Constraining Uncertainties about the Sources and Magnitude of Ambient Air Exposures to Polycyclic Aromatic Hydrocarbons (PAHs): the State of Minnesota as a Case Study

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Abstract (300 words max- 286 here):

Emissions data are often lacking or uncertain for many airborne contaminants. Chemicals, such as 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 and motor vehicle activity) and/or report 'total PAH' or particulate organic matter emissions instead of individual compounds. We measure 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 four major sources of PAHs to outdoor air- (1) on-road motor vehicles, including light-duty gasoline vehicles and diesel-powered buses and medium and heavy duty trucks; (2) residential wood combustion; 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 our emissions and interpret 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 were able to 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.

Key words (max five): gasoline motor vehicles; diesel fuel motor vehicles; external combustion boilers; residential wood combustion; emissions inventory

1. Introduction

Anthropogenic sources appear to be the major contributors to atmospheric polycyclic aromatic hydrocarbon (PAH) emissions. Although estimated emissions of specific anthropogenic sources in the US vary, Baek et al. (1991) report that approximately 10,000 tons of PAHs are emitted to the atmosphere annually in the US. Based on several evaluations of PAH emissions in the current literature [do we need references here, even though they are provided for in Figure 1?], **Figure 1** shows current assumptions

about major sources of PAHs. **Figure 1** reveals that motor vehicles (MVs) are a major source of atmospheric PAH emissions in urban environments (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 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 objectives of this paper are to 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 human activity patterns and emissions factors for specific PAH compounds. From these inputs we compare the relative magnitude and uncertainty of PAH emissions to outdoor air from the following major sources:

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

As our case study, we focus on rural and urban regions of the state of Minnesota. Within a framework represented by **Figure 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 from 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 **Figure 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, Minnesota is 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 less than10 lbs PAH /yr in Minnesota (EPA, TRI-2000 as cited in Scorecard). 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 EPA's list of 16 PAHs (both probable and nonclassifiable carcinogens). 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 proposed emissions inventory approach is designed to provide a highly transparent, easily replicable methodology, which uses the most recent emission factors data, from both the peer reviewed literature and those published by the EPA, 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 Toxics Releases Inventory fail to account for population based activities (such as RWC and on-road MV activity);
2) some emissions databases, such as the US EPA's 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 emission factor 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 emissions factors reported for individual PAH's instead of speciation profiles.

In the following sub-sections 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 measurements derived from a multimedia model.

2.1 Estimates of PAH Emissions

For each of our major source categories we estimate outdoor air emissions from using an emissions factor approach. Where sufficient data are available, we distinguish between urban and rural emissions.

2.1.1 On-road Gasoline and Diesel Fueled Motor Vehicles

For gasoline-powered MVs, we use emissions factors (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 (LDGT1) from 0 to 6000 lb gross vehicle weight and those heavier (LDGT2) up to 8500 lb, and heavy-duty gasoline-powered vehicles (HDGV) we do not explicitly account for these vehicles in our emissions estimates. However,

the contribution 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. But motorcycles are excluded because no EFs are available for PAHs other than BaP.

PAH EFs are available for diesel powered buses and medium and heavy-duty trucks (M+HDTs) with 2 axles and 6-tires or more or combination trucks (single or multiple trailers). We found no EF data for light duty diesel powered vehicles and trucks (0 to 6000 lb. gross vehicle weight). PAH EFs from diesel powered MVs are summarized in Table 1. For the majority of M+HDTs, EFs we combined the reported particulate and gaseous phase EFs.

For PAH emissions from diesel powered motor vehicles, 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, 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:

$$MV\ emissions = activity \times EF \quad (Eq.\ 1)$$

where *activity,* is estimated as the reported VMT for specific MV classes in Minnesota, for urban roads (i.e., passenger vehicles, or LDGVs= 4.18E+10 km/yr, Buses = 8.80E+07 km/yr, and M+HDTs = 2.19E+09 km/yr) and rural roads (i.e., passenger vehicles, or LDGVs = 3.66E+10 km/yr; Buses = 8.26E+07 km/yr; M+HDTs = 4.58E+09 km/yr) (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 *activity* by the following two methods:

(1) estimated urban and rural vehicle miles traveled (VMT) according to:

$$estimated\ VMT = (pop_{est}) \times (cars/household) \times (mpd/car) / (person / household) \quad (Eq.\ 2)$$

where, pop_{est} is defined as the population (of Minnesota) obtained from the 1990 [Can we use 2000 census data?] Census (US BoC, 1990) and, we assume *2 cars/household (US, BoC, 1990 for Minnesota)*, *2.6 persons per household (US BoC, 1990 for Minnesota)*, and *mpd/car* is the average miles driven per day per car, assumed to be 20 [need references for these assumptions- for the 20 mpd/car I still need to find a reference, the other two I found are in the BoC data for 1990, Minnesota specific.];

(2) gasoline fuel usage (GFU) [gallons gasoline/ yr] which is available for on-road LDGVs only, in urban and rural environments based on the 2001 total gasoline highway motor fuel use (including private and commercial and public use) data for Minnesota (US DoT, 2002b), multiplied by the average mil/ gall (mpg) of highway and city driving for LDGVs, 24.6 mpg (stdev = 6.0) summarized for all members of the light duty (i.e., passenger car) motor vehicle 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 derive only from available data on VMT.

Our emissions estimation methodology is based on a transparent, regional-scale approach to estimating 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 Mobile 6 -specific inputs such as volume-percentage aromatic, olefin, benzene content of gasoline; percentage of vapor a given gasoline produces at 200 and/or 300 degrees; or oxygenate type used (MTBE, ETBE, ETOH, TAME) and volume per cent (EPA, 2002).

2.1.2 Residential Wood Combustion (RWC)

We estimated PAH emissions from RWC from both fireplaces and woodstoves. Emissions from pellet stoves were considered negligible and not included since very few are in use in this region. Emissions were estimated for both urban and rural regions based on Eq.3:

$$RWC\ emissions = \sum_{j,k}\left(F_{j,k} \times F_k \times Households \times Consumption_k \times CF_{cords \rightarrow kg} \times EF_{wood}\right) \quad \textbf{(Eq. 3)}$$

where, subscript j refers to the type of RWC (fireplace or woodstove); subscript k indicates whether or not wood is used as the households main heating fuel; $F_{j,k}$ is the percentage of households using fireplaces and those using woodstoves who burn wood, either as a primary or secondary source of fuel (i.e., for those who burn wood as their primary fuel, we assume the national averages of 23% and 77% for fireplace and woodstove (EIA, 1993), respectively, applies for Minnesota; for those households who burn wood, but not as their main heating fuel, we assume half use fireplaces and half use woodstoves); F_k is the percentage of the population using wood as their primary heating fuel (i.e., 4.3% of urban and 16% of rural populations burn wood[1] as their main heating fuel (US BoC, 1990) and the remainder of the urban and rural population use wood as a secondary fuel); *Households* are the number of rural and urban households (for Minnesota these are reported as 72,862 and 1,521,743, respectively, by the most recent available data, US BoC, 1990); $Consumption_k$ is the wood consumption [cords] per household (5.9 cords for urban or rural households who use woods as their main heating fuel, and 1.4 otherwise, assuming West North Central average by EIA, 1993) ; $CF_{cords \rightarrow kg}$ is the conversion from cords of wood to kilograms of wood[2]; and EF_{wood} is the PAH emission factor (EPA, 1998 and McDonald et al, 2000) for wood burning, as summarized in Table 2.

2.1.3 External Combustion Boilers (ECBs)

For power generation, we focus on PAH emissions from external combustion boilers (ECBs). We obtained general information on all electric utility steam generating facilities that burn coal (but not restricted to coal as their primary fuel) for Minnesota. This includes 40 steam generating units, ranging in

[1] 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, 1998, p 4-10).

[2] 1 ton = 0.86 cord, 2000 lbs = 1 ton, and 0.454 kg = 1 lb

electrical power capacity between 7.5 to 855 MWe (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 (199b) was not located, we assume that the reported total MWe capacity (EPA, 1999b) is produced from an even distribution among the fuels reported (coal and petroleum). In the case of Potlatch Corp Minnesota Pulp-Paper division, though coal, oil, natural gas, wood, wood waste, and 'black liquor' are reported by the EPA (1999b) database, only 0.6% of the energy output is provided by coal (DOE, 2000a) and the remaining energy output 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 can be incorporated in our emissions analysis.

PAH emissions were estimated for ECBs as:

$$ECB\ emissions = \frac{MWe_{fuel} \times CF_{MWe \rightarrow Btu/d} \times EF_{fuel}}{E_{fuel}} \times CFs \qquad \text{Eq. (4)}$$

where MWe_{fuel} is the estimated MWe of the particular fuel, as given in Table 3b; $CF_{Mwe \rightarrow Btu/d}$ is the conversion factor from MWe to Btu/d based on the fuel requirements for a 1000 Mwe power plant of 2.4×10^{11} [Btu/day] (Hinrichs, 1996); E_{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, 1998a) (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, i.e., either electrostatic precipitator, or multicyclone, venturi or wet scrubber, or fabric filter or flue gas desulfurization for which the available PAH EFs (summarized in Table 4) apply.

[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 located 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.

[4] 1 lb = 0.454 kg; 1 ton = 1000 kg; 1 yr = 365 days

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

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., 2002; 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 twelve-county urban region that surrounds and includes the Twin Cites, as shown in **Figure 2**. We expect the measured MNCPES samples from the twelve county region to be comparable in terms of the airborne levels of PAHs. We estimated PAH emissions from the twelve county region according to the methods described above, with the following assumptions:

1) for MVs, since the twelve counties encompass the majority of the urban areas of Minnesota, we assume that all urban roads are located in the twelve counties. Thus, we assume the total reported urban VMT applies for estimating MV emissions by Eq. 1. Further, for LDGVs, emissions based on estimated VMT (Eq. 2), we apply the adjusted household population of 952,173 (BoC, 1990);
2) for RWC, since no households are designated as strictly 'rural' (BoC, 1990), we assume that all households (952,173) (BoC, 1990) in the twelve counties are urban and estimate emissions according to Eq.3;
3) for ECBs, we include only four of the plants listed in Table 3a which are located in the 12-county region (i.e., Allen S. King, Black Dog, High Bridge, and Riverside Generating Plant).

Thus, corresponding to our specific emissions estimates, we set the modeled area in CalTOX to represent either the total land and water area of MN (2.3E+11 m^2), or the area of the 12-counties region (1.1E+10 m^2) highlighted in **Figure 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 = 5,000 trials) to generate a distribution of potential C_{air_out} for each of the PAHs, assuming that the sum of our emissions from the major source categories are lognormally distributed, i.e., the GM is the median of our emissions range (we sum the medians, where available, from each particular source category), and the 99th percentile of the distribution is our estimated maximum.

2.2.2 MNCPES

We compare our modeled PAH C_{air_out} with six-day integrated average C_{air_out} 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 oversampled at 55 non-urban residences (Pellizzari et al., 2003). Summary statistics, such as the median and the median method detection limit (mMDL) of the PAH C_{air_out} are reported (Clayton et al., 2003 and Pellizzari et al, 2003, respectively) and were used to develop distributions for comparison with our CalTOX multimedia modeled concentrations.

3. Results and Discussion

3.1Estimated PAH Emissions

We use the methods described above to estimate total (rural & urban) PAH emissions estimates in the state of Minnesota. In **Figure 3 (a-p)** we present our results. If the emissions from a particular source, such as LDGVs, were based on multiple activity scenarios or more than one reported EF, as for RWC, horizontal ranges are given..

As can be seen from **Figure 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). **Figure 3** also reveals that the largest source contributors to PAH emissions appear to be LDGVs and RWC. For the sixteen PAHs presented in **Figure 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 two of the four-ring PAHs (i.e., fluoranthene and pyrene) and B(b)- and B(k)fluoranthene, for which RWC is anywhere from two to three orders of magnitude greater that 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 four out of the nine PAHs with Bus EFs available, i.e., anthracene, BaP, fluoranthene and pyrene, we estimate an approximately equivalent contribution from Buses and ECBs to overall PAH emissions. Among the five remaining PAHs, buses contribute least to overall PAH emissions for benz(a)anthracene, benzo(ghi)perylene, chrysene and indeno (1,2,3-cd)pyrene, but not for phenanthrene. For phenanthrene, we estimate that ECBs contribute least to overall emissions from our five source categories.

Based on the activity scenarios we applied, we estimate the same order of magnitude of LDGV emissions from urban and rural settings when emissions are based on reported VMT (Eq. 1). Not surprisingly, when LDGV emissions are based on population and activity estimates, urban and rural motor vehicle emissions are approximately one order of magnitude less in rural rather than urban settings (proportional to the population size). Similarly, since the activity scenario for RWC depends on population size, the rural emissions from RWC, tended to be an order of magnitude less than urban emissions. Others have reported similar significant distinctions between urban and rural PAH

concentrations, i.e., approximately two orders of magnitude lower ambient PAH concentrations were measured in rural and non-urban areas (Cotham and Bidleman, 1995 and Pirrone et al., 1995).

The results we present in **Figure 3** incorporate both Type A uncertainty, or true variability/randomness, and Type B uncertainty due to a lack of knowledge (Pate-Cornell, 1996). For example, Type A uncertainty in reported EFs for sources with multiple EFs reported, i.e., LDGVs, M+HDTs, and RWC and, in activity scenarios we applied, such as the three for LDGVs. There is also Type B uncertainty due to 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/or poor emissions factor data (EPA, 1995 or EPA, 1998a- L&E document and EPA, 1998b why not use all three? I need to see which document exactly is included here 1998 a or b. For sure EPA 1995, agnes). With the exception of phenanthrene, natural gas fueled ECB EFs for all sixteen 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-or magnitude EF estimate (EPA, 1995 and 1998a; Radian Corporation, 1996). Similarly, EPA gave a rating of E to PAH EFs from woodstoves (conventional, catalytic and noncatalytic) and fireplaces burning seasoned oak and green pine (w/out control devices) (EPA, 1998).

An additional form of Type B uncertainty may be associated with the activity factors we applied. For one, we applied 1990 census data (the most recent available to us at the time of our analysis) to estimate the rural/urban distinctions in emissions from LDGVs and RWC. However, for LDGVs, the total PAH emissions are roughly equivalent regardless of the activity scenario we apply (i.e., population based estimate, actual VMT reported, or GFU), and the ranges for LDGVs in **Figure 3** are influenced primarily by the EF we use. Secondly, in estimating PAH emissions from MVs by reported VMT (Eq. 1), we assume that the proportion of VMT attributable to passenger cars for 2001, i.e., the most recent year for which VMT specific data is available by the US DoT (2002a), is the same as for 1994, the most recent year for which percent of annual VMT driven by passenger cars is available (US DOT, 1996).

A recent emissions inventory on PAHs performed by the Minnesota Pollution Control Agency (MPCA) (MPCA, 2000) provided us with an opportunity to compare our results with an independent study of the same region. A preliminary comparison of our emissions estimates for MVs, for example, with those by the MPCA, reveals that the midpoint of our annual emissions estimate ranges, as shown in **Figure 3**, are at least an order of magnitude greater relative to their 1997 MN-state estimates, with the exception of chrysene which is within an order of magnitude of the MPCA estimate. Although we have not yet made a detailed comparison between our methodology and that of the MPCA for estimating emissions, we believe that the difference is attributable both 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 are based on PAH EFs from speciation profiles of total organic gases (TOGs).

3.2 Evaluation of our Regional Scale Assessment

To evaluate our estimated emissions and assess the degree of comparability between the resulting C_{air_out} and those from MNCPES, we have applied CalTOX regional multimedia fate model as a "melding tool". In **Figure 4**, we present our comparison of predicted concentrations for the 12 –county region with distributions derived from available PAH median and the mMDL concentrations reported from the MNCPES for B(b)fluoranthene, chrysene, fluoranthene, and pyrene (Clayton et al., 2003 and Pellizzari et al, 2003). The remaining PAHs with measured C_{air_out} from the MNCPES, i.e., anthracene, BaP, B(a)anthracene and indeno-1,2,3-cd pyrene have reported medians =< reported mMDLs (we speculate that this is most likely due to the fact that less than half of the samples were above the mMDL) (Pellizzari et al, 2003). Thus, we were unable to incorporate them in this analysis. Whether we assume that the median MDLs reported by the MNCPES are the first or fifth percentile of a lognormal distribution, our predicted C_{air_out} for the 12-county region show reasonable agreement with those measured in MNCPES. As shown by **Figure 4**, the medians of our predicted C_{air_out} agree within an order of magnitude of measured concentrations for all four PAHs.

If we compare our emissions estimates for the entire state of Minnesota, instead of the 12-county region, the median of our modeled C_{air_out} tend to be one to two orders of magnitude less than those reported by the MNCPES for B(b)fluoranthene, chrysene, fluoranthene and pyrene. This indicates that our 12-county emissions estimates better reflect the regional C_{air_out} measured by the MNCPES.

Different combinations of Type A and Type B uncertainty can be assigned to the three "principal" components in our evaluation: 1) the benchmark C_{air_out} provided by the MNCPES, 2) the regional multimedia model CalTOX, and 3) our estimated emission inventory. For example, our emissions estimates, as discussed above, are infused with both Type A and B uncertainty. The MNCPES provides us with benchmark concentrations which, being empirical, consist of randomness or Type A uncertainty as well as Type B uncertainty, with respect to the spatial scale which these samples represent. In contrast to the uncertainty from these measurements, the output from CalTOX, the multimedia model, consists primarily of Type B uncertainty derived from parameter uncertainty (Hertwich, et al., 1999) and, uncertainty in the specification of problem, formulation of conceptual model, and calculation and interpretation of results (Hertwich, et al. 2000). As shown by the estimated 95% confidence intervals in **Figure 4**, by melding our three 'principal elements' of our regional scale evaluation we:

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 12-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, as the amount of Type B uncertainty associated with our emissions estimates appears to be of a lesser degree than that believed 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 result.

However, in neither component do we affect the Type A uncertainties. Thus, by our regional scale evaluation, we achieve a reasonable degree of overlap between predicted concentrations and those measured by MNCPES, thereby leading us to greater confidence in our emissions estimates than if we had solely relied on our estimated emissions.

Further, as a result of our evaluation we can conclude that for at least two of the PAHs, fluoranthene and pyrene, we most consider additional sources, which we did not include in our emissions inventory– for example, tire combustion and asphalt production. Of tire combustion, it has been said, based on the limited research to date, that 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.

5. 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, as we estimate that these sources contribute greatest to outdoor emissions. Though numerous factors contribute to uncertainty in our emissions, such as quality, availability and reliability of EF and activity data, we find that, if our study area is limited to a 12-county region most likely best represented by reported benchmark concentrations from the MNCPES, the range of our predicted C_{air_out} agrees reasonably well 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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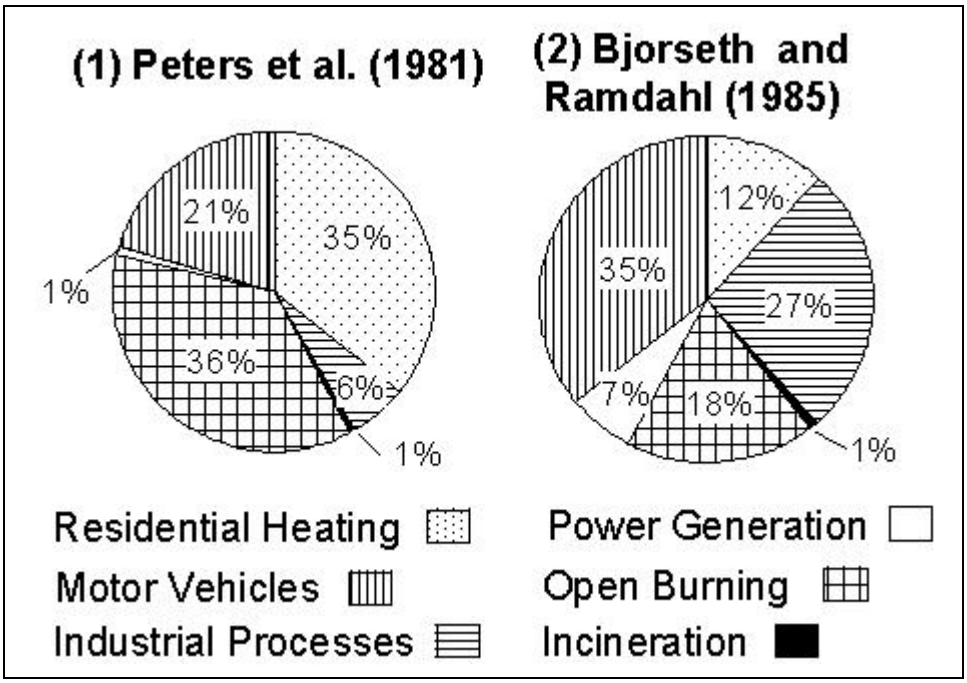

Figure 1: Major anthropogenic contributors to atmospheric PAHs in the US [metric tons/yr].

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 (coal and wood burning is 99% in 1; wood burning is 97% in 2).
Industrial Processes: coke manufacturing (1 and 2), asphalt production (1 and 2), carbon black (1 and 2), aluminum plants (2 only), charcoal manufacturing (uncontrolled batch kilns and continuous furnace production (1 only), and barium processing (black ash rotary kiln) (in 1 only). No petroleum refining emissions.
Incineration: commercial and municipal in 1, municipal only in 2.
Open Burning: agricultural fires (1), forest wildfires (1 and 2), prescribed burning (in 1), coal refuse fires (in 1), land clearing waste burning (1) and structural fires (1).
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).

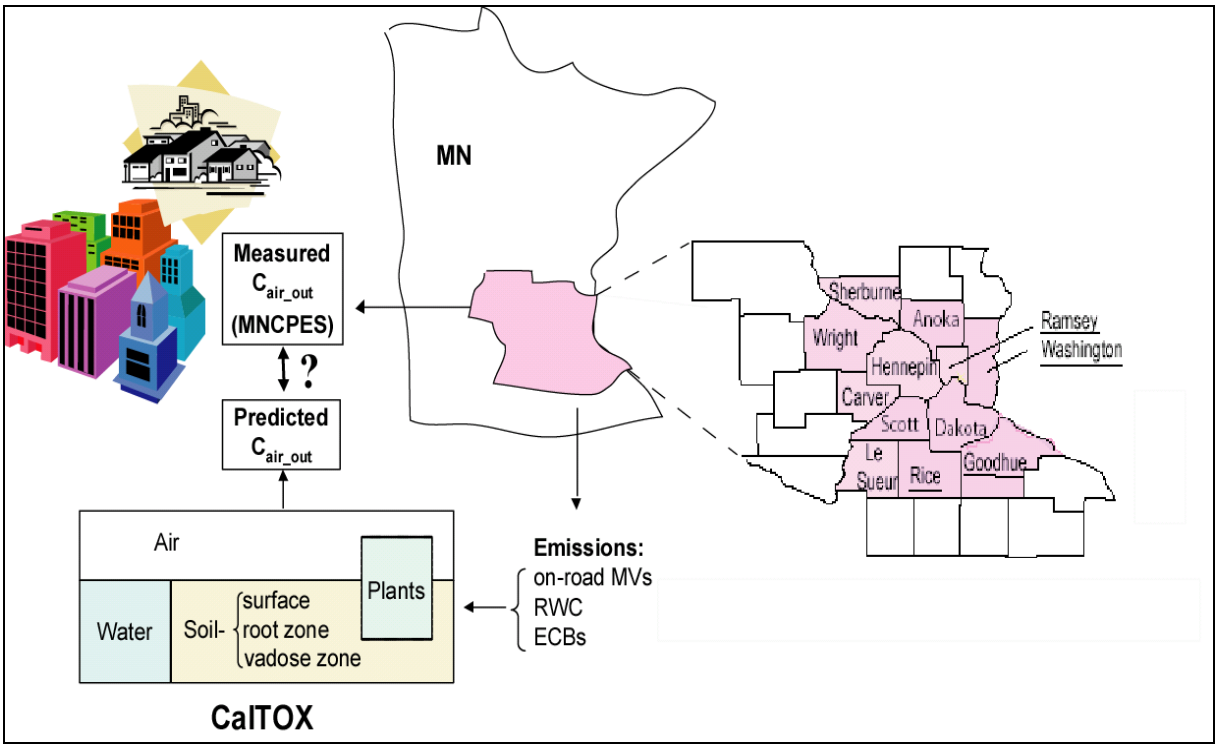

Figure 2: Our general framework for characterizing predicted C_{air_out} and comparison with available empirical concentrations (from the MNCPES). The twelve Minnesota counties that we estimated PAH emissions for separately, in addition to total emissions at the state level, are shaded. Counties underlined had MNCPES C_{air_out} reported (Quakenboss et al., 2000). needs to be black and white (?).

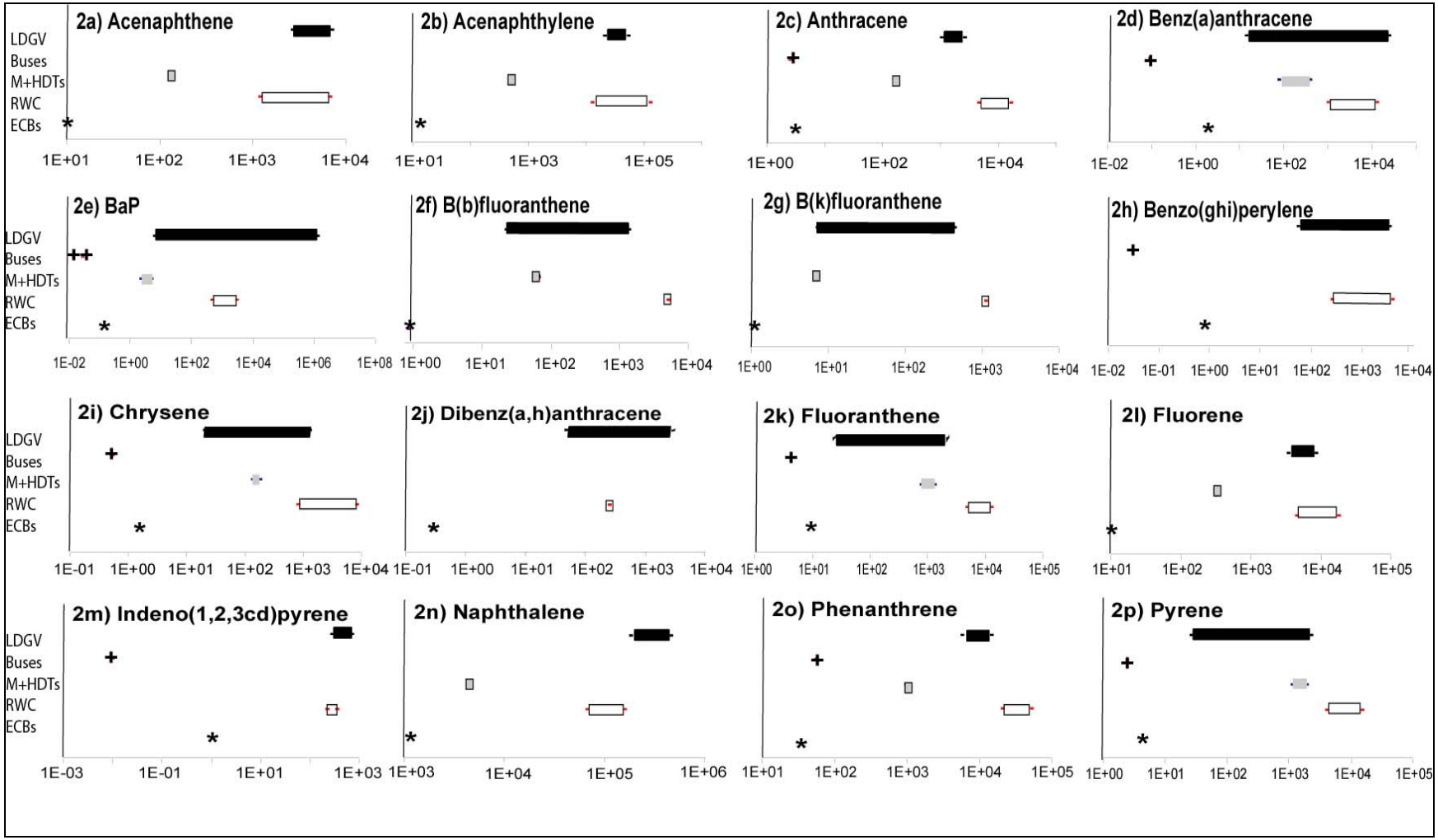

Figure 3(a-p): Estimated emissions [kg/d] for 16 PAHs for the state of Minnesota. Where multiple EFs and/or activity scenarios were available, ranges are presented.

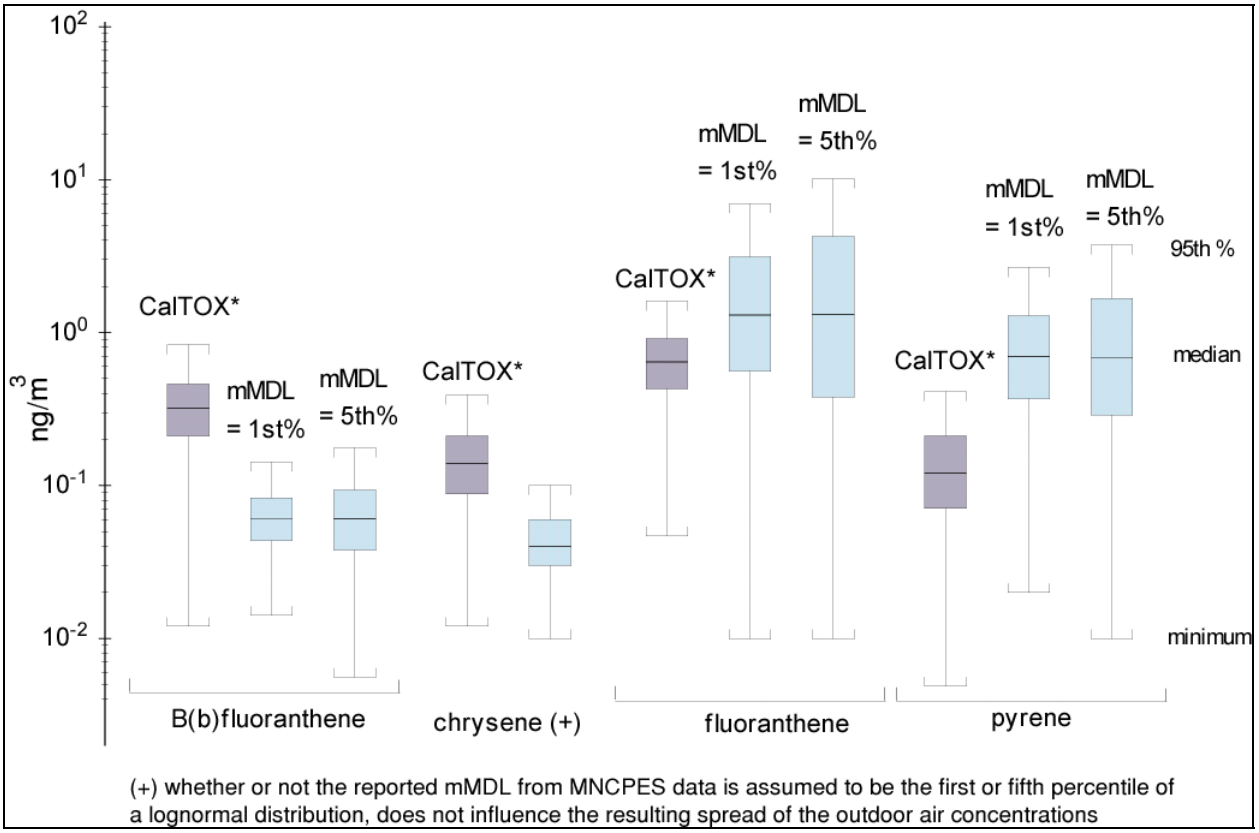

Figure 4: A comparison of our modeled and MNCPES benchmark C_{air_out} [ng/m3]. Ranges predicted from our 12-county emissions estimates (CalTOX*) are a darker shade. Lightly shaded ranges are simulation results based on assuming a lognormal distribution of concentrations measured by the MNCPES, assuming that the median method detection limit (mMDL) is either the first or fifth percentile and the median is the geometric mean.

Table 1: On-road MV PAH EFs [µg/km]

	LDGVs					Buses		MDT	HDT	
	Cadle et al. (2001)[a]	Miguel et al. (1998)[b]	EPA (1998a)[c]	EPA (1998b)[d]	as cited in Westerholm et al. (1994)[e]	Westerholm et al. (1994)[g]	as cited in Westerholm et al. (1994) [h]	Schauer et al. (1999) [i]	Miguel et al. (1998) [j]	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	0.34	0.21			0.44		10.8	54.9	
Benzo(a)pyrene	2.31	0.46		0.43	0.10; 1.9; 11.3	0.06	0.14		NS	0.42[k]; 0.67[l]; 0.31[m]
Benzo(b)fluoranthene		0.54							9.8	
Benzo(k)fluoranthene		0.13							1.1	
Benzo(ghi)perylene		1.31				0.14			NS	
Chrysene	5.08	0.50				2.81		18.9	25.9	
Dibenz(ah)anthracene	12.8 [f]	1.19							NS	
Fluoranthene	21.3	0.58						109.6	188.4	
Fluorene	83.1							44.1		
Indeno(123-cd)pyrene	6.6	0.63				0.05			NS	
Naphthalene	4.5E+03							617		
Phenanthrene	143					295		140.1		
Pyrene	22.1	0.63				13.1		160.4	270.9	

NS:= not a significant source

[a] average EF [µg/mil] 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 [ug PAH/ kg gas]. Converted to per km based on: gasoline density of 743 g/L and average (city and highway) MPG of 24.6 mpg (EPA, 1999a).

[c] average of catalytic and non-catalytic converter controlled LDGVs EFs for b(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] Dibenz(ah+ac)anthracene given in Cadle et al (2001); assume applies to dibenz(ah)anthracene

[g] sum of the mean particle and semivolatile EFs for diluted diesel exhaust from Bus Cycle (simulates Public Transportation conditions in a city).

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

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

[j] diesel fueled HDTs reported originally in units of [ug/gall] and converted to [ug/km] based on avg mpg of diesel HDTs of 5 and diesel density of 830 g/L.

[k] average of HD truck EFs from D1, D6 and D8 type diesel fuel

[l] average of exhaust EFs from diesel fueled HD trucks (in bus cycle) w/out particle trap

[m] average of exhaust EFs from diesel fueled HD trucks (in NY cycle) w/out trap or catalyst

Table 2: RWC PAH EFs [mg PAH/ kg 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 (1998)- L&E			McDonald et al. (2002)	
	Conventional woodstoves [a]	Catalytic and noncatalytic woodstoves [b]	Fireplaces [c]	Fireplaces [d]	Woodstoves [e]
Acenaphthylene	106.0	25	10 [f]	6.8	5.19
Acenaphthene	5.0	4	1.2 [f]	0.65	0.52
Anthracene	7.0	4	9.0	3.1	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	0.2
Benzo(b) fluoranthene	3.0	2	1.9	n/a	n/a
Benzo(k) fluoranthene	1.0	1	n/a	n/a	n/a
Benzo(ghi) perylene	2.0	5.5	1.4	0.15	0.09
Chrysene	6.0	5	1.7 [g]	0.44	0.35
Dibenz(a, h) anthracene	0.0	1.5	0.18 [f]	n/a	n/a
Fluoranthene	10.0	5	1.9	2.9	1.75
Fluorene	12.0	7	4.7 [f]	2.8	1.66
Indeno(1,2,3- cd) pyrene	0.0	6	n/a	0.13	0.08
Naphthalene	144.0	82.5	n/a	38.0	28.1
Phenanthrene	39.0	41.5	9.0	13.5	7.35
Pyrene	12.0	4.5	1.9	2.5	1.49

n/a: not available

[a] EFs reported for conventional woodstoves (w/out control devices; SCC No. 21-04-008-051) (EPA, 1998 L&E doc; Table 4.1-1)
[b] average of EFs from catalytic (SCC No. 21-04-008-030), and noncatalytic (SCC No. 21-04-008-050) woodstoves (EPA, 1998- L&E doc; Tables 4.1-2 and 4.1-3)
[c] average of EFs from fireplaces burning seasoned oak (w/out control device; SCC No. 21-04-008-001), green pine and unspecified wood (EPA, 1998- L&E doc)
[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, 1998- L&E)
[g] EFs available only for fireplaces burning seasoned oak and green pine (EPA, 1998- L&E)

Table 3: a) Total MWe capacity of ECBs in Minnesota and b) total MWE and energy content of specific ECB fuels.

Table 3a: Total MWe capacity of power plants in Minnesota with ECBs. Unless otherwise noted, EPA (1999b) is the primary reference for information provided here.

Plant name [a]	MWe capacity [b]	City	Zip Code	Fuel Source
Allen S. King Generating Plant	542	Bayport	55003	Coal [(c)]
Black Dog Generating Plant	510	Burnsville	55337	Natural gas + Coal [(d)]
Blandin Paper Company	100	Grand Rapids	55744	Natural gas + Coal
Clay Boswell	1072	Cohasset	55721	Oil +Coal
E.W. Davis Works Power Plant	115	Silver Bay	55614	Natural gas + Coal
High Bridge Generating Plant	256	St. Paul	55102	Coal [(f)]
Hoot Lake	136.9	Fergus Falls	56537	Coal [(g)]
Laskin Energy Center	110	Aurora	55705	Coal [(h)]
LTV Steel Mining Company – Schroeder	225	Schroeder	55613	Coal
M.L. Hibbard	70	Duluth	55807	Natural gas + Coal + Other [(e)]
Minnesota Valley	42	Granite Falls	56241	Natural gas + Coal + Oil
NE Station	30	Austin	55912	Natural gas + Coal
Potlatch Corp Minnesota Pulp–Paper Division	70.6	Cloquet	55720	Mostly biomass [(i)]
Riverside Generating Plant	516	Minneapolis	55418	Coal [(j)]
Sartell Mill	44.7	Sartell	56377	Coal [(i)]
Sherburne County Generating Plant	2255	Becker	55308	Coal [(k)]
Silver Lake	54	Rochester	55906	Natural gas + Coal

[a] Question 4a (EPA, 1999b).
[b] If "<#" was reported, included here as '#'
[c] Xcel Energy (2003c)
[d] Xcel Energy (2003a)
[e] other= wood waste, black liquor, used oil, petroleum coke, bark, industrial wastewater, sludge, and/or sludge waste
[f] Xcel Energy (2003d)
[g] OTPCO (2003)
[h] Partners for Affordable Energy (2003)
[i] 0.6% of energy is consumed by burning coal (DOE, 2000a), 80% from burning biomass (i.e., "organic nonfossil 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)).
[j] Xcel Energy (2003e)
[k] Xcel Energy (2003b)

Table 3b: Total estimated MWe (Minnesota and 12-county region) and energy content of specific ECB fuel (E_{fuel}).

	Sub/bituminous coal [a]	Oil	Natural gas	Wood
Estimated total MWe:				
All Minnesota	5.05E+03	5.50E+02	4.25E+02	5.7E+01
12-counties	1.57E+03	0	2.55E+02	0
E_{fuel} [units]	2.6E+07 [kJ/kg] [b]	4.2E+07 [kJ/L residual oil] [c]	3.8E+07 [kJ/m^3] [d]	1.1E+07 [kJ/kg wood, as fired] [e]

[a] if coal reported as fuel reported as sub/bituminous coal by EPA (1999b) and elsewhere (references in Table 3a).
[b] average of bit- and subbituminous coal (as mined and wet, mineral free) (EPA, 1995, Section 1.1)
[c] assume residual oil (EPA, 1995, Vol I, 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] as the midpoint of given energy range (EPA, 1995, Section 1.6.1)

Table 4: Available EFs from ECBs burning specific fuels (EPA, 1995 or EPA, 1998a).

	Coal [a] [kg PAH / ton coal]	Oil [b] [kg PAH/ L oil]	Natural Gas [c] [kg PAH/10^6 m^3 nat gas]	Wood [d] [kg PAH/ ton wood]
Acenapthene	2.32E-07	2.53E-06	2.94E-05 [e]	1.86E-06
Acenaphthylene	1.14E-07	3.03E-08	2.94E-05 [e]	2.16E-05
Anthracene	9.55E-08	1.46E-07	3.92E-05 [e]	1.50E-06
Benzo(a)anthracene	3.64E-08	4.81E-07	2.94E-05 [e]	1.49E-06
BaP	1.73E-08		1.96E-05 [e]	3.07E-08 [e]
Benzo(b)fluroanthene [f]	1.10E-07		2.94E-05 [e]	
Benzo(k)fluroanthene [g]	1.10E-07		2.94E-05 [e]	3.48E-07 [e]
b(ghi)perylene	1.23E-08	2.71E-07	1.96E-05 [e]	6.41E-07
Chrysene	4.55E-08	2.85E-07	2.94E-05 [e]	1.91E-07
Dibenz(a,h)anthracene		2.00E-07	1.96E-05 [e]	
Fluoranthene	3.23E-07	5.80E-07	4.90E-05	8.32E-06
Fluorene	4.14E-07	5.36E-07	4.57E-05	3.74E-06
Indeno(1,2,3-cd)pyrene	2.77E-08	2.57E-07	2.94E-05 [e]	1.64E-07
Naphthalene	5.91E-06	1.36E-04	9.96E-03	1.54E-03
Phenanthrene	1.23E-06	1.26E-06	2.78E-04	2.36E-05
Pyrene	1.50E-07	5.10E-07	8.17E-05 [e]	7.59E-06

[a] Subbituminous and Bituminous Coal are considered to have one EF. Source AP42 (EPA, 1995), Table 1.1-12.
[b] Oil is assumed to be residual oil, or a mixture of distillate and residual, since, by AP42, Section 1.3 (Fuel Oil Combustion), "…residual oils are used mainly in utility, industrial and large commercial applications."
[c] Natural Gas EF Source is AP 42 (EPA, 1995), Table 1.4-3.
[d] Wood: in AP-42, Section 1.6, "In boilers, wood waste is normally burned in the form of hogged wood, bark, sawdust, shavings, chips, mill rejects, sand or dust, or wood trim."
[e] at the method of detection limit.
[f] only natural gas EF reported for benzo(b)fluoranthene (EPA 1995 and 1998). The B(bjk)fluoranthene EF for sub/bituminous coal was applied (EPA, 1995 and 1998).
[g] only natural gas and wood EFs reported specifically for benzo(k)fluoranthene. The B(bjk)fluoranthene EF for sub/bituminous coal was applied (EPA, 1995 and 1998).

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