DBAJANT	6	6	8	9	4	2	2	1	46	11	74	17	47	12	47	16
IP	74	49	62	33	43	16	20	6	161	27	248	48	146	31	159	56
DBAH+ACANT	9	7	10	10	5	3	2	1	23	1	40	7	23	5	26	7
BGHIP	138	103	117	57	71	38	23	7	229	64	323	68	187	30	190	63
ANTHAN	23	10	24	12	18	5	10	4	49	14	71	12	44	8	48	17
COR	50	40	36	23	24	22	ND	ND	69	28	84	23	51	10	47	18
3mPHE	9	5	18	22	7	4	5	4	16	3	19	4	14	3	12	2
2mPHE	9	5	19	23	7	5	5	5	47	10	48	13	23	4	18	2
2mANT	2	1	4	6	1	1	1	1	5	1	7	1	4	1	5	2
9mPHE	8	4	15	19	5	3	3	3	10	2	14	3	10	3	10	2
1mPHE	5	3	11	13	4	2	3	3	18	4	25	4	21	6	18	5
17dmPHE	5	3	10	11	4	3	3	3	22	5	31	3	24	6	21	5
1+3mFL	19	31	13	12	6	3	3	1	47	8	67	14	46	11	43	12
RET	46	86	27	12	12	10	13	4	247	93	495	58	351	64	357	98
4mPYR	27	49	14	9	8	5	3	1	27	7	37	7	23	5	22	5
1mPYR	15	27	8	5	4	3	2	0.4	21	5	31	6	18	3	18	4
3mC	31	16	36	20	20	12	8	2	57	8	97	23	42	9	49	11
6mC	8	4	9	5	5	3	2	0.4	10	3	16	4	7	1	7	2
9FLO	28	18	31	22	16	12	14	7	106	14	128	15	119	31	130	21
ANQ	182	72	219	216	129	48	218	192	454	38	479	51	421	42	460	132
2mANQ	158	63	120	33	102	62	50	9	112	13	115	15	90	10	94	25
23dmANQ	36	39	16	5	15	17	5	2	8	1	14	3	8	2	11	4
BAF	71	100	40	20	28	17	15	5	64	11	83	14	58	7	62	20
9nANT	4	3	11	6	2	1	2	2	10	5	20	8	7	4	9	6
2nFLU	4	2	3	1	3	2	1	0.5	1	0.3	ND	ND	2	1	1	1
norHOP	181	116	126	64	85	63	21	8	83	38	67	26	48	13	25	6
HOP	176	115	126	67	83	65	18	7	73	34	61	26	39	12	20	7
	ng/m ³															
GAL	1.7	0.7	2.0	0.6	1.4	0.4	1.3	0.7	8.7	1.1	15.5	5.2	9.0	1.7	12.8	4.7
MANNO	1.5	0.4	2.2	0.6	1.3	0.4	1.3	0.6	7.3	1.0	14.3	4.8	8.0	1.7	10.3	4.4
LEV	15.3	2.9	21.5	3.5	14.4	4.4	13.3	7.2	116.9	18.8	202.4	75.1	123.2	21.7	148.4	67.5
OXA	4.7	1.5	5.8	2.3	4.7	2.3	6.7	3.4	2.3	1.5	5.1	1.9	1.8	1.3	4.7	1.7
MALA	2.4	1.4	2.5	1.5	3.4	2.2	4.3	1.9	0.6	0.5	0.6	0.5	0.3	0.3	0.9	0.4
SA	16.9	3.8	14.7	3.3	16.9	8.1	15.2	6.9	9.9	1.5	10.7	3.2	8.9	2.3	10.3	4.3
GLU	4.2	1.3	3.2	1.1	3.7	1.5	3.6	1.8	1.7	0.2	1.7	0.3	1.7	0.4	1.9	0.6
ADIA	1.2	0.3	0.9	0.2	1.0	0.3	0.8	0.3	0.5	0.1	0.5	0.1	0.5	0.2	0.6	0.1
PIMA	0.5	0.1	0.4	0.1	0.3	0.0	0.3	0.1	0.2	0.1	0.2	0.1	0.2	0.1	0.2	0.1
SUBA	0.9	0.2	0.9	0.4	0.7	0.2	0.6	0.2	0.3	0.1	0.4	0.2	0.3	0.1	0.4	0.1
AZA	6.0	2.1	6.6	2.4	4.1	1.7	3.3	1.2	2.9	0.6	4.1	2.7	2.9	0.5	2.7	1.1
MA	24.2	6.9	25.0	9.9	34.8	28.9	29.5	12.1	5.5	1.8	7.7	2.4	4.4	2.1	7.6	2.4
TARA	4.8	1.9	6.0	2.1	5.7	2.8	7.7	2.8	0.6	0.4	1.2	0.6	0.5	0.3	1.3	0.5
PHA	2.6	0.7	1.8	0.8	2.4	0.7	1.5	0.5	2.2	0.4	1.6	0.5	1.7	0.5	1.1	0.5
OLEA	2.4	1.5	3.3	4.3	2.9	2.1	1.0	0.4	ND	ND	ND	ND	ND	ND	ND	ND
2MGA	4.3	1.3	3.6	1.1	4.8	1.6	4.6	1.5	1.7	0.3	1.6	0.4	1.8	0.3	1.8	0.5
2MT1	1.9	1.3	1.4	0.7	2.1	1.3	1.8	1.0	0.4	0.1	0.3	0.1	0.4	0.1	0.4	0.1
2MT2	5.7	4.1	4.1	2.2	6.0	4.8	5.5	3.0	1.0	0.3	1.0	0.4	0.8	0.1	0.8	0.1
CPA	6.4	2.3	6.9	2.9	7.1	3.6	11.7	9.7	26.8	12.8	22.9	18.1	45.1	24.7	55.4	46.3
3HGA	9.4	3.5	10.5	4.1	10.1	5.0	11.0	4.9	2.0	0.6	2.5	0.7	1.8	0.6	2.2	0.7
MBTCA	7.1	3.0	6.2	3.1	6.9	3.7	7.3	3.7	1.7	0.5	1.6	0.4	1.6	0.5	1.6	0.5
MANNI	30.6	8.4	25.8	3.1	60.2	22.5	29.4	8.0	3.1	0.5	2.6	0.6	3.0	0.7	2.7	0.7
SOR	1.2	0.4	1.0	0.2	1.6	0.6	0.9	0.4	0.3	0.1	0.3	0.1	0.3	0.1	0.3	0.2
MERY	6.6	3.3	3.8	0.8	6.2	2.7	3.6	1.2	6.3	0.9	8.2	2.1	7.0	1.5	6.4	2.9
AGLU	40.8	20.7	25.1	6.9	82.4	91.7	29.6	8.5	5.4	1.0	4.6	1.3	5.0	0.9	4.1	1.4
BGLU	47.9	24.0	30.3	8.6	105.1	120.8	37.1	11.8	5.4	0.9	4.9	1.3	5.0	1.2	4.3	1.5

Table S2. Concentrations of most of the studied compounds compared with data in the literature in the same region. Abbreviations are defined in Table1. .

Samples	n=15	Elevated site 2022	City site 2022	Elevated site 2023	Vic 2021	Vic 2022	Mollerussa 2021	Mollerussa 2021	Valles 2022	Sierra Nevada Station	BCN 02/08/2019	BCN 16/11/2019	BCN 20/11/2019	BCN 18/12/2019	BCN 22/12/2019	Manlles 02/08/2019	Manlles 16/11/2019	Manlles 20/11/2019	Manlles 18/12/2019	Manlles 22/12/2019	Belver 02/08/2019	Belver 16/11/2019	Belver 20/11/2019	Belver 18/12/2019	Belver 22/12/2019	La pobla 2013	La pobla 2012	BCN 2012	BCN 2013															
Site	Urban	Sub-urban	Urban	Sub-urban	Sub-urban	Sub-urban	Rural	Rural	Industrial	High-altitude	Urban	Urban	Urban	Urban	Urban	Sub-urban	Sub-urban	Sub-urban	Sub-urban	Sub-urban	Rural	Rural	Rural	Rural	Rural	Rural	Rural	Rural	Urban	Urban														
Season	Spring	Spring	Winter	Winter	Summer	Winter	Spring	Spring	Winter	Summer	Summer	Autum	Autum	Autum	Autum	Summer	Autum	Autum	Autum	Autum	Winter	Summer	Autum	Autum	Autum	Autum	Winter	Spring	Spring	Winter														
Fraction	PM ₁₀	PM ₁₀	PM ₁₀	PM ₁₀	TSP	TSP	TSP	TSP	TSP	PM ₁₀	PM ₁₀	PM ₁₀	PM ₁₀	PM ₁₀	PM ₁₀	PM ₁₀	PM ₁₀	PM ₁₀	PM ₁₀	PM ₁₀	PM ₁₀	PM ₁₀	PM ₁₀	PM ₁₀	PM ₁₀	PM ₁₀	TSP	TSP	TSP	TSP														
Reference	Present work											Jaén et al. 2024											Jaén et al. 2021											van Drooge and Grimalt 2015										
	pg/m ³																																											
BAA	8	85	103	0	439	9	314	49	14	674	7	42	72	252	216	45	16	161	1459	1484	41	7	385	376	585	50	20	1790	120	330														
C+T	29	207	247	0	621	22	608	174	49	1127	28	61	152	358	410	84	57	282	1938	3002	73	18	594	490	1008	86	40	2020	220	570														
BBJKFL	37	351	433	0	1060	140	1255	588	158	3449	21	110	303	912	777	101	71	797	7783	8199	86	33	2458	1961	4856	193	140	3610	300	810														
BEP	19	179	232	0	1017	62	749	291	55	1595	9	145	188	534	404	112	60	336	3015	3527	48	25	954	772	1416	129	170	1500	370	650														
BAP	10	168	217	0	596	19	522	87	39	1540	-	59	114	403	335	38	44	249	3355	3240	35	13	969	817	1600	80	120	1490	220	480														
DBAJANT	3	62	65	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	30	460	90	170														
IP	29	177	222	0	402	48	456	236	139	1161	10	51	148	348	311	54	44	411	2331	2493	68	25	999	654	1131	143	130	1580	220	530														
BGHP	33	220	263	0	683	182	797	341	215	2174	15	113	271	650	727	102	49	520	3862	4091	93	30	1165	916	1601	182	210	1250	430	690														
COR	6	64	69	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	90	650	240	370														
3mPHE	11	17	14	0	224	39	117	14	18	101	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-												
2mPHE	14	27	20	0	310	46	159	16	23	150	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-											
9mPHE	9	13	12	0	150	17	71	10	14	85	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-											
1mPHE	9	31	26	0	221	15	119	10	13	164	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-											
17dmPHE	9	33	28	0	259	16	133	14	18	315	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-											
1+3mPHE	3	61	59	0	177	5	158	14	8	235	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-											
RET	19	410	487	0	866	52	861	41	89	4242	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0	3240	10	130														
4mPYR	4	29	28	0	62	4	97	9	7	154	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-											
1mPYR	2	23	23	0	57	5	75	8	6	135	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-											
9FLO	30	173	162	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	10	220	50	120													
ANQ	542	484	660	0	2689	372	318	240	474	678	31	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	30	380	100	160	160													
2mANQ	70	106	128	0	520	152	152	139	168	299	7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	10	220	50	120														
BAF	24	64	88	0	171	13	88	74	19	209	-	28	45	65	69	23	8	41	164	377	14	4	75	75	114	13	10	710	100	270														
norHOP	36	62	36	0	359	18	249	38	48	419	31	91	173	527	460	137	21	28	175	181	9	8	25	48	65	11	460	300	1090	1140														
HOP	29	53	34	0	298	10	217	30	52	377	27	232	230	533	556	124	38	30	179	150	10	12	31	51	56	12	410	260	1070	1090														
	ng/m ³																																											
GAL	3	11	21	0	12	1	23	1	1	75	0.3	0.2	6	6	11	1	0.3	29	93	161	2	1	46	49	79	6	2	190	1	15														
MANNO	2	10	18	0	10 BLD	17	1	1	1	68	0.2	0.4	8	8	12	1	1	29	99	343	97	7	85	98	118	18	1	252	2	13														
LEV	26	150	271	0	128	2	207	12	4	535	2	6	74	92	136	17	6	401	1385	4979	97	37	829	963	1168	290	9	1600	18	156														
MANNI	40	4	4	0	22	41	8	22	47	31	8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	169	10	28	3														
SOR	2	1	0.7	0.0	4	21	1	2	4	2	0.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-												
SA	24	12	18	0	21	30	10	10	20	22	9	5	3	5	10	3	7	3	7	10	3	15	13	13	16	16	74	68	24	47														
GLU	6	2	3	0	1	4	2	1	4	3	3	1	1	1	4	1	1	1	2	4	1	2	3	3	6	3	9	22	6	9														
MA	43	7	10	0	2	12	4	2	11	36	8	8	1	3	2	2	39	5	7	3	1	47	3	3	2	2	99	27	20	35														
PHA	2	2	2	0	1	2	3	10	2	2	2	1	2	1	4	9	16	3	2	11	11	2	4	4	8	2	20	33	22	19														
AZA	6	3	5	0 BLD	14	2	7	3	3	3	2	6	4	14	9	3	6	5	14	15	2	7	11	12	24	6	21	77	18	19														
2MGA	7	2	2	0	1	19	1	5	20	2	15	24	0.3	1	2	1	26	1	2	1	0.3	52	1	2	2	1	98	6	36	9														
2MT1	3	0	0.6	0.0	1	14	1	4	16	1	16	4	0.3	1	2	0.2	3	1	2	1	0.1	20	3	2	8	1	121	2	27	2														
2MT2	8	1	1	0	2	38	1	9	45	2	42	12	1	2	7	1	16	2	3	2	0.1	102	4	3	8	2	381	8	111	14														
CPA	31	88	134	0	19	25	8	7	10	3	8	1	1	2	3	2	1	2	1	1	0.5	1	3	3	4	3	135	48	63	26														
3HGA	17	2	3	0	1	4	2	1	5	2	4	5	1	2	0.4	1	12	1	3	2	0.3	25	1	2	1	1	48	8	6	8														
MBTCA	13	2	2	0	1	2	1 BLD	3 BLD	3	5	3	5	1	0.5	0.1	1	14	1	2	1	0.1	14	0.1	0.5	0.2	0.2	45.4	7.1	7.9	3.3														
AGL	44	6	6	0	25	1	18	37	29	156	6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	258.5	46.4	105.6	49														
BGL	56	7	6	0	23 BLD	20	40	33	193	7	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	296.2	58.9	106.3	57.8														