Interactive comment on "PAH concentrations simulated with the AURAMS-PAH chemical transport model over Canada and the USA" *by* E. Galarneau et al.

Anonymous Referee #1

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General comments: An effort is made to model various semivolatile and non-volatile PAHs in air on short time scales and on the regional spatial scale (North America), including gas-particle partitioning. Such studies are timely as the understanding of the atmospheric fate, long-range transport and distribution of PAHs lags behind the one of other organic substance classes and other criteria pollutants. PAHs are toxic, most of the semivolatile, some of them persistent, hence, air-surface exchange (and multicompartmental cycling) and gas-particle partitioning are key processes for the atmospheric fate and long-range transport. The research field started from box models (e.g. Halsall et al. Atmos. Environ. 2001; Yaffe et al. Risk Analysis 2001; Prevedouros

et al. Chemosphere 2004), while state of the art modelling includes validated dynamic aerosol sub-model and air-surface exchange parameterisations.

Results from the application of an air quality model adopted to PAHs are reported. The adoption to the substances studied is incomplete. The model is not presented in sufficient detail. Deficiencies which render the results more or less inconclusive are an unclear aerosol sub-model (not introduced, references to validation lacking, how many components ? how is its performance with regard to major modes' surface and major components' mass concentrations at background sites ?) and, most severe, lack of air-surface exchange parameterisations (inacceptable for the treatment of semivolatile substances which are long-lived in surface water or soils, which is the case for most of the substances addressed). In the same group another model, appropriate for studies of semivolatiles (including air-surface exchange), had been developed (and used to study of chlorinated semivolatiles; Gong et al., Atmos Chem Phys 2007), but is not used in this study. The results should not be published (in the peer-reviewed literature) at the present development stage of the model, unless limited to the study of non-volatile PAHs (such as benzo(a)pyrene). Unplausible results are found with regard to the predicted particulate fraction and the predicted concentrations using different gas-particle partitioning models. Results determined by the aerosol sub-model would only be meaningful were the sub-model be evaluated and the relevant model output (lifetime of particle size modes/bins, chemical composition and number, surface and mass concentrations) be presented and discussed (see also specific comments, below). The factors influencing the modelled gas-particle partitioning should be presented and then discussed, such that conclusions can be drawn. As is, the results have preliminary character. The discussion of the results in the light of previous knowledge in the field is deficient but could be improved by basing on the results being presented as atmospheric lifetimes and/or deposited and degraded amounts relative to emitted amounts. The evaluation of model results by observational data is obviously biased by the choice of sites: Only background sites can meaningfully be compared with model output regarding the chosen model spatial resolution. Observations at sites influenced by local

sources (urban, residential) will or may reflect strong spatial and temporal gradients, beyond the model resolutions, major aerosol components not included in the aerosol sub-model, and non-equilibrium partitioning. The temporal profile of the emission data (which is not specified) would be needed for discussion and interpretation.

Specific comments and minor corrections:

Introduction, p 18419: It should be mentioned that benzo(a)pyrene is a criteria pollutant in many countries, regulated under a regional UN convention (Arhus protocol to the CLRTAP Convention) and discussed in the context of a global one (UNEP Stockholm or POPs Convention). As to the study region itself: please complement by information on respective policy in Mexico

l 27: also box model applications (Yaffe et al. Risk Analysis 2001; Prevedouros et al. Chemosphere 2004) should be cited; should read 'Shatalov et al.'; this group's modelling, however, has been advanced and Gusev et al. 2011 (Persistent Organic Pollutants in the Environment. EMEP Status Report No. 3/2011, Meteorological Synthesizing Centre – East, Moscow) would be more appropriate to be quoted; Sehili and Lammel's modelling was global; other models in use should be quoted, too: Zhang et al. Atmos. Environ. 2011, 45, 2820-7.

p 18420 ll 19-21: Be more quantitative. Semivolatiles are compounds with partial pressures in the range 1e-6 – 1e-2 Pa at 298K. Rephrase avoiding 'use'. ll 24-26: Not true as several partitioning models have been tested by Aulinger et al. 2007 and Lammel et al 2009.

p 18421, l 8: be more concise, avoid 'usually', introduce and reference aerosol sub-model used

p 18422, l 24-24: unclear which kinetics: first order or second order ? remove 'equilibrium' as misleading here

p 18423, ll 11-15: trivial, drop

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p 18424, ll 1-2: 0.172 J/m2 was suggested by Junge, 1977, as default for all condensable vapours, but 1.71 J/m^2 bei Pankow, 1987 (using other units), for PAHs, which should be preferably used. Here a justification is needed for the selection of Junge's value for the 'constant' and a discussion of the influence of choice of this parameter.

p 18425, l 2: K_aw with temperature dependence (according to Table S1.1), should be noted here

p 18425, ll 10-13: trivial, drop

p 18426, section 2.2: the emission's temporal pattern, spatial resolution, and major limitations (which emissions were neglected) should be explained

l 21: better 'observational data'

section 2.3: number of sites, site type and sampling protocol (e.g. 24 h, were oxidant denuders used or not?) should be mentioned here

p 18427 l 16: 'particulate' rather than 'particle'

p 18428 ll 15-16: be quantitative here: What was the temporal emission pattern like ? Should be discussed in the light of the emissions' temporal resolution

ll 17-19: agreement between partitioning models is very surprising and not plausible regarding that other modelling studies using a model appropriate for semivolatiles with a dynamic aerosol sub-model found very significant differences (e.g. Lammel et al 2009)

ll 17-24: very deficient discussion: How do the differences look like for the entire domain, and at the subset of background sites ? The model resolution (42km) is such that polluted sites cannot be compared with model output, as the gradients can never be reproduced. The comparison between predicted and observed values in this manuscript is strongly biased by the inclusion of a number of urban or industrial site, it seems (cf. p 18430 ll 9-10; which is nowhere told, though). Try for background stations only and

discuss these results.

p 18429 l 9: Is it applicable yes or no ? Losses occur unless oxidant denuders are used, which, nowadays, is the case in many networks.

ll 13-15: Very severe deficiency of the model, renders is unsuitable to simulate fate of semivolatiles. Re-volatilisation is expectedly very significant for the cycling of e.g. fluoranthene and anthracene. Air-surface exchange needs to be included in the processes covered by the model. Why was no appropriate model chosen (e.g. Gong et al Atmos Chem Phys 2007) ?

ll 24-25: conclusion is not justified as the results are biased by the selection of sites

p 18430 ll 9-20: The whole paragraph is not conclusive without a site and emissions' temporal patterns description (which both is not there). Obviously are sites included which are strongly influenced by local sources (see above). Otherwise such large ranges would not occur.

p 18431 l 3: number of sites should be introduced in section 2.3. Here a number is given which differs from the one in section 4. Why?

p 18432 ll 3-10: should be discussed in the light of type of site and model spatial and emission' temporal resolutions

ll 20-22: not true, horizontal concentration gradients within urban areas can be expected even for 24h samples as a consequence of relative position of sites to major sources in the area (subject to wind direction)

ll 27-29: the effective sink process for ozone by reaction with NOx should be mentioned/discussed, too, as the list probably contains sites which are directly influenced by road traffic emissions (?). Then, the characteristic time for ozone formation is not relevant for its temporal variation.

p 18433 ll 3-13: quite trivial and, in particular, known a priori. Hence, move to intro-

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duction or drop section 3.2: should be discussed in the light of predicted atmospheric lifetimes (nowhere given)

p 18434 ll 5-15: Performance of partitioning models should be discussed in the light of the aerosol sub-models performance. Was it evaluated ? What is the range of organic carbon fractions and aerosol surface predicted by the model for various type of sites?

p 18434, l 23: be more concise, replace 'volatility' by the quantity addressed

p 18436 ll 4-27: almost no conclusions in this text (except ll 20-22), drop or move to other section

l 17: be more concise, avoid 'majority'

ll 23-24 a priori knowledge, drop or move to other section

p 18436 ll 1-2: yes: preliminary character of this communication Table 1 caption: n should be explained.

Fig. 2 is it a mix of urban, residential/urban background and continental background stations ?

Fig. 5 caption: the word 'ratio' is missing (as in caption of Fig 4)

Table S1.1: No reference is given for OH degradation rate coefficients. Is it estimated using the EPIsuite model ? Experimentally determined rate coefficients should be used whenever available. The OH degradation rate coefficients for anthracene were determined higher (190e-12) and for fluoranthene lower (11e-12; ; Brubaker and Hites, 1998) than used here.