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PAH concentrations simulated with the AURAMS-PAH chemical transport model over Canada and the USA

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Abstract

The off-line Eulerian AURAMS chemical transport model was adapted to simulate the atmospheric fate of seven PAHs: phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene + triphenylene, and benzo[a]pyrene. The model was then run for the year 2002 with hourly output on a grid covering southern Canada and the continental USA with 42 km horizontal grid spacing. Model predictions were compared to ∼5000 24 h average PAH measurements from 45 sites, eight of which also provided data on particle/gas partitioning which had been modelled using two alternative schemes. This is the first known regional modelling study for PAHs over a North American domain and the first modelling study at any scale to compare alternative particle/gas partitioning schemes against paired field measurements.

Annual average modelled total (gas + particle) concentrations were statistically indistinguishable from measured values for fluoranthene, pyrene and benz[a]anthracene whereas the model underestimated concentrations of phenanthrene, anthracene and chrysene + triphenylene. Significance for benzo[a]pyrene performance was close to the statistical threshold and depended on the particle/gas partitioning scheme employed.

On a day-to-day basis, the model simulated total PAH concentrations to the correct order of magnitude the majority of the time. Model performance differed substantially between measurement locations and the limited available evidence suggests that the model spatial resolution was too coarse to capture the distribution of concentrations in densely populated areas. A more detailed analysis of the factors influencing modelled particle/gas partitioning is warranted based on the findings in this study.

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous air pollutants that tend to be most concentrated in areas of dense human population (Hafner et al., 2005) but are also detected at locations remote from local sources (Hung et al., 2005). Many PAH species have been classified as carcinogens (IARC, 2010) and they are implicated routinely as toxicants in airborne particulate matter (Kelly and Fussell, 2012).

In Canada, PAHs meet the criteria for inclusion on the Toxic Substances List of the Canadian Environmental Protection Act (Environment Canada and Health Canada, 1994), and the resulting government obligation has been to reduce or minimise their release into the environment. Nationwide anthropogenic emissions of benzo[a]pyrene, a commonly-reported species, fell by 70 % between 1990 and 2010 according to estimates made by the National Pollutant Release Inventory (Environment Canada, 2012). Though there are no federal guidelines for PAHs in Canadian air, a recent analysis of ambient monitoring data found that measured PAH concentrations regularly exceed the health-based guidelines set by the Canadian province of Ontario (Galarneau and Dann, 2011).

In the USA, PAHs are listed as Clean Air Act Hazardous Air Pollutants as part of the polycyclic organic matter (POM) class of compounds (US EPA, 2012) and have been identified as a regional cancer concern in the US National-Scale Air Toxics Assessment (US EPA, 2012). Industrial releases to air reported to the US Toxics Release Inventory (TRI) fell by 35 % between 1995 and 2010 (US EPA, 2012). There is no federal US guideline for PAHs in ambient air.

PAH measurements are labour-intensive compared to those of criteria air contaminants such as ozone and particulate matter, and the processes governing their atmospheric fate are not yet well-understood. In an attempt to elucidate the spatiotemporal distributions of PAH sources and ambient concentrations, several numerical modelling studies have been published. Lagrangian frameworks have been used for Europe (Van Jaarsveld et al., 1997; Halsall et al., 2001) and China (Liu et al., 2007; Lang et al., 2007, 2008). Others studies have used box modelling (Prevedouros et al., 2004) and multimedia fate approaches (Prevedouros et al., 2008). Eulerian chemical transport models (CTMs) have been developed for Europe (Shatalov, 2005; Sehili and Lammel, 2007; Aulinger et al., 2007; Matthias et al., 2009; Bieser et al., 2012) and east Asia (Zhang et al., 2009, 2011a,b; Inomata et al., 2012), and two such studies on a global scale have also been published recently (Lammel et al., 2009; Friedman and Selin, 2012).

The aforementioned studies differ in many respects relating to the PAH species examined, the temporal variability of their emissions, and the spatial resolutions and process representations in the models. None has focussed exclusively on North America at the regional scale. As well, although several particle/gas partitioning mechanisms have been explored in other models, including Junge–Pankow adsorption (Junge, 1977; Pankow, 1987), organic matter sorption (Finizio et al., 1997), and combined adsorption/absorption (Dachs and Eisenreich, 2000), no previous studies have evaluated model output against phase-distributed measurements for alternative partitioning expressions on the same domain.

This study presents the results of a chemical transport model, AURAMS-PAH, run over North America at 42 km horizontal grid spacing with hourly output for the year 2002. Seven PAH species were simulated with the model. Three isomer pairs of decreasing volatility and increasing particulate fraction comprise six of the species: phenanthrene (PHEN) and anthracene (ANTH) (178 $\mathrm{g\,mol^{-1}}$), fluoranthene (FLRT) and pyrene (PYR) (202 $\mathrm{g\,mol^{-1}}$), and benz[a]anthracene (BaA) and chrysene/triphenylene (C + T) (228 $\mathrm{g\,mol^{-1}}$). The seventh PAH, benzo[a]pyrene (BaP) (252 $\mathrm{g\,mol^{-1}}$), is not generally considered to be semivolatile but has been included due to its common use as a representative PAH species. Two particle/gas partitioning schemes, Junge–Pankow (JP: Junge, 1977; Pankow, 1987) and Dachs–Eisenreich (DE: Dachs and Eisenreich, 2000),were tested.

Model performance was evaluated against ~5000 measurements from 45 stations in established networks in Canada and the USA. This is the first published model to be run and evaluated for PAH concentrations and their distributions between the particle and gas phases using two partitioning methods. It is also the first such model to be evaluated over a regional North American domain.

2 Methods

2.1 Model description

AURAMS (A Unified Regional Air Quality Modelling System) is an Eulerian CTM originally developed to simulate criteria air contaminants. The standard version of the model uses a sectional approach to represent the size distribution of airborne particles: 12 size bins from 0.01 to 40.96 µm in diameter and 9 particulate species (sulphate, nitrate, ammonium, elemental carbon, primary organic aerosol, secondary organic aerosol, crustal material, sea salt, and aerosol water) are usually considered. The model includes process representations for tropospheric gas-phase oxidative chemistry, the absorptive formation of secondary organic aerosols, inorganic heterogeneous chemistry, particle microphysics (nucleation, condensation, coagulation, etc.), cloud processing of aerosols, advective transport, vertical diffusion, and gas and particle emissions and deposition. Details of its design have been summarized by Gong et al. (2006).

A modified version of the AURAMS CTM known as AURAMS-PAH was developed to incorporate primary semivolatile organic compounds that are subject to sorptive partitioning. Starting from the standard AURAMS CTM had the advantage that a number of required fields for modelling PAHs were already available. These included hydroxyl concentration, total particle surface area, and fractions of particle elemental carbon and organic carbon. The modifications made to AURAMS version 1.3.2 in order to simulate PAHs are described below. Physico-chemical property values used for each PAH in the modified code are found in Table S1.1 of the Supplement.

2.1.1 Dry deposition of gases

Within AURAMS, gaseous dry deposition velocities are modelled using the inverse resistance analogy for several land-use categories (Zhang et al., 2002). Three resistances are assessed in AURAMS and only the first of these (aerodynamic resistance) is independent of the chemical species under consideration. The species-dependent resistances are the quasi-laminar sub-layer resistance and the surface or canopy resistance. The latter both depend on the gas-phase diffusivity of the compound in question, and this quantity was calculated in the model according to the Fuller et al. method described in Reid et al. (1987).

Surface or canopy resistance is the most complex of the three gaseous dry deposition component resistances and tends to dominate total dry deposition (Zhang et al., 2002). One of its sub-components, mesophyll resistance, was set to $100\,\mathrm{s\,m^{-1}}$ for species that are relatively insoluble in water and have small oxidizing capacities, as is the case for PAHs. The remaining sub-components (cuticle and ground resistances) are determined by scaling to O_3 and SO_2 settings based on physico-chemical qualifications. For the PAHs, scaling factors to O_3 and SO_2 for both acetaldehyde and C_3 carbonyls, the least soluble organic compounds considered in AURAMS aside from the PAHs, were used.

Volatilisation of gaseous PAHs can occur from exposed water (Hoff et al., 1996), soil (Jones, 1994), and impervious urban surfaces (Diamond et al., 2000). Net gaseous deposition to the Great Lakes in 2002 was downward (Blanchard et al., 2005) suggesting that PAH fugacities in air exceeded those in surface compartments at the regional scale. Volatilisation was not included in this first-generation version of AURAMS-PAH and the effect of this omission is presented in Sect. 3.1.1.

2.1.2 Gas-phase reactions

Reactions of gas-phase PAHs with hydroxyl radicals are considered in this model. Since these reactions consume relatively little hydroxyl due to the trace concentrations of PAH, their reactions were simulated outside the AURAMS gas-phase chemistry solver. PAH oxidative loss was estimated as a first-order process using the model-predicted OH concentration immediately preceding equilibrium particle-gas partitioning. Only seven new gas-phase concentration fields were added to the CTM; PAH reaction products were not tracked in the model, either as individual gas-phase species or as contributors to SOA.

Hydroxyl reaction rate constants were taken from the program AOPWIN which is part of the US EPA's EPI Suite (US EPA, 2006). Measured constants are available for three low-molecular-weight PAHs considered here (phenanthrene, anthracene, fluoranthene) and these values were represented in AOPWIN. However, measurements for the remaining four PAHs are not available and the software predicted the same hydroxyl reaction rate constant of $50 \times 10^{-12}\,\mathrm{cm^3\,molec^{-1}\,s^{-1}}$ for these species.

2.1.3 Particle representation of PAHs

Seven additional particle species, each with 12 size bins as in the original AURAMS configuration, were added to the model to represent the particle-bound PAH mass.

2.1.4 Particle/gas partitioning of PAHs

A new algorithm was developed for AURAMS-PAH to account for the sorptive particle/gas partitioning of PAHs. It is fully adaptable to other semivolatile species with similar atmospheric partitioning behaviour to PAHs such as dioxins and furans, PCBs, and organochlorine pesticides. The partitioning of PAHs to airborne particles was assumed to be fully reversible.

Two instantaneous equilibrium sorptive partitioning expressions were incorporated in the new partitioning subroutine. The first treated particle/gas partitioning as a Langmuirian adsorption process on a uniform particle surface (JP: Junge, 1977; Pankow, 1987). The model calculations began by adding the particulate PAH concentrations in all size bins (ΣC_p) and the gas-phase PAH concentration (C_g) to give a total PAH concentration (C_TOT) for each species. An updated bulk particulate fraction (φ) was then assigned according to the first part of Eq. (1):

$$\varphi = \frac{c\Sigma\theta}{c\Sigma\theta + p_\mathrm{L}^0} = \frac{\Sigma C_\mathrm{p}}{C_\mathrm{TOT}}, \quad (1)$$

where c is a constant set at $0.173\,\mathrm{J\,m^{-2}}$ (estimated from Fig. 3 in Junge, 1977), $\Sigma\theta$ is the total particle surface area concentration ($\mathrm{m^2\,m^{-3}}$) and p_L^0 is the saturated vapour pressure of the sub-cooled liquid (Pa) taken from the temperature-dependent values measured by Offenberg and Baker (1999; see Table S1.1). The total particulate PAH concentrations dictated by φ were then redistributed among the particle size bins by prorating to the proportion of total aerosol surface area concentration within each size bin. The redistributed gas-phase PAH concentration was determined by difference between C_TOT and $\Sigma\mathrm{C_p}$.

The second equilibrium partitioning expression available in the partitioning subroutine developed a partition coefficient (K_p, $\mathrm{m^3\,\mu g^{-1}}$) based on the contributions of two additive processes: absorption into particulate organic matter and adsorption onto particulate soot (DE: Dachs and Eisenreich, 2000)

$$K_\mathrm{p} = 10^{-12}\left(1.5 f_\mathrm{OC}/\rho_\mathrm{oct} K_\mathrm{OA} + f_\mathrm{EC} K_\mathrm{SA}\right) = \frac{\left(\Sigma C_\mathrm{p}/C_\mathrm{TSP}\right)}{C_\mathrm{g}}, \tag{2}$$

where ρ_oct is the bulk density of octanol ($0.82\,\mathrm{kg\,L^{-1}}$), f_OC is the organic carbon fraction of the particulate matter (the 1.5 multiplier converts organic carbon to organic matter which is assumed to be well-represented by octanol), K_OA is the octanol-air partition coefficient (dimensionless), f_EC is the elemental carbon fraction of the particulate matter, K_SA is the soot-air partition coefficient ($\mathrm{L\,kg^{-1}}$), ΣC_p is the particulate PAH concentration across all the size bins ($\mathrm{ngm^{-3}}$), C_TSP is the total particulate matter concentration ($\mathrm{\mu g\,m^{-3}}$), and C_g is the gas-phase concentration ($\mathrm{ngm^{-3}}$).

Soot-air partition coefficients (K_SA, $\mathrm{L\,kg^{-1}}$) were estimated as the ratios of soot-water (K_SW) to air-water partition (K_AW) coefficients since direct K_SA measurements are not available for PAHs. K_SW values from Jonker and Koelmans (2002) were used in this model. These values vary substantially (up to a factor of 47) between relevant soots for the PAHs considered here. Since a single K_SW was needed for each PAH in the model, representative values were determined by weighting the reported K_SW values by the contribution of their related combustion processes to the total emitted fine particulate matter ($PM_{2.5}$) used in the inventory of Galarneau et al. (2007). K_{AW} values were taken from Bamford et al. (1999). K_{OA} values were taken from the temperature-dependent expressions determined by Odabasi et al. (2006).

PAH partition coefficients were calculated according to the first part of Eq. (2). By determining the contribution of each size bin's organic matter and soot carbon to the totals across all size bins, the total particulate PAH was apportioned to each size bin. For example, if a total partition coefficient had contributions from the organic matter and soot carbon of 20 % and 80 %, respectively, and size bin 1 held 10 % of the total particulate organic matter and 15 % of the total soot carbon, the fraction of total particulate PAH assigned to size bin 1 would be 14 % (viz., $0.2 \times 0.1 + 0.8 \times 0.15$). Gas-phase concentrations were then determined by difference between C_{TOT} and ΣC_p.

2.1.5 Below-cloud (precipitation) scavenging

Scavenging of gas and particle PAHs by liquid precipitation was calculated as per Gong et al. (2006). Particle scavenging assumed that particle-bound PAHs do not dissolve in falling rain; particle-bound PAHs were thus treated as passive aerosol tracers. Snow scavenging was not considered in this version of AURAMS.

2.1.6 Cloud processing

Cloud processing in the model was treated in a similar manner to precipitation scavenging whereby gas-phase mass transfer to cloud water is species-dependent, whereas particulate interactions with cloud droplets are only affected by the presence of PAHs in terms of the size (mass and volume) that they represent as part of the overall aerosol. Solid-phase densities used to relate aerosol PAH mass to volume were taken from Mackay et al. (2006; see Table S1.1).

2.2 Model domain, emissions, and boundary conditions

The model domain included southern Canada and the continental USA (see Fig. 1). It was run on a 42 km polar stereographic grid using off-line meteorology generated with the Global Environmental Multiscale numerical weather prediction model (GEM v 3.2.0: Côté et al., 1998a,b).

Emissions of PAHs were taken from the inventory of Galarneau et al. (2007) that had been updated from 2000 to 2002 and to which benzo[a]pyrene had been added using identical methods and data sources. All PAHs were emitted exclusively in the gas phase. Particle/gas partitioning took place at each 15 min CTM time step according to the partitioning module described in Sect. 2.1.5. Emissions of SO_2, NO_x, NH_3, CO, volatile organic compounds (VOCs), and particulate matter were derived using Environment Canada and US EPA databases and methods for the year 2002.

Initial PAH concentrations at all lateral boundaries were set to zero in anticipation of pronounced spatial gradients away from localised source regions. As a result, modelled concentrations in Mexico and near its border with the US are not expected to be reliable, particularly since PAH emissions from Mexico have not been included in the model. Model output along the northern edge of the domain over western Canada is similarly expected to be unreliable since emission sources are located close to the model boundary in that region. The development of representative non-zero boundary concentrations is anticipated as part of future model development.

2.3 Evaluation data

PAH measurement data used for comparison with model output were collected from four measurement networks: NAPS (Canada), IADN (Canada-US), CARB (California), and Rio Tinto Alcan (Kitimat, British Columbia, Canada). The measurement stations are depicted in Fig. 2 and described in Sect. 2 of the Supplement.

Measurement data were available from a total of 45 stations, 23 in Canada and 22 in the USA. Particle/gas partitioning was assessed at eight stations, three in Canada and five in the USA, all of which were operated by IADN.

The IADN phase-distributed data were also combined to yield total concentrations. These combined IADN data, along with NAPS and Rio Tinto data, yielded a total of 28 sites at which total PAH concentration for all the modelled PAHs could be assessed. Particulate PAH measurements from the latter networks were determined from samples of total suspended particles (TSP). CARB provided data for benzo[a]pyrene in particles smaller than 2.5 µm in diameter ($PM_{2.5}$) at a further 17 locations.

Four model grid squares (Kitimat, Toronto, Hamilton, and Montreal) contained two or more measurement stations thus allowing for an assessment of the adequacy of modelling all seven PAHs at 42 km grid spacing.

3 Results

3.1 Total PAH concentration

3.1.1 Overall spatiotemporal domain

Total PAH concentration refers to the sum of the gas and particle concentrations whether these have been analysed together (e.g., NAPS) or separately (e.g., IADN). For stations at which the gas and particle phases were analysed separately, a valid total concentration was assumed to exist if at least one of the gas and particle phase concentrations was greater than the detection limit. Non-detectable values were assumed equal to zero for the calculation of total concentrations.

A representative plot of the spatial distribution of modelled annual average concentrations is presented in Fig. 1 for fluoranthene. The remaining PAHs show similar spatial distributions and maps of their modelled concentrations are found in Sect. 3 of the Supplement. All the PAHs show spatial distributions of their modelled concentrations that are consistent with regional dispersion of their emissions as depicted in Galarneau et al. (2007).

A summary of annual mean modelled and measured values over the entire spatiotemporal model domain is shown in Table 1. Only modelled values for which there was a corresponding measurement were included.

In comparing modelled results to measurements, the overall means were statistically indistinguishable at the 95 % confidence level for FLRT, PYR, BaA, and BaP (JP) whereas they were statistically different for PHEN, ANTH, C + T, and BaP (DE). For PHEN, ANTH, and C + T, modelled values were underestimated relative to measurements whereas they were overestimated for DE BaP.

The model's temporal variability tended to be smaller than that of the corresponding measurements; the relative standard deviations of the measurements were 1.3 to 2.7 times greater than those of the modelled values. This effect was also seen by Matthias et al. (2009) who concluded that temporal variability in PAH emissions was not adequately represented by their inventory. This is a plausible contributing factor in the current study as well.

Differences in mean modelled values between the two partitioning versions (JP and DE) were statistically indistinguishable at 95 % significance despite the finding that the two BaP model results differed in their comparison to measured values. The latter anomaly indicates that the BaP distributions were close to the 95 % confidence threshold. As a result, no conclusion can be drawn about which partitioning mechanism was superior in simulating overall total PAH concentrations. Phase partitioning of semivolatile organic compounds (SVOCs) is a major determinant of their potential for long-range transport (Bidleman, 1988), yet it does not appear to have a large effect on the simulation of their total concentrations at the regional scale. Model performance in simulating phase partitioning is discussed in Sect. 3.2.

The model's performance was also more closely evaluated by examining the pertinent data distributions. Figure 3 depicts frequency distributions of the ratios of modelled-to-measured concentrations for all of the valid data pairs available for the model evaluation. Four PAH species (ANTH, FLRT, PYR, and C + T) yielded median values of the modelled-to-measured concentration ratio that were close to the ideal value of unity (1.1, 1.1, 1.5, and 1.4, respectively). PHEN showed an overall tendency toward underestimation by the model (0.2), whereas BaA and BaP tended toward overestimation (3.2/3.5 and 3.0/3.5 JP/DE, respectively).

BaA and BaP are reactive PAHs (Behymer and Hites, 1985) and the exclusion of particle-bound reactions in this first-generation model may explain a portion of their overestimation in AURAMS-PAH as suggested in a comparable model for Europe (Matthias et al., 2009). However, BaP is subject to losses during sampling (Menichini, 2009) and some portion of the apparent model overestimation may in fact be due to measured values that are biased low. This presents a priority for future research since many jurisdictions use BaP as an indicator PAH when setting air quality standards.

As presented in Sect. 2.1.2, volatilisation of gaseous PAHs from surface compartments such as air and soil was not included in this first-generation version of AURAMS-PAH. If such volatilisation were significant to the balance of PAHs in ambient air relative to the other processes simulated, one would expect an overall bias in model results whereby the most volatile PAHs, which are found predominantly in the gas phase, would be underestimated and the least volatile particulate species would be unaffected. Summary results provide indefinite evidence. Volatile phenanthrene is systematically underestimated yet its similarly volatile isomer, anthracene, shows an ambiguous central tendency toward underestimation whereby its mean values are underestimated by the model (Table 1) but its median values are not (Fig. 3). Less volatile but nonetheless predominantly gaseous fluoranthene and pyrene show no tendency toward underestimation. These results warrant further investigation but suggest that volatilisation of gaseous PAHs from surface comparments is not significant at the regional scale when model results are compared to 24 h measurements.

The range of modelled-to-measured concentration ratios shown in Fig. 3 varied substantially by species. The ratios of 90th to 10th percentile values for PHEN, FLRT, PYR, BaA, and C + T spanned fewer than, or close to, two orders of magnitude (55, 59, 67/68, 67/63, and 100/93, respectively). The ratio for BaP was larger (180/270) and that for ANTH was very large (5900/7400), with extreme values tending toward underestimation for the latter species. As seen with the comparison of means, the two partitioning parametrizations used by AURAMS-PAH led to similar model performance overall when considering the distribution of total PAH concentrations.

Additional quantitative performance metrics are presented for the two particle/gas partitioning parametrizations in Tables S4.1 and S4.2 of the Supplement. Normalized mean bias and error have been included for completeness, but their utility in this evaluation is questionable given the large range of measured values. Measured maximum to minimum concentration ratios range from $4.7 \times 10^{+06}$ (PYR) to $1.3 \times 10^{+09}/1.4 \times 10^{+09}$ (C + T). Therefore, the mean measured concentrations used to normalize the bias and error do not represent the dataset well.

The correspondence between individual modelled-measured data pairs is weak as demonstrated by the low coefficients of determination, non-unity slopes, and high intercepts listed in Tables S4.1 and S4.2. However, the ability of the model to simulate observed concentrations within a certain tolerance is reasonable, especially when considering that PAHs are trace organic compounds subject to numerous sampling artefacts (McDow, 1999) and poor measurement precision (Galarneau, 2008). Depending on PAH species, 22–34 % of modelled-measured data pairs fell within a factor of 2 of each other. This increased to 61–86 % when considering a factor of 10. As a result, it can be stated with confidence that, on average, AURAMS-PAH was able to simulate atmospheric PAH concentrations in North America to the correct order of magnitude.

3.1.2 Site-specific performance

Model performance was not spatially uniform. Figure 4 depicts the variation in distributions of individual modelled-to-measured concentration ratios across measurement sites for fluoranthene, the PAH species for which overall performance was best as determined by the median and spread in modelled-to-measured concentration ratios.

Note that only JP partitioning values have been plotted since these are visually indistinguishable from those for DE partitioning.

Of the 30 sites depicted in Fig. 4, the median modelled-to-measured concentration ratio ranged from 0.061 (St. John's) to 4.0 (Hamilton – Confederation Park), whereas the median value for all sites was 1.1. The variability at individual sites is itself highly variable, with ratios of 90th to 10th percentile values of the modelled-to-measured concentration ratio ranging from 5.8 (Toronto – Junction Triangle) to 105 000 (Haul Road, near the Rio Tinto Alcan smelter in Kitimat, British Columbia). A low value of 1.1 was observed for Saint John, but this was based on only two modelled-measured data pairs. Sixteen of the 30 sites (53 %) had median modelled-to-measured ratios that fell within a factor of two of the median value for all sites.

The other compounds varied spatially in a manner similar to fluoranthene with the following exceptions. ANTH exhibited atypically large underestimation at the three sites near the Rio Tinto Alcan smelter in Kitimat, suggesting that inaccurately low ANTH emissions are associated with the dominant source there. The reporting threshold for point-source ANTH emissions through the Canadian National Pollutant Release Inventory (NPRI) system is higher than the thresholds for other commonly-measured PAHs and no ANTH emissions were reported to the NPRI by Rio Tinto Alcan for 2002. The C + T performance at Jonquière, home to aluminum smelting facilities, suggests that reported emissions there are also too low. Emissions for other PAHs were reported from this location for 2002 but not so for chrysene, which is called benzo[a]phenanthrene in the NPRI.

3.1.3 Model grid squares containing multiple measurement sites

The smoother the spatial distribution of a pollutant, the coarser the model resolution that can be used to simulate it. Four AURAMS-PAH model grid squares contain more than one measurement site, thus allowing for an assessment of the 42 km spatial resolution used for the evaluation runs. The multi-site grid squares are all located in Canada, and from west to east, they encompass sites in Kitimat (2 sites), Hamilton (2), Toronto (3), and Montreal (2) (see Tables S2.1 and S2.4).

Kitimat is a town 650 km northwest of Vancouver with approximately 9000 residents whose largest employer is the aluminum smelter complex operated by Rio Tinto Alcan (District of Kitimat, 2009). Two measurement sites (Haul Road and Kitamaat Village) are located in the same model grid square and a third site (Whitesail) lies in an adjacent square even though it is only a few kilometers away. Hamilton is a city at the western end of Lake Ontario that is known colloquially as the Steel Capital of Canada and had a population of approximately 700 000 in 2010. It is part of the so-called "Golden Horseshoe" conurbation at the western end of Lake Ontario whose 2010 population, estimated as the sum of the populations of Oshawa, Toronto, Hamilton, and St. Catharines-Niagara, was over 7 million (Statistics Canada, 2011). Toronto and Montreal are the largest cities in Canada having 2010 populations of 5.7 and 3.9 million, respectively.

Table 2 lists the variability in contemporaneously measured concentrations at the four grid squares as represented by their coefficients of variation (COV). At any given site, the average COVs for the different PAH species tend to be similar to each other. Substantial differences exist between sites, however, particularly when grouping the urban sites (Hamilton, Toronto, and Montréal) against the industrial site at Kitimat. This is not unexpected. Urban areas include complex mixtures of point, area, and mobile sources that are distributed over distances similar to the scale of the model. Kitimat houses industrial operations within a relatively small area of otherwise rural land and wilderness. Steep spatial gradients in pollutant concentrations are expected there as a result.

The COVs for ozone and total suspended particles (TSP) have also been included in Table 2 as comparative gaseous and particulate pollutants, respectively. Both vary less between sites in the same grid square than do PAHs. Ozone and a portion of TSP are secondary pollutants created by the mixing and reaction of precursor compounds. The atmospheric residence times required for their creation is consistent with a smoothing of the spatial variability in their concentrations. Conversely, unsubstituted PAHs are primary pollutants whose concentrations would be expected to vary in space over a finer resolution when multiple sources are found close by.

The results presented above suggest that a 42 km spatial resolution is not sufficiently fine to represent PAH concentrations in areas close to sources such as cities and industrial areas if an average model accuracy better than an order of magnitude is desired. AURAMS modelling of fine particulate matter has shown substantial improvement when grid spacing has been reduced to 2.5 km (Stroud et al., 2011), and similar results can be expected for the modelling of PAHs. No 42 km model grid squares in rural or background areas away from sources contain multiple measurement stations and, as a result, a comparison cannot be made for these areas. However, it is expected that spatial variation in PAH concentrations will be less in such areas and, as such, a 42 km resolution model may be sufficient there.

3.2 Particle/gas partitioning

As noted in Sect. 3.1, the choice of partitioning expression (JP or DE) had little effect on the simulation of total PAH concentrations. This implies that the partitioning from each approach is sufficiently similar that regional-scale differences in removal rates between gaseous and particulate PAHs have little effect. However, differences between the two expressions with respect to simulating phase-resolved concentrations were noted.

3.2.1 Overall spatiotemporal domain

Figure 5 shows frequency distributions of the ratios of individual modelled-to-measured particulate fraction for all data pairs available to the model evaluation. Note that only the eight IADN stations are included since the gas and particle phases are analysed separately only at those sites.

Figure 5 shows that PAH particulate fraction is underestimated for all species except BaP. The degree of underestimation decreases with increasing molecular weight.

The particulate fractions of volatile PHEN and ANTH (178 g mol^{-1}) are underestimated by approximately two orders of magnitude whereas equipartitioning BaA and C + T (228 g mol^{-1}) have particulate fractions that are underestimated by only a factor of two. A similar pattern appears when examining the partition coefficient, K_p (not shown).

For all species other than BaP, Dachs–Eisenreich partitioning performs slightly better than Junge–Pankow partitioning in simulating measured particulate fractions. The all-site median particulate fraction simulated using DE is between 1.1 (PYR) and 2.9 (ANTH) times higher than that using JP. However, the performance of the partitioning expressions is highly dependent on the physico-chemical property values used. For example, estimated soot-air partition coefficients vary by more than an order of magnitude (Galarneau et al., 2006) and translate directly to variations in predicted partitioning by the Dachs–Eisenreich expression. For Junge–Pankow partitioning, the value of the constant, c, in Eq. (1) and the estimation of aerosol surface area also introduce uncertainties. A full analysis of the sensitivity of modelled partitioning is beyond the scope of this paper and will be the subject of future study using AURAMS-PAH.

3.2.2 Site-specific performance

As was the case for total concentration, there is substantial variability in the simulation of partitioning between sites. Figure 6 shows the variation in frequency distribution of individual modelled-to-measured particulate fraction for fluoranthene using Dachs–Eisenreich partitioning. Model performance for particulate fraction simulation is better at urban (Chicago) or urban-influenced (Sturgeon Point, Egbert) sites than at those that are remote (Eagle Harbor). An analysis of measured partitioning at IADN stations (Galarneau et al., 2006) found that the proportionality between partitioning and volatility varied between sites, and in some cases, over the annual cycle. Volatility is included in both the JP (through p_L^0) and DE (through K_{OA} and K_{SA}) partitioning expressions and the proportionality between it and partitioning magnitude is much smaller in model outputs than in measurements. As noted earlier, factors involved in the performance of model partitioning such as modelled particulate matter concentration and composition will be explored in future AURAMS-PAH studies.

4 Conclusions

This study described the first known regional modelling results for atmospheric PAHs at the regional scale over North America. AURAMS-PAH, an off-line Eulerian chemical transport model, was developed and used to simulate the atmospheric fate of seven PAHs for the year 2002 with hourly output at 42 km grid spacing. Model predictions were compared to ~5000 24 h average PAH measurements from 45 sites, eight of which also provided data on particle/gas partitioning which had been modelled using two alternative schemes.

Annual average modelled total (gas + particle) concentrations were statistically indistinguishable from measured values for fluoranthene, pyrene and benz[a]anthracene whereas the model underestimated concentrations of phenanthrene, anthracene and chrysene + triphenylene. Significance for benzo[a]pyrene performance was close to the statistical threshold and depended on the particle/gas partitioning scheme employed.

On a day-to-day basis, the model simulated total PAH concentrations to the correct order of magnitude the majority of the time. The model output showed less temporal variability than the measurements indicating that model inputs may not have adequately represented temporal variations in actual PAH emissions. Reactive particulate PAH species tended toward overestimation by the model, suggesting the need to account for their reactions with atmospheric oxidants in subsequent modelling studies and measurements. Model performance differed substantially between measurement locations and the limited available evidence suggested that the model spatial resolution was too coarse to capture the distribution of concentrations in densely populated areas. The Junge–Pankow and Dachs–Eisenreich particle/gas partitioning schemes that were tested showed similar performance, with both expressions increasingly underestimating particle-bound concentrations with increasing PAH volatility. A more detailed analysis of the factors influencing modelled particle/gas partitioning is needed to improve the distribution of PAHs between the gas and particle phases in the atmosphere.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/13/18417/2013/ acpd-13-18417-2013-supplement.pdf.

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Table 1. Summary of 2002 annual modelled and measured total PAH concentration mean (standard deviation) values (ng m^{-3}).

PAH	Modelled – JP	Modelled – DE	Measured	*n*
PHEN	12.75 (36.44)	12.76 (36.44)	36.06 (131.8)	790
ANTH	0.9123 (1.757)	0.9104 (1.759)	2.804 (11.56)	701
FLRT	6.781 (14.40)	6.888 (14.66)	9.179 (32.44)	789
PYR	5.727 (12.23)	6.009 (13.40)	5.733 (21.57)	785
BaA	1.227 (2.438)	1.328 (2.704)	1.326 (6.081)	610
C + T	1.511 (3.964)	1.473 (3.569)	3.303 (21.95)	721
BaP	1.173 (2.002)	1.424 (2.455)	0.9047 (3.238)	595

Table 2. Average coefficient of variation (%) between contemporaneous measurements at sites falling within the same 42 km AURAMS-PAH grid square.

Station	PHEN	ANTH	FLRT	PYR	BaA	C + T	BaP	O_3[2]	TSP
Kitimat	106	101	96.5	93.7	87.4	91.3	93.2	N/A	N/A
Hamilton	52.1	59.0	59.2	58.8	73.1	117	62.8	24.9	30.5
Toronto3[1]	36.2	48.7	42.5	39.6	42.2	32.9	43.0	N/A	22.1
Toronto2[1]	36.5	45.4	39.3	35.7	32.9	25.0	38.0	12.2	24.6
Montréal	49.2	52.9	45.8	44.6	55.2	55.3	51.6	35.3	29.0

[1] Toronto3 includes data from all three Toronto measurement sites. Toronto2 includes only data from the Gage Institute and Judson and Etona because O_3 data were not available from Junction Triangle.
[2] Ozone data have been aggregated to 24 h values contemporaneous with PAH measurements.

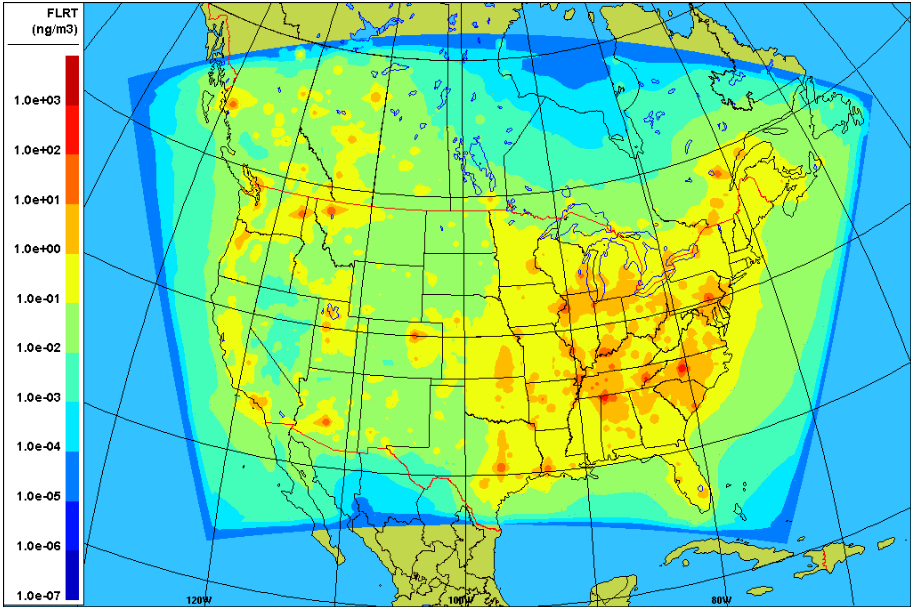

Fig. 1. Map of modelled (JP) annual average total (gas + particle) fluoranthene concentrations (ng m^{-3}).

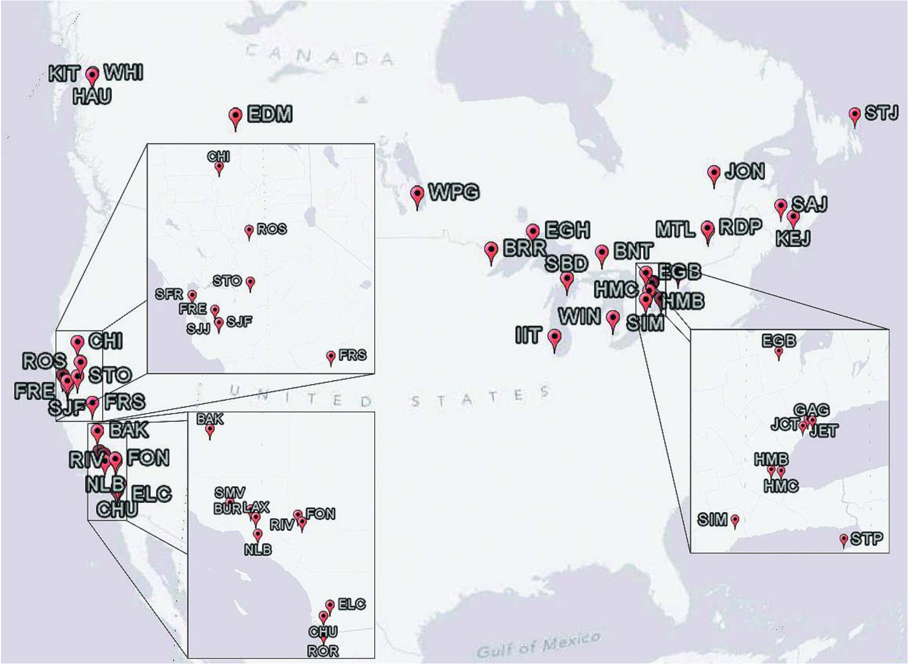

Fig. 2. Map of measurement stations used in AURAMS-PAH evaluation.

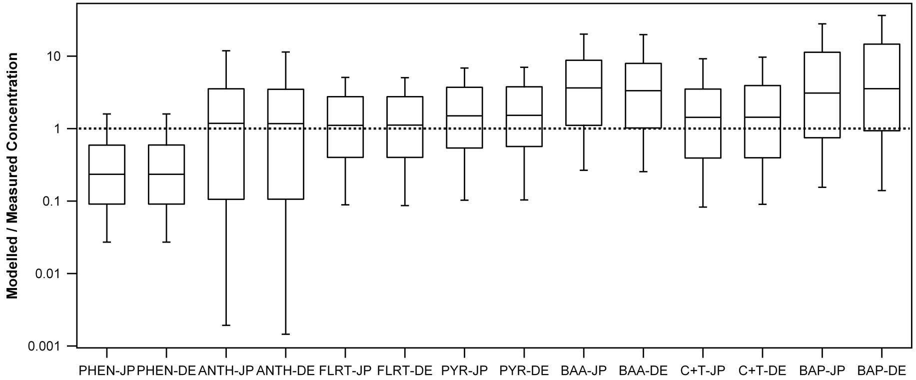

Fig. 3. All-site ensemble of modelled-to-measured concentration ratios for total (gas + particle) PAHs using JP and DE partitioning expressions.

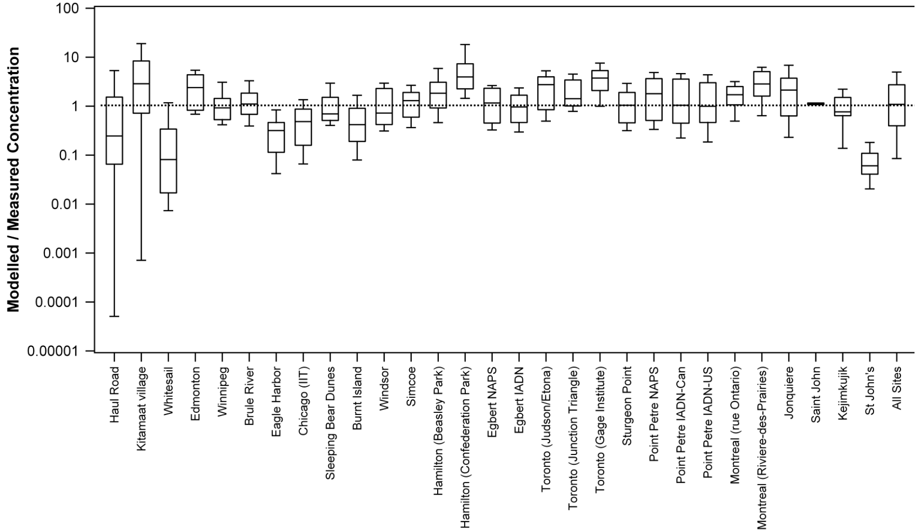

Fig. 4. Site-specific modelled-to-measured concentration ratios for total (gas + particle) fluoranthene for JP partitioning.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◄ | ►
◄ | ►
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

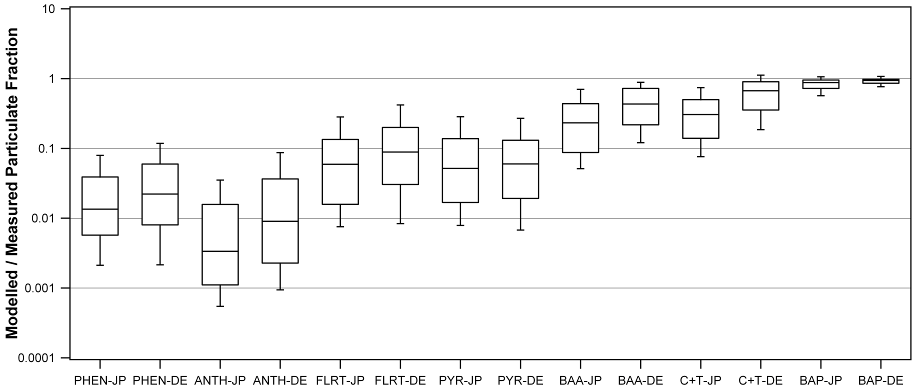

Fig. 5. All-site ensemble of modelled-to-measured PAH particulate fractions for JP and DE partitioning expressions.

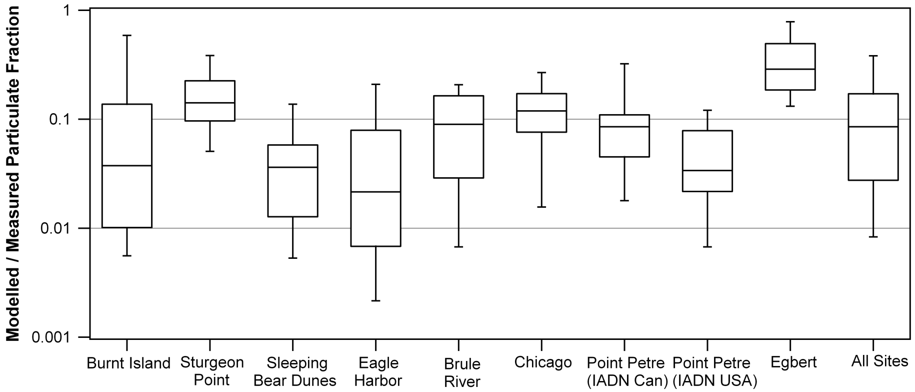

Fig. 6. Site-specific modelled-to-measured partition coefficients for fluoranthene for DE partitioning for eight IADN sites.