



*Supplement of*

## **Regional modelling of polycyclic aromatic hydrocarbons: WRF-Chem-PAH model development and East Asia case studies**

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Table S1. Configurations of WRF-Chem v3.6.1

Physics	WRF option
Microphysics	Lin scheme
Surface layer	Eta Monin–Obukhov (Janjic) scheme
Planetary boundary layer	Mellor–Yamada–Janjic (MJY) TKE scheme
Cumulus parameterisation	Grell 3-D ensemble scheme
Land-surface model	Unified Noah land-surface model
Shortwave radiation	Goddard scheme
Longwave radiation	RRTMG scheme
Chemistry	Chem option
Gas-phase mechanism	RACM with aqua-phase reactions
Aerosol module	MADE/SORGAM
Photolytic rate	Fast-J photolysis scheme

Table S2. Parameterization of heterogeneous reaction rate for the ozonolysis of BaP. First-order reaction rate coefficients  $k$  ( $s^{-1}$ ) are given by the Hill equation  $k = \text{base} + \frac{\text{max}-\text{base}}{1+(\frac{\text{xhalf}}{[\text{O}_3]})^{\text{rate}}}$  with  $[\text{O}_3]$  in ppbv. For each grid cell, the parameters are read from the look-up table with temperature and relative humidity (RH) closest to the temperature and humidity of the grid cell. When equally close, the smaller parameter value is adopted.

70% RH				
Temperature (°C)	base	max	rate	xhalf
40	1.67e-4	1.29e-2	0.682	1.25e3
35	1.19e-4	1.29e-2	0.682	1.25e3
30	8.52e-5	9.02e-3	0.696	1.23e3
25	5.94e-5	6.33e-3	0.707	1.27e3
23	4.84e-5	5.14e-3	0.700	1.25e3
15	2.55e-5	2.72e-3	0.711	1.29e3
10	1.58e-5	1.68e-3	0.706	1.27e3
5	9.49e-6	1.00e-3	0.698	1.24e3
0	6.85e-6	5.64e-4	0.704	1.11e3
-5	5.31e-6	3.10e-4	0.713	1.01e3
-10	3.83e-6	1.48e-4	0.731	7.33e2
-15	8.93e-7	1.05e-4	0.580	1.88e3
-20	1.16e-6	2.58e-5	0.673	3.35e2

50% RH				
Temperature (°C)	base	max	rate	xhalf
40	1.65e-4	1.80e-2	0.672	1.21e3
35	1.16e-4	1.27e-2	0.678	1.24e3
30	8.24e-5	8.68e-3	0.688	1.22e3
25	5.44e-5	5.71e-3	0.688	1.21e3
23	2.64e-5	3.08e-3	0.618	7.97e2
15	2.20e-6	1.10e-3	0.544	5.83e2
10	7.84e-7	2.60e-4	0.559	7.50e1
5	-4.79e-7	7.19e-5	0.564	1.31e1
0	-7.02e-6	2.18e-5	0.464	1.05e0
-5	-4.06e-6	6.54e-6	0.459	1.24e-1
-10	-1.89e-6	2.02e-6	0.429	1.44e-2
-15	2.58e-7	7.22e-7	0.175	1.28e-1
-20	1.79e-7	2.60e-7	0.689	1.11e3

Dry				
Temperature (°C)	base	max	rate	xhalf
40	1.61e-4	1.74e-2	0.667	1.19e3
35	1.10e-4	1.19e-2	0.667	1.21e3
30	6.75e-5	7.31e-3	0.653	1.11e3
25	2.3e-5	3.10e-3	0.586	7.02e2
23	-1.90e-5	9.28e-4	0.446	1.59e2
15	-2.65e-5	3.09e-4	0.341	8.38e1
10	-4.28e-5	1.03e-4	0.191	4.41e0
5	-1.12e-5	3.49e-5	0.142	4.33e0
0	3.39e-6	1.03e-5	0.382	8.85e2
-5	1.37e-6	5.67e-6	0.780	2.96e3

-10	4.53e-7	1.57e-6	0.979	1.63e3
-15	1.44e-7	2.10e-6	0.924	1.39e4

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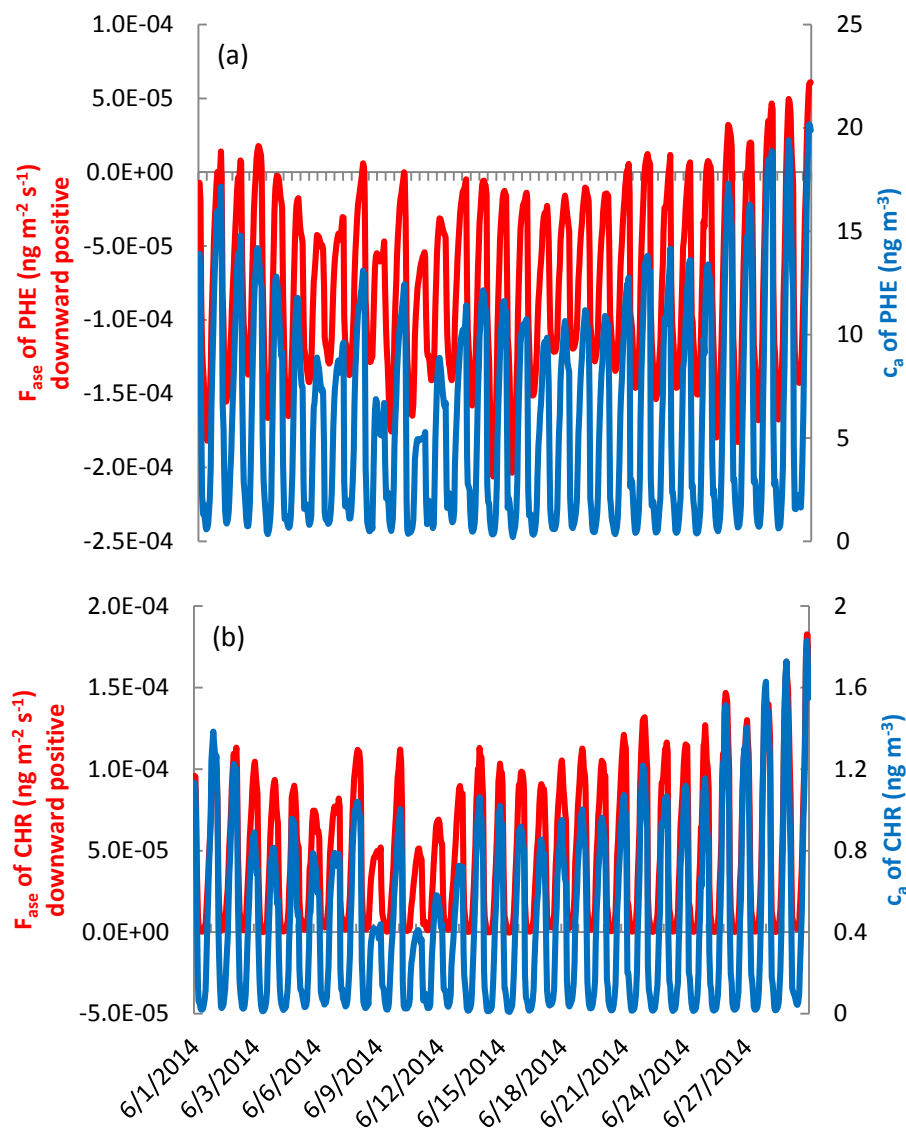


Figure S1. Air-soil gas exchange flux ( $F_{ase}$ , positive is defined downward, negative is defined upward) and near-ground air concentration ( $c_a$ ) at a receptor site.

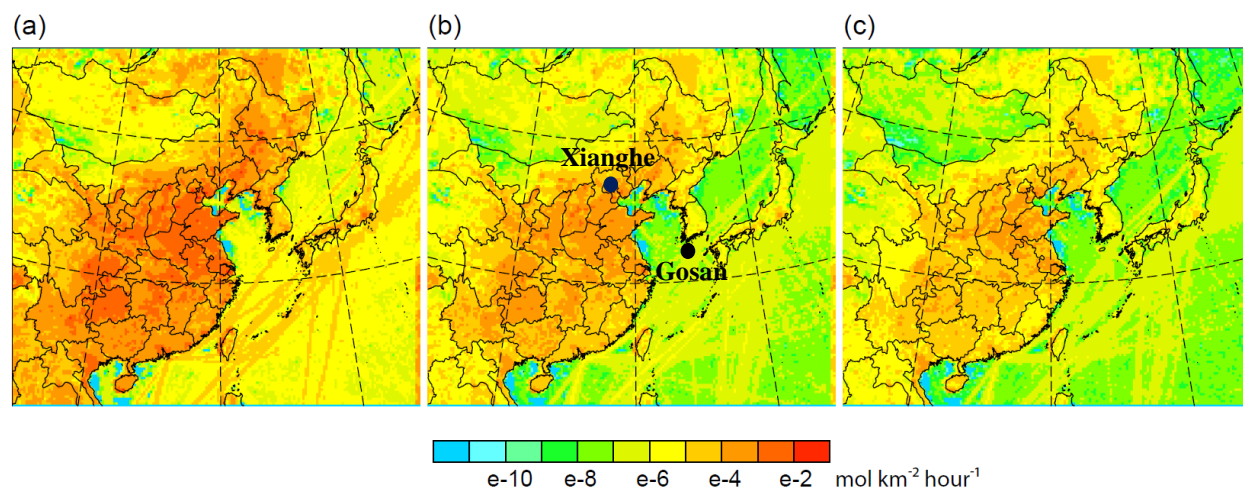


Figure S2. Emissions of (a) PHE, (b) CHR and (c) BaP in July 2013. The locations of Xianghe and Gosan are also shown.

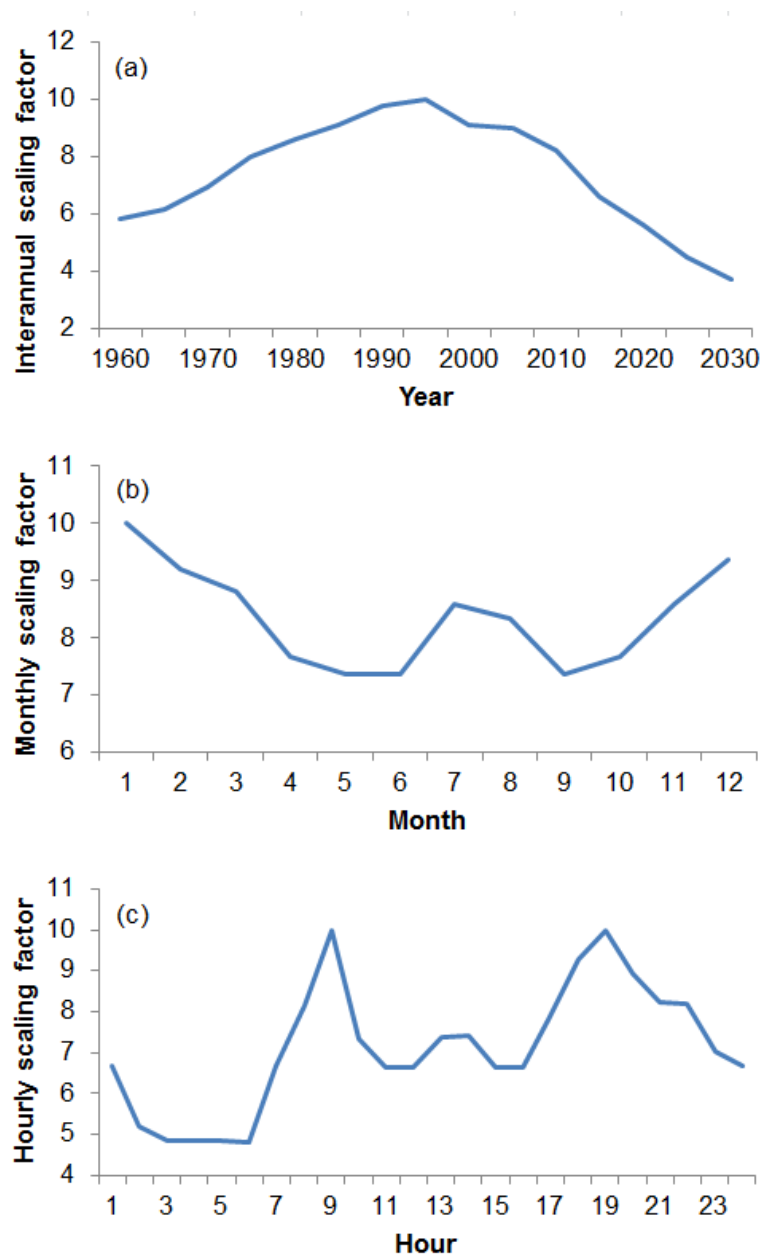


Figure S3. (a) Inter-annual, (b) monthly and (c) hourly scaling factors of PAH emissions.



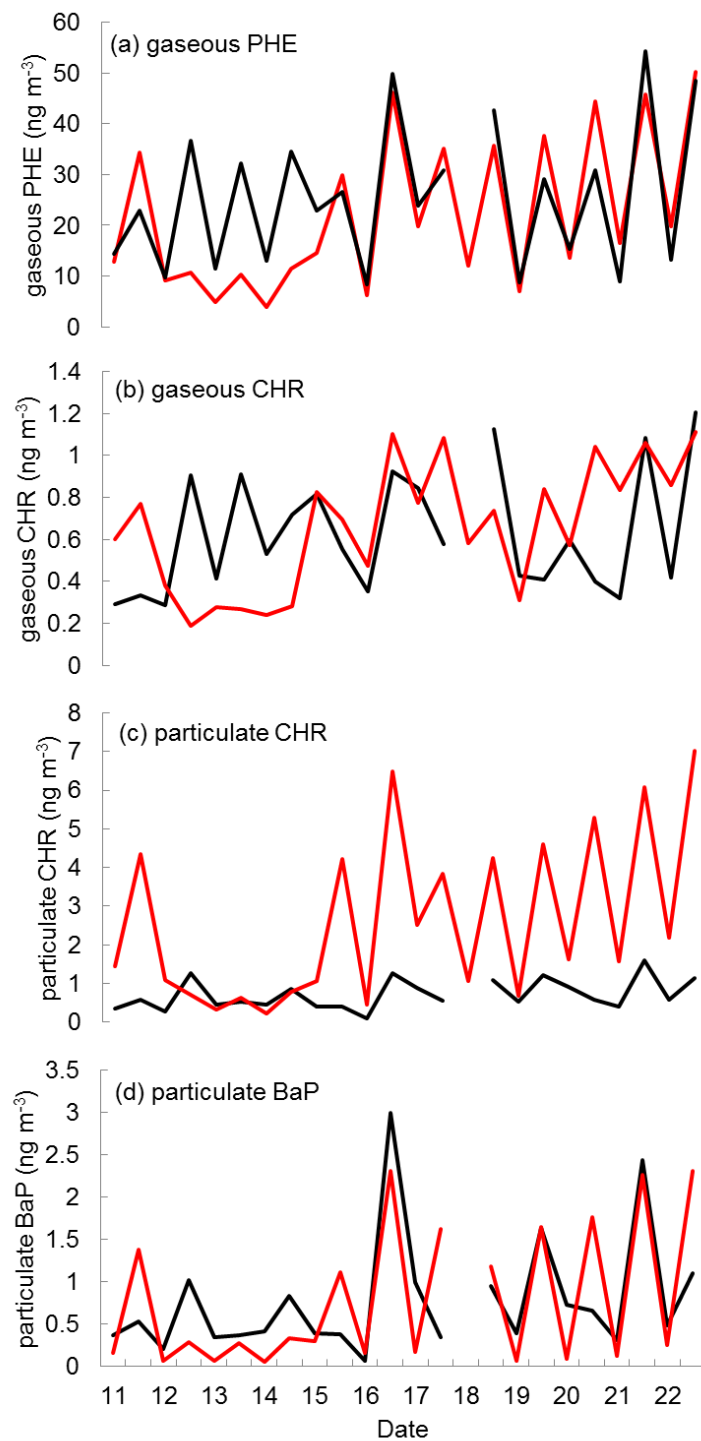


Figure S4. Simulated (red) and observed (black) concentrations of (a) gaseous PHE, (b) gaseous CHR, (c) particulate CHR and (d) particulate BaP at the Xianghe site during 11–22 July, 2013.

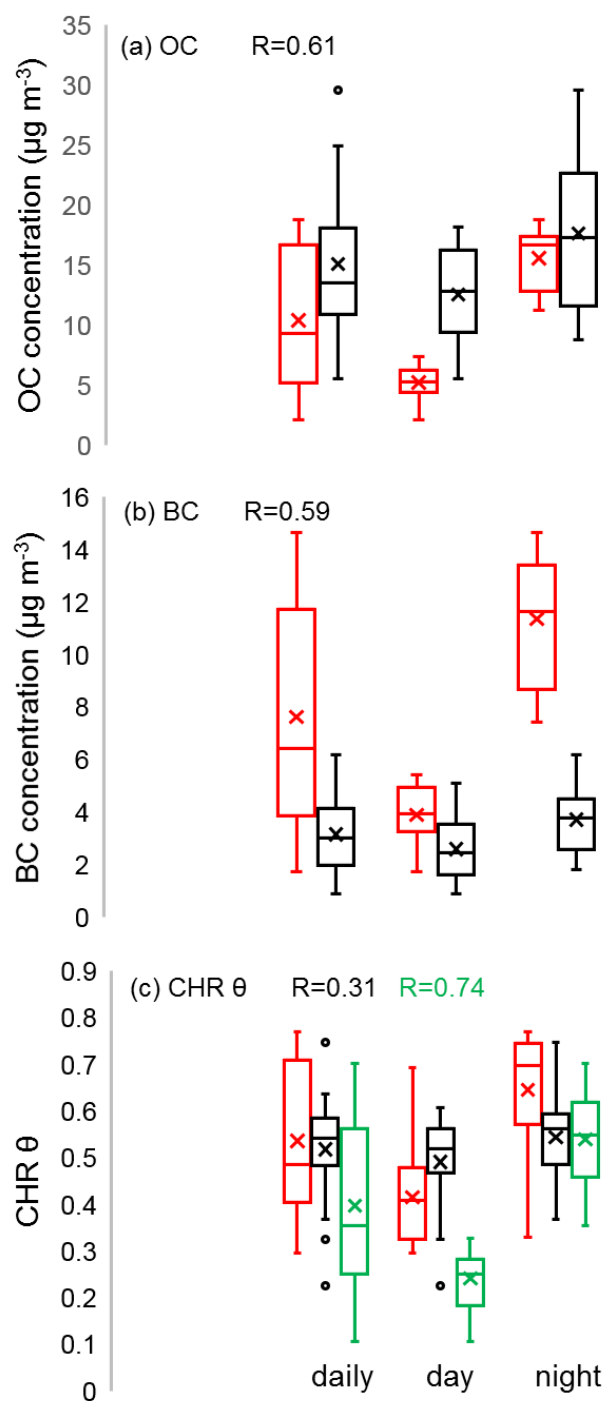


Figure S5. Simulated (red) and observed (black) daily, day and night concentrations of (a) OC, (b) BC and (c) particulate mass fraction of CHR at the Xianghe site during 11–22 July, 2013. Calculated particulate mass fraction of CHR based on the observed BC and OC is shown in (c) green column. The line and “X” in each box are the median and mean, while the boxes represent the 25<sup>th</sup> and 75<sup>th</sup> percentiles. Upper whisker is quartile 3 (Q3) + 1.5 x interquartile range (IQR) or maximum value, whichever is smaller; lower whisker is quartile 1 (Q1) - 1.5 x IQR or minimum value, whichever is larger. The Spearman's rank correlation coefficients R use combined daytime and nighttime data sets.

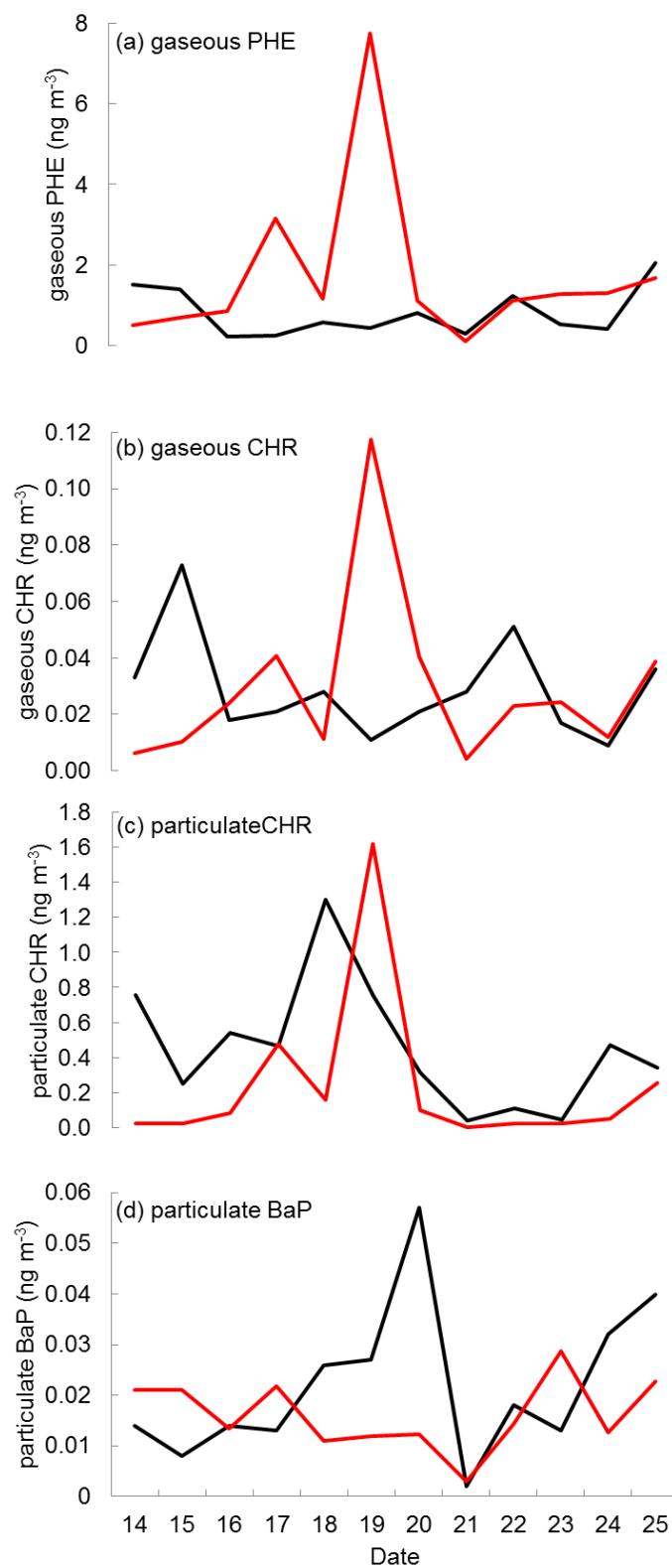


Figure S6. Simulated (red) and observed (black) concentrations of (a) gaseous PHE, (b) gaseous CHR, (c) particulate CHR and (d) particulate BaP at the Gosan site during 14–25 February, 2003.

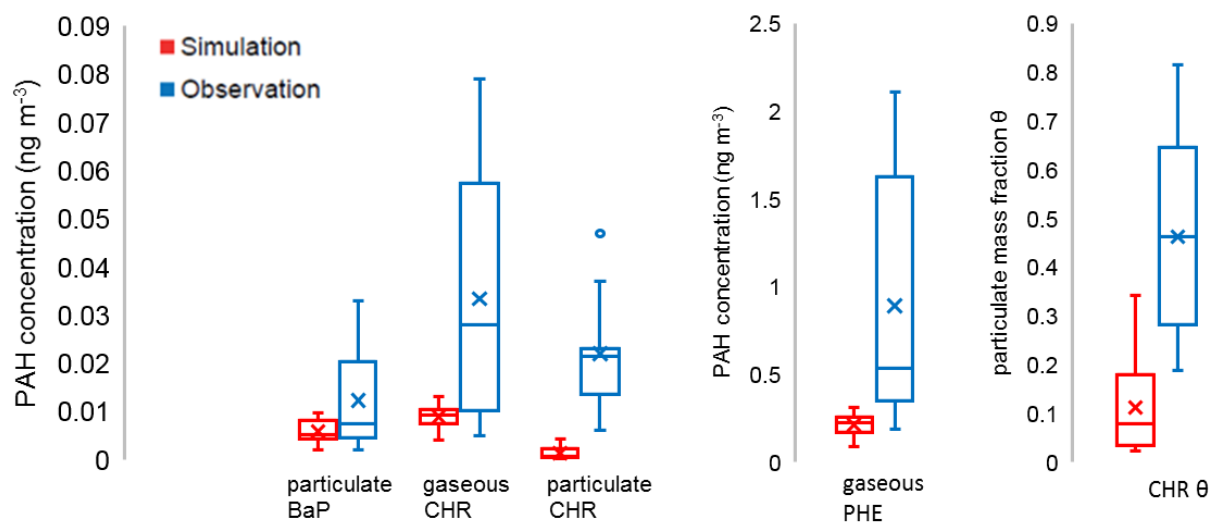


Figure S7. Simulated (red) and observed (blue) concentrations of gaseous PHE and CHR, particulate BaP and CHR, and particulate mass fraction of CHR at the Gosan site averaged over 6–17 June 2003 (summer case). The line and “X” in each box are the median and mean, while the boxes represent the 25<sup>th</sup> and 75<sup>th</sup> percentiles. Upper whisker is quartile 3 (Q3) + 1.5 x interquartile range (IQR) or maximum value, whichever is smaller; lower whisker is quartile 1 (Q1) - 1.5 x IQR or minimum value, whichever is larger.

Table S3. Observed (obs) and simulated (sim) median, mean bias (MB), root mean square error (RMSE), mean absolute deviation (MAD) in unit  $\text{ng m}^{-3}$  and Spearman's rank correlation coefficient (R) at the Xianghe site averaged over 11–22 July, 2013. R use combined daytime and nighttime data sets.

gaseous PHE												
	daily				day				night			
	obs	sim	sim-obs	(sim-obs)/obs	obs	sim	sim-obs	(sim-obs)/obs	obs	sim	sim-obs	(sim-obs)/obs
Median	23.9	15.5	-8.5	-35.5%	13.0	12.5	-0.5	-4.2%	33.3	35.3	2.0	6.0%
MB	-3.0				-2.0				-3.9			
RMSE	10.5				5.4				13.6			
MAD	7.9				4.5				11.1			
R	0.69											
gaseous CHR												
	daily				day				night			
	obs	sim	sim-obs	(sim-obs)/obs	obs	sim	sim-obs	(sim-obs)/obs	obs	sim	sim-obs	(sim-obs)/obs
Median	0.56	1.08	0.52	94.0%	0.42	0.61	0.19	45.5%	0.81	1.98	1.17	143.8%
MB	0.67				0.16				1.14			
RMSE	0.97				0.35				1.31			
MAD	0.74				0.30				1.14			
R	0.42											
particulate CHR												
	daily				day				night			
	obs	sim	sim-obs	(sim-obs)/obs	obs	sim	sim-obs	(sim-obs)/obs	obs	sim	sim-obs	(sim-obs)/obs

	obs	sim	sim-obs	(sim-obs)/obs	obs	sim	sim-obs	(sim-obs)/obs	obs	sim	sim-obs	(sim-obs)/obs
Median	0.58	0.98	0.40	69.1%	0.45	0.45	0.00	0.7%	0.97	4.89	3.92	404.4%
MB	1.83				0.03				3.48			
RMSE	3.07				0.46				4.23			
MAD	2.00				0.35				3.51			
R	0.54											

## particulate BaP

	daily				day				night			
	obs	sim	sim-obs	(sim-obs)/obs	obs	sim	sim-obs	(sim-obs)/obs	obs	sim	sim-obs	(sim-obs)/obs
Median	0.49	0.29	-0.20	-41.1%	0.39	0.13	-0.26	-67.1%	1.50	0.89	-0.61	-40.6%
MB	0.002				-0.29				0.27			
RMSE	0.61				0.38				0.76			
NMB	0.48				0.31				0.63			
R	0.62											

Table S4. Same as SI Table S3 but at the Gosan site averaged over 14–25 February, 2003.

gaseous PHE				
	obs	sim	sim-obs	(sim-obs)/obs
Median	0.54	1.14	0.60	109.8%
MB	0.92			
RMSE	2.35			
MAD	1.32			
gaseous CHR				
	obs	sim	sim-obs	(sim-obs)/obs
Median	0.02	0.02	0.00	-4.6%
MB	0.00			
RMSE	0.04			
MAD	0.03			
particulate CHR				
	obs	sim	sim-obs	(sim-obs)/obs
Median	0.40	0.06	-0.34	-84.1%
MB	-0.21			
RMSE	0.51			
MAD	0.36			
particulate BaP				
	obs	sim	sim-obs	(sim-obs)/obs
Median	0.016	0.018	0.002	13.8%
MB	0.000			
RMSE	0.021			
MAD	0.016			

## Text S1. Overview of the heterogeneous degradation of BaP

In the atmosphere, BaP resides almost entirely in the particle phase of aerosols and undergoes heterogeneous reaction with ozone, but the reactivity is not well characterized for particles of complex composition and morphology. Laboratory experiments have shown that the reaction with ozone is fast on the surface of solid particles but decreases substantially on liquid substrates and in the presence of coatings that can shield BaP from the oxidant (Pöschl et al., 2001; Kwamena et al., 2004; Kahan et al., 2006; Shiraiwa et al., 2009; Zhou et al., 2012; Zhou et al., 2013). So far, however, laboratory data are available only at room temperature and some of the experiments were performed at unrealistically high ozone concentrations (up to 3 orders of magnitude above tropospheric levels). Field experiments indicate substantial but not very fast degradation of BaP on aerosols in ambient air (Schauer et al. 2003), and recent studies suggest that the phase state can strongly influence the rates of gas uptake, oxidation, and chemical aging of organic aerosol particles depending on temperature and relative humidity (e.g., Shiraiwa et al. 2011, Berkemeier et al. 2016). Following up on the laboratory experiments of Zhou et al. (2012) and Zhou et al. (2013), Shrivastava et al. (2017) applied a highly simplified parameterization to investigate the influence of temperature and humidity on the atmospheric degradation and transport of BaP and concluded that organic aerosol coatings can have a strong influence on lung cancer risks.



**Text S2. Sampling at the Xianghe site and data quality control**

Particulate- and gas-phase samples were collected twice a day (day time samples 8:00 – 18:00 LT, night time samples 20:00 – 6:00 LT) during 11–22 July 2013 using a low volume sampler at a flow rate of  $2.3 \text{ m}^3 \text{ h}^{-1}$  (Leckel LVS,  $\text{PM}_{10}$  inlet) equipped with a quartz filter (Whatman QMA 47 mm) and 2 polyurethane foam (PUF) plugs (Gumotex Břeclav, density  $0.030 \text{ g cm}^{-3}$ , 55 mm diameter, total depth 10 cm, cleaned by extraction in acetone and dichloromethane, 8 h each, placed in a glass cartridge) in series. Field blanks were prepared (4 for particulate phase and 3 for gas-phase) following the standard protocol for mounting QFF and PUF plugs without turning on the sampler. PAHs were analyzed using gas-chromatography coupled to a mass spectrometer operated in the electron impact ionization mode. Breakthrough of the PUFs was not expected based on estimation of the safe sample volume (Kamprad and Goss, 2007; Melymuk et al., 2016), but nevertheless was controlled by separate analysis of PUF plugs in series and confirmed to not occur.

Limits of quantification (LOQ) were calculated based on instrument detection limits, which in turn are determined using 3 times the chromatogram baseline noise level:  $\text{LOQ} = \text{mean blank concentrations} + 3 * \text{standard deviations (SD)}$ . PAH concentrations are reported after subtraction of the mean field blank level (see Table S5). Only data points for which the concentrations exceeded the LOQ were considered. Therefore, gaseous PHE and CHR, and particulate phase CHR and BaP were used for the model evaluation, when all the samples with concentration exceeding LOQ. The field blank level of selected species corresponded to about 3-10% of the amounts collected in samples.

Table S5. Field blank concentrations (G: gas-phase; P: particulate phase; based on typical sampling volume) and percentage of samples with concentrations exceeding LOQ.

Species	Field blank concentrations (ng $\text{m}^{-3}$ )	Percentage of samples >LOQ
	Mean $\pm$ SD	
PHE	G: $2.46 \pm 0.57$	100%
	P: $0.56 \pm 0.06$	34%
CHR	G: $0.07 \pm 0.006$	100%
	P: $0.03 \pm 0.004$	100%
BaP	G: 0.03	0

P: < 0.03	100%
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EC and OC samples were collected by a Digitel high volume air sampler DHA-80 (Riemer, Hausen, Germany) on quartz fiber filters (MK 360, Munktell, Falun, Sweden) at a flow rate of 0.5 m<sup>3</sup> min<sup>-1</sup>. For analyses of quartz filters the EUSAAR 2 temperature-protocol was used and a charring correction using light transmission was applied (Cavalli et al., 2010).

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