

Supplementary materials for

**Influence of source apportionment of PAHs occurrence in
aquatic suspended particulate matter at a typical post-
industrial city: A case study of Freiburger Mulde River**

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Section S1. Sample analysis

The water samples were collected from 2002 to 2016 at 6 measuring stations in the Freiburger Mulde River. It should be noted that some stations in the midstream (such as Dobeln) were only used for several years. The main sampling frequency is 4 times a year, and the sampling time is relatively evenly distributed in each season. The sample sizes for the different sites (Katzenstein, Hilbersdorf, Halsbrücke, Siebenlehn, Dobeln, and Erlin) were 10, 49, 23, 51, 20, and 54, respectively. Variances in sampling periods are the main reason for the differences in the number of samples at different stations. As one of the important tributaries of the Elbe, the Freiburger Mulde River's sample set is affected by changes in the Elbe monitoring program (<http://www.fgg-elbe.de>). **Table S1** provides details of the spatiotemporal distribution of the samplings.

All the sample detections were conducted by the state operating company for environment and agriculture (BfUL, Staatliche Betriebsgesellschaft für Umwelt und Landwirtschaft). Details on sample collection and quality control are available on the online website of the office of the FGG Elbe (<https://www.fgg-elbe.de>). Sample collection and chemical analysis would be briefly described here. Water samples were collected by a stainless-steel centrifugal pump, in which coarse particles larger than 1 mm in diameter were excluded. The suspension was separated using a flow-through centrifuge (15,000 rpm). Suspended solids retention was higher than 80% in most samples. After centrifugation, the suspension was collected in glass containers and stored sealed at -20°C before being transported to the laboratory for analysis. Suspension samples were extracted on a modified SUPREX SFE 50 extraction unit

using an acetone/n-hexane (1:1) solvent mixture. A sample amount of approximately 0.5 g of the suspended matter was mixed with 200 mg of activated copper powder and statically extracted in a 10 mL extraction cell at a temperature of 100 °C and a pressure of 150 atm for 15 min. The extracted material was rinsed with 20 mL of mixed solvent, and the remaining solvent was blown out of the extraction cell with nitrogen. Dynamic extraction is then performed using ultrasound. Water was extracted and the n-hexane phase was dried over sodium sulfate. After concentration to 100 µL, the suspended solid extract was pre-washed using HPLC.

Quantification in the extracts was carried out on a GC (Hewlett Packard 5890 Series II) with a mass selective detector (MSD 5971 A) and KAS 3 cold application system (Gerstel GmbH, Mühlheim). A 5% phenylmethyl silicone capillary column with 0.25 µm ID, 0.5 µm film thickness, and 25 m length (SE 52, Macherey/Nagel, Dülmen) was used, with helium being used as the carrier gas. The GC temperature program was: 40 °C initial temperature, 5 °C/min to 310 °C, 310 °C for 20 min. Parameters for the cold feed system were: 40 °C initial temperature; 1 °C/s to 70 °C; 70 °C for 20 s; 12 °C/s to 320 °C; 320 °C for 600 s; splitless time 120 s; Injection volume 2 µL (suspended matter extracts). The uncertainty of sample detection is within acceptable limits [32].

Section S2. Mann-Kendall trend test

Mann-Kendall (MK) trend test was used for the long-term trend analysis of trace elements in sediments [89,90]. MK trend test is a nonparametric rank-based method, thus, the effect of outliers in data on the trend results could be ignored [91]. The statistic S of the MK test which represented the trend value of the series is determined by:

$$S = \sum_{i=1}^{n-1} \sum_{j=i+1}^n \text{sign}(x_j - x_i) = \begin{cases} 1 & x_i < x_j \\ 0 & x_i = x_j \\ -1 & x_i > x_j \end{cases} \quad \text{Eq. S1}$$

where n is the number of samples; x_i and x_j are the time series data in chronological order. The mean of S is zero in the null hypothesis, and the variance $V(S)$ should be constant, which is calculated by Equation 2:

$$V(S) = \left[n(n-1)(2n+5) - \sum_i^P t_i(t_i-1)(2t_i+5) \right] / 18 \quad \text{Eq. S2}$$

where P is the number of tied groups; t_i is the value of the i_{th} group; the standardized test statistics Z can be calculated by Eq. 3 ($P > 40$):

$$Z = \begin{cases} \frac{S-1}{\sqrt{V(S)}} & \text{if } S > 0 \\ 0 & \text{if } S = 0 \\ \frac{S+1}{\sqrt{V(S)}} & \text{if } S < 0 \end{cases} \quad \text{Eq. S3}$$

where $|Z|$ is higher than the determined significance level (0.05), the null hypothesis (no trend) should be rejected.

Section S3. Wavelet analysis

Wavelet analysis is a useful technique for figuring out various time scales or changes in the variance of time series data [45]. For a long-term data set, the wavelet function could accurately extract the local characteristics of the data and obtain the periodic change characteristics of the pollutants at a specific scale [1,92–94]. Suppose that $\psi(t)$ is a square-integrable function in the real number domain, the basic wavelet function satisfies [94]:

$$\int_{-\infty}^{+\infty} \psi(t) dt = 0 \quad \text{Eq. S4}$$

where $\psi(t)$ is the mother wavelet. The sub-wavelets are obtained through the translation and expansion of the mother wavelet:

$$\psi_{a,b}(x) = |a|^{\frac{1}{2}} \psi(at - b) \quad \text{Eq. S5}$$

where a is the scaling factor, b is the translation factor. Wavelet transform is divided into discrete wavelet transform and continuous wavelet transform. The continuous wavelet transform which was more applicable in the extraction time sequence data signal characteristics was used in this study [92].

Furthermore, the variation of the wavelet coefficient can be used to determine the time scale of the specific period of the time series signal [94]. The equation is shown as follows:

$$Var(a) = \int_{-\infty}^{+\infty} |W_x(a, f)|^2 df \quad \text{Eq. S6}$$

where a represents the scale factor of the periodicity of the original data series at various time scales. The peak value of $Var(a)$ represents the main time scale (primary period) of the series. All the calculation and analysis processes were carried out in MATLAB and Suffer.

Table S1 The sampling information for stations

Station	Period (year)	Number of samples
Katzenstein	2002, 2008, 2010, 2015	10
Hilbersdorf	2004-2009, 2011, 2013- 2015	49
Halsbrucke	2002-2006, 2008-2009, 2013	23
Siebenlehn	2003-2010, 2015-2016	51
Dobeln	2006-2007, 2009, 2013, 2016	20
Erlin	2002-2016	54

Table S2. Proposed toxicity equivalency factors (TEFs) for individual PAHs

Individual PAH	TEF from USEPA (1984)	TEF from Nisbet and Lagoy (1992)
Naphthalene	0	0.001
Acenaphthylene	0	0.001
Acenaphthene	0	0.001
Fluorene	0	0.001
Phenanthrene	0	0.001
Anthracene	0	0.01
Fluoranthene	0	0.001
Pyrene	0	0.001
Benz(a)anthracene	1	0.1
Chrysene	1	0.01
Benzo(b)fluoranthene	1	0.1
Benzo(k)fluoranthene	1	0.1
Benzo(a)pyrene	1	1
Dibenzo(a,h)anthracene	1	1
Indeno(1,2,3-cd)pyrene	1	0.1
Benzo(g,h,i)perylene	0	0.01

Table S3. Global review of PAHs concentrations

Location	n^a	Σ PAHs (µg kg⁻¹ dry weight)	Pollution level	References
Taranto Gulf, Italy	8	335-5193	Moderate to very high	[57]
Xiamen Harbor, China	9	2900-61000	High to very high	[53]
Victoria Harbor, Hong Kong	9	1200-14000	High to very high	[53]
Commercial ports from Spain	12	260-66710	Moderate to very high	[95]
Gemlik Bay, Turkey	14	50.8-13482	Low to very high	[96]
Boston Harbor, USA	16	7300-358000	Very high	[59]
Olbia Harbor, Italy	16	160-770	Moderate	[97]
Genoa-Voltri Harbor, Italy	16	4500-20800	High to very high	[98]
Norwegian Harbor, Norway	16	2000-76000	High to very high	[60]
Santander Bay, Northern Spain	16	20-25800	Low to very high	[99]
Kaohsiung Harbor, Taiwan	17	472-16207	Moderate to very high	[54]
Izmit Bay, Turkey	17	2500-25000	High to very high	[100]
Western Harbor, Alexandria, Egypt	20	8-131150	Low to very high	[61]
Baltimore Harbor, USA	21	2944-29590	High to very high	[101]
Incheon Harbor, Korea	23	12-1400	Low to moderate	[58]
Hsin-ta Harbor, Taiwan	30	1156-3382	high	[102]
The River Tiber basion, Italy	6	1663.1-15472.9	High to very high	[103]
Pearl River estuary and coastal areas, China	15	515.4-16489	Moderate to very high	[55]
Henan Reach of Yellow River, Middle China	16	506.6-10510	Moderate to very high	[56]
Hun River, Dalian River watershed, China	18	375.48-2310.07	Moderate to high	[23]

Taizi River, Dalian River watershed, China	18	317.5-238518.7	Moderate to very high	[23]
Dalian River, China	18	655.34-10477.19	Moderate to very high	[23]
Langat River, Peninsular Malaysia	18	308-7970	Moderate to very high	[104]
Barcelona, France	16	47.9-4210	Low to high	[105]
Banyuls-sur-Mer, France	16	117-2514	Moderate to high	[105]
Seine River and Estuary, France	25	1000-14000	High to very high	[106]
York River, VA Estuary, USA	20	199-1153	Moderate to high	[107]
Elbe river, Sachsen, Germany	16	5994-9566	Very high	[83]
Freiberger Mulde river, Sachsen, Germany	16	3147-8162	High to very high	This study

^a: the number of selected PAHs

Table S4. The correlation coefficient (R^2) values between observed and predicted concentrations of the PMF model

Species	R^2		
	2002-2006	2007-2011	2012-2016
NAP	0.9	0.8	1.0
ACY	0.7	0.9	0.8
ACE	0.8	0.8	0.9
FLU	0.4	0.7	1.0
PHE	0.9	0.9	1.0
ANT	0.7	0.8	1.0
FLUH	0.8	0.7	1.0
PYR	0.9	0.8	1.0
BaA	0.9	0.9	0.9
CHR	0.9	0.9	1.0
BbF	0.9	0.8	1.0
BkF	0.8	0.9	1.0
BaP	0.9	0.8	1.0
DBA	0.9	0.9	0.6
IDP	0.9	0.8	1.0
BgP	0.9	0.9	1.0

Notes: R^2 : The correlation coefficient values between observed and predicted concentrations of individual PAHs.

Table S5. The results of Displacement (DISP) and Bootstrap (BS) by PMF model

Period		Coke oven	Gasoline	Diesel
2002–2006	BS mapping (%)	88	100	96
	Drop of Q (%) in DISP		-0.003	
	Swaps by factor in DISP	0	0	0
2007–2011	BS mapping (%)	100	94	100
	Drop of Q (%) in DISP		-0.002	
	Swaps by factor in DISP	0	0	0
2012–2016	BS mapping (%)	93	100	98
	Drop of Q (%) in DISP		-0.006	
	Swaps by factor in DISP	0	0	0

Table S6. Effects range-low (ERL), effects range-median (ERM), mean and maximumconcentration of 16 PAHs in $\mu\text{g kg}^{-1}$

PAHs	ERL	ERM	Mean	Maximum
NAP	160.0	2100.0	101.0	820.0
ACY	44.0	640.0	39.0	110.0
ACE	16.0	500.0	36.0	140.0
FLU	19.0	540.0	70.0	470.0
PHE	240.0	1500.0	590.0	2000.0
ANT	853.0	1100.0	170.0	1300.0
FLUH	600.0	5100.0	1028.0	2400.0
PYR	665.0	2600.0	822.0	1600.0
CHR	384.0	2800.0	474.0	1600.0
BaA	261.0	1600.0	461.0	1300.0
BbF	n.a.	n.a.	442.0	1100.0
BkF	n.a.	n.a.	349.0	1100.0
BaP	430.0	1600.0	428.0	270.0
DBA	63.4	260.0	84.0	1100.0
IDP	n.a.	n.a.	375.0	760.0
BgP	n.a.	n.a.	301.0	1100.0
$\Sigma_{16}\text{PAHs}$	4000.0	44792.0	5770.0	17170.0

n.a.: not available

Table S7. Hazard quotients (HQ) and mean hazard quotient (MHQ) of 16 PAHs from 2002-2016

PAHs	Ring Number	HQ					
		Katzenstein	Hilbersdorf	Halsbrücke	Siebenlehn	Dobeln	Erlbn
NAP	2	0.02	0.08	0.05	0.04	0.02	0.04
ACY	3	0.03	0.10	0.07	0.05	0.03	0.04
ACE	3	0.04	0.11	0.07	0.07	0.04	0.05
FLU	3	0.04	0.25	0.10	0.11	0.04	0.09
PHE	3	0.22	0.65	0.45	0.39	0.17	0.26
ANT	3	0.08	0.26	0.16	0.17	0.07	0.09
FLUH	4	0.14	0.29	0.26	0.22	0.11	0.12
PYR	4	0.23	0.48	0.39	0.33	0.17	0.19
CHR	4	0.15	0.22	0.22	0.18	0.09	0.12
BaA	5	0.25	0.38	0.36	0.31	0.16	0.21
BbF	5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
BkF	5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
BaP	6	0.26	0.34	0.34	0.28	0.16	0.19
DBA	5	0.51	0.44	0.39	0.33	0.17	0.21
IDP	5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
BgP	6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
$\Sigma 16\text{PAHs}$	/	0.10	0.18	0.16	0.14	0.07	0.09
MHQ	/	0.16	0.30	0.24	0.20	0.10	0.13

n.a.: not available

Table S8. TEQ values of PAHs at different locations

Location	TEQ (ng TEQ g⁻¹ dry weight)	Reference
External area	2-1629	[108]
Eastern area	2-1973	[108]
Industrial area	4-4723	[108]
Commerical area	6-4528	[108]
Touristic area	10-2250	[108]
Shipping area	45-3578	[108]
Guba Pechenga	18-300	[108]
Korsfjord	18-60	[108]
Jarfjord	19-35	[108]
Vard Harbor	40-66	[108]
Vars Harbor	472-733	[108]
Kola Bay	71-583	[108]
Kaohsiung Harbor, Taiwan	55-1964	[54]
Meiliang Bay, China	94-845	[109]
Elbe river, Sachsen, Germany	872-1123	[83]
Eastern Mediterranean Sea, Lebanon	17-872	[110]
Freiberger Mulde river, Germany	407-1180	This study