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Constraining uncertainties about the sources and magnitude of polycyclic aromatic hydrocarbon (PAH) levels in ambient air: the state of Minnesota as a case study

Agnes B. Lobscheid[a,b,*], Thomas E. McKone[a,b]

[a]*Environmental Health Sciences, School of Public Health, University of California, Berkeley, CA 94720, USA*
[b]*Lawrence Berkeley National Laboratory, Indoor Environment Department, Environmental Energy Technologies Division, One Cyclotron Road, MS 90R3058, Berkeley, CA 94720, USA*

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Abstract

Emissions data are often lacking or uncertain for many airborne contaminants. Polycyclic aromatic hydrocarbons (PAHs) emitted from combustion sources fall into this category. Currently available ambient-air emission inventories of PAHs either fail to account for population-based activities, such as residential wood combustion (RWC) and motor vehicle (MV) activity, and/or report "total PAH" or particulate organic matter emissions, instead of individual compound emissions. We assess the degree of overlap between predicted concentrations from estimated emissions with measured concentrations. Our analysis is based on probabilistic analysis of measured outdoor air concentrations with those predicted from mass-balance models. Based on available information, we estimate the relative magnitude of emissions from three major sources of PAHs to outdoor air: (1) on-road MVs, including light-duty gasoline vehicles and diesel-powered buses and medium and heavy-duty trucks; (2) RWC; and (3) power generation from external combustion boilers. We use the CalTOX regional multimedia mass-balance model to evaluate our emissions estimates in rural and urban regions of the state of Minnesota, USA. We compare model estimates of outdoor PAH airborne concentrations with those reported by the Minnesota Children's Pesticide Exposure Study (MNCPES). With these measured concentrations we probabilistically evaluate the reliability of our emissions estimates for specific PAHs. The median estimates of our predicted outdoor air concentrations agree within an order of magnitude of measured concentrations. For four representative PAHs, we obtain a reasonable degree of overlap between empirical and predicted distributions of outdoor air concentrations. Our combination of models, emissions estimates, and empirical concentration data estimate exposure in a manner that is more reliable than any of these tools alone. Thereby, we increase our confidence about our plausible ranges of emissions and predicted concentrations.

Keywords: Gasoline motor vehicles; Diesel fuel motor vehicles; External combustion boilers; Residential wood combustion; Emissions inventory

*Corresponding author. Lawrence Berkeley National Laboratory, Indoor Environment Department, Environmental Energy Technologies Division, One Cyclotron Road, MS 90R3058, Berkeley, CA 94720, USA. Tel.: +1-510-486-4919; fax: +1-510-486-6658.
E-mail address: ablobscheid@lbl.gov (A.B. Lobscheid).

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Nomenclature

C_{air_out}	outdoor air concentrations
ECBs	external combustion boilers
E_{fuel}	energy content of fuel
EFs	emissions factors
EPA	Environmental Protection Agency
GFU	gasoline fuel usage
LDGVs	light-duty gasoline vehicles
M + HDTs	medium and heavy-duty trucks
mMDL	median method detection limit
MNCPES	Minnesota Children's Pesticide Exposure Study
MPCA	Minnesota Pollution Control Agency
MVs	motor vehicles
MWe	megawatts electric
NHEXAS	National Human Exposure Assessment Survey
PAH	polycyclic aromatic hydrocarbon
RWC	residential wood combustion
TOGs	total organic gases
VKT	vehicle kilometers traveled

1. Introduction

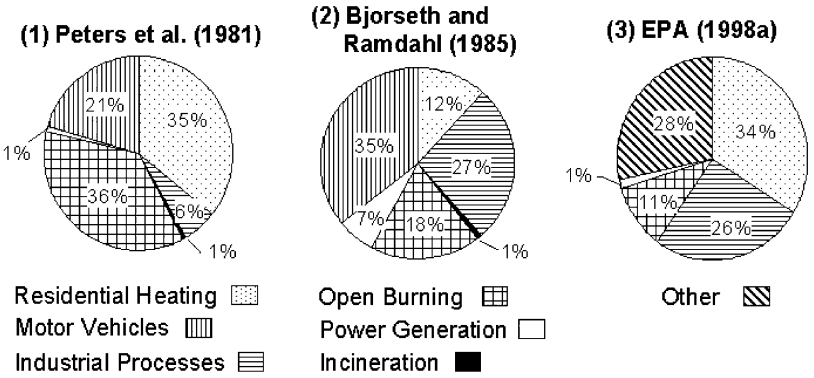
Polycyclic aromatic hydrocarbons (PAHs), such as benzo(*a*)pyrene (BaP) and naphthalene, are important contributors to potential human health risk (EPA, 2001). Anthropogenic sources appear to be the major contributors to atmospheric PAH emissions. Although estimated emissions of specific anthropogenic sources in the US vary, between 10,000 and 30,000 tons of PAHs are emitted to the atmosphere annually in the US (Baek et al., 1991; EPA 1998a). Based on several evaluations of PAH emissions in the literature (Peters et al., 1981; Bjorseth and Ramdahl, 1985), Fig. 1 shows three representative estimates of major sources of PAHs. These estimates reveal that motor vehicles (MVs) are considered a major source of atmospheric PAH emissions (Smith and Harrison, 1996; Van Metre et al., 2000; Nielsen, 1996). Menichini (1992) reports that, in addition to MVs, domestic heating, in general, and residential wood combustion (RWC), in particular, are another major source of PAHs to outdoor urban and rural air. In a 1996 estimate of the inventory of toxic-chemical emissions to air, approximately 60% of all PAH emissions from point, area, and mobile sources in the Great Lakes States were attributed to RWC (GLC, 2000). Additionally, emissions studies have also identified contributions to atmospheric PAH levels from industrial sources, such as coke-oven emissions, asphalt production facilities, carbon black manufacturing, aluminum smelters, blast furnaces, steel mills, and petroleum refineries.

The objective of this paper is to demonstrate, using the state of Minnesota as our case study, how emissions inventories and measured concentrations can be reconciled with each other using a mass balance framework to reduce uncertainties in emission inventories. In order to achieve our objective we: (1) develop regional-scale estimates of PAH airborne emissions, (2) predict the resulting ambient outdoor air concentrations (C_{air_out}) with a multimedia mass-balance model, and (3) assess the degree of comparability between predicted concentrations and regional-scale ambient-air measurements. Key inputs to this process are available data for population activities relating to emissions and emissions factors (EFs) for specific PAH compounds. From these inputs we evaluate the relative magnitude and uncertainty of PAH emissions to outdoor air from the following major sources:

- on-road gasoline and diesel-fueled MVs, including light-duty gasoline vehicles (LDGVs); diesel-powered buses and diesel-powered medium and heavy-duty trucks (M + HDTs);
- RWC;
- power generation, with a primary focus on external combustion boilers (ECBs).

As a case study, we focus on rural and urban regions of the state of Minnesota. Within a framework represented by Fig. 2, we apply a regional multimedia mass-balance model to evaluate our emissions estimates by comparing model-based estimates of outdoor PAH airborne concentrations with those reported by the Minnesota Children's Pesticide Exposure Study (MNCPES) (Clayton, et al., 2003; Pellizzari et al., 2003). The recent availability of these measured C_{air_out} enables us to evaluate the available emissions data and interpret the reliability of our emissions estimates. Within this framework we evaluate the degree of match between observed C_{air_out} and those predicted using a model parameterized to best represent the area for which the measurements apply.

In order to carry out this analysis, we make a number of assumptions. Important among these is our assumption that PAH contributions to the Minnesota region from open burning, such as agricultural fires, household waste burning, and forest fires, are not major contributors to the overall regional mass balance. Although these sources have been estimated to contribute nationally up to 36% of total annual PAH emissions (as shown by Fig. 1), their contribution to the Minnesota region is considered negligible since numerous agricultural and other open burning prohibitions exist in the state (Minnesota Statutes, 2002) and because Minnesota is



Motor Vehicles: on-road gasoline and diesel engines; (2) is not corrected for cars with emission control devices (approximately 50% when estimated).
Residential Heating: including gas, oil, coal and wood burning at a residence (coal and wood burning is 99% in 1 and 100% in 3; wood burning is 97% in 2).
Industrial Processes: coke manufacturing (1, 2 and 3), asphalt production (1 and 2), carbon black (1 and 2), aluminum plants (2 and 3), charcoal manufacturing (uncontrolled batch kilns and continuous furnace production (1 only), and barium processing (black ash rotary kiln) (1), petroleum refining (all processes) emissions (3); also included in (3) are emissions from: aerospace industry (surface coating); pulp and paper manufacturing- Kraft recovery furnaces, fabricated rubber products and metal product manufacturing and plastic foam manufacturing as well as gasoline distribution and chemicals manufacturing (including industrial organic chemicals and cyclic crude and intermediates).
Incineration: commercial and municipal (1), municipal only (2).
Open Burning: agricultural fires (1), forest wildfires (1, 2, and 3), prescribed burning (1 and 3), coal refuse fires (1), land clearing waste burning (1) and structural fires (1), scrap tire burning (3).
Power generation: utility boilers/power plants (coal, oil and gas-fired in 1; coal and oil-fired in 2) and industrial boilers (in 1 and 2), commercial and industrial coal combustion (3).
Other: includes consumer product usage, blast furnace and steel mills, wood treatment/wood preserving and on-road MVs (3 only), and 'other' sources as given (3)

Fig. 1. Major anthropogenic contributors to atmospheric PAHs in the US.

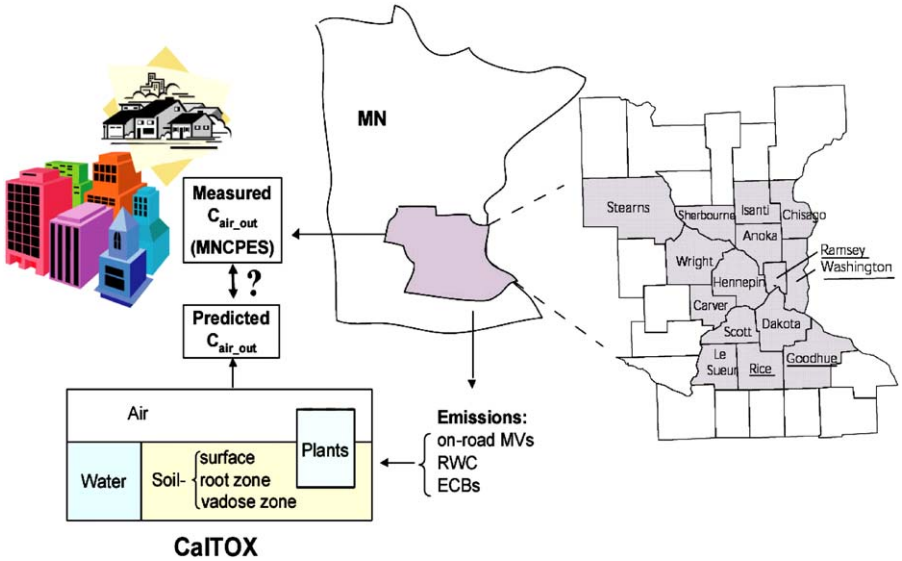


Fig. 2. Our general framework for developing a modeled C_{air_out} and comparing it with available empirical concentrations (from the MNCPES). The 15-county region for which we estimated PAH emissions separately (in addition to emissions at the state-wide level) are shaded. Counties underlined had MNCPES C_{air_out} reported (Quakenboss et al., 2000).

not part of a major forest fire region (as compared to the South or Western portion of the US). In addition, Minnesota lacks any major blast furnaces and steel mills (GLC, 2000). Other major industrial processes such as coke manufacturing and aluminum smelting contribute $<5\,\mathrm{kg\ PAH\ yr^{-1}}$ in Minnesota (EPA, 2000). Therefore,

we exclude industrial processes, other than ECBs, from our emission estimates.

2. Materials and methods

We construct our emissions inventory using individual emissions from the Environmental Protection Agencies (EPAs) list of 16 PAHs (both probable and nonclassifiable carcinogens) (EPA, 1998b). This list includes acenaphthene; acenaphthylene; anthracene; benz(*a*)anthracene; benzo(*a*)pyrene, benzo(*b*)fluoranthene; benzo(*k*)fluoranthene; benzo(*ghi*)perylene; chrysene; dibenz(*a*,*h*)anthracene; fluoranthene; fluorene; indeno(1,2,3-*cd*)pyrene; naphthalene; phenanthrene; and pyrene. Our emissions inventory approach is designed to provide a highly transparent, easily replicable methodology, which uses the most recent EFs data, from both the peer reviewed literature and from EPA publications, combined with activity factors specific to the emissions source. We adapted this particular methodology in order to accommodate the following issues:

(1) existing emissions inventories, such as the Toxic Release Inventory fail to account for population-based activities (such as RWC and on-road MV activity);
(2) some emissions databases, such as the US EPAs National Emissions Inventory, do not report on individual PAH emissions but instead report 'total PAH' or POM emissions;
(3) since published emissions inventories apply PAH EF speciation profiles, which are based on measured concentrations of PM or total organic gases (TOGs), the reliability of the emissions predicted for specific PAHs is reduced. Wherever possible we base our emissions estimates on EFs reported for individual PAHs instead of speciation profiles.

In the following subsections we first provide details on the methods by which we estimate PAH emissions to outdoor air for each of the four major source categories. We next describe how we evaluate the emissions estimates in the context of reported measured C_{air_out} compared with levels derived from a multimedia model.

2.1. Estimates of PAH emissions

For each of our major source categories we estimate outdoor air emissions using an EF approach. Where sufficient data are available, we distinguish between urban and rural emissions, assuming that counties with <35 persons km^{-2} (90 persons $mile^{-2}$) are rural.

2.1.1. On-road gasoline and diesel-fueled MVs

For gasoline-powered MVs, we use EFs obtained from several references for PAH emissions from LDGVs, which are primarily passenger vehicles. These EFs and corresponding references are summarized in Table 1. Because there appears to be a lack of EF data available for light-duty gasoline-powered trucks, which includes popular sport utility vehicles, and heavy-duty gasoline-powered vehicles, we do not separately categorize these vehicles in our emissions estimates. However, the contributions of SUVs are accounted for to a large degree in our 16-PAH emission estimates by our use of activity rates based on passenger vehicles, which includes SUVs, to capture LDGV emissions. Motorcycles are excluded because no EFs were located for PAHs other than BaP.

PAH EFs are available for diesel-powered buses and M + HDTs with two axles and six tires or more and combination trucks (single or multiple trailers). We found no EF data for light-duty diesel-powered vehicles and trucks (0–6000 lb gross vehicle weight). PAH EFs from diesel-powered MVs are summarized in Table 1. For the majority of M + HDT EFs, we use combined particulate and gaseous phase EFs.

For PAH emissions from diesel-powered MVs, we assume that all buses and M + HDTs are diesel powered. However, since diesel-powered vehicles emit more of the lighter PAHs than their gasoline-powered counterparts, we note that this assumption could bias the emissions estimates toward more of the lighter PAHs.

Based on the EFs in Table 1, we estimate PAH emissions from on-road MVs as

$$\text{MV emissions} = \text{activity} \times \text{EF}, \quad (1)$$

where activity is estimated as the reported vehicle kilometers traveled (VKT) for specific MV classes in Minnesota for urban roads (passenger vehicles, or LDGVs $= 4.18 \times 10^{10}$ km yr^{-1}; buses $= 8.80 \times 10^{7}$ km yr^{-1}; and M + HDTs $= 2.19 \times 10^{9}$ km yr^{-1}) and rural roads (passenger vehicles, or LDGVs $= 3.66 \times 10^{10}$ km yr^{-1}; buses $= 8.26 \times 10^{7}$ km yr^{-1}; and M + HDTs $= 4.58 \times 10^{9}$ km yr^{-1}) (US DoT, 1996 and US DoT, 2002a); and EF is the emission factor for a specific PAH (in μg of PAH emitted per km driven), as summarized for each vehicle class in Table 1. Because of additional activity factors available specifically for LDGVs, we also estimate the activity by the following two methods:

(1) estimated urban and rural VKT according to:

$$\text{estimated VKT} = (\text{MVs/household}) \times \text{households} \times (\text{km/day} - \text{vehicle}), \quad (2)$$

where we use 1.89 and 1.99 MVs/household in rural and urban counties, respectively (US BoC, 2002); 692,188 and 1,204,016 households in rural and urban counties, respectively (US BoC, 2002); and the average kilometers driven per day per vehicle are

Table 1
On-road MV PAH EFs ($\mu g\,km^{-1}$)

	LDGVs				Buses		MDT		HDT	
	Cadle et al. (2001)[a]	Miguel et al. (1998)[b]	EPA (1998c)[c]	EPA (1998d)[d]	As cited in Westerholm et al. (1994)[e]	Westerholm et al. (1994)[f]	As cited in Westerholm et al. (1994)[g]	Schauer et al. (1999)[h]	Miguel et al. (1998)[i]	Westerholm et al. (1994)
Acenapthene	68.8							19.3		
Acenaphthylene	495							70.1		
Anthracene	25.4					13.3		23.4		
Benz(*a*)anthracene	3.3	0.3	0.21			0.4		10.8	55	
Benzo(*a*)pyrene	2.3	0.5		0.43	0.1; 1.9; 11.3	0.06	0.14		NS	0.42[j]; 0.7[k]; 0.31[l]
Benzo(*b*)fluoranthene		0.5							10	
Benzo(*k*)fluoranthene		0.1							1.1	
Benzo(*ghi*)perylene		1.3				0.1			NS	
Chrysene	5.1	0.5				2.8		18.9	26	
Dibenz(*ah*)anthracene	12.8[m]	1.2							NS	
Fluoranthene	21.3	0.6						109.6	189	
Fluorene	83.1							44.1		
Indeno(123-*cd*)pyrene	6.6	0.63				0.05			NS	
Naphthalene	4500							617		
Phenanthrene	143					295		140.1		
Pyrene	22.1	0.63				13.1		160.4	271	

NS = not a significant source.

[a]Average EF ($\mu g\,ml^{-1}$) from oxygenated fuel (mandated in Minnesota in 1997) tests for LDGV (tier 0, tier 1, and high emitter each run in two driving cycles, FTP and REP05); EFs based on particulate matter emissions.

[b]Original EFs in (μg PAH $kg\ gas^{-1}$). Converted to per km based on: gasoline density of $743\,g\,l^{-1}$ and average (city and highway) mpg of 24.6 (EPA, 1999a).

[c]Average of catalytic and non-catalytic converter controlled LDGVs EFs for benz(*a*)anthracene only.

[d]Average of LDGVs with and without I/M, speciated from total organic gases EF for BaP only.

[e]EFs at various speeds, temperature, and combination of oxygenates in fuels. Only available for BaP.

[f]Sum of the mean particle and semivolatile EFs for diluted diesel exhaust from bus cycle (simulates public transportation conditions in a city).

[g]Average EFs for diesel fuel (D1, D6, and D8 type) for BaP only.

[h]Sum of gas and particle phase EFs for diesel-fueled MDT.

[i]Diesel-fueled HDTs reported originally in units of ($\mu g\,gallon^{-1}$) and converted to ($\mu g\,km^{-1}$) based on average mpg of diesel HDTs of 5 and diesel density of $830\,g\,l^{-1}$.

[j]Average of HDT EFs from D1-, D6-, and D8-type diesel fuel.

[k]Average of exhaust EFs from diesel-fueled HD trucks (in bus cycle) without particle trap.

[l]Average of exhaust EFs from diesel-fueled HD trucks (in NY cycle) without trap or catalyst.

[m]Dibenz(*ah* + *ac*)anthracene given in Cadle et al. (2001); assume applies to dibenz(*ah*)anthracene.

assumed to be 32 (or, 20 miles day^{-1}, from mileage information from ORNL, 1995);

(2) gasoline fuel usage (L gasoline yr^{-1}), which is available for on-road LDGVs only, in urban and rural environments based on the 2001 total gasoline highway motor fuel use data for Minnesota (US DoT, 2002b), multiplied by an average km l^{-1} of 10.4 (24.6 miles gallon^{-1}, with standard deviation of 6.0) of highway and city driving for LDGVs, summarized for all members of the light duty (i.e., passenger car) MV class including two-seaters, minicompact, subcompact, compact, midsize, and large cars, as well as small and midsize station wagons (EPA, 1999a).

For diesel-powered buses and M + HDTs, *activity* is derived only from available reported data on VKT.

Our emissions estimation methodology for MV EFs is based on a transparent, regional-scale approach to estimate emissions, in contrast to other, more vehicle-specific methodologies that employ computer models, such as Mobile6 for MV emission factors (EPA, 2002). For the regional analysis we were not able to make use of the Mobile6-specific inputs such as volume-percentage aromatic, olefin, benzene content of gasoline; percentage of vapor of a given gasoline produced at 200 and/or 300 °C; or oxygenate type used, and volume percent (EPA, 2002).

2.1.2. RWC

We estimated PAH emissions from RWC from both fireplaces and woodstoves. Emissions were estimated for both urban and rural regions based on Eq. (3):

$$\text{RWC emissions} = \sum_{j,k} (F_{j,k} \times F_k \times \text{households} \times \text{consumption}_k \times \text{CF}_{\text{cords}\rightarrow\text{kg}} \times \text{EF}_{\text{wood}}), \quad (3)$$

where subscript j refers to the type of RWC (fireplace or woodstove); subscript k indicates whether or not wood is used as the household's main heating fuel; $F_{j,k}$ is the percentage of households using fireplaces or those using woodstoves that burn wood, either as a primary or secondary source of fuel; F_k is the percentage of the population using wood as their primary heating fuel; households are the number of rural and urban households (as given under Eq. (2)); consumption$_k$ is the wood consumption (cords) per household; $\text{CF}_{\text{cords}\rightarrow\text{kg}}$ is the conversion from cords of wood to kilograms of wood;[1] and EF_{wood} is the PAH emission factor (EPA, 1998b and McDonald et al., 2000) for wood burning, as summarized in Table 2. For those households that burn wood as their primary fuel, we assume national average $F_{j,k}$ values of 23% and 77%, respectively, for fireplace and woodstoves (EIA, 1993). For those households that burn wood, but not as their main heating fuel, we assume half-use fireplaces and half-use woodstoves. For F_k we assume that 4.3% of urban and 16% of rural populations burn wood[2] as their main heating fuel (US BoC, 1990) and the remainder of the urban and rural population use wood as a secondary fuel. For consumption$_k$ we use 5.9 cords for urban or rural households that use wood as their main heating fuel, and 1.4 otherwise, assuming the "West North Central" average reported by the EIA (1993).

2.1.3. ECBs

For power generation, we focus on PAH emissions from ECBs. We obtained general information for Minnesota on all electric utility steam generating facilities that burn coal, but did not restrict our focus to those using coal as their primary fuel. This group includes 40 steam generating units, ranging in electrical power capacity between 7.5 and 855 MWe (megawatts electric) (EPA, 1999b). Three small plants that did not report MWe capacity were excluded from our PAH emissions inventory. In most cases, multiple steam generating units were reported for a given facility. Table 3a summarizes the total MWe per power plant.

All power plants summarized in Table 3a report burning a mixture of fuels[3] (EPA, 1999b). Based on available additional information, we summarize, in the last column of Table 3a, the particular fuel or contribution of fuels burned that are incorporated in our emissions estimates. For the Sherburne County Generating Plant, for example, both coal and oil are reported as fuel (EPA, 1999b; Question 9). However, we assume coal (subbituminous and bituminous) is the sole fuel source since this plant is the largest coal consuming generating plant in Minnesota, burning approximately 30,000 tons of coal per day (Xcel Energy, 2003b). For plants such as Clay Boswell, for which information beyond that provided by EPA (1999b) was not located, we assume that the reported total MWe capacity (EPA, 1999b) is produced from an equal distribution among the fuels reported (coal and petroleum). In the case of Potlatch Corp Minnesota Pulp-Paper division, for which

[1] 1 ton = 0.86 cord, 2000 lbs = 1 ton, and 0.454 kg = 1 lb.

[2] This is actually the percent of Minnesota households who use either coal or wood (US BoC, 1990), but here we assume that this is the percent of households who use wood, since "coal is not a widely used source of fuel for residential heating purposes in the US" (EPA, 1998a).

[3] Either coal (lignite, subbituminous, bituminous, or anthracite), oil, natural gas, or other (specified as either wood, wood waste, petroleum coke, or wastewater, sludge) (EPA, 1999b; Question 9). Since we were unable to locate PAH EFs from ECBs burning the latter two fuels (e.g., in the AP42 or the FIREV6.1 database), we exclude them from our PAH emissions inventory.

Table 2
RWC PAH EFs (mg PAH kg^{-1} wood burned) based on the average EF for those RWC units that had specific household use data such as conventional woodstoves, catalytic and non-catalytic woodstoves, and fireplaces

	EPA (1998b)			McDonald et al. (2000)	
	Conventional woodstoves[a]	Catalytic and non-catalytic woodstoves[b]	Fireplaces[c]	Fireplaces[d]	Woodstoves[e]
Acenaphthylene	106.0	25.0	10.0[f]	6.80	5.19
Acenaphthene	5.0	4.0	1.2[f]	0.65	0.52
Anthracene	7.0	4.0	9.0	3.10	1.43
Benz(*a*)anthracene	10.0	6.5	1.8	0.38	0.56
Benzo(*a*)pyrene	2.0	2.5	0.73[f]	0.25	0.20
Benzo(*b*)fluoranthene	3.0	2.0	1.9	n/a	n/a
Benzo(*k*) fluoranthene	1.0	1.0	n/a	n/a	n/a
Benzo(*ghi*) perylene	2.0	5.5	1.4	0.15	0.09
Chrysene	6.0	5.0	1.7[g]	0.44	0.35
Dibenz(*a*,*h*)anthracene	0.0	1.5	0.2[f]	n/a	n/a
Fluoranthene	10.0	5.0	1.9	2.90	1.75
Fluorene	12.0	7.0	4.7[f]	2.80	1.66
Indeno(1,2,3-*cd*)pyrene	0.0	6.0	n/a	0.13	0.08
Naphthalene	144.0	82.5	n/a	38.0	28.10
Phenanthrene	39.0	41.5	9.0	13.50	7.35
Pyrene	12.0	4.5	1.9	2.50	1.49

n/a: not available.
[a]EFs reported for conventional woodstoves (without control devices; SCC No. 21-04-008-051) (EPA, 1998b; Table 4.1-1).
[b]Average of EFs from catalytic (SCC No. 21-04-008-030) and non-catalytic (SCC No. 21-04-008-050) woodstoves (EPA, 1998b; Tables 4.1-2 and 4.1-3).
[c]Average of EFs from fireplaces burning seasoned oak (without control device; SCC No. 21-04-008-001), green pine, and unspecified wood (EPA, 1998b).
[d]Average of reported mean measured hardwood and softwood burning fireplace PAH EFs (McDonald et al., 2000).
[e]Reported mean PAH EFs from hardwood woodstoves (McDonald et al., 2000).
[f]EFs available only for fireplaces burning unspecific wood (EPA, 1998b).
[g]EFs available only for fireplaces burning seasoned oak and green pine (EPA, 1998b).

coal, oil, natural gas, wood, wood waste, and 'black liquor' are reported by the EPA (1999b) database as fuels, only 0.6% of the energy output is provided by coal (DOE, 2000a) and the remaining energy output is produced mostly by burning biomass (DOE, 2000a). Since we did not locate EFs for biomass fuels in ECBs, only the contribution of coal from the Potlatch Corp Minnesota Pulp-Paper Division incorporated in our emissions analysis.

PAH emissions were estimated for ECBs as

$$\text{ECB emissions} = \frac{\text{MWe}_{\text{fuel}} \times \text{CF}_{\text{MWe}\rightarrow\text{Btu day}^{-1}} \times \text{EF}_{\text{fuel}}}{\text{F}_{\text{fuel}}} \times \text{CFs}, \quad (4)$$

where MWe_{fuel} is the estimated MWe of the particular fuel, as given in Table 3b; $\text{CF}_{\text{MWe}\rightarrow\text{Btu day}^{-1}}$ is the conversion factor from MWe to Btu day^{-1} based on the fuel requirements for a 1000 Mwe power plant of 2.4×10^{11} (Btu day^{-1}) (Hinrichs, 1996); F_{fuel} is the energy content of the particular fuel, as given in Table 3b; EF_{fuel} is the PAH EF from the particular fuel from the AP42 (EPA, 1995) or FIRE V6.1 (EPA, 1998c) (both sources report identical EFs), as summarized in Table 4; and CFs are applicable conversion factors.[4] All ECBs listed in Table 3a report the use of some form of pollution control technology; that is, electrostatic precipitator; multicyclone, venturi, or wet scrubber; fabric filter; or flue gas desulfurization. These are systems for which the available PAH EFs apply (as summarized in Table 4).

2.2. An evaluation of our regional-scale emissions assessment

We evaluate our emissions assessment based on a benchmark comparison of predicted and measured concentrations for PAHs in outdoor air. According to Webster's Dictionary, a 'benchmark' is a point of reference from which measurements, calculations, or

[4]1 lb = 0.454 kg; 1 ton = 2000 lbs; 1 yr = 365 days.

Table 3a
Total MWe capacity of power plants in Minnesota with ECBs

Plant name[a]	County	MWe capacity[b]	Fuel source[c]
Allen S. King Generating Plant	Washington	542	Coal[d]
Black Dog Generating Plant	Dakota	510	Natural gas + coal[e]
Blandin Paper Company	Itasca	100	Natural gas + coal
Clay Boswell	Itasca	1072	Oil + coal
E.W. Davis Works Power Plant	Lake	115	Natural gas + coal
High Bridge Generating Plant	Ramsey	256	Coal[f]
Hoot Lake	Otter Tail	137	Coal[g]
Laskin Energy Center	Saint Louis	110	Coal[h]
LTV Steel Mining Company-Schroeder	Cook	225	Coal
M.L. Hibbard	Saint Louis	70	Natural gas + coal + other[i]
Minnesota Valley	Yellow Medicine	42	Natural gas + coal + oil
NE Station	Mower	30	Natural gas + coal
Potlatch Corp Minnesota Pulp-Paper Division	Carlton	71	Mostly biomass[j]
Riverside Generating Plant	Hennepin	516	Coal[k]
Sartell Mill	Stearns	45	Coal
Sherburne County Generating Plant	Sherburne	2255	Coal[l]
Silver Lake	Olmsted	54	Natural gas + coal

[a]Question 4a (EPA, 1999b).
[b]If "<#" was reported, included here as '#' (EPA, 1999b).
[c]Unless otherwise noted, EPA (1999b) is the primary reference.
[d]Xcel Energy (2003a).
[e]Xcel Energy (2003b).
[f]Xcel Energy (2003c).
[g]OTPCO (2003).
[h]Partners for Affordable Energy (2003).
[i]Other = wood waste, black liquor, used oil, petroleum coke, bark, industrial wastewater, sludge, and/or sludge waste.
[j]0.6% of energy is consumed by burning coal (DOE, 2000a), 80% from burning biomass (i.e., "organic non-fossil material of biological origin constituting a renewable energy source"; DOE, 2000b), and the remaining 19% by 'other' (i.e., "agricultural byproducts such as straw, digester gas and methane, fish oil, liquid acetonitrite, waste, tall oil, waste alcohol, medical waste, solid byproducts; sludge waste and tires" (DOE, 2000b).
[k]Xcel Energy (2003d).
[l]Xcel Energy (2003e).

Table 3b
Total estimated MWe (Minnesota and 15-county region) and energy content of specific ECB fuel (E_{fuel})

	Sub/bituminous coal[a]	Oil	Natural gas	Wood
Estimated total MWe				
All Minnesota	5.1×10^3	5.5×10^2	4.3×10^2	5.7×10^1
15 counties	3.9×10^3	0	2.6×10^2	0
E_{fuel} (units)	2.6×10^4 (kJ kg^{-1})[b]	4.2×10^7 (kJ m^{-3} residual oil)[c]	3.8×104 (kJ m^{-3})[d]	1.1×10^4 (kJ kg^{-1} wood, as fired)[e]

[a]If coal is reported as fuel, reported as sub/bituminous by EPA (1999b) and elsewhere by references in Table 3a.
[b]Average of subituminous and bituminous coal (as mined and wet, mineral free) (EPA, 1995, Section 1.1).
[c]Assume residual oil (EPA, 1995, Appendix A: Miscellaneous Data and Conversion Factors) since "residual oils are used mainly in utility, industrial and large commercial applications" (EPA, 1995, Section 1.3).
[d]Average gross heating value of natural gas (EPA, 1995, Section 1.4).
[e]Midpoint of given energy range (EPA, 1995, Section 1.6.1).

assessments may be made. As described in the following sections, our predicted values of C_{air_out} rely on our emissions estimates and are derived from the CalTOX multimedia model. We compare these with the available measured PAH C_{air_out} values as reported by the MNCPES.

Table 4
Available EFs from ECBs burning specific fuels

	Coal[a] (kg PAH ton^{-1} coal)	Oil[b] (kg PAH l^{-1} oil)	Natural Gas[c] (kg PAH 10^{-6} m^{-3} nat. gas)	Wood[d] (kg PAH ton^{-1} wood)
Acenapthene	2.32×10^{7}	2.53×10^{6}	2.94×10^{5e}	1.86×10^{6}
Acenaphthylene	1.14×10^{7}	3.03×10^{8}	2.94×10^{5e}	2.16×10^{5}
Anthracene	9.55×10^{8}	1.46×10^{7}	3.92×10^{5e}	1.50×10^{6}
Benzo(*a*)anthracene	3.64×10^{8}	4.81×10^{7}	2.94×10^{5e}	1.49×10^{6}
BaP	1.73×10^{8}		1.96×10^{5e}	3.07×10^{8e}
Benzo(*b*)fluroanthene	1.10×10^{7f}		2.94×10^{5e}	
Benzo(*k*)fluroanthene	1.10×10^{7f}		2.94×10^{5e}	3.48×10^{7e}
Benz(*ghi*)perylene	1.23×10^{8}	2.71×10^{7}	1.96×10^{5e}	6.41×10^{7}
Chrysene	4.55×10^{8}	2.85×10^{7}	2.94×10^{5e}	1.91×10^{7}
Dibenz(*a,h*)anthracene		2.00×10^{7}	1.96×10^{5e}	
Fluoranthene	3.23×10^{7}	5.80×10^{7}	4.90×10^{5}	8.32×10^{6}
Fluorene	4.14×10^{7}	5.36×10^{7}	4.57×10^{5}	3.74×10^{6}
Indeno(1,2,3-*cd*)pyrene	2.77×10^{8}	2.57×10^{7}	2.94×10^{5e}	1.64×10^{7}
Naphthalene	5.91×10^{6}	1.36×10^{4}	9.96×10^{3}	1.54×10^{3}
Phenanthrene	1.23×10^{6}	1.26×10^{6}	2.78×10^{4}	2.36×10^{5}
Pyrene	1.50×10^{7}	5.10×10^{7}	8.17×10^{5e}	7.59×10^{6}

[a]Subbituminous and bituminous coal are considered to have one EF (EPA, 1995, Table 1.1–12).
[b]Oil is assumed to be residual oil or a mixture of distillate and residual, since "…residual oils are used mainly in utility, industrial and large commercial applications" (EPA, 1995, Section 1.3).
[c](EPA, 1995, Table 1.4–3).
[d]Wood, defined in boilers as "… wood waste is normally burned in the form of hogged wood, bark, sawdust, shavings, chips, mill rejects, sand or dust, or wood trim" (EPA, 1995, Section 1.6).
[e]At the method of detection limit.
[f]Not explicitly reported, therefore, the benz(*bjk*)fluoranthene EF for sub/bituminous coal was applied (EPA, 1995).

2.2.1. CalTOX multimedia model

To predict C_{air_out} based on our emissions estimates, we applied the CalTOX (version 4.0) quasi-dynamic regional-scale multimedia mass-balance model (McKone et al., 2003; McKone and Enoch, 2002). Algorithms to estimate environmental concentrations in the CalTOX model are described in detail elsewhere (McKone, 1993; McKone and Daniels, 1991).

Since CalTOX is a regional multimedia model and does not make urban and non-urban distinctions, we assess C_{air_out} from two different sets of estimated emissions, i.e., one based on the entire state of Minnesota and another estimated for the 15-county urban region that surrounds and includes the seven counties of the Twin Cities metropolitan region, as shown in Fig. 2. We expect the measured MNCPES concentrations from the 15-county region to be comparable to CalTOX results in terms of the airborne levels of PAHs. We estimated PAH emissions from the 15-county region according to the methods described above, with the following assumptions:

(1) because our urban and rural distinction leads to the inclusion of all but one urban county in Minnesota in the 15-county region, we assume for MV emissions that all urban roads are located in the 15 counties. Thus, we assume the total reported urban VKT applies for estimating MV emissions by Eq. (1). Further, for LDGV, emissions based on estimated VKT (Eq. (2)), we apply the rural (26,622) and urban (1,093,978) household populations (US BoC, 2002) and average MVs/household of 2.0 (US BoC, 2002);
(2) for RWC, we estimate emissions according to Eq. (3), based on the adjusted rural and urban household populations given under assumption (1);
(3) for ECBs, we include six plants listed in Table 3a that are located in the 15-county region, i.e., Allen S. King, Black Dog, High Bridge, Sartell Mill, Sherburne County, and Riverside Generating Plant.

To match our specific emissions estimates, we set the modeled area in CalTOX to represent either the total land and water area of MN (2.3×10^{11} m^2) or the area of the 15-counties region (2.00×10^{10} m^2) highlighted in Fig. 2. For both cases, we parameterized CalTOX with average meteorological and landscape parameters for Minnesota (McKone et al., 1998). We ran a Monte Carlo analysis ($n = 5000$ trials) to generate a distribution of potential C_{air_out} for each of the PAHs, by using default parameter distributions in CalTOX and by fitting a lognormal distribution to the sum of emissions

from the major source categories. We construct this distribution by matching the median and maximum emissions estimates from our data to the geometric mean and 99th percentiles, respectively, of a standard lognormal.

2.2.2. MNCPES

We compare our modeled PAH C_{air_out} values with 6-day integrated average C_{air_out} values measured by the MNCPES, an adjunct study to the National Human Exposure Assessment Survey (NHEXAS). The MNCPES is a probabilistic sample in which outdoor air PAH concentrations were sampled from 55 urban and non-urban residences within the 15-county region (Pellizzari et al., 2003). We used summary statistics, such as the median and the median method detection limit (mMDL) of the PAH C_{air_out} reported, respectively, in Clayton et al. (2003) and Pellizzari et al. (2003) to develop concentration distributions for comparison with our CalTOX multimedia model concentrations.

3. Results and discussion

3.1. Estimated PAH emissions

With the methods described above, we estimate total (rural and urban) PAH emissions estimates by source category in the state of Minnesota. Fig. 3(a–p) summarizes our results. If the emissions from a particular source, such as LDGVs, are based on multiple activity scenarios or more than one reported EF, as for RWC, we use horizontal bars to show the estimated range.

As can be seen from Fig. 3, two- and three-ring PAHs make up the majority of our estimated emissions for the 16 PAHs we focus on. This corresponds with prior results from studies of outdoor PAH levels (Khalili et al., 1995). Fig. 3 also reveals that the largest source contributors to PAH emissions appear to be LDGVs and RWC. For the 16 PAHs presented in Fig. 3, the range of LDGV emissions tends to either overlap RWC emissions or are within an order of magnitude of them. Exceptions to this trend appear for three of the four-ring PAHs—chrysene, fluoranthene, and pyrene—and for benzo(*b*)- and benzo(*k*)fluoranthene, for which RWC is anywhere from two to three orders of magnitude greater than the minimum emissions of LDGV estimated. For those PAHs with M + HDT EFs available, ECBs tend to contribute less to emissions than M + HDTs. Furthermore, for six out of the nine PAHs for which bus EFs are available (anthracene, BaP, chrysene, fluoranthene, phenanthrene, and pyrene), we estimate an approximately equivalent contribution from buses and ECBs to overall PAH emissions. Among the three remaining PAHs considered, buses contribute least to total emissions by at least one order of magnitude for benz(*a*)anthracene, benzo(*ghi*)perylene, chrysene, and indeno (1,2,3-*cd*)pyrene.

Based on the activity scenarios considered here, we estimate the same order of magnitude of LDGV emissions from urban and rural settings when emissions are based on reported VKT (Eq. (1)). Based on our definition of urban and rural counties, when LDGV emissions are based on population and activity estimates, total MV emissions are approximately equal in rural and urban settings. We observe a similar trend for RWC.

The results we present in Fig. 3 incorporate both Type A uncertainty (attributable to variability/randomness) and Type B uncertainty (attributable to lack of knowledge). For example, Type A uncertainty in reported the EFs for sources with multiple EFs reported, i.e., LDGVs, M + HDTs, and RWC, as well as in activity methods we applied, such as the three for LDGVs. We find Type B uncertainty resulting from a lack of knowledge associated with inputs to our emissions estimates. For example, the fuel-specific EFs for both ECBs and for RWC are based on limited and sometimes inaccurate EF data (EPA, 1995, 1998b, c). With the exception of phenanthrene, natural gas-fueled ECB EFs for all 16 PAHs have a rating of "E", or a "poor factor"—one that was based on tests from either an unproven or new methodology, or a generally unacceptable method which could provide at most an order of magnitude EF estimate (EPA, 1995 and 1998c; Radian Corporation, 1996). Similarly, EPA gave an "E" rating to PAH EFs from woodstoves (conventional, catalytic, and noncatalytic) and fireplaces burning seasoned oak and green pine (without control devices) (EPA, 1998b).

An additional source of Type B uncertainty is associated with our activity factors, even with the use of the most recently available data. For example, we use MVs as a proxy measure for LDGVs to estimate LDGV emissions from estimated VKT (Eq. (2)). Additionally, we use the proportion of VKT attributable to passenger cars for 2001, the most recent year for which total VKT data is available from the US DoT (2002a), combined with the percent of annual VKT driven by passenger vehicles for 1994, the most recent year for the percent distribution of VKT is available (US DoT, 1996). Nevertheless, we find that the contribution of LDGVs to total PAH emissions are roughly equivalent regardless of the activity scenario we apply, and the ranges in Fig. 3 are influenced primarily by the EF we use.

We have compared our emissions estimates with a recent emissions inventory on PAHs performed by the Minnesota Pollution Control Agency (MPCA) (MPCA, 2000) and found some significant differences. For example, a preliminary comparison of our emissions estimates for MVs, with those by the MPCA, reveals

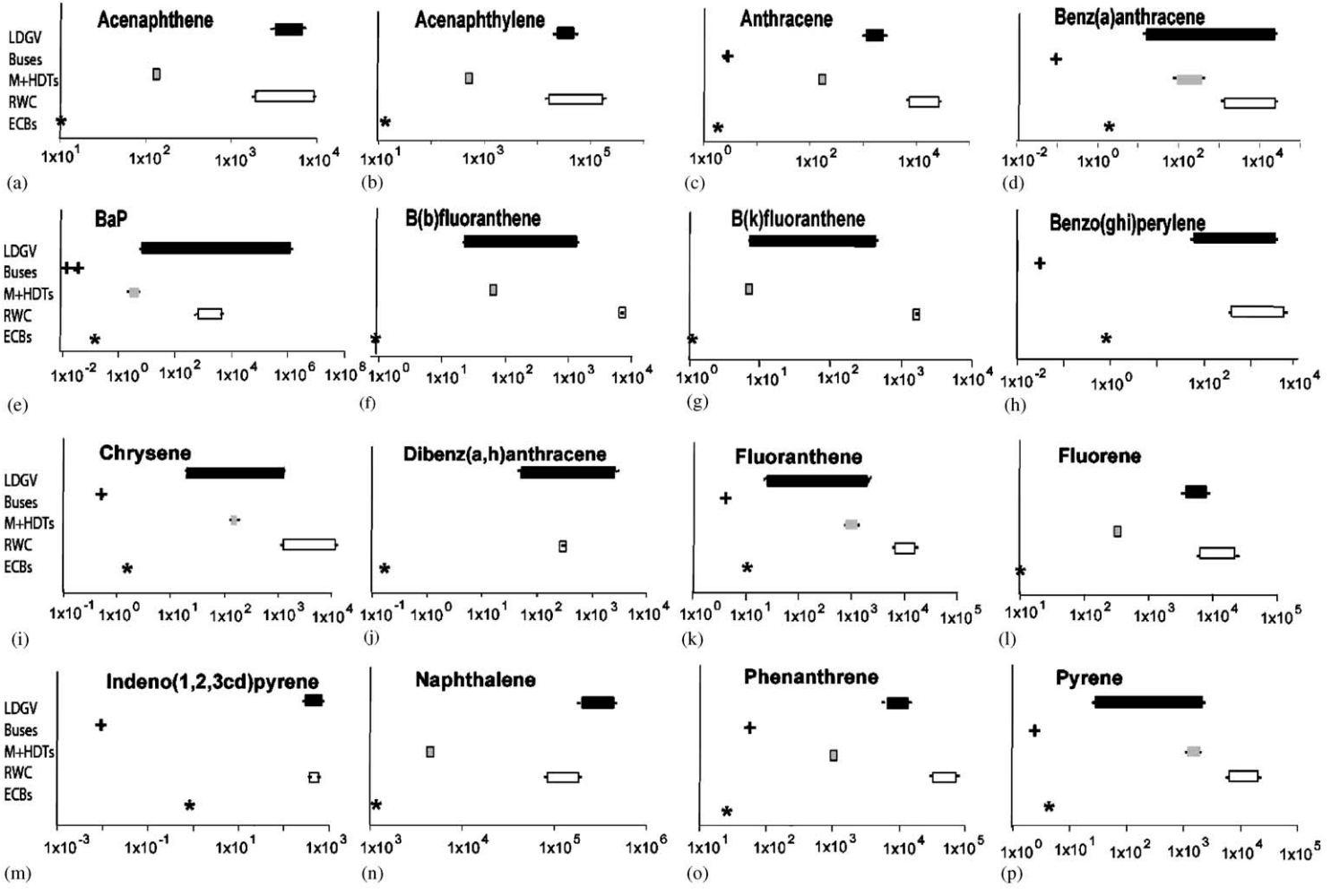


Fig. 3. (a–p) Estimated emissions ($kg\,yr^{-1}$) for 16 PAHs for the state of Minnesota. Where multiple EFs and/or activity scenarios were available, ranges are presented.

that, with the exception of chrysene, the midpoint of our annual emissions estimate ranges, as shown in Fig. 3, are at least an order of magnitude greater than the 1997 MN-state estimates. Chrysene is within an order of magnitude of the MPCA estimate. We have yet to make a detailed comparison between our methodology and that of the MPCA for estimating emissions, but believe that the main sources of these differences are attributable to different choices of activity factors and our use of PAH-specific EFs. For example, in contrast to our PAH-specific approach, the MPCA estimated inventories of specific PAHs based on models that use PAH EFs from speciation profiles of TOGs.

3.2. Evaluation of our regional-scale assessment

To evaluate the degree of comparability between the modeled C_{air_out} and those from MNCPES, we applied the CalTOX regional multimedia fate model as a "melding tool." In Fig. 4, we present our comparison of modeled concentrations for the 15-county region with distributions derived from available PAH median and the mMDL concentrations reported from the MNCPES for benz(*b*)fluoranthene, chrysene, fluoranthene, and pyrene (Clayton et al., 2003 and Pellizzari et al., 2003). Anthracene, BaP, benz(*a*)anthracene and indeno (1,2,3-*cd*)pyrene are not included in our comparison because the median C_{air_out} from the MNCPES are reported as equal to or below the reported mMDLs (Pellizzari et al., 2003). For benz(*b*)fluoranthene, chrysene, fluoranthene, and pyrene, our predicted C_{air_out} ranges for the 15-county region show reasonable agreement with ranges derived from MNCPES measurements. As shown in Fig. 4, the median values of our predicted C_{air_out} agree within an order of magnitude of measured concentrations for all four PAHs. We constructed the MNCPES ranges by assuming that the reported median MDLs are either the first or fifth percentile of a lognormal distribution of concentrations and found our comparison insensitive to this choice.

If we use the entire state of Minnesota and state-wide emissions estimates in our regional model, instead of the 15-county region, the median values of our modeled C_{air_out} tend to be one to two orders of magnitude less than those reported by the MNCPES for benz(*b*)fluoranthene, chrysene, fluoranthene, and pyrene. This indicates that our 15-county emissions estimates better reflect the regional C_{air_out} measured by the MNCPES. Although we did not include PAH emissions attributable to regional sources outside of Minnesota in our model, we achieve good agreement between the mostly urban 15-county region C_{air_out} estimates and those measured in the MNCPES. Therefore, we do not believe that long-range transport of PAHs are a significant contributor to C_{air_out} in this region, and that we can ignore background levels attributable to long-range transport. However, this may not be the case at the state-wide level.

Furthermore, as a result of our 15-county regional evaluation we can conclude that for at least two of the

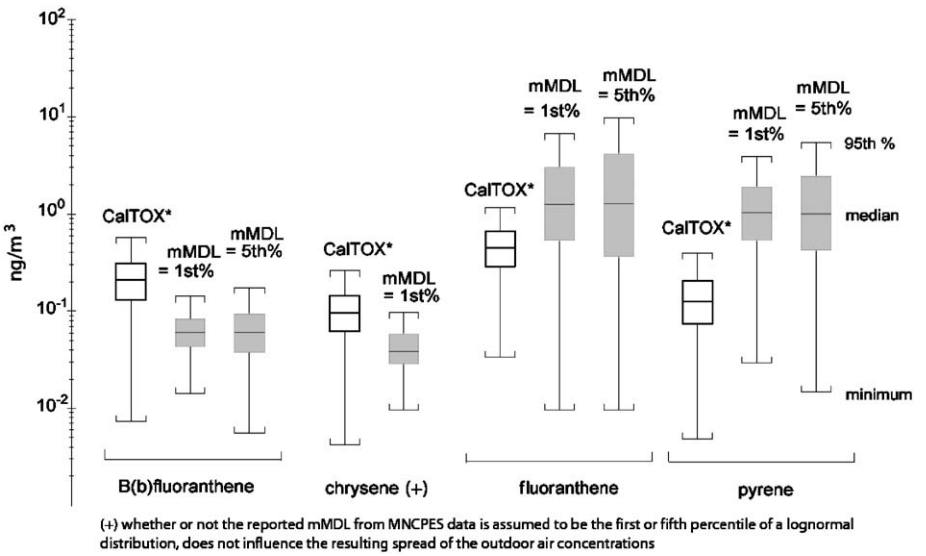


Fig. 4. A comparison of our modeled C_{air_out} (ng m^{-3}) and MNCPES-based benchmark C_{air_out} (ng m^{-3}). Ranges predicted from our 15-county emissions estimates (CalTOX*) are not shaded. Shaded ranges reflect the use of a lognormal distribution to fit concentrations measured by the MNCPES, and treating the median as the geometric mean and the mMDL as either the first or fifth percentile.

PAHs, fluoranthene and pyrene, additional emissions sources, most likely other than emissions migrating from other regions, should be characterized, for example, tire combustion and asphalt production. The contribution of these sources may result in even better overlap between the distributions derived from the reported MNCPES measurements and those from the CalTOX model, as shown in Fig. 4. Of tire combustion, it has been said, based on the limited research to date, that in comparison with coal, the "highest PAH emissions were produced with tire as a fuel" (Mastral and Callan, 2000). However, the availability of activity and EF data for these PAH emitting activities is extremely limited and precludes us from including them as sources in our emissions inventory.

In an effort to evaluate sources of uncertainty, we assign combinations of Types A and B uncertainty to the three principal elements in our evaluation: (1) the benchmark C_{air_out} reported from the MNCPES, (2) the C_{air_out} derived from the CalTOX model, and (3) our estimated emissions inventory. The empirical MNCPES provides us with benchmark concentrations, which consist of randomness or Type A uncertainty, as well as Type B uncertainty that derives from an absence of knowledge about the spatial scale that these samples represent. In contrast to the uncertainty from these measurements, the output from CalTOX consists primarily of Type B uncertainty derived from parameter uncertainty (Hertwich et al., 1999) and from the specification of the problem, formulation of conceptual model, and calculation and interpretation of results (Hertwich et al., 2000). However, as shown by the estimated 95% confidence intervals in Fig. 4, by melding our three principal elements of our regional-scale evaluation we are able to:

(1) reduce the Type B uncertainty associated with the MNCPES in terms of the region represented by the empirical concentrations. We see a much greater degree of overlap between predicted and empirical C_{air_out} based on the 15-county emissions estimate than if we base our predicted concentrations on emissions estimated for the entire state of MN;
(2) increase the confidence in our emissions estimates, because the amount of Type B uncertainty associated with our emissions estimates decreases relative to our uncertainty prior to the regional-scale evaluation;
(3) reduce the Type B model prediction uncertainty in terms of specification of problem and estimation of C_{air_out} and interpretation of results.

By achieving a reasonable degree of overlap between model-predicted concentrations and those derived from the MNCPES, we have reduced Type B uncertainty and gained greater confidence in our emissions estimates. However, we do not see a reduction in the Type A uncertainties. The variability inherent in the data and giving rise to Type A uncertainty remains, since reducing this uncertainty requires collecting more basic data. One cannot "model" ones way out of Type A uncertainty.

4. Conclusions

Our objective was to compare estimates of PAH airborne emissions from major sources and to predict and evaluate C_{air_out} based on a regional multimedia transport and fate mass-balance model. We conclude that efforts to reduce PAH emissions should focus on controlling emissions from RWC and LDGVs, since we estimate that these sources are the largest contributors overall to outdoor emissions. Though numerous factors contribute to uncertainty in our emissions, such as availability, reliability, and quality of EF and activity data, we find that, if our study area is limited to a 15-county region most likely best represented by reported benchmark concentrations from the MNCPES, the range of our predicted C_{air_out} agrees within our expected uncertainty with those measured. Lastly, our analysis expresses the need for more data collected for specific PAHs in a spatially resolved manner.

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