

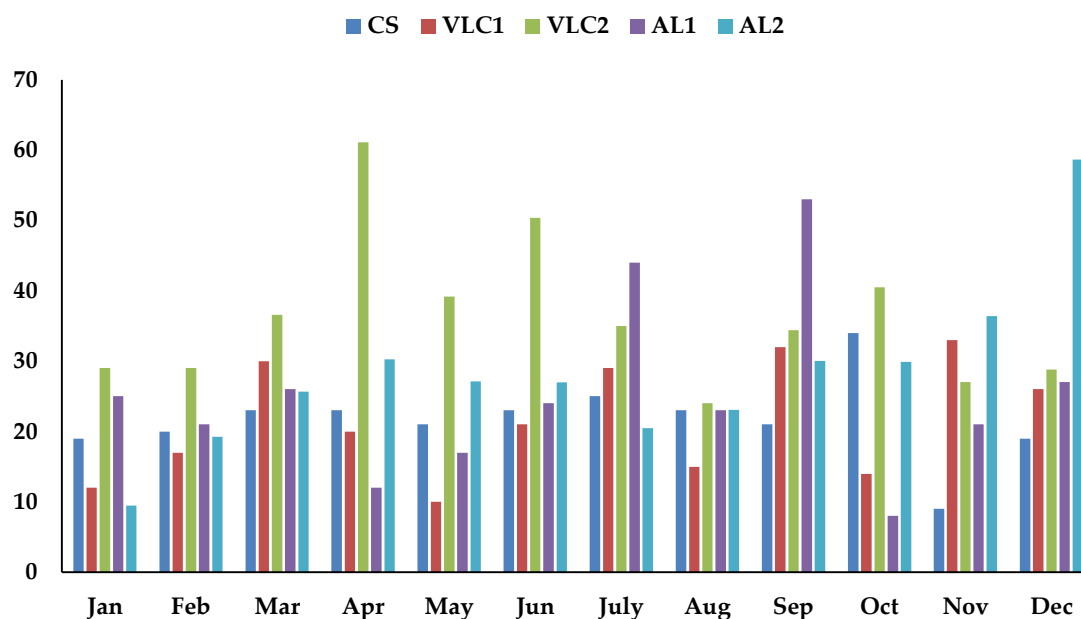
Supplementary Materials: Multi-oxygenated organic compounds in fine particulate matter collected in the Western Mediterranean Area

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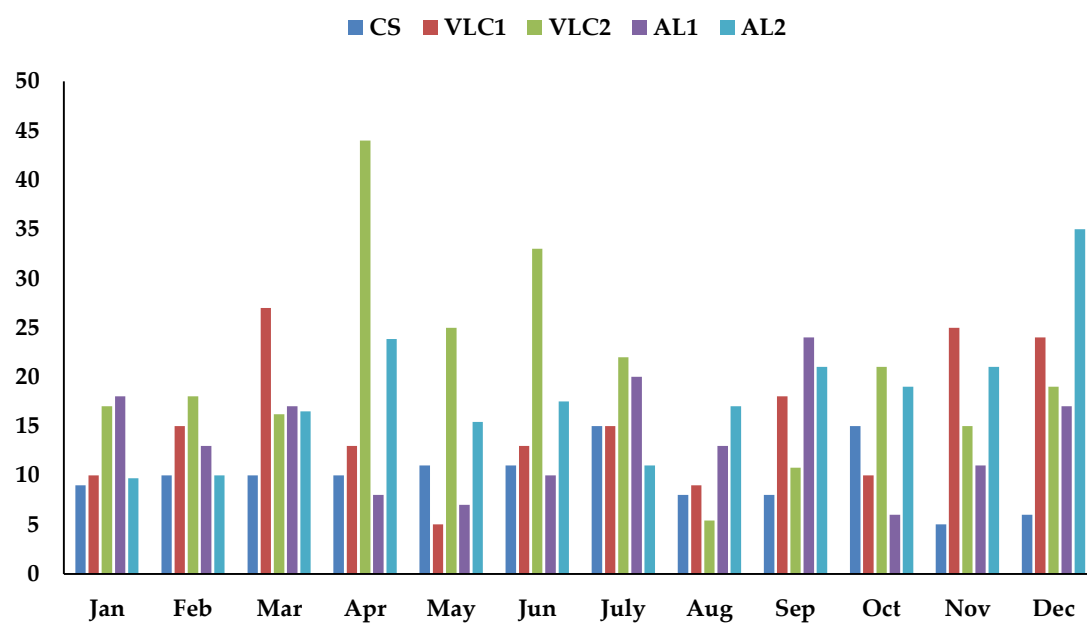


Figure S1. Map showing the locations of the sampling sites of Western Mediterranean Area, Spain.

a)



b)



c)

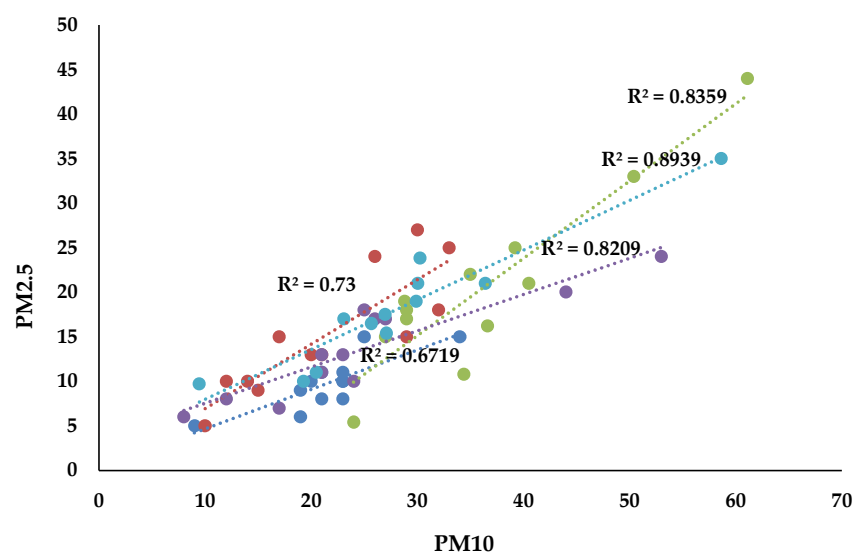


Figure S2. Correlations between PM10 to PM2.5 monthly in 5 locations (a) PM10 data; (b) PM2.5 data; (c) Correlations PM10 to PM2.5.

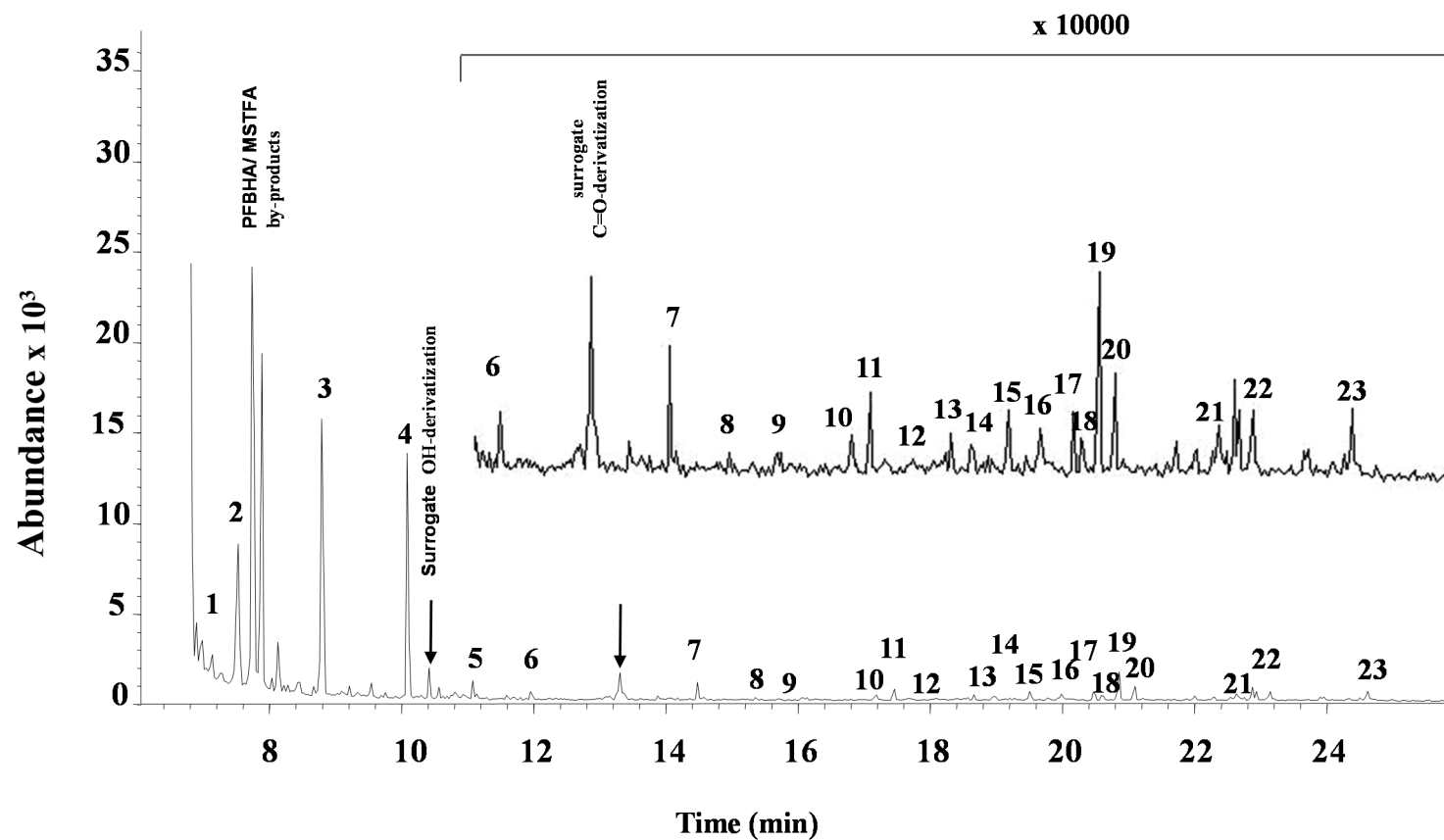


Figure S3. GC-MS extracted ion chromatogram (m/z 73+181) obtained from sub-urban sample (Valencia 1). 1. Phenol, 2. Oxalic acid, 3. Benzoic acid, 4. Succinic acid, 5. Glutaric acid, 6. Malic acid, 7. Levoglucosan, 8. Phtalic acid, 9. Azelaic acid, 10. Myristic acid, 11. Glyoxal, 12. Pentadecanoic acid, 13. Palmitoleic acid, 14. Palmitic acid, 15. Margaric acid, 16. Tetradecanoic acid, 17. Oleic acid, 18. Linoelic acid, 19. Stearic acid, 20. Nonadecanoic acid, 21. Eicosanoic acid, 22. Heneicosanoic acid, and 23. Tricasanoic acid.

Table S1. Classification of detected oxygenated organic compounds based on functional groups.

Family	Number	Compounds
n-Alcohol	8	phenol, o-cresol, m-cresol, p-cresol, benzyl alcohol, resorcinol, pyrocatechol, hydroquinone
Anhydrosugar	1	levoglucosan
Aldehydes	9	furfural, benzaldehyde, butanal, p-tolualdehyde, glyoxal, methylglyoxal, 2,3-butadione, hexanal, octanal
MCA	22	C6-carboxylic acid, C6-carboxylic acid, C7-carboxylic acid, benzoic acid, octanoic acid, C14-carboxylic acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitoleic acid, palmitic acid, margaric acid, acid, linoleic acid, stearic acid, nonadecanoic acid, C19-Carboxylic acid, eicosanoic acid, heneicosanoic acid, docosanoic acid, tricosanoic acid
DCA	18	oxalic acid, malonic acid, maleic acid, succinic acid, glutaric acid, 2-methylglutaric acid, C8-carboxylic acid, 3-methylglutaric acid, malic acid, adipic acid, pimelic acid, C7-diacid compound, phthalic acid, sebacic acid, azelaic acid, tetradecanoic acid, pentadecanedioic acid, C12-carboxylic acid
Hydroxy-aldehyde compound	7	2-hydroxybenzaldehyde, 3-hydroxybenzaldehyde, 4-hydroxybenzaldehyde, 2,3-dihydroxybenzaldehyde, 2,5-dihydroxybenzaldehyde, 2,4-dihydroxybenzaldehyde, 3,4-dihydroxybenzaldehyde
Hydroxyl-MCA	3	hydroxypentanoic acid, C19-carboxylic cid, C19-carboxylic cid
Keto-MCA	4	4-oxobutanoic acid, n-oxopentenoic acid, n-oxopentanoic acid, 5-oxopentanoic acid
Keto-DCA	1	4-oxopimelic acid

MCA: mono-carboxylicacid; DCA: dicarboxylicacid.

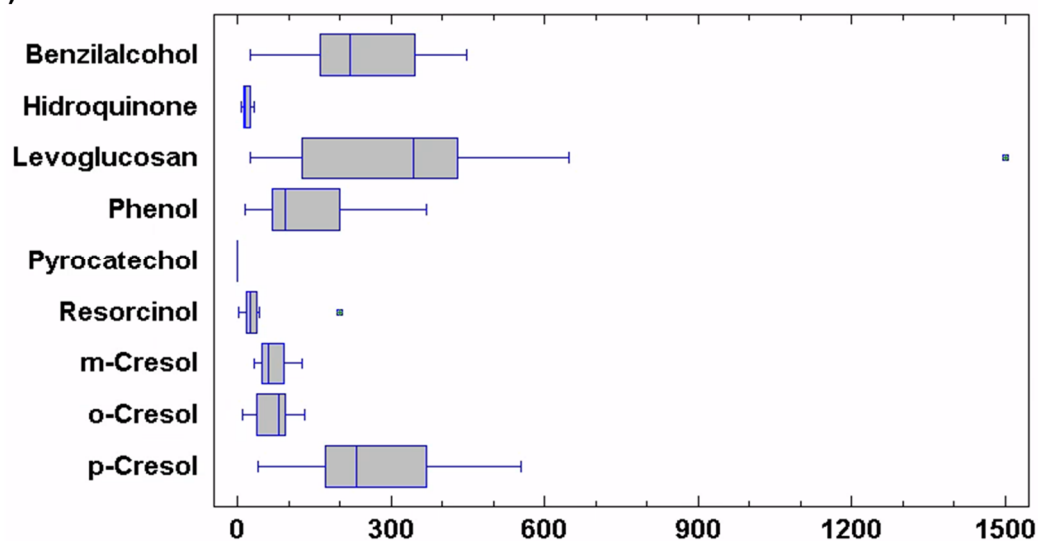
Table S2. Concentration average and mean concentration (ng m⁻³) of oxygenated compounds of the fine PM.

Species	Formula	Code	MW	Cases	Range	Average	Median
Glyoxal	C ₂ H ₂ O ₂	a	58	53	3-43	15	11
Butanal	C ₄ H ₈ O	a	72	14	6-64	28	10
Methylglyoxal	C ₃ H ₄ O ₂	a	72	53	0.3-11	1.6	1.0
Oxalic acid	C ₂ H ₂ O ₄	d	90	41	0.9-31	10	10
Phenol	C ₆ H ₆ O	o	94	30	14-368	98	46
Furfural	C ₅ H ₄ O ₂	a	96	31	0.3-5	0.8	0.3
4-Oxobutanoic acid	C ₄ H ₆ O ₃	a-m	102	1	0-48	48	10
Malonic acid	C ₃ H ₄ O ₄	d	104	38	0-152	14	8
Benzaldehyde	C ₇ H ₆ O	a	106	31	1.5-4	1.8	1.0
o-Cresol	C ₇ H ₈ O	o	108	13	11-131	55	27
m-Cresol	C ₇ H ₈ O	o	108	11	32-126	61	35
p-Cresol	C ₇ H ₈ O	o	108	11	41-555	246	146
Benzylalcohol	C ₇ H ₈ O	o	108	7	24-447	232	127
Resorcinol	C ₆ H ₆ O ₂	o	110	15	1.9-199	25	7
Pyrocatechol	C ₆ H ₆ O ₂	o	110	12	0.02-0.6	0.2	0.1
Hydroquinone	C ₆ H ₆ O ₂	o	110	11	8-32	17	10
C6-Carboxylic acid Is.1	C ₆ H ₁₀ O ₂	m	114	31	2-28	7	5
C6-Carboxylic acid Is.2	C ₆ H ₁₀ O ₂	m	116	13	1.9-14	7	1.3
Maleic acid	C ₄ H ₄ O ₄	d	116	30	1.6-95	16	5
n-Oxopentanoic acid	C ₅ H ₈ O ₃	a-m	116	1	0-6	6	1.1
5-Oxopentanoic acid	C ₅ H ₈ O ₃	a-m	116	1	0-7	7	1.4
Succinic acid	C ₄ H ₆ O ₄	d	118	48	10-470	122	110
n-Hydroxypentanoic acid	C ₅ H ₁₀ O ₃	o-m	118	1	0-50	55	10
p-Tolualdehyde	C ₈ H ₈ O	a	120	3	0.01-0.06	0.04	0.01
2-Hydroxybenzaldehyde	C ₇ H ₆ O ₂	o-a	122	32	0.6-218	23	9
4-Hydroxybenzaldehyde	C ₇ H ₆ O ₂	o-a	122	25	0.5-3	2	1.3
3-Hydroxybenzaldehyde	C ₇ H ₆ O ₂	o-a	122	9	3-4	3	0.6
Benzoic acid	C ₇ H ₆ O ₂	m	122	53	3-367	54	26
Octanal	C ₈ H ₁₆ O	a	128	33	4-55	13	6
C7-Carboxylic acid	C ₇ H ₁₄ O ₂	m	130	18	1.9-13	4	1.2
Glutaric acid	C ₅ H ₈ O ₄	d	132	32	0-244	23	12
Malic acid	C ₄ H ₆ O ₅	d	134	31	0.8-103	10	4
3,4-Dihydroxybenzaldehyde	C ₇ H ₆ O ₃	o-a	138	31	0.1-21	6	4
2,5-Dihydroxybenzaldehyde	C ₇ H ₆ O ₃	o-a	138	33	5-6	5	3
2,3-Dihydroxybenzaldehyde	C ₇ H ₆ O ₃	o-a	138	18	0.2-0.4	0.3	0.1
2,4-Dihydroxybenzaldehyde	C ₇ H ₆ O ₃	o-a	138	9	4-28	14	2
Octanoic acid	C ₈ H ₁₆ O ₂	m	144	3	24-48	40	24
2-Methylglutaric acid	C ₆ H ₁₀ O ₄	d	146	26	4-85	24	13
3-Methylglutaric acid	C ₆ H ₁₀ O ₄	d	146	34	11-175	58	35
Adipic acid	C ₆ H ₁₀ O ₄	d	146	35	4-263	35	21
Pimelic acid	C ₇ H ₁₂ O ₄	d	160	54	3-998	226	174
C7-Dicarboxylic acid	C ₇ H ₁₂ O ₄	d	160	3	21-404	196	33
Levogluconan	C ₆ H ₁₀ O ₅	o	162	33	25-2274	431	149
Phtalic acid	C ₈ H ₆ O ₄	d	166	28	8-235	46	17
C8-Dicarboxylic acid	C ₈ H ₁₂ O ₄	d	172	6	9-92	44	41
4-Oxopimelic acid	C ₇ H ₁₀ O ₅	a-d	174	28	18-835	215	119
Azelaic acid	C ₉ H ₁₆ O ₄	d	188	43	8-649	84	51

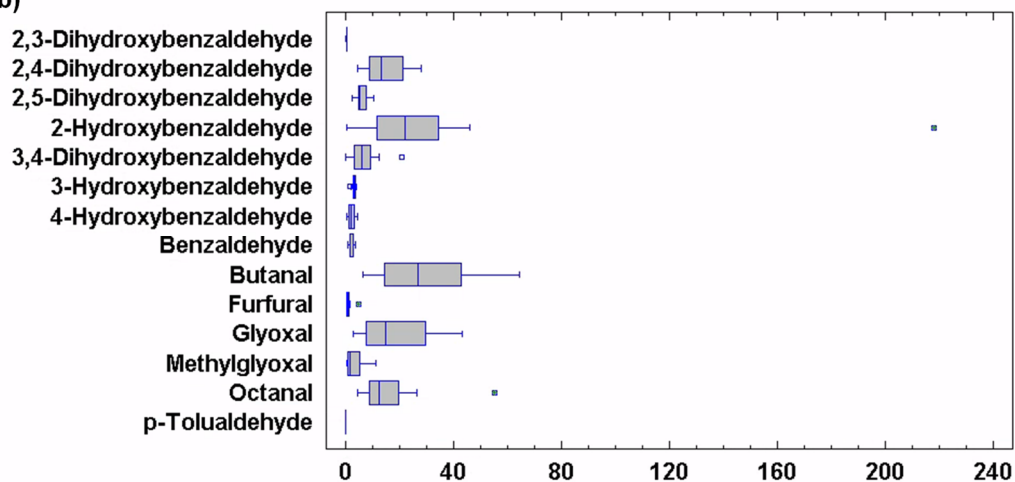
Lauric acid	C ₁₂ H ₂₄ O ₂	m	200	2	46-141	94	19
Sebacic acid	C ₁₀ H ₁₈ O ₄	d	202	39	2-696	197	182
Tridecanoic acid	C ₁₃ H ₂₆ O ₂	m	214	1	0-5	5	1.1
C14-Carboxylic acid	C ₁₄ H ₂₄ O ₂	m	224	2	16-52	34	7
Myristic acid	C ₁₄ H ₂₈ O ₂	m	228	58	6-259	52	47
C12-Dicarboxylic acid	C ₁₂ H ₂₀ O ₄	d	228	20	21-176	104	60
Pentadecanoic acid	C ₁₅ H ₃₀ O ₂	m	242	57	5-179	39	36
Palmitoleic acid	C ₁₆ H ₃₀ O ₂	m	254	33	14-621	133	107
Palmitic acid	C ₁₆ H ₃₂ O ₂	m	256	59	0-864	105	40
Tetradecanoic acid	C ₁₄ H ₂₆ O ₄	d	258	39	0-815	127	44
Margaric acid	C ₁₇ H ₃₄ O ₂	m	270	50	3-631	162	137
Pentadecanedioic acid	C ₁₅ H ₂₈ O ₄	d	272	1	0-11	11	2
Linoleic acid	C ₁₈ H ₃₂ O ₂	m	280	34	19-989	180	102
Oleic acid	C ₁₈ H ₃₄ O ₂	m	282	51	0-541	192	156
Stearic acid	C ₁₈ H ₃₆ O ₂	m	284	52	0-414	42	120
C19-Carboxylic acid	C ₁₉ H ₃₆ O ₂	m	296	7	28-194	102	54
Nonadecanoic acid	C ₁₉ H ₃₈ O ₂	m	298	52	0-737	122	90
C19-Hydroxy-carboxylic acid Is.1	C ₁₉ H ₂₆ O ₃	o-m	302	15	6-271	64	45
C19-Hydroxy-carboxylic acid Is.2	C ₁₉ H ₂₈ O ₃	o-m	304	14	10-382	111	61
Eicosanoic acid	C ₂₀ H ₄₀ O ₂	m	312	36	0-780	136	85
Heneicosanoic acid	C ₂₁ H ₄₂ O ₂	m	326	38	0-880	223	125
Docosanoic acid	C ₂₂ H ₄₄ O ₂	m	340	17	3-195	65	62
Tricosanoic acid	C ₂₃ H ₄₆ O ₆	m	354	25	0-458	100	67

Alcohol (o), Aldehyde (a), MCA (m), DCA (d), Hydroxy-aldehyde (o-a), Hydroxy-MCA (o-m), Keto-MCA (a-m), Keto-DCA (a-d).

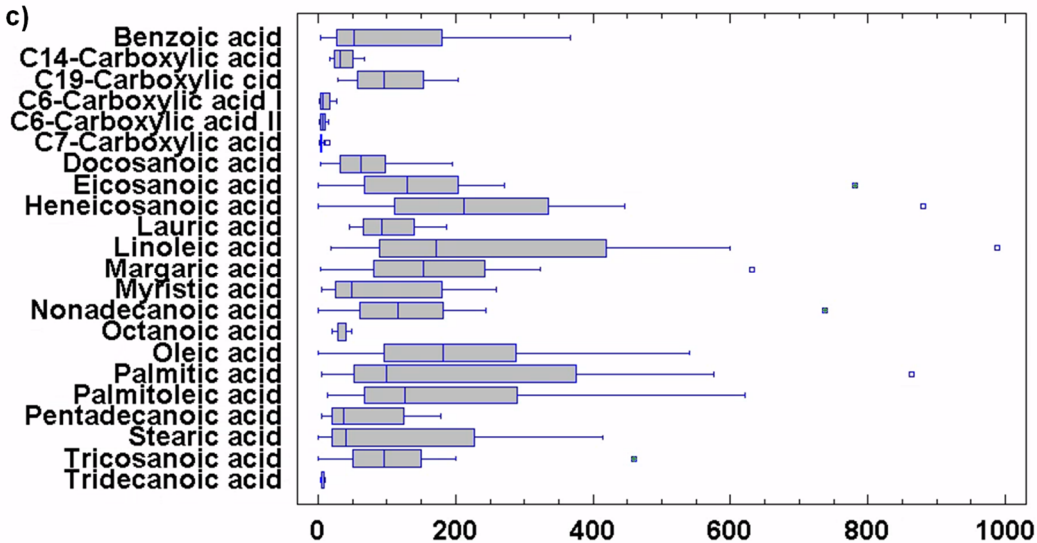
a)



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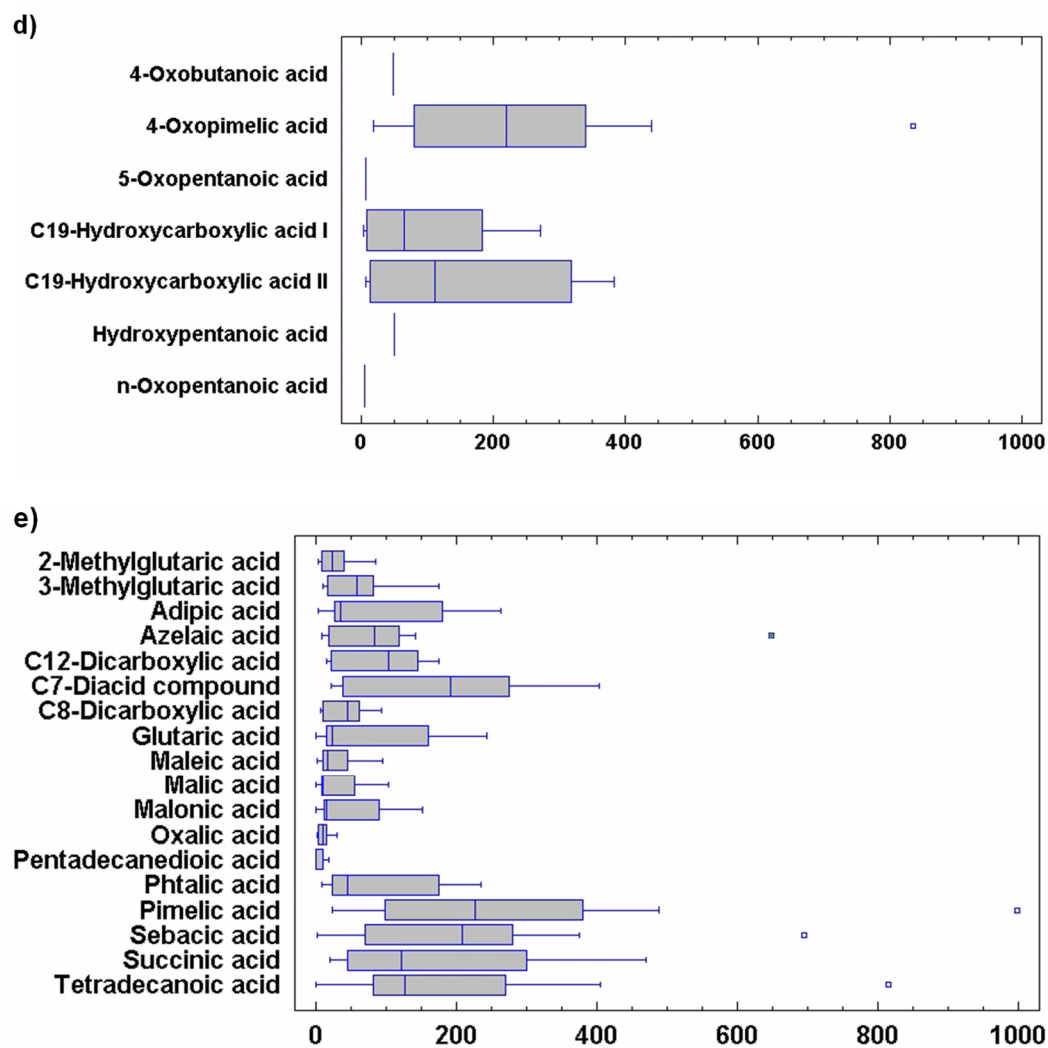


Figure S4. Box plot data with a detailed concentration values (in ng m⁻³) for each specie.

Table S3. Average ratios of concentrations of dicarboxylic acids collected at different locations and seasons.

dicarboxylic acids	Castellón				Valencia 1				Valencia 2				Alicante 1				Alicante 2			
	winter	spring	summer	autumn	winter	spring	summer	autumn	winter	spring	summer	autumn	winter	spring	summer	autumn	winter	spring	summer	autumn
C6/C9	0.36	0.50	0.27	0.52	0.32	0.62	0.44	0.36	N.D	N.D	N.D	N.D	0.52	0.39	0.38	0.18	N.D	N.D	N.D	N.D
C8/C9	0.48	0.48	0.31	0.68	0.22	0.72	0.47	0.38	N.D	N.D	N.D	N.D	0.43	0.51	0.28	0.48	N.D	N.D	N.D	N.D
C18:0/C18:1	0.04	0.08	0.14	0.05	0.07	0.09	0.09	0.04	0.64	1.02	0.54	1.20	0.17	0.14	0.13	0.12	0.18	N.D	N.D	N.D
C3/C4	0.14	0.06	0.71	0.22	0.10	0.10	0.27	0.14	N.D	0.01	0.12	0.03	0.05	0.06	0.21	0.11	N.D	N.D	N.D	N.D
C18/C16	0.30	0.73	0.47	0.14	0.24	0.69	0.42	0.17	0.94	1.63	1.39	2.02	0.78	0.41	0.42	0.69	0.06	1.12	0.99	N.D

N.D: not determined

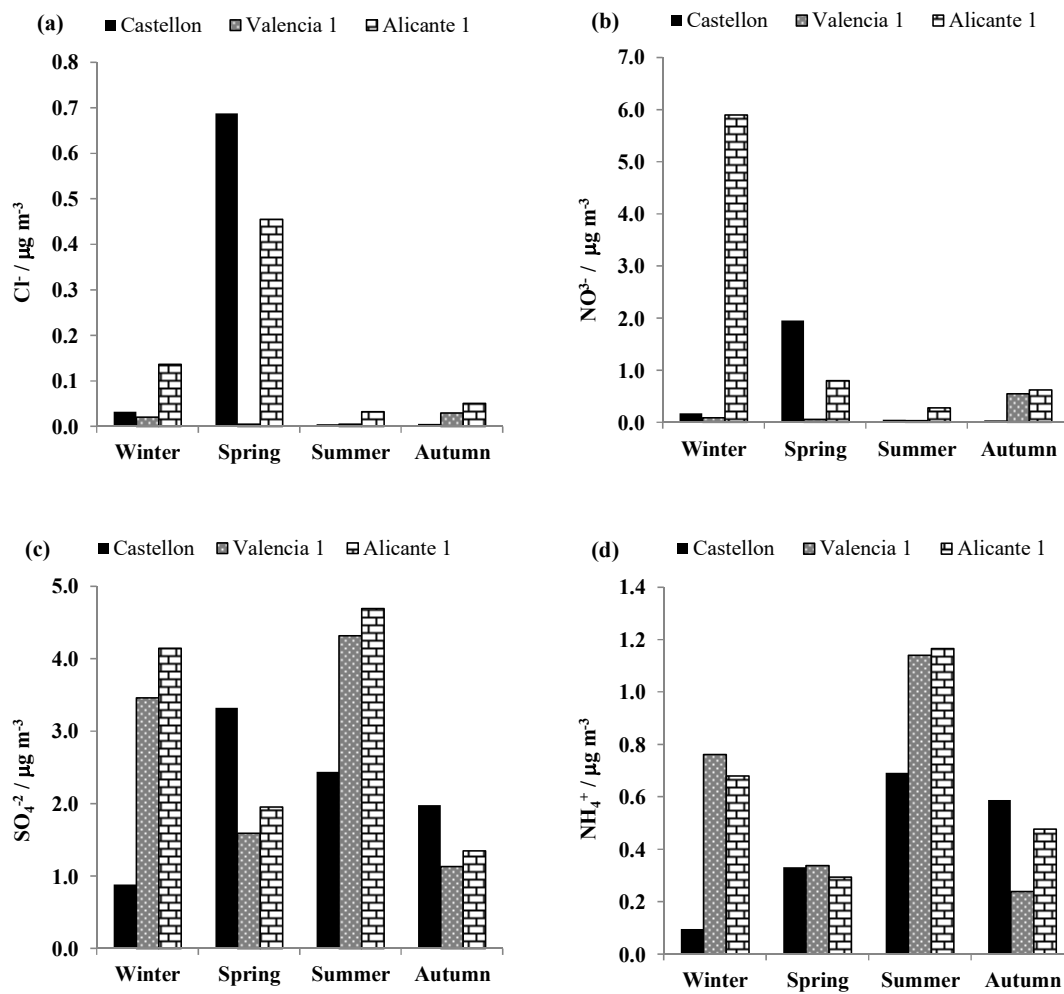


Figure S5. Seasonal trend of inorganic anions.