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Supplement of

Composition and mass size distribution of nitrated and oxygenated aromatic compounds in ambient particulate matter from southern and central Europe – implications for the origin

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Section S1. Chemicals and solutions

Solvents including methanol (MeOH, Chromasolv, LC-MS grade; Fluka, Buchs, Switzerland), tetrahydrofuran (THF, LiChrosolv, HPLC grade; Merck, Darmstadt, Germany), high-purity water (18.2 M Ω cm; Elga PURELAB, Veolia Water Technologies, Celle, Germany), ethylenediaminetetraacetic acid (EDTA, trace metals basis; Sigma-Aldrich, St. Louis, USA), formic acid and ammonium formate (grade eluent additive for LC-MS; Fluka) were used for LC-MS mobile phase and sample preparation for NMAHs. Dichloromethane (DCM), *n*-hexane, and ethyl acetate (Suprasolv, GC-MS grade, Merck) were used for N/OPAH analysis. Analytical standards used in our study, their acronyms, and suppliers are listed in Tables 1 and S1. The internal standards (IS) of 2,4,6-trinitrophenol (picric acid, aqueous solution 1.0%; Sigma-Aldrich) and 4-nitrophenol-d₄ (4-NP-d₄; LGC, Teddington, UK) were used for NMAH quantification, whereas 1-nitronaphthalene-d₇, 2-nitrofluorene-d₉, 9-nitroanthracene-d₉, 3-nitrofluoranthene-d₉, 1-nitropyrene-d₉, 6-nitrochrysene-d₁₁, 9,10-anthraquinone-d₈, and 9-fluorenone-d₈ (Chiron, Norway) were used for N/OPAH quantification. Individual stock solutions of NMAH standards were prepared in methanol at concentrations of 200 $\mu\text{g mL}^{-1}$, whereas those for N/OPAHs were prepared in toluene at 10 $\mu\text{g mL}^{-1}$. Standard mixtures were prepared for each substance class from individual stock solutions, and further used for preparation of calibration standards of NMAHs in methanol/water mixture (3/7, v/v) containing 5 mM ammonium formate buffer pH 3 and 400 μM EDTA (injection solvent), and calibration standards of N/OPAHs in ethyl acetate. NMAH and N/OPAH calibration standards were prepared in the concentration range of 0.1 to 500 and 0.25 to 1000 $\text{pg } \mu\text{L}^{-1}$, with a fixed IS concentration of 100 and 200 $\text{pg } \mu\text{L}^{-1}$, respectively.

Table S1. Target analytes, their acronyms, and suppliers

Analyte	Abbreviation	Supplier
3-Nitrosalicylic acid	3-NSA	Sigma-Aldrich
5-Nitrosalicylic acid	5-NSA	Sigma-Aldrich
4-Nitrocatechol	4-NC	Sigma-Aldrich
4-Nitroguaiacol	4-NG	Sigma-Aldrich
4-Methyl-5-nitrocatechol	4-M-5-NC	Santa Cruz Biotechnologies
4-Nitrophenol	4-NP	(>96%) Sigma-Aldrich
2,4-Dinitrophenol	2,4-DNP	Sigma-Aldrich
3-Methyl-4-nitrophenol	3-M-4-NP	Sigma-Aldrich
3-Methyl-5-nitrocatechol	3-M-5-NC	(>95%) Chemhere Co. Ltd
2-Methyl-4-nitrophenol	2-M-4-NP	Sigma-Aldrich
Dinitro-ortho-cresol	DNOC	Sigma-Aldrich
1-Nitronaphthalene	1-NNAP	Chiron
2-Nitronaphthalene	2-NNAP	Chiron
5-Nitroacenaphthene	5-NACE	Chiron
2-Nitrofluorene	2-NFLN	Chiron
9-Nitroanthracene	9-NANT	Chiron
9-Nitrophenanthrene	9-NPHE	Chiron
3-Nitrophenanthrene	3-NPHE	Chiron
2-Nitrofluoranthene	2-NFLT	Chiron
3-Nitrofluoranthene	3-NFLT	Chiron
1-Nitropyrene	1-NPYR	Chiron
2-Nitropyrene	2-NPYR	Chiron
7-Nitrobenz(a)anthracene	7-NBAA	Chiron
6-Nitrochrysene	6-NCHR	Chiron
1,3-Dinitropyrene	1,3-N ₂ PYR	Chiron
1,6-Dinitropyrene	1,6-N ₂ PYR	Chiron
1,8-Dinitropyrene	1,8-N ₂ PYR	Chiron
6-Nitrobenz(a)pyrene	6-NBAP	Chiron
1,4-Naphthoquinone	1,4-O ₂ NAP	Chiron
9-Fluorenone	9-OFLN	Chiron
9,10-Anthraquinone	9,10-O ₂ ANT	Chiron
2-Nitro-9-fluorenone	2-N-9-OFLN	Chiron
Benz(a)fluorenone	BaOFLN	Chiron
Benz(b)fluorenone	BbOFLN	Chiron
Benzanthrone	OBAT	Chiron
1,2-Benzanthraquinone	1,2-O ₂ BAA	Chiron

Table S2. Limits of quantification ($\mu\text{g } \mu\text{L}^{-1}$)

	Back-up filters MZ	Slotted filters MZ	Back-up filters TK	Slotted filters TK
1-Nitronaphthalene	0.5	2.0	1.1	1.2
2-Nitronaphthalene	1.0	2.0	1.0	1.0
5-Nitroacenaphthene	1.0	1.0	1.0	1.0
2-Nitrofluorene	1.0	1.0	1.0	1.0
9-Nitroanthracene	1.0	1.0	1.0	1.0
9-Nitrophenanthrene	1.0	1.0	1.0	1.0
3-Nitrophenanthrene	1.0	1.0	1.0	1.0
2-Nitrofluoranthene	1.0	1.0	1.0	1.0
3-Nitrofluoranthene	5.0	5.0	5.0	5.0
1-Nitropyrene	1.0	1.0	1.0	1.0
2-Nitropyrene	5.0	5.0	5.0	5.0
7-Nitrobenz(a)anthracene	1.0	1.0	1.0	1.0
6-Nitrochrysene	1.0	1.0	1.0	1.0
1,4-Naphthoquinone	0.5	0.5	0.5	0.5
9-Fluorenone	11.9	11.4	4.6	7.9
9,10-Anthraquinone	13.5	12.3	5.0	6.7
2Nitro-9-Fluorenone	1.0	1.0	1.0	1.0
Benz(a)fluorenone	0.5	0.5	0.5	0.5
Benz(b)fluorenone	1.0	1.0	1.0	1.0
Benzanthrone	1.0	1.0	1.0	1.0
1,2-Benzanthraquinone	1.0	1.0	1.0	1.0

Table S3. Concentration ranges of the studied compounds in total PM

Analyte	Units	Mainz ^a	Thessaloniki ^b
		min-max (mean)	min-max (mean)
3-Nitrosalicylic acid	ng m ⁻³	0.009 – 0.18 (0.10*)	0.19 – 0.91 (0.58*)
5-Nitrosalicylic acid	ng m ⁻³	0.04 – 0.27 (0.19)	0.52 – 1.84 (1.24)
4-Nitrocatechol	ng m ⁻³	0.05 – 3.90 (2.46)	5.89 – 36.33 (22.11)
4-Methyl-5-nitrocatechol	ng m ⁻³	0.006 – 1.30 (0.79)	2.54 – 16.05 (9.79)
3-Methyl-5-nitrocatechol	ng m ⁻³	0.003 – 0.88 (0.53)	1.57 – 11.15 (6.52)
3-Methyl-4-nitrocatechol	ng m ⁻³	n.d. – 0.25 (0.14)	0.40 – 2.69 (1.62)
4-Nitrophenol	ng m ⁻³	0.24 – 1.27 (0.83)	0.75 – 3.80 (2.64)
3-Methyl-4-nitrophenol	ng m ⁻³	0.09 – 0.29 (0.23)	0.09 – 0.80 (0.58)
2-Methyl-4-nitrophenol	ng m ⁻³	0.07 – 0.38 (0.26)	0.11 – 0.88 (0.67)
4-Nitroguaiacol	ng m ⁻³	n.d.	n.d. – 0.36 (0.07)
2,4-Dinitrophenol	ng m ⁻³	n.d. – 0.02 (0.009)	0.02 – 1.53 (0.43)
Dinitro-ortho-cresol	ng m ⁻³	n.d.	n.d. – 0.47 (0.12)
1-Nitronaphthalene	pg m ⁻³	n.d. – 0.75 (0.19)	1.53 – 5.2 (2.92)
2-Nitronaphthalene	pg m ⁻³	n.d.	n.d.
5-Nitroacenaphthene	pg m ⁻³	n.d.	n.d.
2-Nitrofluorene	pg m ⁻³	n.d.	n.d.
9-Nitroanthracene	pg m ⁻³	n.d. – 43.31 (23.58)	42.13 – 224.53 (130.41)
9-Nitrophenanthrene	pg m ⁻³	n.d.	n.d.
3-Nitrophenanthrene	pg m ⁻³	n.d.	0.20 – 9.43 (5.98)
2-Nitrofluoranthene	pg m ⁻³	n.d. – 38.17 (26.34)	21.19 – 154.3 (105.32)
3-Nitrofluoranthene	pg m ⁻³	n.d.	n.d. – 35.48 (12.18)
1-Nitropyrene	pg m ⁻³	n.d.	2.16 – 21.8 (10.93)
2-Nitropyrene	pg m ⁻³	n.d.	n.d. – 57.07 (27.54)
7-Nitrobenz(a)anthracene	pg m ⁻³	n.d. – 7.82 (5.77)	8.34 – 70.64 (40.35)
6-Nitrochrysene	pg m ⁻³	n.d.	n.d.
1,3-Dinitropyrene	pg m ⁻³	n.d.	n.d.
1,6-Dinitropyrene	pg m ⁻³	n.d.	n.d.
1,8-Dinitropyrene	pg m ⁻³	n.d.	n.d.
6-Nitrobenz(a)pyrene	pg m ⁻³	n.d.	n.d.
1,4-Naphthoquinone	pg m ⁻³	n.d. – 4.60 (1.20)	n.d. – 4.52 (1.60)
9-Fluorenone	pg m ⁻³	n.d. – 56.41 (26.69)	37.84 – 87.72 (62.18)
9,10-Anthraquinone	pg m ⁻³	10.28 – 220.99 (95.94)	166.16 – 354.38 (256.87)
2-Nitro-9-fluorenone	pg m ⁻³	n.d.	n.d.
Benz(a)fluorenone	pg m ⁻³	14.93 – 205.84 (94.69)	169.87 – 780.92 (423.40)
Benz(b)fluorenone	pg m ⁻³	1.95 – 299.36 (98.39)	195.59 – 830.82 (473.22)
Benzanthrene	pg m ⁻³	n.d. – 712.17 (179.52)	27.29 – 1733.94 (684.13)
1,2-Benzanthraquinone	pg m ⁻³	19.85 – 137.01 (79.66)	261.69 – 513.65 (420.66)

^a Sum of size fractions 0.49-0.95, 0.95-1.5, 1.5-3, 3-7.2, 7.2-10 μm

^b Sum of size fractions 0.49-0.95, 0.95-1.5, 1.5-3, 3-7.2, >7.2 μm

Table S4. Correlation analysis for the analytes determined in winter total PM samples from Thessaloniki (TK; Greece). Numbers given are calculated values of the determination coefficient adjusted for the degrees of freedom of the correlation model (R^2_{adj}). Bolded numbers represent statistically significant correlations at $p < 0.05$ ($n=5$)

Analyte	3-NSA	5-NSA	4-NC	4-M-5-NC	3-M-5-NC	3-M-4-NC	4-NP	2-M-4-NP	3-M-4-NP	2,4-DNP	WSOC	HULIS	Nitrate	Sulfate	Potassium
3-NSA	1														
5-NSA	0.87	1													
4-NC	0.14	-0.06	1												
4-M-5-NC	0.12	-0.06	0.98	1											
3-M-5-NC	0.17	-0.06	0.98	0.94	1										
3-M-4-NC	0.20	-0.02	0.99	0.98	0.98	1									
4-NP	0.69	0.83	0.27	0.26	0.24	0.28	1								
2-M-4-NP	0.37	0.46	0.40	0.47	0.29	0.40	0.76	1							
3-M-4-NP	0.13	0.12	0.74	0.78	0.63	0.69	0.57	0.83	1						
2,4-DNP	0.25	0.34	-0.23	-0.28	-0.18	-0.23	0.27	-0.22	-0.23	1					
WSOC	0.60	0.60	0.33	0.24	0.36	0.32	0.79	0.33	0.35	0.65	1				
HULIS	0.59	0.59	0.34	0.24	0.37	0.33	0.78	0.32	0.35	0.65	1.00	1			
Nitrate	0.37	0.61	0.08	0.13	0.00	0.08	0.81	0.91	0.58	-0.13	0.32	0.31	1		
Sulfate	0.05	-0.12	0.02	-0.10	0.14	0.03	-0.09	-0.32	-0.25	0.53	0.40	0.42	-0.33	1	
Potassium	0.82	0.81	0.38	0.34	0.38	0.40	0.94	0.60	0.48	0.39	0.90	0.89	0.58	0.13	1

Abbreviations: 3-NSA = 3-nitrosalicylic acid; 5-NSA = 5-nitrosalicylic acid; 4-NC = 4-nitrocatechol; 4-M-5-NC = 4-methyl-5-nitrocatechol; 3-M-5-NC = 3-methyl-5-nitrocatechol; 3-M-4-NC = 3-methyl-4-nitrocatechol; 4-NP = 4-nitrophenol; 2-M-4-NP = 2-methyl-4-nitrophenol; 3-M-4-NP = 3-methyl-4-nitrophenol; 2,4-DNP = 2,4-dinitrophenol; WSOC = water soluble organic carbon; HULIS = humic-like substances;

4-nitroguaiacol (4-NG) and dinitro-o-cresol (DNOC) were not consistently detected in TK sample sets and therefore were not included.

Table S5. Correlation analysis for the analytes determined in winter $PM_{0.97}$ from Thessaloniki (TK; Greece). Numbers given are calculated values of the determination coefficient adjusted for the degrees of freedom of the correlation model (R^2_{adj}). Bolded numbers represent statistically significant correlations at $p < 0.05$ ($n=5$)

Analyte	3-NSA	5-NSA	4-NC	4-M-5-NC	3-M-5-NC	3-M-4-NC	4-NP	2-M-4-NP	3-M-4-NP	2,4-DNP	WSOC	HULIS	Nitrate	Sulfate	Potassium
3-NSA	1														
5-NSA	0.80	1													
4-NC	0.21	0.03	1												
4-M-5-NC	0.19	0.01	0.98	1											
3-M-5-NC	0.28	0.04	0.98	0.94	1										
3-M-4-NC	0.29	0.05	0.99	0.98	0.99	1									
4-NP	0.76	0.93	0.22	0.23	0.20	0.24	1								
2-M-4-NP	0.43	0.58	0.24	0.31	0.16	0.25	0.83	1							
3-M-4-NP	0.30	0.32	0.74	0.79	0.64	0.71	0.60	0.75	1						
2,4-DNP	0.54	0.47	-0.21	-0.26	-0.14	-0.18	0.20	-0.20	-0.24	1					
WSOC	0.75	0.89	0.23	0.16	0.27	0.23	0.81	0.41	0.39	0.56	1				
HULIS	0.77	0.88	0.28	0.21	0.32	0.29	0.81	0.42	0.42	0.55	1.00	1			
Nitrate	0.12	0.41	0.36	0.32	0.29	0.28	0.53	0.45	0.67	-0.12	0.59	0.59	1		
Sulfate	-0.31	-0.32	-0.22	-0.28	-0.13	-0.21	-0.29	-0.10	-0.32	-0.06	-0.30	-0.29	-0.33	1	
Potassium	0.70	0.71	0.58	0.50	0.60	0.57	0.75	0.46	0.64	0.34	0.91	0.93	0.68	-0.27	1

Abbreviations: 3-NSA = 3-nitrosalicylic acid; 5-NSA = 5-nitrosalicylic acid; 4-NC = 4-nitrocatechol; 4-M-5-NC = 4-methyl-5-nitrocatechol; 3-M-5-NC = 3-methyl-5-nitrocatechol; 3-M-4-NC = 3-methyl-4-nitrocatechol; 4-NP = 4-nitrophenol; 2-M-4-NP = 2-methyl-4-nitrophenol; 3-M-4-NP = 3-methyl-4-nitrophenol; 2,4-DNP = 2,4-dinitrophenol; WSOC = water soluble organic carbon; HULIS = humic-like substances;

Table S6. Correlation analysis for the analytes determined in winter PM_{3-0.97} from Thessaloniki (TK; Greece). Numbers given are calculated values of the determination coefficient adjusted for the degrees of freedom of the correlation model (R^2_{adj}). Bolded numbers represent statistically significant correlations at $p < 0.05$ ($n=5$)

Analyte	3-NSA	5-NSA	4-NC	4-M-5-NC	3-M-5-NC	3-M-4-NC	4-NP	2-M-4-NP	3-M-4-NP	2,4-DNP	WSOC	HULIS	Nitrate	Sulfate	Potassium
3-NSA	1														
5-NSA	0.97	1													
4-NC	0.01	-0.11	1												
4-M-5-NC	-0.03	-0.14	0.98	1											
3-M-5-NC	0.00	-0.12	0.99	0.97	1										
3-M-4-NC	0.05	-0.07	0.99	0.98	0.99	1									
4-NP	0.59	0.45	0.49	0.47	0.43	0.50	1								
2-M-4-NP	0.07	-0.02	0.59	0.67	0.51	0.61	0.70	1							
3-M-4-NP	-0.16	-0.23	0.68	0.77	0.60	0.67	0.49	0.92	1						
2,4-DNP	0.62	0.53	0.19	0.09	0.23	0.23	0.22	-0.17	-0.25	1					
WSOC	0.58	0.41	0.54	0.46	0.51	0.53	0.90	0.45	0.31	0.44	1				
HULIS	0.41	0.24	0.40	0.32	0.37	0.37	0.79	0.31	0.22	0.28	0.94	1			
Nitrate	0.40	0.46	-0.23	-0.21	-0.26	-0.20	0.43	0.30	-0.01	-0.22	0.13	0.02	1		
Sulfate	0.33	0.16	0.39	0.31	0.35	0.35	0.77	0.32	0.25	0.19	0.91	0.99	0.01	1	
Potassium	0.72	0.62	0.17	0.13	0.12	0.18	0.91	0.42	0.17	0.23	0.84	0.78	0.54	0.76	1

Abbreviations: 3-NSA = 3-nitrosalicylic acid; 5-NSA = 5-nitrosalicylic acid; 4-NC = 4-nitrocatechol; 4-M-5-NC = 4-methyl-5-nitrocatechol; 3-M-5-NC = 3-methyl-5-nitrocatechol; 3-M-4-NC = 3-methyl-4-nitrocatechol; 4-NP = 4-nitrophenol; 2-M-4-NP = 2-methyl-4-nitrophenol; 3-M-4-NP = 3-methyl-4-nitrophenol; 2,4-DNP = 2,4-dinitrophenol; WSOC = water soluble organic carbon; HULIS = humic-like substances;

Table S7. Correlation analysis for the analytes determined in winter PM₁₀ samples from Mainz (MZ; Germany). Numbers given are calculated values of the determination coefficient adjusted for the degrees of freedom of the correlation model (R^2_{adj}). Bolded numbers represent statistically significant correlations at $p < 0.05$ ($n=4$)

Analyte	3-NSA	5-NSA	4-NC	4-M-5-NC	3-M-5-NC	3-M-4-NC	4-NP	2-M-4-NP	3-M-4-NP	2,4-DNP	WSOC	HULIS	Nitrate*	Sulfate*	Potassium*
3-NSA	1														
5-NSA	0.88	1													
4-NC	0.79	0.98	1												
4-M-5-NC	0.86	0.98	0.95	1											
3-M-5-NC	0.83	0.99	0.98	0.99	1										
3-M-4-NC	0.91	0.94	0.87	0.98	0.95	1									
4-NP	0.99	0.93	0.86	0.90	0.88	0.92	1								
2-M-4-NP	0.92	0.92	0.90	0.85	0.86	0.82	0.96	1							
3-M-4-NP	0.74	0.91	0.95	0.82	0.86	0.72	0.82	0.93	1						
2,4-DNP	0.78	0.48	0.32	0.53	0.44	0.69	0.70	0.48	0.20	1					
WSOC	0.90	0.60	0.47	0.58	0.52	0.68	0.85	0.74	0.46	0.87	1				
HULIS	0.98	0.80	0.68	0.80	0.75	0.89	0.95	0.83	0.61	0.88	0.94	1			
Nitrate*	0.95	0.15	-0.28	0.07	-0.12	0.38	0.89	0.94	-0.11	0.98	0.95	0.97	1		
Sulfate*	-0.94	-0.75	-0.39	-0.69	-0.54	-0.88	-0.97	-0.95	-0.54	-0.87	-0.52	-0.91	-0.77	1	
Potassium*	-0.40	0.62	0.90	0.69	0.81	0.42	-0.27	-0.37	0.81	-0.53	-0.88	-0.46	-0.67	0.05	1

* $n=3$, due to lack of data for the PM_{3-0.95}.

Abbreviations: 3-NSA = 3-nitrosalicylic acid; 5-NSA = 5-nitrosalicylic acid; 4-NC = 4-nitrocatechol; 4-M-5-NC = 4-methyl-5-nitrocatechol; 3-M-5-NC = 3-methyl-5-nitrocatechol; 3-M-4-NC = 3-methyl-4-nitrocatechol; 4-NP = 4-nitrophenol; 2-M-4-NP = 2-methyl-4-nitrophenol; 3-M-4-NP = 3-methyl-4-nitrophenol; 2,4-DNP = 2,4-dinitrophenol; WSOC = water soluble organic carbon; HULIS = humic-like substances;

4-nitroguaiacol (4-NG) and dinitro-o-cresol (DNOC) were not detected in MZ sample sets.

Table S8. Correlation analysis for the analytes determined in winter PM_{0.95} from Mainz (MZ; Germany). Numbers given are calculated values of the determination coefficient adjusted for the degrees of freedom of the correlation model (R^2_{adj}). Bolded numbers represent statistically significant correlations at $p < 0.05$ ($n=4$)

Analyte	3-NSA	5-NSA	4-NC	4-M-5-NC	3-M-5-NC	3-M-4-NC	4-NP	2-M-4-NP	3-M-4-NP	2,4-DNP	WSOC	HULIS	Nitrate	Sulfate	Potassium
3-NSA	1														
5-NSA	0.86	1													
4-NC	0.76	0.98	1												
4-M-5-NC	0.85	0.99	0.95	1											
3-M-5-NC	0.83	0.99	0.97	1.00	1										
3-M-4-NC	0.91	0.94	0.86	0.97	0.95	1									
4-NP	1.00	0.89	0.80	0.87	0.85	0.92	1								
2-M-4-NP	0.98	0.85	0.77	0.80	0.79	0.84	0.98	1							
3-M-4-NP	0.85	0.94	0.94	0.87	0.89	0.81	0.88	0.90	1						
2,4-DNP	0.80	0.83	0.73	0.90	0.87	0.96	0.80	0.67	0.62	1					
WSOC	0.91	0.59	0.47	0.57	0.54	0.68	0.89	0.91	0.65	0.56	1				
HULIS	0.97	0.71	0.59	0.71	0.68	0.82	0.95	0.93	0.71	0.73	0.97	1			
Nitrate	0.50	0.75	0.84	0.65	0.69	0.50	0.56	0.62	0.88	0.28	0.27	0.32	1		
Sulfate	0.47	0.28	0.26	0.16	0.17	0.16	0.48	0.63	0.55	-0.06	0.60	0.47	0.47	1	
Potassium	0.41	0.73	0.73	0.81	0.81	0.73	0.44	0.32	0.48	0.79	0.06	0.25	0.34	-0.31	1

Abbreviations: 3-NSA = 3-nitrosalicylic acid; 5-NSA = 5-nitrosalicylic acid; 4-NC = 4-nitrocatechol; 4-M-5-NC = 4-methyl-5-nitrocatechol; 3-M-5-NC = 3-methyl-5-nitrocatechol; 3-M-4-NC = 3-methyl-4-nitrocatechol; 4-NP = 4-nitrophenol; 2-M-4-NP = 2-methyl-4-nitrophenol; 3-M-4-NP = 3-methyl-4-nitrophenol; 2,4-DNP = 2,4-dinitrophenol; WSOC = water soluble organic carbon; HULIS = humic-like substances;

Table S9. Correlation analysis for the analytes determined in winter PM_{3-0.95} from Mainz (MZ; Germany). Numbers given are calculated values of the determination coefficient adjusted for the degrees of freedom of the correlation model (R^2_{adj}). Bolded numbers represent statistically significant correlations at $p < 0.05$ ($n=4$). N.A. not available due to concentrations being <LOQ

Analyte	3-NSA	5-NSA	4-NC	4-M-5-NC	3-M-5-NC	3-M-4-NC	4-NP	2-M-4-NP	3-M-4-NP	2,4-DNP	WSOC	HULIS	Nitrate*	Sulfate*	Potassium*
3-NSA	1														
5-NSA	0.85	1													
4-NC	0.81	0.99	1												
4-M-5-NC	0.55	0.89	0.92	1											
3-M-5-NC	0.84	0.95	0.95	0.79	1										
3-M-4-NC	0.63	0.94	0.96	0.99	0.86	1									
4-NP	0.80	1.00	1.00	0.93	0.94	0.97	1								
2-M-4-NP	0.88	0.80	0.78	0.50	0.91	0.59	0.75	1							
3-M-4-NP	0.84	0.73	0.71	0.42	0.88	0.52	0.68	0.99	1						
2,4-DNP	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1					
WSOC	0.31	0.29	0.24	0.24	0.04	0.24	0.28	-0.08	-0.15	N/A	1				
HULIS	0.84	0.88	0.88	0.66	0.98	0.74	0.85	0.97	0.95	N/A	-0.07	1			
Nitrate*	-0.10	-0.49	-0.21	-0.15	0.64	-0.13	-0.35	-0.48	-0.80	N/A	-0.70	0.99	1		
Sulfate*	-0.86	0.42	0.66	0.71	1.00	0.72	0.55	0.00	0.02	N/A	0.01	0.44	0.59	1	
Potassium*	0.23	-0.75	-0.52	-0.47	0.35	-0.45	-0.64	-0.16	-0.56	N/A	-0.42	0.99	0.94	0.29	1

* $n=3$, due to lack of data for the PM_{3-0.95}.

Abbreviations: 3-NSA = 3-nitrosalicylic acid; 5-NSA = 5-nitrosalicylic acid; 4-NC = 4-nitrocatechol; 4-M-5-NC = 4-methyl-5-nitrocatechol; 3-M-5-NC = 3-methyl-5-nitrocatechol; 3-M-4-NC = 3-methyl-4-nitrocatechol; 4-NP = 4-nitrophenol; 2-M-4-NP = 2-methyl-4-nitrophenol; 3-M-4-NP = 3-methyl-4-nitrophenol; 2,4-DNP = 2,4-dinitrophenol; WSOC = water soluble organic carbon; HULIS = humic-like substances;

Table S10. Correlation analysis for the N/OPAHs determined in winter total PM samples from Thessaloniki (TK). The given values are the calculated determination coefficients adjusted for the degrees of freedom of the correlation model (R^2_{adj}). The numbers in bold represent statistically significant correlations at $p < 0.05$ ($n=5$). N.A. not available due to concentrations being $< LOQ$.

Analyte	1,4-O2NAP	9-OFLN	9,10-O2ANT	BaOFLN	BbOFLN	OBAT	1,2-O2BAA	1-NNAP	9-NANT	3-NPHE	2-NFLT	3-NFLT	1-NPYR	2-NPYR	7-NBAA	WSOC	HULIS	Nitrate	Sulfate	Potassium
1,4-O2NAP	1																			
9-OFLN	0.59	1																		
9,10-O2ANT	-0.16	0.39	1																	
BaOFLN	0.44	0.24	-0.07	1																
BbOFLN	0.73	0.65	0.26	0.27	1															
OBAT	0.61	0.23	-0.02	0.20	0.86	1														
1,2-O2BAA	-0.07	0.51	0.87	0.19	0.20	-0.10	1													
1-NNAP	-0.30	-0.24	-0.29	-0.04	-0.31	-0.13	-0.30	1												
9-NANT	0.07	-0.19	-0.29	-0.32	-0.08	-0.05	-0.24	-0.26	1											
3-NPHE	-0.30	0.09	0.14	-0.02	-0.30	-0.31	0.50	-0.18	-0.02	1										
2-NFLT	-0.17	0.35	0.30	0.15	-0.17	-0.33	0.68	-0.21	-0.17	0.94	1									
3-NFLT	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1								
1-NPYR	0.34	0.18	-0.12	0.98	0.14	0.06	0.16	-0.07	-0.29	0.06	0.21	N.A.	1							
2-NPYR	0.28	0.14	-0.25	0.82	-0.05	-0.16	0.01	-0.22	-0.31	0.16	0.28	N.A.	0.89	1						
7-NBAA	-0.05	-0.33	0.04	-0.33	-0.27	-0.17	0.08	-0.33	0.74	0.23	0.07	N.A.	-0.32	-0.33	1					
WSOC	0.11	0.17	0.24	0.83	0.22	0.13	0.49	-0.06	-0.18	0.11	0.26	N.A.	0.80	0.50	-0.14	1				
HULIS	0.11	0.15	0.23	0.83	0.21	0.13	0.48	-0.05	-0.17	0.10	0.25	N.A.	0.80	0.50	-0.15	1.00	1			
Nitrate	-0.27	0.22	0.59	0.04	-0.16	-0.32	0.85	-0.25	-0.02	0.83	0.87	N.A.	0.07	0.02	0.37	0.32	0.31	1		
Sulfate	0.14	-0.26	-0.32	0.59	0.02	0.25	-0.28	0.65	-0.33	-0.33	-0.33	N.A.	0.54	0.29	-0.30	0.40	0.42	-0.33	1	
Potassium	0.06	0.28	0.27	0.76	0.08	-0.09	0.62	-0.26	-0.14	0.46	0.61	N.A.	0.79	0.64	-0.06	0.90	0.89	0.58	0.13	1

Abbreviations: 1,4-O2NAP = 1,4-Naphthoquinone; 9-OFLN = 9-Fluorenone; 9,10-O2ANT = 9,10-Anthraquinone; BaOFLN = Benz(a)fluorenone; BbOFLN = Benz(b)fluorenone; OBAT = Benzanthrone; 1,2-O2BAA = 1,2-Benzanthraquinone; 1-NNAP = 1-Nitronaphthalene; 9-NANT = 9-Nitroanthracene; 3-NPHE = 3-Nitrophenanthrene; 2-NFLT = 2-Nitrofluoranthene; 3-NFLT = 3-Nitrofluoranthene; 1-NPYR = 1-Nitropyrene; 2-NPYR = 2-Nitropyrene; 7-NBAA = 7-Nitrobenz(a)anthracene; WSOC = water soluble organic carbon; HULIS = humic-like substances;

Table S11. Correlation analysis for the N/OPAHs determined in winter PM_{0.97} from Thessaloniki (TK). The given values are the calculated determination coefficients adjusted for the degrees of freedom of the correlation model (R^2_{adj}). The numbers in bold represent statistically significant correlations at $p < 0.05$ ($n=5$). N.A. not available due to concentrations being <LOQ.

Analyte	1,4-O2NAP	9-OFLN	9,10-O2ANT	BaOFLN	BbOFLN	OBAT	1,2-O2BAA	1-NNAP	9-NANT	3-NPHE	2-NFLT	3-NFLT	1-NPYR	2-NPYR	7-NBAA	WSOC	HULIS	Nitrate	Sulfate	Potassium	
1,4-O2NAP	1																				
9-OFLN	0.22	1																			
9,10-O2ANT	-0.23	0.30	1																		
BaOFLN	0.59	-0.07	-0.21	1																	
BbOFLN	0.61	0.41	0.30	0.21	1																
OBAT	0.65	-0.03	-0.06	0.26	0.82	1															
1,2-O2BAA	-0.17	0.52	0.87	-0.09	0.23	-0.15	1														
1-NNAP	-0.33	0.34	-0.19	-0.32	-0.33	-0.24	0.02	1													
9-NANT	0.01	-0.02	-0.33	-0.33	-0.06	-0.09	-0.33	-0.21	1												
3-NPHE	-0.31	0.00	-0.04	0.00	-0.32	-0.31	0.31	0.07	-0.07	1											
2-NFLT	-0.20	0.16	0.04	0.19	-0.23	-0.33	0.42	0.05	-0.19	0.95	1										
3-NFLT	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1									
1-NPYR	0.50	-0.15	-0.28	0.98	0.07	0.13	-0.17	-0.32	-0.32	0.01	0.18	N.A.	1								
2-NPYR	0.24	-0.22	-0.33	0.78	-0.21	-0.19	-0.27	-0.33	-0.29	0.15	0.28	N.A.	0.87	1							
7-NBAA	-0.08	-0.32	-0.03	-0.33	-0.29	-0.20	-0.02	-0.33	0.70	0.20	0.05	N.A.	-0.33	-0.33	1						
WSOC	0.27	-0.09	0.02	0.85	0.20	0.17	0.15	-0.32	-0.23	0.16	0.34	N.A.	0.80	0.54	-0.17	1					
HULIS	0.24	-0.12	-0.02	0.85	0.15	0.13	0.12	-0.31	-0.21	0.17	0.34	N.A.	0.82	0.57	-0.16	1.00	1				
Nitrate	-0.27	-0.27	0.31	0.14	-0.10	-0.16	0.29	-0.29	0.17	0.14	0.19	N.A.	0.10	-0.09	0.43	0.59	0.59	1			
Sulfate	-0.25	0.12	0.06	-0.22	-0.33	-0.17	0.20	0.73	-0.33	0.04	-0.03	N.A.	-0.19	-0.23	-0.17	-0.30	-0.29	-0.33	1		
Potassium	-0.02	-0.28	-0.12	0.69	-0.10	-0.08	-0.02	-0.27	0.01	0.20	0.30	N.A.	0.70	0.53	0.00	0.91	0.93	0.68	-0.27	1	

Abbreviations: 1,4-O2NAP = 1,4-Naphthoquinone; 9-OFLN = 9-Fluorenone; 9,10-O2ANT = 9,10-Anthraquinone; BaOFLN = Benz(a)fluorenone; BbOFLN = Benz(b)fluorenone; OBAT = Benzanthrone; 1,2-O2BAA = 1,2-Benzanthraquinone; 1-NNAP = 1-Nitronaphthalene; 9-NANT = 9-Nitroanthracene; 3-NPHE = 3-Nitrophenanthrene; 2-NFLT = 2-Nitrofluoranthene; 3-NFLT = 3-Nitrofluoranthene; 1-NPYR = 1-Nitropyrene; 2-NPYR = 2-Nitropyrene; 7-NBAA = 7-Nitrobenz(a)anthracene; WSOC = water soluble organic carbon; HULIS = humic-like substances;

Table S12. Correlation analysis for the N/OPAHs determined in winter PM_{3-0.97} from Thessaloniki (TK). The given values are the calculated determination coefficients adjusted for the degrees of freedom of the correlation model (R^2_{adj}). The numbers in bold represent statistically significant correlations at $p < 0.05$ ($n=5$). N.A. not available due to concentrations being <LOQ.

Analyte	1,4-O2NAP	9-OFLN	9,10-O2ANT	BaOFLN	BbOFLN	OBAT	1,2-O2BAA	1-NNAP	9-NANT	3-NPHE	2-NFLT	3-NFLT	1-NPYR	2-NPYR	7-NBAA	WSOC	HULIS	Nitrate	Sulfate	Potassium
1,4-O2NAP	1																			
9-OFLN	0.49	1																		
9,10-O2ANT	0.84	0.81	1																	
BaOFLN	0.60	0.97	0.90	1																
BbOFLN	-0.08	0.38	0.21	0.44	1															
OBAT	0.05	-0.02	-0.07	-0.10	-0.27	1														
1,2-O2BAA	0.88	0.74	0.96	0.81	0.00	0.11	1													
1-NNAP	-0.30	-0.33	-0.33	-0.33	-0.22	-0.30	-0.33	1												
9-NANT	0.30	-0.20	-0.04	-0.20	-0.19	0.64	0.15	-0.33	1											
3-NPHE	0.84	0.07	0.47	0.19	-0.21	-0.11	0.50	-0.13	0.32	1										
2-NFLT	0.53	-0.08	0.18	0.01	-0.17	-0.26	0.15	0.27	0.06	0.85	1									
3-NFLT	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1								
1-NPYR	0.64	0.75	0.83	0.86	0.60	-0.27	0.66	-0.23	-0.26	0.40	0.31	N.A.	1							
2-NPYR	-0.13	0.04	0.01	0.13	0.84	-0.12	-0.16	0.03	-0.16	-0.15	0.00	N.A.	0.47	1						
7-NBAA	0.34	-0.24	-0.06	-0.22	-0.23	0.43	0.09	-0.28	0.93	0.49	0.30	N.A.	-0.23	-0.26	1					
WSOC	0.81	0.65	0.75	0.72	0.22	-0.06	0.69	-0.11	0.00	0.66	0.59	N.A.	0.84	0.15	0.08	1				
HULIS	0.65	0.66	0.60	0.66	0.16	0.05	0.57	-0.07	0.00	0.48	0.46	N.A.	0.70	0.06	0.07	0.94	1			
Nitrate	0.09	-0.32	-0.20	-0.29	-0.29	-0.33	-0.21	0.47	-0.12	0.54	0.83	N.A.	-0.07	-0.09	0.13	0.13	0.02	1		
Sulfate	0.63	0.62	0.56	0.61	0.08	0.13	0.55	-0.08	0.06	0.46	0.45	N.A.	0.62	-0.02	0.13	0.91	0.99	0.01	1	
Potassium	0.59	0.22	0.36	0.30	0.08	-0.22	0.30	0.28	-0.06	0.71	0.87	N.A.	0.59	0.20	0.11	0.84	0.78	0.54	0.76	1

Abbreviations: 1,4-O2NAP = 1,4-Naphthoquinone; 9-OFLN = 9-Fluorenone; 9,10-O2ANT = 9,10-Anthraquinone; BaOFLN = Benz(a)fluorenone; BbOFLN = Benz(b)fluorenone; OBAT = Benzanthrene; 1,2-O2BAA = 1,2-Benzanthraquinone; 1-NNAP = 1-Nitronaphthalene; 9-NANT = 9-Nitroanthracene; 3-NPHE = 3-Nitrophenanthrene; 2-NFLT = 2-Nitrofluoranthene; 3-NFLT = 3-Nitrofluoranthene; 1-NPYR = 1-Nitropyrene; 2-NPYR = 2-Nitropyrene; 7-NBAA = 7-Nitrobenz(a)anthracene; WSOC = water soluble organic carbon; HULIS = humic-like substances;

Table S13. Correlation analysis for the N/OPAHs determined in winter PM₁₀ samples from Mainz (MZ). The given values are the calculated determination coefficients adjusted for the degrees of freedom of the correlation model (R^2_{adj}). The numbers in bold represent statistically significant correlations at $p < 0.05$ ($n=4$). N.A. not available due to concentrations being <LOQ.

Analyte	1,4-O2NAP	9-OFLN	9,10-O2ANT	BaOFLN	BbOFLN	OBAT	1,2-O2BAA	1-NNAP	9-NANT	3-NPHE	2-NFLT	3-NFLT	1-NPYR	2-NPYR	7-NBAA	WSOC	HULIS	Nitrate*	Sulfate*	Potassium*	
1,4-O2NAP	1																				
9-OFLN	0.48	1																			
9,10-O2ANT	0.56	0.80	1																		
BaOFLN	0.73	0.93	0.75	1																	
BbOFLN	0.88	0.76	0.88	0.87	1																
OBAT	0.99	0.53	0.58	0.77	0.89	1															
1,2-O2BAA	-0.07	0.63	0.72	0.37	0.34	-0.04	1														
1-NNAP	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1													
9-NANT	0.25	0.86	0.41	0.81	0.44	0.32	0.33	N.A.	1												
3-NPHE	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1											
2-NFLT	-0.25	0.53	0.03	0.35	-0.05	-0.20	0.26	N.A.	0.80	N.A.	1										
3-NFLT	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1									
1-NPYR	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1								
2-NPYR	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1							
7-NBAA	-0.39	0.29	-0.19	0.12	-0.25	-0.35	0.05	N.A.	0.64	N.A.	0.96	N.A.	N.A.	N.A.	1						
WSOC	0.57	0.97	0.71	0.98	0.77	0.63	0.44	N.A.	0.91	N.A.	0.52	N.A.	N.A.	N.A.	0.30	1					
HULIS	0.36	0.99	0.77	0.88	0.67	0.41	0.69	N.A.	0.87	N.A.	0.61	N.A.	N.A.	N.A.	0.38	0.94	1				
Nitrate*	0.76	0.99	0.90	0.92	0.98	0.75	0.12	N.A.	0.83	N.A.	0.93	N.A.	N.A.	N.A.	0.83	0.95	0.97	1			
Sulfate*	-0.17	-0.09	0.01	-0.45	-0.64	-0.15	0.14	N.A.	-0.29	N.A.	0.02	N.A.	N.A.	N.A.	0.002	-0.52	-0.91	-0.77	1		
Potassium*	0.01	0.19	-0.28	0.04	0.10	0.003	0.65	N.A.	0.01	N.A.	-0.35	N.A.	N.A.	N.A.	-0.16	-0.88	-0.46	-0.67	0.05	1	

* n=3, due to lack of data for the PM_{3-0.95}.

Abbreviations: 1,4-O2NAP = 1,4-Naphthoquinone; 9-OFLN = 9-Fluorenone; 9,10-O2ANT = 9,10-Anthraquinone; BaOFLN = Benz(a)fluorenone; BbOFLN = Benz(b)fluorenone; OBAT = Benzanthrene; 1,2-O2BAA = 1,2-Benzanthraquinone; 1-NNAP = 1-Nitronaphthalene; 9-NANT = 9-Nitroanthracene; 3-NPHE = 3-Nitrophenanthrene; 2-NFLT = 2-Nitrofluoranthene; 3-NFLT = 3-Nitrofluoranthene; 1-NPYR = 1-Nitropyrene; 2-NPYR = 2-Nitropyrene; 7-NBAA = 7-Nitrobenz(a)anthracene; WSOC = water soluble organic carbon; HULIS = humic-like substances;

Table S14. Correlation analysis for the N/OPAHs determined in winter PM_{0.95} from Mainz (MZ). The given values are the calculated determination coefficients adjusted for the degrees of freedom of the correlation model (R^2_{adj}). The numbers in bold represent statistically significant correlations at $p < 0.05$ ($n=4$). N.A. not available due to concentrations being <LOQ.

Analyte	1,4-O2NAP	9-OFLN	9,10-O2ANT	BaOFLN	BbOFLN	OBAT	1,2-O2BAA	1-NNAP	9-NANT	3-NPHE	2-NFLT	3-NFLT	1-NPYR	2-NPYR	7-NBAA	WSOC	HULIS	Nitrate	Sulfate	Potassium	
1,4-O2NAP	1																				
9-OFLN	0.08	1																			
9,10-O2ANT	0.47	0.69	1																		
BaOFLN	0.68	0.66	0.61	1																	
BbOFLN	0.89	0.46	0.80	0.84	1																
OBAT	0.99	0.15	0.49	0.76	0.91	1															
1,2-O2BAA	-0.17	0.83	0.68	0.25	0.22	-0.13	1														
1-NNAP	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1													
9-NANT	0.23	0.66	0.24	0.83	0.41	0.33	0.17	N.A.	1												
3-NPHE	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1											
2-NFLT	-0.28	0.57	-0.08	0.37	-0.09	-0.20	0.18	N.A.	0.79	N.A.	1										
3-NFLT	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1									
1-NPYR	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1								
2-NPYR	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1							
7-NBAA	-0.39	0.37	-0.26	0.17	-0.26	-0.34	0.00	N.A.	0.65	N.A.	0.97	N.A.	N.A.	N.A.	1						
WSOC	0.53	0.79	0.62	0.98	0.75	0.61	0.38	N.A.	0.89	N.A.	0.52	N.A.	N.A.	N.A.	0.32	1					
HULIS	0.41	0.91	0.71	0.91	0.71	0.49	0.58	N.A.	0.83	N.A.	0.54	N.A.	N.A.	N.A.	0.32	0.97	1				
Nitrate	-0.43	0.44	-0.22	0.11	-0.29	-0.38	0.14	N.A.	0.57	N.A.	0.95	N.A.	N.A.	N.A.	0.97	0.27	0.32	1			
Sulfate	0.08	0.23	-0.16	0.58	0.12	0.17	-0.23	N.A.	0.87	N.A.	0.68	N.A.	N.A.	N.A.	0.63	0.60	0.47	0.47	1		
Potassium	-0.45	0.62	0.20	-0.10	-0.22	-0.43	0.83	N.A.	0.01	N.A.	0.26	N.A.	N.A.	N.A.	0.15	0.06	0.25	0.34	-0.31	1	

Abbreviations: 1,4-O2NAP = 1,4-Naphthoquinone; 9-OFLN = 9-Fluorenone; 9,10-O2ANT = 9,10-Anthraquinone; BaOFLN = Benz(a)fluorenone; BbOFLN = Benz(b)fluorenone; OBAT = Benzanthrene; 1,2-O2BAA = 1,2-Benzanthraquinone; 1-NNAP = 1-Nitronaphthalene; 9-NANT = 9-Nitroanthracene; 3-NPHE = 3-Nitrophenanthrene; 2-NFLT = 2-Nitrofluoranthene; 3-NFLT = 3-Nitrofluoranthene; 1-NPYR = 1-Nitropyrene; 2-NPYR = 2-Nitropyrene; 7-NBAA = 7-Nitrobenz(a)anthracene; WSOC = water soluble organic carbon; HULIS = humic-like substances;

Table S15. Correlation analysis for the N/OPAHs determined in winter PM_{3-0.95} from Mainz (MZ). The given values are the calculated determination coefficients adjusted for the degrees of freedom of the correlation model (R^2_{adj}). The numbers in bold represent statistically significant correlations at $p < 0.05$ ($n=4$). N.A. not available due to concentrations being <LOQ.

Analyte	1,4-O2NAP	9-OFLN	9,10-O2ANT	BaOFLN	BbOFLN	OBAT	1,2-O2BAA	1-NNAP	9-NANT	3-NPHE	2-NFLT	3-NFLT	1-NPYR	2-NPYR	7-NBAA	WSOC	HULIS	Nitrate*	Sulfate*	Potassium*	
1,4-O2NAP	1																				
9-OFLN	N.A.	1																			
9,10-O2ANT	N.A.	0.91	1																		
BaOFLN	N.A.	0.87	0.85	1																	
BbOFLN	N.A.	-0.50	-0.44	-0.49	1																
OBAT	N.A.	0.62	0.41	0.80	-0.19	1															
1,2-O2BAA	N.A.	0.89	0.98	0.93	-0.48	0.54	1														
1-NNAP	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1													
9-NANT	N.A.	0.41	0.73	0.37	-0.02	-0.17	0.66	N.A.	1												
3-NPHE	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1											
2-NFLT	N.A.	0.33	0.61	0.16	0.17	-0.31	0.48	N.A.	0.93	N.A.	1										
3-NFLT	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1									
1-NPYR	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1								
2-NPYR	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1							
7-NBAA	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	1						
WSOC	N.A.	0.57	0.20	0.37	-0.22	0.62	0.20	N.A.	-0.34	N.A.	-0.36	N.A.	N.A.	N.A.	N.A.	1					
HULIS	N.A.	0.42	0.49	0.05	-0.07	-0.30	0.30	N.A.	0.50	N.A.	0.73	N.A.	N.A.	N.A.	N.A.	N.A.	-0.07	1			
Nitrate*	N.A.	-0.77	-0.12	-0.58	-0.31	0.02	-0.20	N.A.	0.92	N.A.	1.00	N.A.	N.A.	N.A.	N.A.	N.A.	-0.70	0.99	1		
Sulfate*	N.A.	0.05	0.73	0.31	0.02	-0.38	0.67	N.A.	0.86	N.A.	0.56	N.A.	N.A.	N.A.	N.A.	N.A.	0.01	0.44	0.59	1	
Potassium*	N.A.	-0.94	-0.44	-0.82	0.02	0.00	-0.51	N.A.	0.73	N.A.	0.95	N.A.	N.A.	N.A.	N.A.	N.A.	-0.42	0.99	0.94	0.29	1

* n=3, due to lack of data for the PM_{3-0.95}.

Abbreviations: 1,4-O2NAP = 1,4-Naphthoquinone; 9-OFLN = 9-Fluorenone; 9,10-O2ANT = 9,10-Antraquinone; BaOFLN = Benz(a)fluorenone; BbOFLN = Benz(b)fluorenone; OBAT = Benzanthrone; 1,2-O2BAA = 1,2-Benzanthraquinone; 1-NNAP = 1-Nitronaphthalene; 9-NANT = 9-Nitroanthracene; 3-NPHE = 3-Nitrophenanthrene; 2-NFLT = 2-Nitrofluoranthene; 3-NFLT = 3-Nitrofluoranthene; 1-NPYR = 1-Nitropyrene; 2-NPYR = 2-Nitropyrene; 7-NBAA = 7-Nitrobenz(a)anthracene; WSOC = water soluble organic carbon; HULIS = humic-like substances;

Table S16. Mean particulate N/O-PAH and NMAH concentrations detected in size-resolved PM ($\mu\text{g m}^{-3}$)

Particle size	Mainz					Thessaloniki				
	<0.49	0.49-0.95	0.95-3	3-10	Total	<0.49	0.49-0.95	0.95-3	>3	Total
1,4-O ₂ NAP	0.68	0.16	0.31	0.05	1.20	1.3	0.14	0.07	0.09	1.6
9-OFLN	10.55	3.60	8.23	4.31	26.7	36.3	11.3	10.2	4.4	62.2
9,10-O ₂ ANT	57.7	12.9	13.1	12.2	95.9	123	66	44	23	257
OBAT	154	21.8	1.6	2.1	179.5	519	115	38	12	684
BaOFLN	68.3	13.5	10.1	2.8	94.7	208	133	59	23	423
BbOFLN	112	20.7	4.8	6.1	143.6	360	139	59	15	573
1,2-O ₂ BAA	56.8	13.8	7.9	1.1	79.7	227	113	65	16	421
1-NNAP	<LOQ	<LOQ	<LOQ	0.2	0.2	1.4	0.52	0.44	0.57	2.9
3-NPHE	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2.6	2.5	0.78	0.13	6.0
9-NANT	18.8	3.1	1.4	0.10	23.6	68	47	14	1.6	130
2-NFLT	20.3	4.8	1.2	0.05	26.3	65	28	10	1.9	105
3-NFLT	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	6.9	5.1	<LOQ	0.22	12.2
1-NPYR	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	6.5	3.1	0.88	0.44	10.9
2-NPYR	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	15.8	10.3	1.5	<LOQ	27.5
7-NBAA	4.8	0.9	0.05	<LOQ	5.8	23.8	12.9	3.6	0.07	40.4
2,4-DNP	5.5	1.7	0.7	3.0	12.7	27	13	15	388	443
DNOC	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	4	115	119
3-NSA	64	19	15	2.9	102	280	156	115	26	577
5-NSA	109	38	23	8.9	189	623	290	234	94	1241
4-NP	377	127	179	144	826	1009	559	560	517	2644
4-NG	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	82	82
3-M-4-NP	107	33	52	38	230	250	130	137	116	633
2-M-4-NP	127	41	57	43	264	270	136	169	148	723
4-NC	1663	598	188	14	2463	11625	7054	3217	214	22110
4-M-5-NC	518	201	64	5.5	789	5492	2937	1289	74	9792
3-M-4-NC	90	39	14	2.9	145	842	522	233	26	1623
3-M-5-NC	343	140	44	4.4	531	3502	2044	902	68	6516
∑ OPAHs	460	86	46	29	621	1475	577	275	93	2422
∑ NPAHs	44	9	3	0	56	190	109	31	5	335
∑ NPs*	616	203	290	224	1333	1556	838	881	1169	4444
∑ NCs	2613	977	311	27	3928	21461	12557	5642	382	40041
∑ NSAs	174	58	48	12	292	903	446	348	120	1818

Figure S1. NMAH mass size distribution in Mainz (MZ) samples.

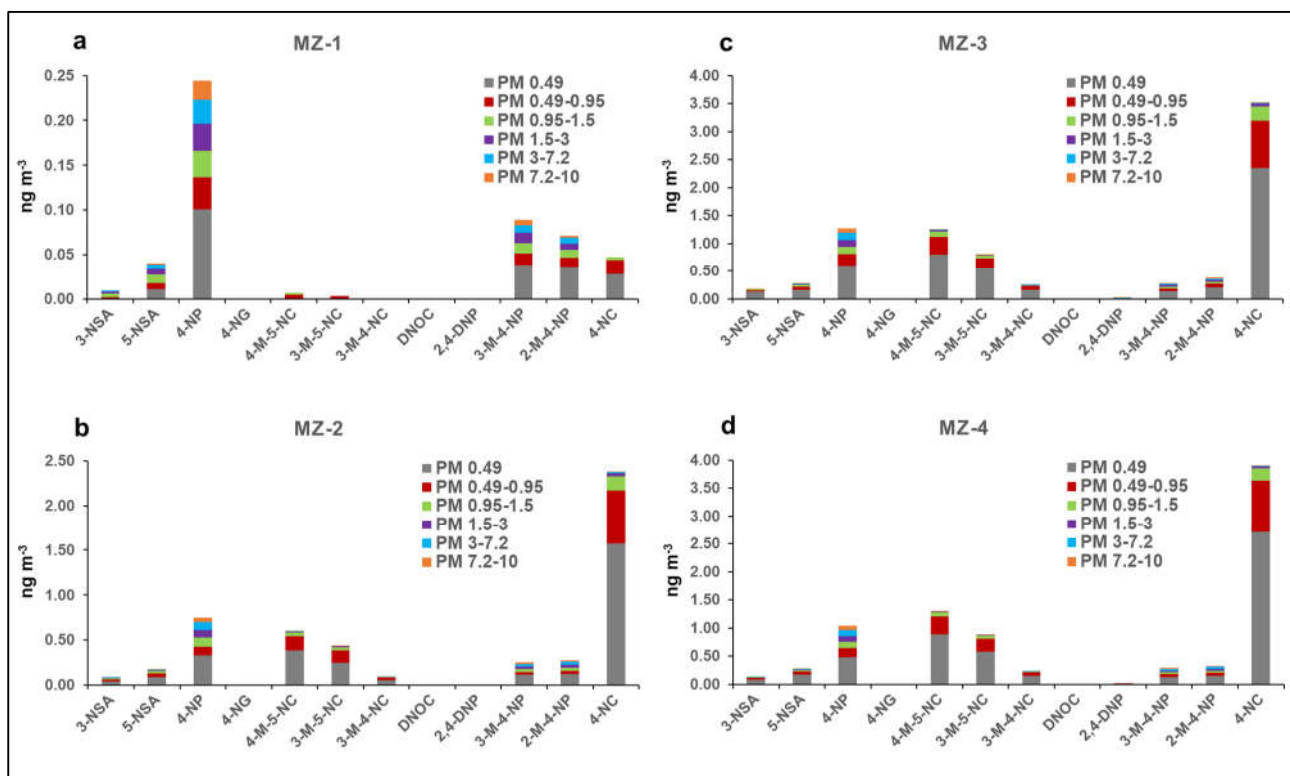


Figure S2. NMAH mass size distribution in Thessaloniki (TK) samples.

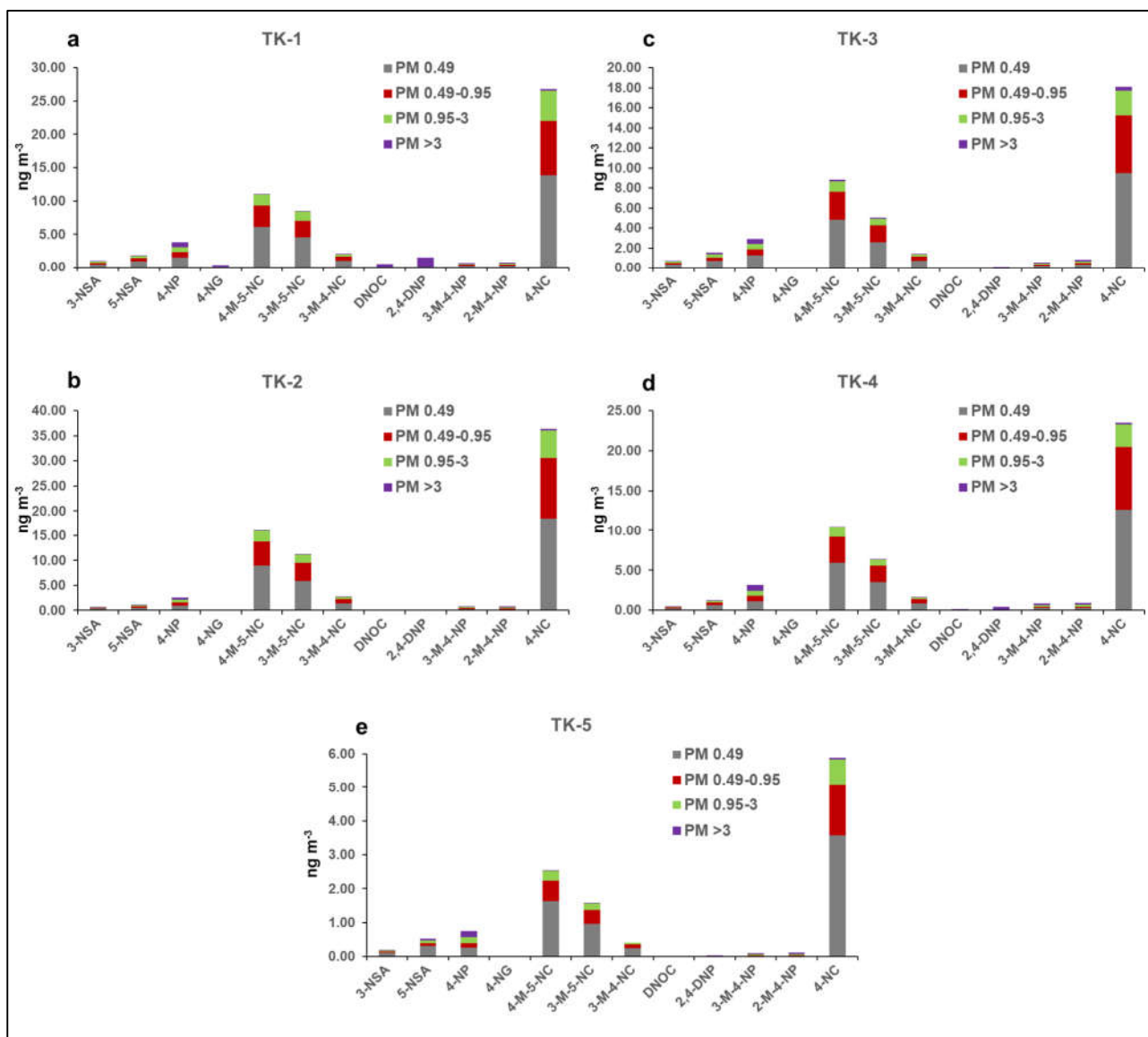


Figure S3. N/OPAH mass size distribution in Mainz (MZ) samples. The substances in each subclass, NPAHs and OPAHs, are sorted in the order of their predicted partitioning in PM.

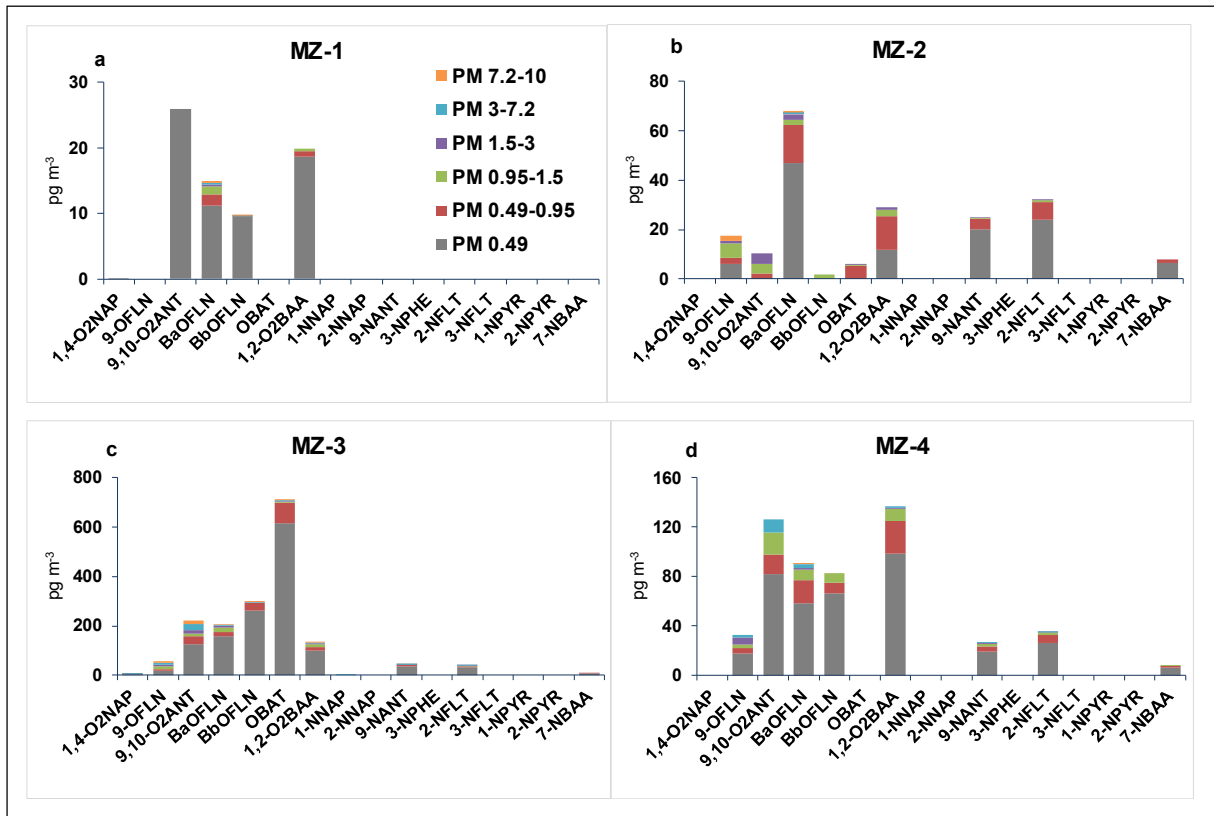


Figure S4. N/OPAH mass size distribution in Thessaloniki (TK) samples. The substances in each subclass, NPAHs and OPAHs, are sorted in the order of their predicted partitioning in PM.

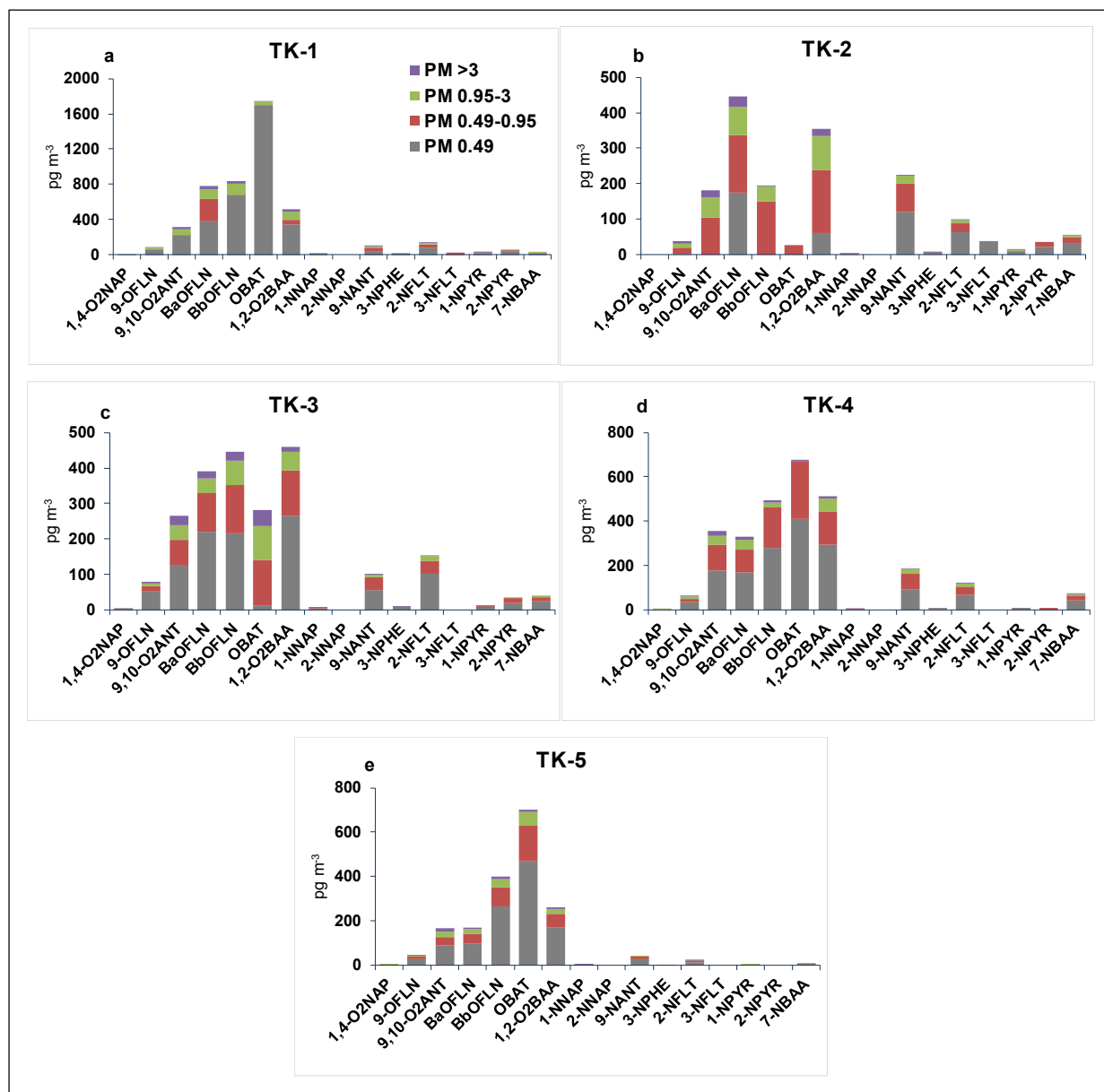


Figure S5. Time-weighted mean NMAH and N/OPA mass fractions accumulated over particle size

