Supplemental information

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PAH Analysis Method

The exposed PUF disk and Quartz filters, respectively, are inserted in the automatic extractor Büchi B-811 and a defined amount of a defined standard mixture, composed of 7 deuterated PAHs, is added to individual samples. PUF disks are extracted using 150 mL of 7% diethyl ether in hexane; QFs are extracted in 100 mL of 7% methanol in dichloromethane. In the next step, individual extracts are thickened to the volume of approx. 20 mL and are analytically transferred to tubes. Then the samples are concentrated using a combined concentrator to reach the volume of approx. 0.5 mL. Subsequently, the samples are purified by column chromatography using deactivated silica gel with an exact water content. The prepared sample is then analysed by gas chromatography with mass detection (GC/MS). The weight detector works as a simple quadrupole. Separation is done using the column Rxi-PAH (30 m × 0.25 mm × 0.1 μm); He 1.5 mL/min is used as the carrier gas; the temperature program is: 80 °C, 15 °C/min to 180 °C (0 min), 5 °C/min to 310 °C (20 min). Splitless injection at 280 °C is used. The limit of quantification can be determined from the chromatography record for the calibration solution with the lowest concentration according to the signal / noise (S/N) ratio [1,2]. The above described processing of samples is done at a CHMI laboratory – Ústí nad Labem branch office.

Table S1. Overall uncertainty and detection limit of measured PAHs (taken from monitoring CHMI).

PAH	Overall uncertainty (%)	Detection limit (ng·m^{-3})
ANT	17.6	0.02
BaA	20.3	0.06
BaP, BeP	22.8	0.06
BbF	28.2	0.06
BghiP	19.7	0.06
BkF	25.2	0.06
CHRY	21.5	0.06
DBahA	27.2	0.06
PHE	24.3	0.22
FLT	26.8	0.20
FLA	28.2	0.04
IP	27.0	0.06
PY	23.8	0.04

Table S2. Diagnostic ratios, their typical values and characteristic sources (taken from [3,4]), observed trends, together with stat significance level.

DRs	Value	Sources	p	trend (ng·m⁻³year⁻¹)
FLA/(FLA + PY)	>0.5	solid fuels comb.	0.05	+0.01
ANT/(ANT + FEN)	<0.1	pyrogenic sources	-	-
BaP/BghiP	>1.25, <0,5	brown coal, traffic	-	-
LMW/HMW[1]	<1	pyrogenic sources	-	-
COMB/SUM[2]	~1	solid fuels comb.	0.01	+0.01

[1](ANT+PHE+FLA+FLT) / (BaA+BaP+BbF+BghiP+BkF+DBahA+PHE+FLA+FLT+CHRY+IP+PY).

[2](BaA+BaP+BbF+BghiP+BkF+ DBahA+PHE+ FLA+FLT +CHRY+ IP+PY) / ∑all PAHs.

Table S3. Summary of the mean and standard deviations of BaP and PAH SUM between 1996 and 2016; the BaP and PAH SUM concentrations for 1996–2005 are based on the study of Dvorská et al. [5].

Year	Mean BaP (ng·m⁻³)	Mean SUM (ng·m⁻³)
1996	0.3 ± 0.6	33.9 ± 32.6
1997	0.7 ± 2.0	36.3 ± 80.4
1998	0.3 ± 0.6	17.3 ± 21.2
1999	0.3 ± 0.3	14.6 ± 14.2
2000	0.2 ± 0.3	13.2 ± 14.1
2001	0.2 ± 0.4	14.3 ± 13.9
2002	0.6 ± 1.0	23.4 ± 29.8
2003	0.4 ± 0.7	19.8 ± 28.3
2004	0.3 ± 0.5	16.8 ± 17.2
2005	0.4 ± 0.6	19.7 ± 23.6
2006	0.9 ± 1.1	32.1 ± 40.8
2007	0.7 ± 0.9	22.0 ± 24.8
2008	0.4 ± 0.5	17.4 ± 18.0
2009	0.5 ± 0.5	18.4 ± 22.2
2010	0.4 ± 0.9	23.3 ± 28.2
2011	0.4 ± 0.7	19.1 ± 22.6
2012	0.6 ± 1.1	23.9 ± 37.5
2013	0.7 ± 1.0	23.7 ± 27.1
2014	0.4 ± 0.5	16.3 ± 15.6
2015	0.4 ± 0.4	13.5 ± 11.5
2016	0.4 ± 0.4	12.7 ± 12.2

Table S4. Summary of PMF diagnostics for PAHs composition.

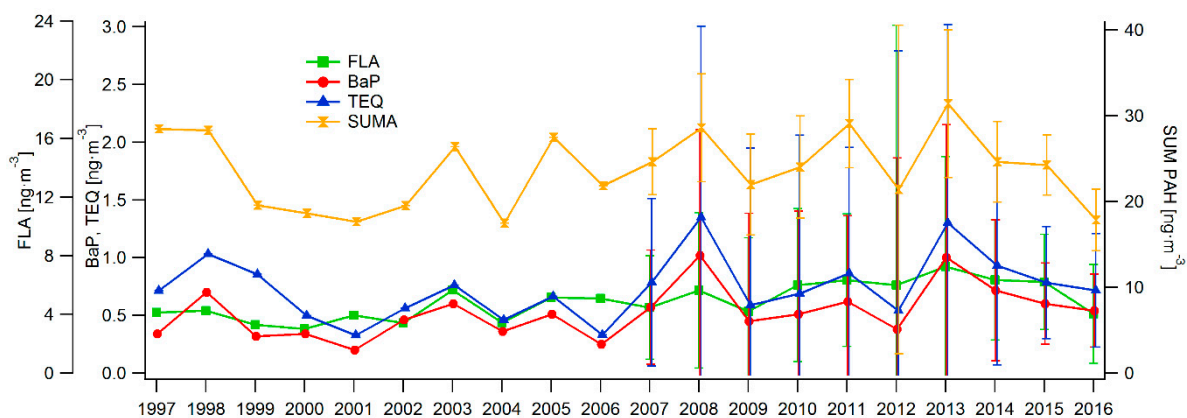| Diagnostic	NAOK PAH Summer	NAOK PAH Winter
Qexpected/theoretical	4191	4128
Qtrue	4222	4241
Qrobust	4222	4241
Species Q/Qexpected >2	4 samples	8 samples
Extra modeling uncertainty	2.3%	0%
DISP swaps	0	0
BS mapping	100%	100%

Figure S1. The median concentrations (±standard deviation calculated for this study) of BaP, TEQ, FLA and PAH SUM concentrations in the cold half-year (October - March). 2007 stands for winter season 2006 – 2007 etc. Data till 2006 are from Dvorská at al. [5]. The markers are shifted for a better readability.
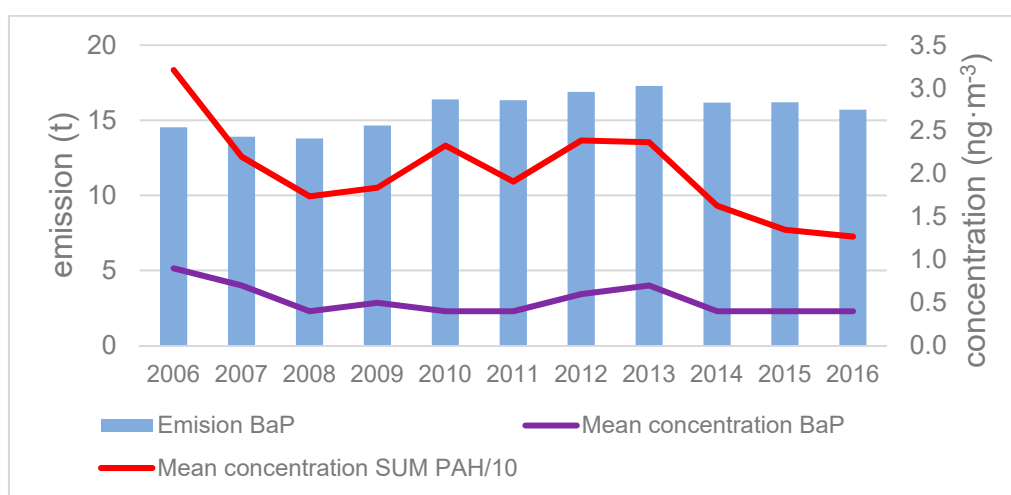

Figure S2. BaP emission production and concentration of BaP and PAH SUM/10 in the Czech Republic between the years 2006 and 2016 (taken from: [6]).
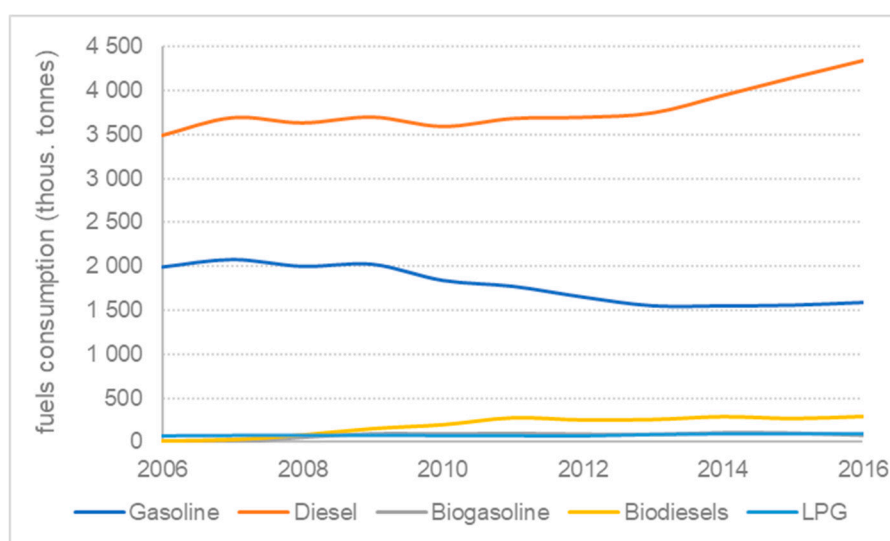

Figure S3. Fuels consumption used for transportation in the Czech Republic between the years 2006 and 2016 (taken from: [7]).
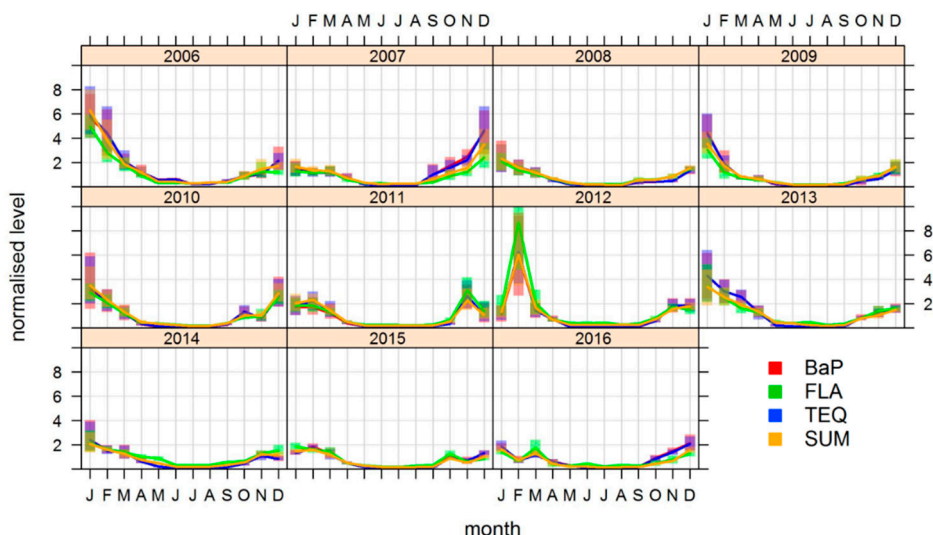
Figure S4. Annual cycles of selected PAHs (BaP, TEQ, FLA and PAH SUM) for the years from 2006 to 2016.

Table S5. Diagnostic ratios for PMF factors for warm (W) and cold (C) part of the year.

DRs	Combustion W; C	Mixed W; C	Nat. gas combustion W; C
FLA/(FLA + PY)	0.75; 0.79	0.60; -	-; 0.57
ANT/(ANT + FEN)	0.01; 0.01	0.16; 0.73	0.06; -
BaP/BghiP	20.40; 3.21	2.70; 0.08	0.39; 27.47
LMW/HMW[1]	6.54; 5.42	0.34; 0.25	6.54; 1.04
COMB/SUM[2]	0.98; 0.97	0.76; 0.77	0.82; 0.87

[1](ANT+PHE+FLA+FLT) / (BaA+BaP+BbF+BghiP+BkF+DBahA+PHE+FLA+FLT+CHRY+IP+PY).

[2](BaA+BaP+BbF+BghiP+BkF+ DBahA+PHE+ FLA+FLT +CHRY+ IP+PY) / ∑all PAHs.

References

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