Supplementary Material of "$PM_{2.5}$-bound Organosulfates in two Eastern Mediterranean cities: The dominance of isoprene organosulfates"

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Table S1. Mean concentrations of O_3, NO_x and SO_2 for each seasonal period at both sampling sites.

Athens	Winter	Spring	Summer	Autumn
O_3 (μg m^{-3})	20.8 ± 9.49	34.2 ± 10.6	29.9 ± 13.1	23.2 ± 14.0
NO_x (μg m^{-3})	77.7 ± 33.3	71.2 ± 27.5	72.6 ± 20.8	130 ± 80.6
SO_2 (μg m^{-3})	14.0 ± 2.61	3.34 ± 2.44	2.92 ± 1.71	3.02 ± 1.37
Patra	Winter	Spring	Summer	Autumn
O_3 (μg m^{-3})	32.4 ± 7.57	34.2 ± 8.33	80.8 ± 15.5	54.7 ± 6.57
NO_x (μg m^{-3})	98.1 ± 29.2	53.9 ± 11.5	31.6 ± 5.81	86.9 ± 27.9

*SO_2 levels in Patra were not available

Table S2. Mass spectrometry parameters of the standards compounds.

Compounds/ Purity (%)	Molecular ion $[M-H]^-$	Exact mass	Mass error (ppm)	Product ions (m/z)	Collision Energy (eV)
MeS	$CH_3O_4S^-$	110.9758	-2.70	$\cdot SO_3^-$(79.9572) $\cdot SO_4^-$(95.9523)	27
EtS	$C_2H_5O_4S^-$	124.9914	+0.80	HSO_4^-(96.9601) $\cdot SO_3^-$(79.9572)	16
PrS (94%)	$C_3H_7O_4S^-$	139.0071	-2.88	HSO_4^- (96.9601) $\cdot SO_3^-$ (79.9572)	17
OctS (95%)	$C_8H_{17}O_4S^-$	209.0853	-0.48	HSO_4^- (96.9601) $\cdot SO_3^-$ (79.9572)	23
BS (>99%)	$C_7H_7O_4S^-$	187.0071	+1.07	$\cdot SO_4^-$ (95.9523) $\cdot SO_3^-$ (79.9572)	25
PhS (98%)	$C_6H_5O_4S^-$	172.9914	+2.89	$C_6H_5O\cdot$(93.0340) $\cdot SO_3^-$ (79.9572)	17
m-MBS (>99%)	$C_8H_9O_4S^-$	201.0227	-1.60	$\cdot SO_4^-$(95.9523) $\cdot SO_3^-$ (79.9572)	27
p-MBS (>99%)	$C_8H_9O_4S^-$	201.0227	+4.48	$\cdot SO_4^-$(95.9523) $\cdot SO_3^-$ (79.9572)	27
p-MPhS (85%)	$C_7H_7O_4S^-$	187.0071	+3.48	$C_7H_7O\cdot$(107.0497) $\cdot SO_3^-$ (79.9572)	17
HAS (95%)	$C_3H_5O_5S^-$	152.9863	-1.56	$\cdot SO_3^-$(79.9572) HSO_4^-(96.9601)	21
GAS (40%)	$C_2H_3O_6S^-$	154.9656	+2.58	HSO_4^-(96.9601) $C_2H_3O_3\cdot$(75.0082)	19
LAS (13%)	$C_3H_5O_6S^-$	168.9812	+0.59	HSO_4^-(96.9601) $C_3H_5O_3$ (75.0082)	14
Et-d5S	$C_2D_5O_4S^-$	130.0228	+3.87	DSO_4^-(97.9658) $\cdot SO_3^-$(79.9572)	22
10-CSA	$C_{10}H_{15}O_4S^-$	231.0697	+1.30	-	-

Table S3. Validation data of the applied method for the determination of OS.

Compound	Linear range	Linearity	R^2	Precision, RSD% (intraday)		Accuracy ± SD (%)		LOD	LOQ
				25.0 ppb	100 ppb	25.0 ppb	100 ppb	ng sample^{-1}	
MeS	34.0-500	y=0.0052(±0.00023) x-0.0117(±0.0589)	0.9961	7.83	2.61	86.1 ± 5.67	81.1 ± 3.98	11	34
EtS	1.7-500	y=0.0081(±0.00012) x-0.0242(±0.0234)	0.9988	1.20	2.00	98.1 ± 5.02	85.8 ± 4.40	0.57	1.7
PrS	2.4-500	y=0.0174(±0.00027) x-0.0569(±0.0536)	0.9986	2.76	2.27	82.0 ± 4.26	78.5 ± 3.52	0.80	2.4
OctS	1.5-250	y=0.0394(±0.00035) x-0.0484(±0.0037)	0.9996	1.60	0.44	89.2 ±4.32	83.2 ± 4.14	0.51	1.5
BS	1.8-250	y=0.0346(±0.00032) x-0.0386(±0.0332)	0.9996	1.83	1.09	91.9 ± 3.92	104 ± 5.09	0.59	1.8
PhS	2.3-250	y=0.0215(±0.00018) x-0.0132(±0.0191)	0.9997	1.42	0.76	83.4 ± 4.72	77.5 ± 3.41	0.77	2.3
m+p-MBS	2.4-250	y=0.0695(±0.00064) x-0.0090(±0.0067)	0.9995	1.39	0.37	85.0 ± 3.24	94.5 ± 4.43	0.78	2.4
p-MPhS	8.0-250	y=0.0068(±0.00005) x+0.0221(±0.0048)	0.9998	4.06	2.04	82.1 ± 5.03	90.6 ± 1.22	2.6	8.0
HAS	1.00-500	y=0.0029(±0.00002) x-0.0087(±0.0048)	0.9996	8.81	1.79	92.3 ± 5.45	85.8 ± 1.63	0.12	0.37
GAS*	11.0-5000	y=0.0003(±0.000006) x-0.0240(±0.0125)	0.9969	6.42	4.87	91.3 ± 2.14	83.2 ± 2.75	3.5	11
LAS*	100-5000	y=0.0004(±0.000007) x-0.0409(±0.0158)	0.9988	9.30	8.98	108 ± 3.77	103 ± 6.36	27	81
10-CSA	2.2-250	y=0.0040(±0.00004) x+0.0104(±0.0042)	0.9995	3.72	0.39	86.7 ± 5.46	89.4 ± 3.52	0.72	2.2

*The respective concentrations of GAS and LAS for the precision and accuracy experiments were 250 ppb and 1000 ppb

**The RSD of the precision experiments for the internal standard (ethyl-d5 sulfate) was <5.00%

Table S4. Identification and quantification data about the studied OS compounds

Compound	Molecular ion $[M\text{-}H]^-$	Exact mass $[M\text{-}H]^-$	Possible precursor	Quantification
iOS139	$C_2H_3SO_5^-$	138.9707	Isoprene [a]	HAS
iOS167	$C_4H_7SO_5^-$	167.0014	MACR, MVK [b]	HAS
iOS171	$C_3H_7SO_6^-$	170.9969	Isoprene [c]	HAS
iOS183	$C_4H_7SO_6^-$	182.9963	Isoprene, MACR, MVK [b, d]	LAS
iOS185	$C_3H_5SO_7^-$	184.9761	Isoprene [c]	LAS
iOS197	$C_5H_9SO_6^-$	197.0112	Isoprene, MACR, MVK [a]	LAS
iOS199	$C_4H_7SO_7^-$	198.9918	Isoprene, MVK [a, d, e]	LAS
iOS211	$C_5H_7SO_7^-$	210.9918	Isoprene [a, d]	LAS
iOS213	$C_5H_9SO_7^-$	213.0074	Isoprene [a, d]	LAS
iOS215	$C_5H_{11}SO_7^-$	215.0231	Isoprene [a, d]	LAS
iOS229	$C_5H_9SO_8^-$	229.0024	Isoprene [c]	LAS
iOS231	$C_5H_{11}SO_8^-$	231.0180	Isoprene [c]	LAS
mtOS249	$C_{10}H_{17}SO_5^-$	249.0802	Monoterpenes [f]	10-CSA
mtOS251	$C_9H_{15}SO_6^-$	251.0589	Limonene, β-caryophyllene [a, h]	10-CSA
mtOS267	$C_9H_{15}SO_7^-$	267.0544	Limonene, α-pinene [a, f]	10-CSA
mtOS279	$C_{10}H_{15}SO_7^-$	279.0544	Monoterpenes [e, g]	10-CSA
mtOS281	$C_9H_{14}O_8S^-$	281.0338	α-Pinene [i]	10-CSA
iNOS260	$C_5H_{10}NSO_9^-$	260.0082	Isoprene [a, d]	OctS
mtNOS294	$C_{10}H_{16}NSO_7^-$	294.0653	Monoterpenes [a, d]	OctS
lNOS296	$C_9H_{14}NSO_8^-$	296.0446	Limonene [a, d]	OctS
mtNOS310	$C_{10}H_{16}NSO_8^-$	310.0602	α+β-Pinene [a]	OctS
dNOS326	$C_{10}H_{16}NSO_9^-$	326.0551	decalin [j]	OctS
napOS257	$C_{10}H_9SO_6^-$	257.0139	naphthalene [k]	PhS
napOS273	$C_{10}H_9SO_8^-$	273.0063	naphthalene [k]	PhS
napOS275	$C_{10}H_{11}SO_8^-$	275.0228	naphthalene [k]	PhS
napOS320	$C_{10}H_{10}NSO_9^-$	320.0021	naphthalene [k]	PhS
mnapOS217	$C_6H_4NSO_6^-$	217.9751	2-methylnaphthalene [k]	PhS
mnapOS231	$C_9H_{11}SO_5^-$	231.0333	2-methylnaphthalene [k]	PhS
mnapOS287	$C_{11}H_{11}SO_7^-$	287.0243	2-methylnaphthalene [k]	PhS
mnapOS289	$C_{11}H_{13}SO_7^-$	289.0387	2-methylnaphthalene [k]	PhS
cdOS251	$C_{10}H_{19}SO_5^-$	251.0950	cyclodecane [j]	OctS
cdOS265	$C_{10}H_{17}SO_6^-$	265.0751	cyclodecane [j]	OctS
dOS269	$C_9H_{17}SO_7^-$	269.0700	decalin [j]	OctS
dOS295	$C_{10}H_{15}SO_8^-$	295.0493	decalin [j]	OctS
doOS279	$C_{12}H_{23}SO_5^-$	279.1272	dodecane [j]	OctS

[a]Surrat et al., 2008 [b] Schindelka et al., 2013 [c] Chen et al., 2020 [d] Hettiyadura et al., 2019 [e] Nozière et al., 2010 [f] Wang et al., 2017 [g] Kristensen and Glasius 2011 [h] Chan et al., 2011 [i] Brüggemann et al., 2019 [j] Riva et al., 2016 [k] Riva et al., 2015

Table S5. Mean concentrations of PAHs and inorganic ions for each seasonal period at both sampling sites.

Athens	Winter	Spring	Summer	Autumn
Naphthalene (pg m^{-3})	9.72 ± 0.44	9.50 ± 0.34	9.63 ± 0.31	9.66 ± 0.34
Acenaphthylene (pg m^{-3})	17.2 ± 0.78	16.8 ± 0.61	17.0 ± 0.54	17.1 ± 0.60
Acenaphthene (pg m^{-3})	4.49 ± 0.20	4.38 ± 0.16	32.5 ± 45.8	101 ± 205
Fluorene (pg m^{-3})	15.5 ± 16.6	4.01 ± 8.16	25.2 ± 44.9	1.86 ± 0.07
Phenanthrene (pg m^{-3})	4.11 ± 0.19	46.9 ± 44.5	191 ± 236	43.8 ± 55.7
Anthracene (pg m^{-3})	6.38 ± 0.29	68.6 ± 61.4	26.3 ± 51.7	6.31 ± 0.22
Patra	Winter	Spring	Summer	Autumn
Naphthalene (pg m^{-3})	248±832	13.1 ± 0.99	41.4 ± 75.9	13.7 ± 1.1
Acenaphthylene (pg m^{-3})	331 ± 1147	23.3 ± 1.74	39.7 ± 5.91	24.3 ± 1.92
Acenaphthene (pg m^{-3})	247 ± 901	6.08 ± 0.45	26.0 ± 47.8	6.34 ± 0.50
Fluorene (pg m^{-3})	220 ± 696	28.6 ± 39.3	4.26 ± 0.64	2.64 ± 0.21
Phenanthrene (pg m^{-3})	182 ± 547	160 ± 68.8	91.2 ± 123	5.82 ± 0.46
Anthracene (pg m^{-3})	237 ± 727	208 ± 85.3	14.5 ± 2.18	8.99 ± 0.71
Na^+ (μg m^{-3})	0.89 ± 0.65	0.24 ± 0.23	ND	0.010 ± 0.024
NH_4^+ (μg m^{-3})	0.34 ± 0.41	1.50 ± 0.55	0.53 ± 0.37	1.15 ± 0.93
K^+ (μg m^{-3})	0.78 ± 0.43	0.43 ± 0.39	0.04 ± 0.14	0.30 ± 0.26
Mg^{+2} (μg m^{-3})	0.03 ± 0.05	0.02 ± 0.06	0.05 ± 0.08	ND
Ca^{+2} (μg m^{-3})	1.25 ± 0.90	0.68 ± 0.53	1.22 ± 0.60	0.07 ± 0.20
Cl^- (μg m^{-3})	0.78 ± 0.73	0.64 ± 0.44	0.40 ± 0.42	ND
NO_3^- (μg m^{-3})	3.38 ± 1.88	1.97 ± 1.04	1.23 ± 0.66	0.66 ± 0.45
SO_4^{-2} (μg m^{-3})	2.71 ± 1.48	4.12 ± 1.72	1.25 ± 1.71	3.29 ± 2.82

Non-sea salt sulfate (NSS) was calculated using the following equation, as described in (Mukherjee et al., 2021)

$NSS = [SO_4^{-2}]_{total} – [Na^+] \times 0.25$

where 0.25 is the weight ratio of SO_4^{-2}/Na^+ in seawater

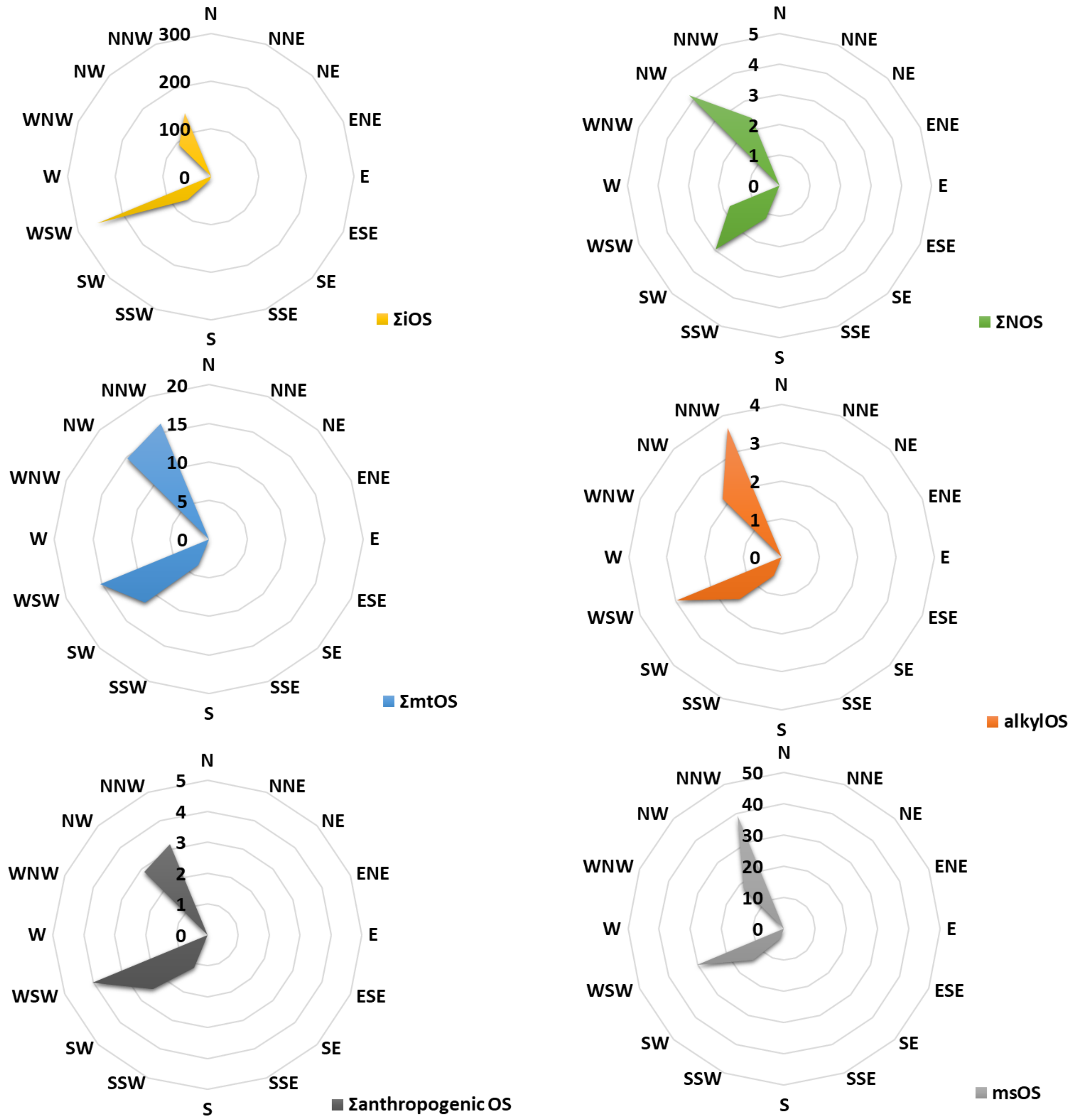

Fig. S1. Correlation of the different OS groups mean concentrations (ng m-3) with the wind patterns.

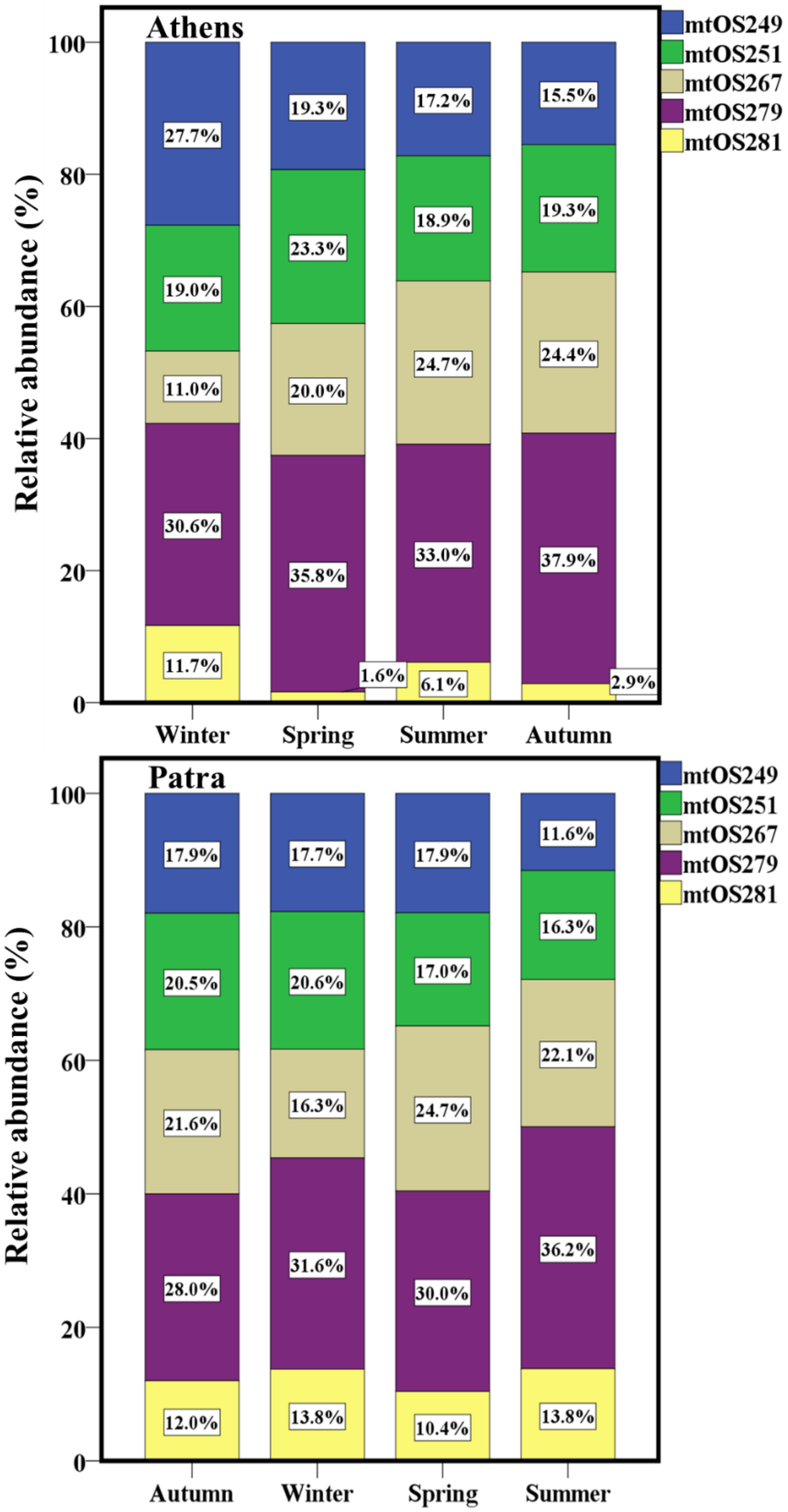

Fig. S2. Mean relative abundance (%) of the different mtOS species at both sampling sites.

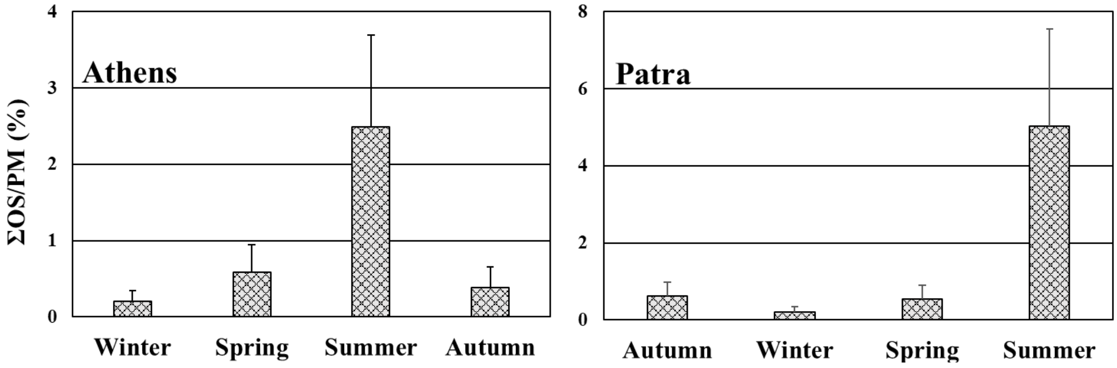

Fig. S3. Mean contribution of ΣOS to PM during each seasonal period at both sampling sites.

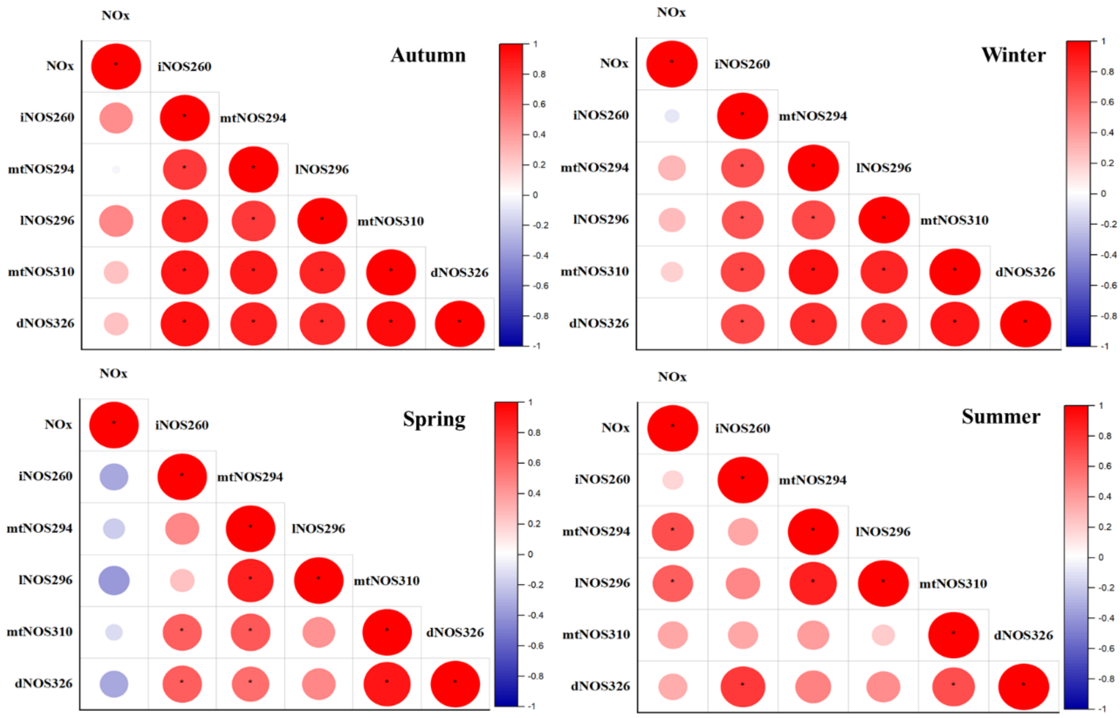

Fig. S4. Correlations between each individual NOS compound, SO_2 and NO_x during each sampling period in Patra (* indicate p<0.05).

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