SUPPORTING INFORMATION FOR:

Direct quantification of PAHs and nitro-PAHs in atmospheric PM by thermal desorption gas chromatography with electron ionization mass spectroscopic detection

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Table S1. Groups of ions with respective dwell times.

Group	*m/z*	Dwell time
1	152.1	90
	166.1	90
	165.1	50
2	178.1	100
3	101.1	50
	202.1	100
4	101.1	50
	114.1	50
	202.1	50
	228.1	50
5	252.1	50
	264.1	50
6	138.1	50
	139.1	50
	267.1	50
	276.1	50
	278.1	50
7	193.1	100
	223.1	100
8	189.1	40
	217.1	90
	247.1	40
9	243.1	90
	273.1	40

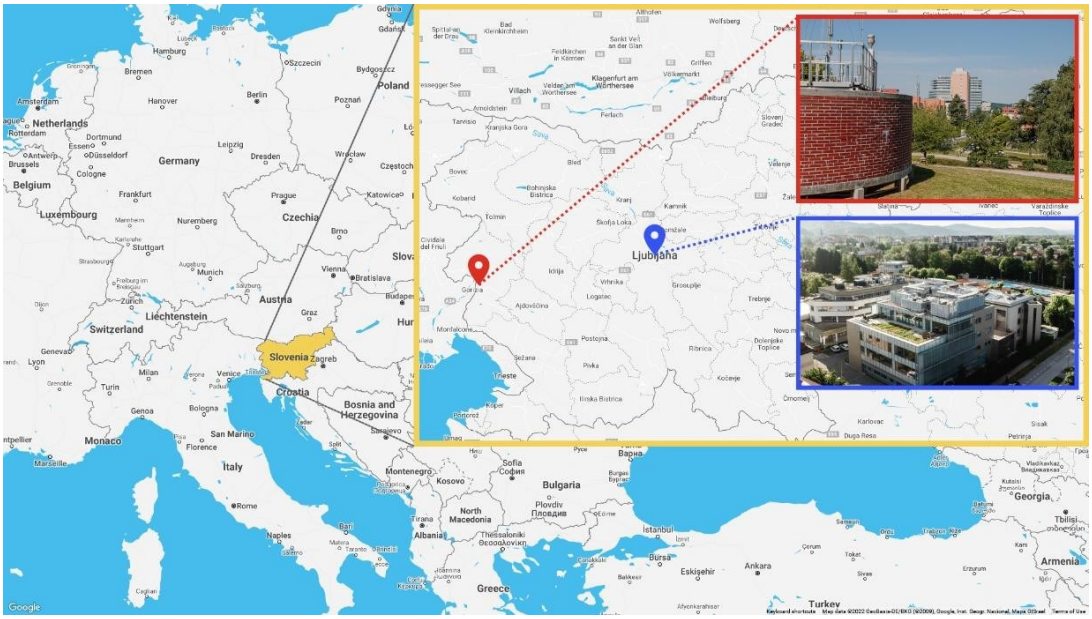

Figure S1. Figure Sampling locations: the red label denotes ARSO campaign site in Nova Gorica (45°57'19 – North, 13°39'8'' – East), while the National Institute of Chemistry in Ljubljana, Slovenia (46°2'36 – North, 14°29'41'' – East) is depicted with the blue label.

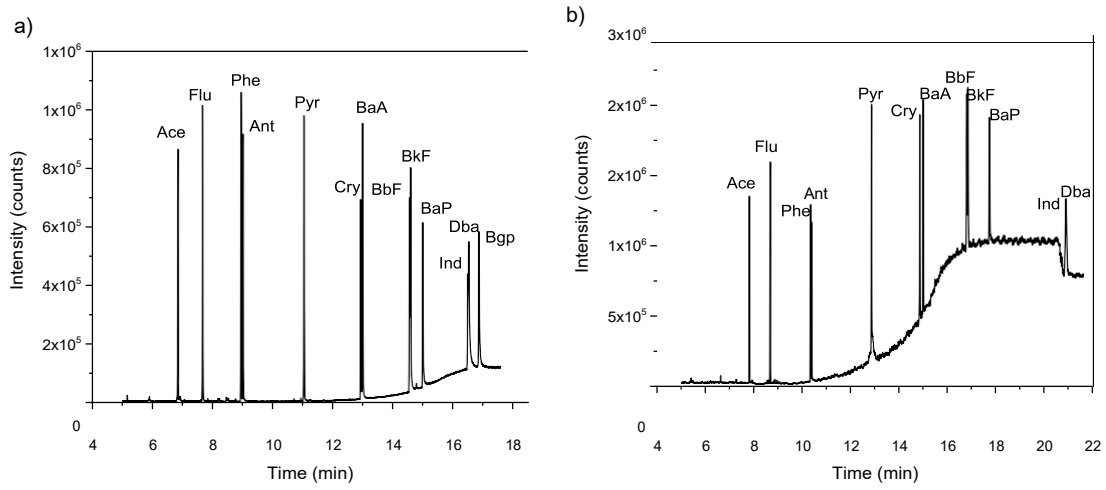

Figure S2. Liquid injection chromatograms using different columns: a) HP-5MS, b) DB-EUPA

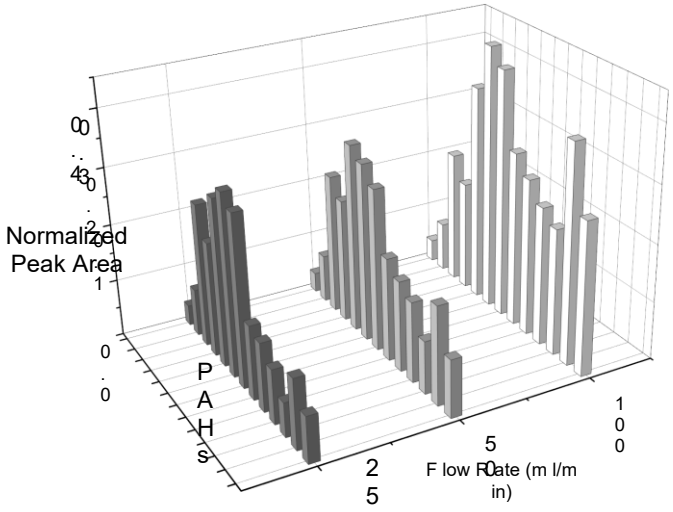

Figure S3. Optimization of TD desorption flowrate: analyte recovery is shown at three tested gas flows (25, 50 and 100 ml min^{-1}). Peak areas are normalized with the corresponding Splitless liquid injection outputs.

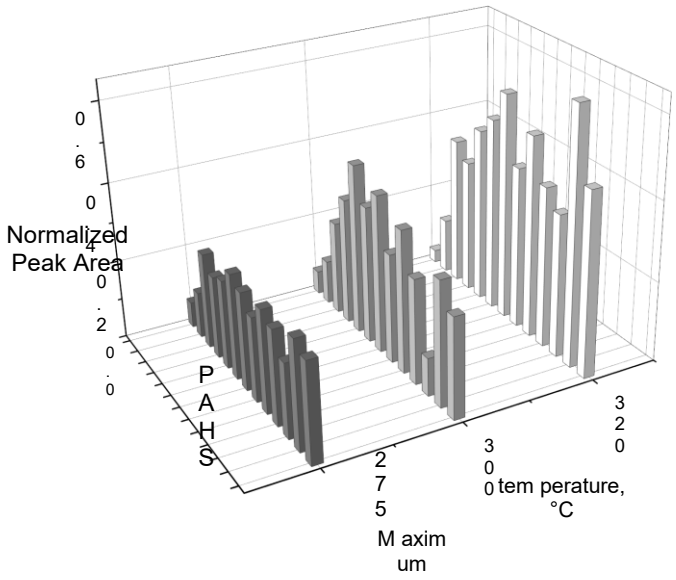

Figure S4. Optimization of TD desorption temperature: analyte recovery is shown at three tested maximum temperatures (275, 300 and 320 °C). Peak areas are normalized with the corresponding Splitless liquid injection outputs.

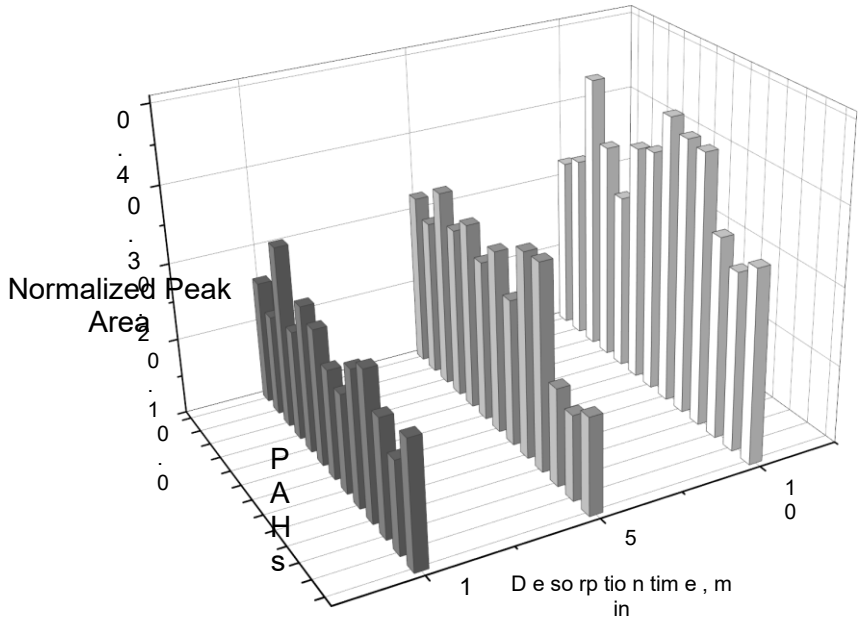

Figure S5. Optimization of TD desorption time: analyte recovery is shown at three tested hold times (1, 5 and 10 min). Peak areas are normalized with the corresponding Splitless liquid injection outputs.

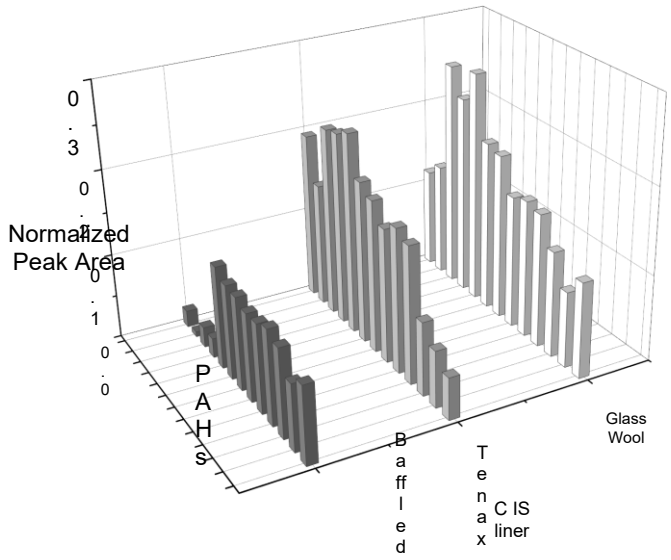

Figure S6. CIS liner perfomance: analyte recovery is shown with respect to three different liner types (baffled, Tenax and glass wool). Trap temperature was held at 5 °C, while the maximal temperature used corresponded to the specified maximum temperature of every liner (see main text for explanation). Peak areas are normalized with the corresponding Splitless liquid injection outputs.

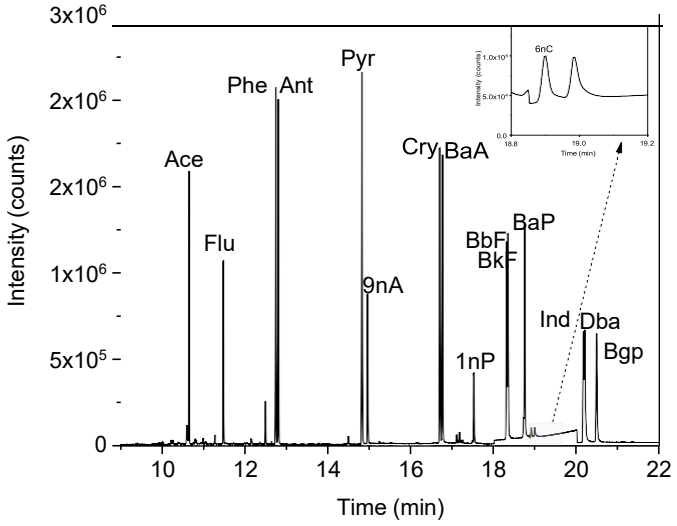

Figure S7. Standard chromatogram (5000 pg filter^{-1}) obtained with the optimized method parameters.

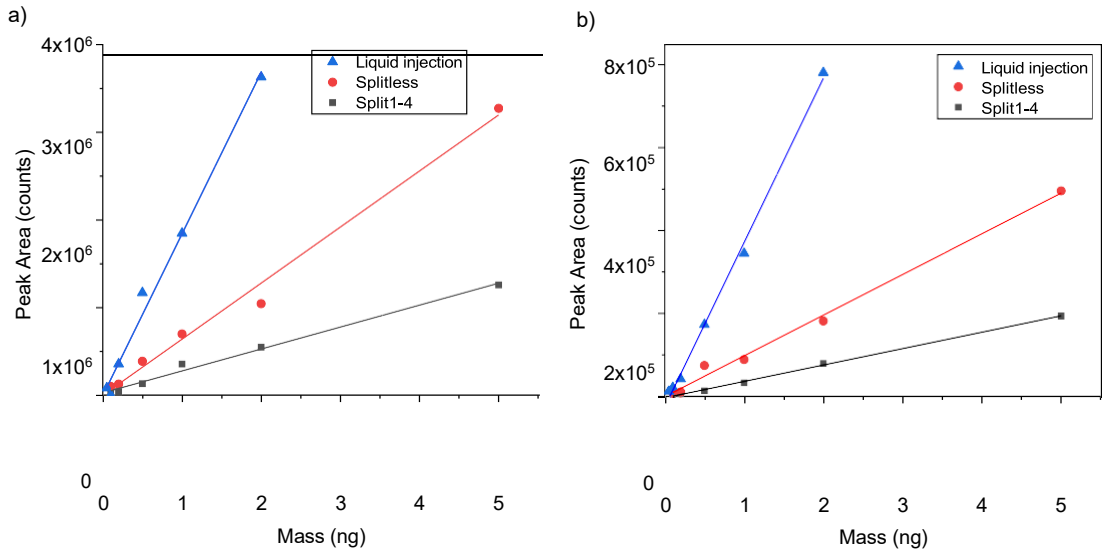

Figure S8. Exemplary linear calibration curves for a) 1nP and b) B(a)P: liquid injection (blue), TD-Splitless (red) and TD-Split 1-4 (black).

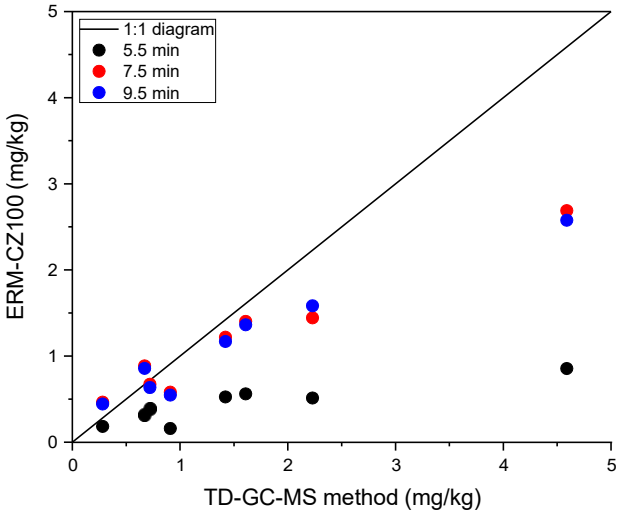

Figure S9. Optimization of CIS hold time: analyte recovery is shown with three different CIS hold times (5.5 min (black), 7.5 min (red) and 9.5 min (blue)).

Table S2. F-test results with 95 % confidence.

Analyte	SD^2_{max}	SD^2_{min}	F_{cal}	F_{theor}*	Homoscedasticity
Acy	4.57E+10	2.9E+08	157.4905	6.338	No
Flu	9.91E+10	9.28E+07	1067.573516	6.338	No
Phe	1.09E+11	6.11E+08	178.9957	6.338	No
Ant	2.79E+11	4.95E+08	564.4738	6.338	No
Pyr	2.35E+10	2.68E+08	87.70063	6.338	No
Cry	7.91E+10	4.24E+08	186.5777	6.338	No
BaA	1.02E+11	4.07E+08	250.7089	6.338	No
BbF	3.18E+11	6.24E+08	509.9101	6.338	No
BkF	2.71E+11	7.63E+08	355.7157	6.338	No
BaP	2.16E+11	1.40E+09	154.518	6.338	No
Ind	7.18E+11	8.97E+09	80.05825	6.338	No
DbA	3.78E+11	5.10E+09	74.17631	6.338	No
BghP	4.95E+11	7.28E+09	67.9817	6.338	No
9nA	4.16E+09	1.73E+07	240.7103	6.338	No
1-nP	8.96E+09	3.12E+06	2874.896	6.338	No
6nC	3.34E+09	1.95E+04	171087.9	6.338	No

*F_{theor} - a critical value of F for a one-tailed test (P=0.05) with 9 degrees of freedom [28]

Table S3. Quantification of selected PAHs in ambient PM_{10} filters from Nova Gorica, Slovenia; concentrations in ng m^{-3} are reported for every analyte. In brackets, concentrations as measured by the conventional liquid extraction method at ARSO are also given.

	BaA (ARSO)	BbF, BkF (ARSO)	BaP (ARSO)	DbA (ARSO)	Ind (ARSO)	Total PAH conc., ng m^{-3}	PM conc., µg m^{-3}
PM10(Q)NG - 02032021	0.67±0.05 (1.206)	1.5±0.2 (3.602)	0.56±0.09 (1.245)	n.a. (0.265)	n.a. (1.505)	2.7±0.3	22
PM10(Q)NG - 03032021	0.96±0.08 (1.247)	2.6±0.4 (4.109)	0.8±0.1 (1.899)	0.7±0.2 (0.317)	0.035±0.008 (1.505)	5.1±0.8	33
PM10(Q)NG - 04032021	0.63±0.05 (0.878)	2.2±0.3 (3.230)	0.47±0.07 (1.489)	n.a. (0.254)	n.a. (1.376)	3.3±0.4	40
PM10(Q)NG - 05032021	0.62±0.05 (0.362)	2.0±0.3 (2.719)	0.49±0.08 (0.982)	0.13±0.03 (0.214)	0.08 ±0.02 (1.019)	3.3±0.7	41
PM10(Q)NG - 22042021	0.072±0.005 (0.105)	0.15±0.02 (0.597)	0.10±0.02 (0.223)	n.a. (0.041)	n.a. (0.282)	0.32±0.05	12
PM10(Q)NG - 23042021	0.113±0.009 (0.110)	0.60±0.09 (0.648)	0.18±0.03 (0.228)	n.a. (0.039)	n.a. (0.300)	0.9±0.1	12
PM10(Q)NG - 24042021	0.064±0.005 (0.068)	0.38±0.06 (0.448)	0.09±0.02 (0.121)	n.a. (0.028)	n.a. (0.192)	0.53±0.08	14
PM10(Q)NG - 25042021	0.063±0.005 (0.063)	0.39±0.06 (0.473)	0.13±0.02 (0.174)	0.016±0.004 (0.036)	0.24±0.06 (0.245)	0.8±0.1	15
PM10(Q)NG - 26042021	0.16±0.01 (0.104)	0.8±0.1 (0.541)	0.23±0.04 (0.195)	0.030±0.006 (0.030)	0.33±0.08 (0.233)	1.6±0.2	14

Table S4. Quantification of PAHs and nitro-PAHs in ambient $PM_{2.5}$ filters from Ljubljana, Slovenia; concentrations in ng m^{-3} are reported for every analyte.

PAH/nitro-PAH	PM2.5(Q)20210224	PM2.5(Q)20210225	PM2.5(Q)20210226	PM2.5(Q)20210227	PM2.5(Q)20210228	PM2.5(Q)20210524	PM2.5(Q)20210525	PM2.5(Q)20210526	PM2.5(Q)20210527	PM2.5(Q)20210528
Ace	0.043±0.006	0.06±0.01	0.06±0.01	0.014±0.002	0.07±0.01	n.a.	n.a.	n.a.	n.a.	n.a.
Flu	n.a.	n.a.	n.a.	n.a.	0.005±0.001	0.012±0.003	0.005±0.001	0.004±0.001	0.004±0.001	0.003±0.001
Phe	0.21±0.02	0.17±0.02	0.14±0.01	0.031±0.003	0.12±0.01	0.082±0.007	0.017±0.002	0.015±0.001	0.016±0.002	0.012±0.001
Ant	0.008±0.002	0.004±0.001	0.006±0.002	0.008±0.002	0.022±0.006	0.013±0.004	0.007±0.002	0.006±0.002	0.006±0.002	0.007±0.002
Pyr	1.49±0.06	1.97±0.08	1.52±0.07	0.36±0.01	1.08±0.04	0.139±0.006	0.041±0.002	0.039±0.002	0.033±0.001	0.053±0.002
BaA	1.6±0.1	2±0.2	2±0.2	0.34±0.03	1.2±0.1	0.12±0.01	0.024±0.002	0.026±0.002	0.014±0.001	0.030±0.003
Cry	2.2±0.2	2.6±0.2	2.4±0.2	0.56±0.04	1.8±0.1	0.24±0.02	0.064±0.004	0.063±0.004	0.038±0.003	0.057±0.004
BbF	1.9±0.3	1.8±0.3	1.8±0.3	0.7±0.1	1.3±0.2	n.a.	0.13±0.02	0.12±0.02	0.07±0.01	0.12±0.02
BkF	1.7±0.2	2.0±0.3	1.8±0.3	0.8±0.1	1.6±0.2	0.45±0.06	0.08±0.01	0.10±0.01	0.045±0.006	0.11±0.01
BaP	1.8±0.3	1.9±0.3	1.8±0.3	0.7±0.1	1.1±0.2	0.32±0.06	0.030±0.005	0.032±0.005	0.014±0.002	0.038±0.006
Ind	0.5±0.1	0.6±0.1	0.15±0.03	0.5±0.1	0.6±0.2	0.33±0.07	0.09±0.02	0.06±0.01	0.035±0.008	0.07±0.02
DbA	0.21±0.05	0.26±0.06	0.42±0.09	0.21±0.05	0.30±0.07	0.09±0.02	0.021±0.004	0.017±0.004	0.008±0.002	0.014±0.003
BghP	n.a.	n.a.	1.3±0.3	0.7±0.2	0.8±0.2	0.35±0.09	0.11±0.03	0.08±0.02	0.05±0.01	0.08±0.02
9nA	0.26±0.02	0.29±0.02	0.24±0.01	0.034±0.002	0.29±0.02	n.a.	n.a.	n.a.	n.a.	n.a.
1nP	0.07±0.02	0.07±0.02	0.14±0.02	0.037±0.008	0.15±0.03	n.a.	n.a.	n.a.	n.a.	n.a.
6nC	0.20±0.04	0.11±0.02	0.09±0.02	0.14±0.03	0.08±0.02	0.05±0.01	n.a.	n.a.	n.a.	n.a.
Total PAH and nitro-PAH conc., ng m^{-3}	12±1	14±2	14±2	5.1±0.8	11±1	2.2±0.4	0.62±0.08	0.56±0.08	0.33±0.05	0.59±0.09
PM conc., µg m^{-3}	29	37	40	19	10	5	10	5	7	9