Response to comments of referee #1

General comment:

Thank you for your revisions, they were helpful in answering some of the questions I had in the previous version. I was disappointed that a table of results was not provided.

Response:

Thanks for the constructive comments on both our current and previous versions, which help us to improve our manuscript.

Upon requests, we now add the Table R1 (SI Table S3) and Table R2 (SI Table S4) to show detailed statistic metrics about the Xianghe summer case and the Gosan winter case, respectively. Please kindly find more details in our point-to-point reply to your specific comments.

Also, in this response and the revised manuscript,

(1) We summarize the motivation of model development and new features in the newly developed WRF-Chem-PAH mode.

(2) Regarding model evaluation, we clarify the selection of evaluation data sets in detail. For model performance on seasonal bases, we added Gosan summer case and compared the model performance with previous global models. To further demonstrate that our model performs at least similarly with previous regional models in East Asia, we choose the same simulation period in Beijing as by Inomata et al. (2012) and compare the daily concentrations of the same species (total CHR and total BaP) with that study. The comparisons show that the two models perform quite similar and more details will be presented in the following response.

Specific comments:

I am still unconvinced by the model performance data. For example, in Fig.3, the authors present 11 days of data. These can be examined full day, daytime only, and nighttime only. The only metric produced to compare these two data sets is a correlation coefficient. It's not clear which two sets of data the correlation is between and it's not clear to me that a simple correlation is meaningful here. For Fig3c, the correlation for particulate chrysene is provided as 0.59, but the night time simulation looks completely uncorrelated in the graph. The only graph where all three - full day, day, night - look reasonably similar are the gas-phase phenanthrene comparisons. Some of the poor performance may be due to using summer samples, when chrysene and benzo[a]pyrene concentrations are relatively low. More clarification is definitely needed and perhaps a metric that takes into account absolute differences as well.

Response:

The correlation coefficients shown in Fig. 3 use combined daytime and nighttime data sets, i.e., between 24 observation and 24 simulation samples (12 daytime and 12 nighttime). These correlation coefficients have all passed the Student's t-test with a significance level of 0.05. Correlation coefficients for only daytime or nighttime samples are not included, because of small data sets. In Fig. 5, correlation coefficients are also not shown for the same reason. We have added the clarifications of correlation coefficients to the caption of Fig. 3: *The correlation coefficients use combined daytime and nighttime data sets, passing the Student's t-test with a significance level of 0.05.*

We add the Table R1 (SI Table S3) and Table R2 (SI Table S4) to show detailed statistic metrics about the Xianghe summer case and the Gosan winter case, respectively. Table R1 (SI Table S3) shows that our model performance in Xianghe summer is as good as the previous modeling study in Beijing (Xianghe is a semi-urban town in the Beijing metropolitan area) comparing with daily PAH observation (Inomata et al., 2012). Their simulated daily average/median concentrations of PAH are 0.1–2 factors of observation, while in our summer case these are a factor of 0.7–3; their correlation coefficients between simulation and observation are 0.30–0.58, while in our summer case these are 0.42–0.72. Our diurnal comparisons reveal that the overestimate of daily CHR concentrations mainly comes from nighttime rather than daytime, both for gaseous and particulate CHR. The following discussion was added: Page 9 line 8, "*PAH diurnal variabilities are well captured for both gas- and particulate-phase species at the Xianghe site, with correlation coefficients of 0.42–0.72 (Fig. 3, Table S3) compared with 0.30–0.58 in Beijing (Xianghe is a semi-urban town in the Beijing metropolitan area) by Inomata et al. (2012)".* Page 9 line 14, "*The model well catches the observed daily average concentration of particulate BaP (observation 0.78 ng* m^{-3}*, simulation 0.78 ng* m^{-3}*), while Inomata et al. (2012) underestimated daily concentration of BaP in Beijing by about a factor of 2.* Page 9 line 18, *"Further diurnal comparisons reveal that such overestimate of daily CHR concentrations mainly comes from nighttime rather than daytime (Table S3)."*

Motivation and new feature of the model:

The WRF/Chem-PAH model has been developed to resolve detailed transport and transformation processes of PAHs, particularly in high temporal and spatial resolution. Regarding the model development, our WRF/Chem-PAH model reflects the state-of-the-art and the up-to-date understanding of current PAHs studies with several new or updated features. (1) The gas-phase reactions include not only reactions with OH but also reactions with previous neglected O_3 and NO_3 radical. We found that during nights with high NO_3, the NO_3 reaction causes a significant night-time drop of gaseous PAH levels by about -50 – -75%. (2) The heterogeneous degradation of particulate BaP is treated with a new elaborated kinetic scheme, which considers

aerosol phase change and chemical reactivity under different temperature and humidity. Compared with previous BaP degradation schemes, the new scheme greatly improves model performance in both near source summer time (e.g., Xianghe site) and remote winter time (e.g., Gosan site) cases (on-going project). (3) The gas/particle partitioning considers absorption into organic matter and adsorption onto soot, which is an improvement from the commonly used adsorption to unspecific aerosol surfaces i.e., Junge-Pankow scheme. (4) The air-soil gas exchange process embedded in the WRF/Chem-PAH module is important for semi-volatile PAHs under certain atmospheric conditions (another on-going project), but neglected by some previous models. (5) We have successfully demonstrated an example to implement low concentrated tracers in WRF/Chem (Section 2.1) and solved the crucial transport problem of low concentrated tracers (Section 3). The method and solution can be adapted to other atmospheric low concentrated species by WRF/Chem users.

Model evaluation:

Previous global or regional models have demonstrated their ability to reproduce seasonal or annual variations of PAHs in the atmosphere, but to our knowledge, none of them compared with observation data on a diurnal basis, let alone in both atmospheric phases.

We use the Xianghe summer data since it is the only available observation in East Asia that provides continuous measurement both in daytime and nighttime and in both gaseous and particulate phases. Previous modeling studies (e.g. Zhang et al., 2011a; Zhang et al., 2011b; Inomata et al., 2012; Inomata et al., 2013; Sehili and Lammel, 2007; Lammel et al., 2009; Friedman and Selin, 2012; Friedman et al., 2014; Shen et al., 2014) were not able to do so. Simultaneous EC and OC data are also available for evaluation of gas/particle partitioning. Moreover, since East Asia in summer often experiences complex atmospheric conditions (e.g. East Asia summer monsoon), the model's good performance in Xianghe summer case implies its ability in representing complex atmospheric conditions.

The Gosan winter data is used to validate model performance in winter. An important reason to choose a winter episode at the Gosan site is that the continental outflow and emissions are both strongest in this season. This winter episode is designated as "continental outflow conditions" and "pollution period" which transports PAH from continental sources to Gosan (Kim et al., 2007; Kim et al., 2012).

However, to evaluation model performance in a seasonal basis, we do have included a simulation of a summer episode at the Gosan site (Fig. S7, continuous summer period 6–17 June 2003 when all the simulated species are available). In winter, our simulated average BaP concentration is ≈ 0.022 ng m^{-3} at Gosan site, in good agreement with the observed 0.020 ng m^{-3}, while the simulated BaP was underestimated by about 50% in Zhang et al. (2011a). For the summer case, our simulated average BaP concentration is ≈ 0.006 ng m^{-3}, much closer to the

observed value of 0.012 ng m^{-3} (Fig. S7) than the previously simulated BaP concentration of 0.001 ng m^{-3} in Zhang et al. (2011a). No simulated values of other species have been reported by Zhang et al. (2011a). In general, WRF/Chem-PAH model shows good/reasonable agreement with observations in both winter and summer seasons.

The simulation periods are short in Gosan because only few periods could be covered from November 2001 to August 2003 with the longest consecutive measurements in each season not exceeding 15 days (Kim et al., 2012). Only total PAHs without consideration of single species have been used for model evaluation in several previous studies (Zhang et al., 2009; Zhang et al., 2011a; Zhang et al., 2011b). In Kim et al. (2012), even larger data gaps apply for monitoring of individual PAH species at Gosan: the spring episode (28 March – 11 April 2002) missed 6 out of total 15 samples of gaseous PHE, the summer episode (18 August – 1 September 2003) missed all data of particulate CHR and the fall episode (12–26 November 2001) missed all data of gaseous BaP. Only the winter episode (14–25 February 2003) has the complete daily observation of the simulated PAH species in both particulate and gaseous phases. Data availability is upon personal communication with Prof. Young-Sung Ghim.

In general, the observation data set is much smaller in Asia, unlike in North America or Europe where continuous monitoring of PAH at many background sites are available. There is no PAH monitoring in China, while the one in Korea (only one Gosan site) and Japan are discontinuous (e.g. 1 day/month in Japan) and/or cover only particulate phase. Campaigns are also limited. For example in Inomata et al. (2012), the simulated concentrations of nine particulate PAHs agreed very well with the measured concentrations, but it is a pity that there were only particulate PAH observation available and the Noto site was monitored at 1-week intervals. Hence, more model process evaluation in East Asia on the seasonal scale is only possible when more observation data is available in the future.

To further demonstrate that our model performs at least similarly with previous regional models in East Asia, we choose the same simulation period in Beijing as by Inomata et al. (2012) and compare the daily concentrations of the same species (total CHR and total BaP) with that study. Figure R1 shows that the RAQM2-POP model underestimated average CHR by about 15% while our WRF/Chem-PAH model overestimated by 3%; the RAQM2-POP model overestimated average BaP by about 50% while our WRF/Chem-PAH model underestimated by about 50%. It is worth noticing that, without knowing the exact starting and ending hours of the daily samples, we arbitrarily choose 08:00 (local hour) to the next day 08:00 as our simulated daily averages, which may lead to a slight time shift in the comparison with observations. Apparently, the two models perform quite similar.

Table S1 (SI Table S3). Observed (obs) and simulated (sim) mean concentration, median, standard deviation (σ), mean bias (MB), root mean square error (RMSE), mean absolute deviation (MAD) in unit ng m^{-3} and correlation coefficient (R) at the Xianghe site averaged over 11–22 July, 2013. The correlation coefficients use combined daytime and nighttime data sets, passing the Student's t-test with a significance level of 0.05.

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
Mean	25.6	22.2	-3.4	-13.4%	13.6	11.7	-1.9	-14.1%	36.5	32.6	-3.9	-10.7%
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%
σ	13.8	14.8	0.9	6.7%	5.1	5.2	0.1	2.5%	9.6	13.8	4.2	43.8%
MB	-3.0				-2.0				-3.9			
RMSE	10.5				5.4				13.6			
MAD	7.9				4.5				11.1			
R	0.72											

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
Mean	0.63	1.27	0.65	102.8%	0.48	0.65	0.17	34.5%	0.76	1.90	1.14	149.2%
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%
σ	0.28	0.77	0.49	170.9%	0.19	0.27	0.08	42.6%	0.29	0.57	0.28	97.5%
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
Mean	0.85	2.46	1.61	189.6%	0.78	0.52	-0.26	-33.4%	0.92	4.40	3.48	378.0%
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%

σ	0.75	2.65	1.90	252.7%	0.99	0.35	-0.64	-64.7%	0.37	2.52	2.15	579.3%
MB	1.83				0.03				3.48			
RMSE	3.07				0.46				4.23			
MAD	2.00				0.35				3.51			
R	0.59											

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
Mean	0.78	0.78	0.00	0.3%	0.43	0.14	-0.29	-68.1%	1.10	1.37	0.27	24.5%
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%
σ	0.81	0.70	-0.12	-14.5%	0.24	0.08	-0.16	-67.5%	0.81	0.73	-0.08	-10.1%
MB	0.002				-0.29				0.27			
RMSE	0.61				0.38				0.76			
NMB	0.48				0.31				0.63			
R	0.69											

Table R2 (SI 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
Mean	0.81	1.73	0.92	113.6%
Median	0.54	1.14	0.60	109.8%
σ	0.57	1.95	1.38	242.1%
MB	0.92			
RMSE	2.35			
MAD	1.32			

gaseous CHR				
	obs	sim	sim-obs	(sim-obs)/obs
Mean	0.03	0.03	0.000520	1.8%
Median	0.02	0.02	0.00	-4.6%
σ	0.02	0.03	0.01	69.8%
MB	0.00			
RMSE	0.04			
MAD	0.03			

particulate CHR				
	obs	sim	sim-obs	(sim-obs)/obs
Mean	0.45	0.24	-0.21	-47.5%
Median	0.40	0.06	-0.34	-84.1%
σ	0.35	0.44	0.09	26.2%
MB	-0.21			
RMSE	0.51			
MAD	0.36			

particulate BaP				
	obs	sim	sim-obs	(sim-obs)/obs
Mean	0.020	0.022	0.002	8.3%
Median	0.016	0.018	0.002	13.8%
σ	0.015	0.019	0.004	29.9%
MB	0.000			
RMSE	0.021			
MAD	0.016			

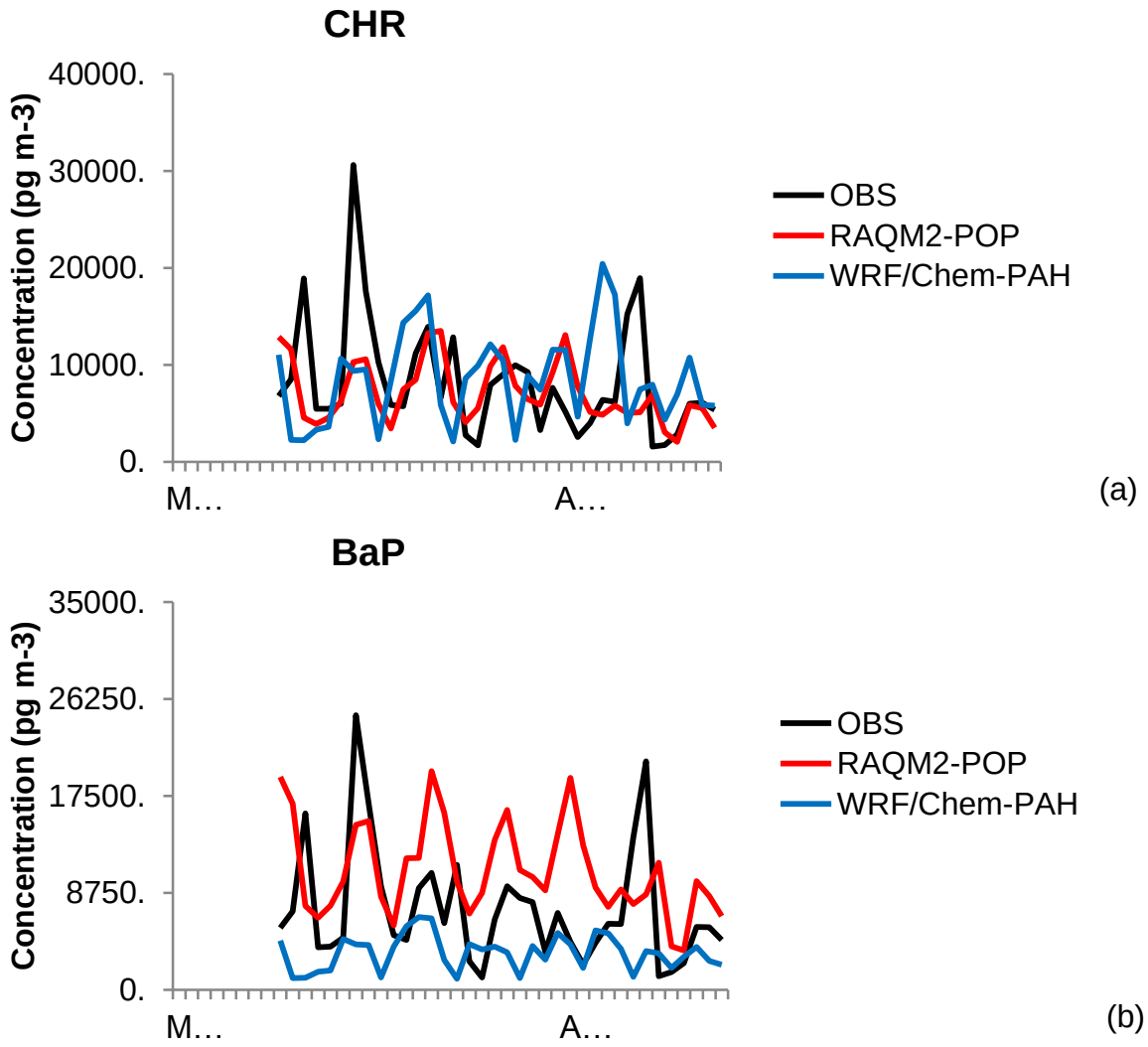

Figure R1. Comparison of the observed and simulated concentrations of (a) total (gas + particulate) CHR and (b) total BaP at Beijing. The data at Beijing were daily, March-April 2005. Simulated results of RAQM2-POP model and WRF/Chem-PAH model are from Inomata et al. (2012) and this study, respectively.

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