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Ultrafine Particulate Matter Emissions Inventory Prepared for the San Francisco Bay Area

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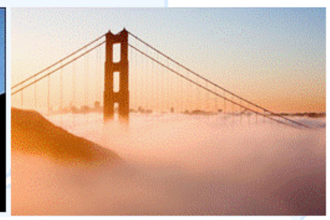

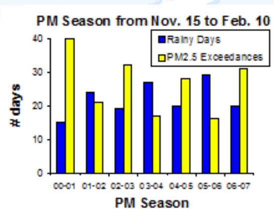

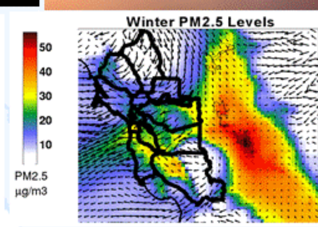

Prepared by:
Saffet Tanrikulu, Research and Modeling Manager, BAAQMD
Cuong Tran, Senior Atmospheric Modeler, BAAQMD

Significant contributors:
Steve Reid, STI

Reviewed and approved by:
Henry Hilken, Director of Planning, Rules and Research Division

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Introduction

Ultrafine particulate matter (UFP) refers to particles with aerodynamic diameter less than 0.1 micrometer or 100 nanometers. It is currently unregulated but has known harmful effects on human health. Because of its potentially significant adverse health impacts, the Bay Area Air Quality Management District (BAAQMD) has been studying UFP, with the goal of better understanding this pollutant and reducing its health impacts in the Bay Area. The key components of this study, previously described in a BAAQMD document (BAAQMD, 2010), include ambient monitoring, data analysis, emissions inventory development, air quality simulation, and estimating exposure and health impacts. In the current report, we document the development of UFP emissions inventories for the San Francisco Bay Area.

1. Background

For criteria pollutants and their precursors, large facilities are required to report their annual emissions. For the remaining sources, these pollutants' emissions are estimated and regularly updated by regulatory agencies. Emissions are typically estimated as a product of emission factors, expressed as mass of pollutant emitted per unit of activity, and some corresponding measure of activity. In some cases, emission factors are unavailable and emissions must be estimated relative to a pollutant for which emissions are known. In this case the relationship between the pollutants must be known. If emission factors are available, the former approach is generally preferred.

UFP emissions will be estimated in this study using a two-prong approach. In the first, emissions are estimated from size fractionation of existing $PM_{2.5}$ emissions using a tool known as mode2sec, which was developed by Atmospheric and Environmental Research Corporation and funded the US EPA (Pun et al., 2005). In the second, UFP emission factors will be obtained for available sources from the scientific literature. Emissions for these sources will then be directly estimated using emission factors. Both approaches are being taken partly because UFP emission factors for some sources are unknown. Another reason for this two-prong approach is so that the two estimates can be compared and reconciled for sources with known emission factors. Results from the first approach are complete and presented in this report while results from the second approach will be completed by March 2013.

The mode2sec software tool was originally intended to prepare PM emissions inputs with multiple sizes for air quality modeling. In particular it was developed to be compatible with a modified version of the US EPA's Community Multiscale Air Quality (CMAQ) model called CMAQ-MADRID. The next section details how mode2sec was used to fractionate $PM_{2.5}$ and PM_{10} to various sizes including UFP.

2. Ultrafine PM Emissions Estimation Using mode2sec

The CMAQ-MADRID model builds on the existing CMAQ model and includes new modules for aerosol processes and gas- and aqueous-phase chemistry. If users provide CMAQ-MADRID with PM emissions that are defined by size section, the model is capable of producing sectional PM concentrations (Electric Power Research Institute, 2002). Previous versions of CMAQ required $PM_{2.5}$ emissions speciated into sulfate (PSO4), nitrate (PNO3), elemental carbon (PEC), organic aerosols (POA), and other fine PM (PMFINE), as well as coarse PM (PMC) calculated as the difference between PM_{10} and $PM_{2.5}$ emissions. The speciation of $PM_{2.5}$ and calculation of PMC is typically handled by the Sparse Matrix Operator Kernel Emissions (SMOKE) model.

However, because CMAQ-MADRID requires speciated and size-specific PM emissions inputs, the typical SMOKE emissions processing stream is incomplete. Therefore, CMAQ-MADRID comes with an emissions preprocessor, mode2sec, that can be used to generate speciated and size-specific PM emission inputs based on $PM_{2.5}$ and PM_{10} emissions (Pun et al., 2005). This preprocessor performs the following steps on gridded, hourly $PM_{2.5}$ and PM_{10} emissions (in netCDF format):

1. Subtracts $PM_{2.5}$ mass from PM_{10} mass to calculate $PM_{10-2.5}$ mass.
2. Splits $PM_{2.5}$ and $PM_{10-2.5}$ emissions into 6 species: SO_4, elemental carbon (EC), organic material (OM), sodium (Na), chlorine (Cl), and crustal material (OI). This speciation is done using the species fractions shown in Table 1, which are based on a 1987 speciated, size-resolved PM emissions inventory for the Los Angeles Air Basin (Jacobson, 1997).
3. Apportions the speciated $PM_{2.5}$ emissions into nuclei (0.1%) and accumulation (99.9%) modes.
4. Converts mass to number concentration for each species.
5. Divides the total PM mass into the 8 size sections defined in Table 2.

By summing mode2sec's outputs for sections 1 and 2 in Table 2, UFP emissions estimates are obtained.

Table 1. Speciation profiles applied to $PM_{2.5}$ and $PM_{10-2.5}$ emissions in CMAQ-MADRID.

Species	$PM_{2.5}$	$PM_{10-2.5}$
Crustal material	0.648	0.812
OM	0.105	0.150
SO4	0.130	0.009
EC	0.082	0.015
Cl	0.034	0.010
Na	0.002	0.004

Table 2. Default PM section definitions in mode2sec.

Section Number	Size range (μm)
1	0.02 -0.05
2	0.05 – 0.10
3	0.10 – 0.22
4	0.22 – 0.46
5	0.46- 1.0
6	1.0 – 2.15
7	2.15 – 4.64
8	4.64 – 10.0

In our study, the default size ranges in Table 2 were modified to include more resolution, particularly for particles below 100 nanometers (0.1 μm). This decision was motivated by more recent research which successfully simulated as many as 24 size bins (Zhang et al., 2010). The number of sections used in our study, however, was selected to ensure optimal model accuracy without incurring excessive computing resources. The corresponding size ranges were selected based on empirical logarithmic distributions of particle sizes. The final number of bins and the associated size cut-offs are shown in Table 3. Under this modified scheme, summing sections 1 through 5 in Table 3 yields estimates of ultrafine PM emissions.

Table 3. Revised PM section definitions, used in BAAQMD preliminary UFP modeling.

Section Number	Size range (μm)
1	0.001 -0.007
2	0.007 – 0.014
3	0.014 – 0.026
4	0.026 – 0.051
5	0.051- 0.10
6	0.10 – 0.185
7	0.185 – 0.341
8	0.341 – 0.63
9	0.63 – 1.164
10	1.164 – 2.15
11	2.15 – 4.637
12	4.637 – 10.0

3.1 Ultrafine PM Speciation Profiles

It should be noted that the default speciation shown in Table 1 is based on an aggregated PM inventory for Los Angeles that dates to 1987. Therefore, this speciation scheme was updated by developing individual speciation profiles for the various source sectors included in the District's 2015 inventory, as described below.

District staff prepared separate files containing PM_{10} and $PM_{2.5}$ emissions data for four individual source sectors: (1) area sources; (2) on-road mobile sources; (3) non-road mobile sources; and (4) point sources. Speciation profiles for each of the four source sectors listed above were developed to update the default speciation in the mode2sec preprocessor.

To accomplish this step, 2015 emissions data for the BAAQMD[1] and PM speciation profiles from the California Air Resources Board (ARB) were used. ARB speciation profiles were assigned to each source category in the 2015 emissions data using ARB's speciation cross-reference file, and then the associated speciation profiles were applied to develop speciated PM inventories.

[1] The 2015 data was obtained from the California Emissions Forecasting System (CEFS): http://www.arb.ca.gov/app/emsinv/fcemssumcat2009.php.

Using these results, weighted average speciation profiles for each source sector for both $PM_{2.5}$ and PM_{10} were generated. The resulting profiles are shown in Tables 4 and 5.

Table 4. $PM_{2.5}$ speciation profiles by source sector.

Species	Area	Non-road	On-road	Point
Crustal material	0.349	0.000	0.000	0.062
OM	0.293	0.561	0.360	0.009
SO4	0.082	0.151	0.321	0.588
EC	0.262	0.272	0.271	0.329
Cl	0.011	0.016	0.048	0.011
Na	0.002	0.000	0.000	0.001

Table 5. PM_{10} speciation profiles by source sector.

Species	Area	Non-road	On-road	Point
Crustal material	0.660	0.000	0.000	0.084
OM	0.165	0.539	0.451	0.007
SO4	0.046	0.169	0.250	0.614
EC	0.118	0.272	0.261	0.285
Cl	0.007	0.020	0.038	0.009
Na	0.004	0.000	0.000	0.001

The speciation profiles in Tables 4 and 5 were incorporated into the mode2sec preprocessor, and the program was then used to process the source sector-specific emissions inventories. Each sector-based netCDF file was processed through mode2sec using the appropriate speciation profiles from Tables 4 and 5. As a result, the original PM species ($PM_{2.5}$ and PM_{10}) in the BAAQMD's emissions files were divided into 72 new species-size bin combinations (i.e., six chemical species time twelve size bins).

3. Summary of Results

Table 6 and Table 7 show the breakdown of 2015 wintertime $PM_{0.1}$ emissions by sub-category for the entire BAAQMD (Table 6) and by county (Table 7). Note that the values shown in these tables are the sum of emissions in sections 1 through 5, as defined in Table 3.

4. Discussion

As shown in the two tables above, 2015 wintertime UFP emissions in the Bay Area total 5.8 tons per day based upon mode2sec. Alameda County has the highest emissions, followed closely by Contra Costa and Santa Clara. Given that mode2sec estimates UFP mainly from $PM_{2.5}$, it is not surprising that the county-to-county variations are similar between the two pollutants. It should be noted that the distribution of UFP by source category is also the same as that of $PM_{2.5}$; therefore, area sources (particularly wood burning) dominate the inventory. Furthermore, categories from which little, if any, UFP are expected are shown to have significant UFP. An example is road dust.

The observations above elucidate an inherent limitation in mode2sec, which is that it is not suitable for use in quantifying emissions from individual source categories. This limitation arises from the fact that $PM_{2.5}$ mass from all sources are split 999 to 1 between accumulation and nuclei modes, respectively. Although this assumption may be applicable to total $PM_{2.5}$ mass, it can mask important differences among emission sources. For instance road dust is handled in the exact manner as onroad vehicle emissions, essentially assigning them the same particle size distribution. Because of this limitation, a complementary approach to estimating UFP emissions is needed.

5. Ongoing and Future Work

BAAQMD staff is in the process of developing an emissions inventory using direct emission factors (see Table 8). Although the resulting inventory is not adequate for use in air quality modeling because it is not chemically speciated and it is not distributed into more resolved size bins required by the air quality model, it can be used to adjust the more resolved mode2sec results discussed above. As noted previously, we plan to complete this work by March, 2013. Since the emission factors in Table 8 do not cover all known sources of ultrafine PM emissions, staff will continue to update these factors as more data become available in the scientific literature.

Table 6. 2015 Bay Area winter $PM_{0.1}$ emissions (tons/day) by sub-category

Sector	Source Category	% of Sector Emissions	$PM_{0.1}$
Nonroad	Aircraft	8%	0.021
	CNG	1%	0.003
	Marine Vessels, Commercial	31%	0.082
	Off-highway Vehicle Diesel	14%	0.036
	Off-highway Vehicle Gasoline	16%	0.041
	Pleasure Craft	26%	0.068
	Railroad Equipment	5%	0.013
Area	Industrial Processes	21%	0.981
	Agriculture Production	11%	0.518
	Other Combustion	8%	0.375
	Paved Roads	20%	0.904
	Unpaved Roads	2%	0.100
	Geogenic	2%	0.085
	Commercial/Institutional	3%	0.135
	Industrial	0%	0.005
	Residential fuel combustion	33%	1.507
	Waste Disposal	0%	0.011
Mobile	Heavy Duty Diesel	29%	0.112
	Heavy Duty Gasoline	1%	0.005
	Light Duty Diesel	1%	0.002
	Light Duty Gasoline	69%	0.266
	Motorcycles (MC)	1%	0.002
Point	External Combustion Boilers	4%	0.020
	Industrial Processes	76%	0.411
	Internal Combustion Engines	20%	0.105
	Waste Disposal	0%	0.002
Total			**5.809**

Table 7. 2015 Bay Area winter $PM_{0.1}$ emissions (tons/day) by sub-category and county

Sector	Source Category	Alameda	Contra Costa	Marin	Napa	San Francisco	San Mateo	Santa Clara	Solano	Sonoma	Total
Nonroad	Aircraft	0.003	0.000	0.000	0.000	0.000	0.003	0.005	0.010	0.000	**0.021**
	CNG	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	**0.003**
	Marine Vessels, Commercial	0.039	0.006	0.003	0.000	0.012	0.020	0.000	0.002	0.000	**0.082**
	Off-highway Vehicle Diesel	0.007	0.005	0.001	0.001	0.005	0.003	0.008	0.003	0.003	**0.036**
	Off-highway Vehicle Gasoline	0.008	0.005	0.002	0.001	0.005	0.008	0.009	0.001	0.002	**0.041**
	Pleasure Craft	0.006	0.011	0.016	0.008	0.007	0.006	0.002	0.008	0.005	**0.068**
	Railroad Equipment	0.003	0.003	0.000	0.001	0.001	0.001	0.003	0.001	0.001	**0.013**
Area	Industrial Processes	0.200	0.116	0.030	0.027	0.157	0.094	0.219	0.067	0.071	**0.981**
	Agriculture Production	0.056	0.044	0.048	0.084	0.019	0.025	0.076	0.017	0.150	**0.518**
	Other Combustion	0.300	0.049	0.002	0.003	0.001	0.005	0.006	0.004	0.005	**0.375**
	Paved Roads	0.200	0.142	0.035	0.023	0.071	0.105	0.228	0.040	0.059	**0.904**
	Unpaved Roads	0.005	0.008	0.009	0.003	0.000	0.013	0.054	0.004	0.004	**0.100**
	Geogenic	0.006	0.009	0.002	0.010	0.000	0.004	0.016	0.026	0.010	**0.085**
	Commercial/Institutional	0.017	0.062	0.002	0.001	0.007	0.011	0.026	0.005	0.003	**0.135**
	Industrial	0.001	0.001	0.000	0.000	0.001	0.001	0.002	0.000	0.000	**0.005**
	Residential fuel combustion	0.202	0.413	0.108	0.058	0.037	0.092	0.316	0.071	0.211	**1.507**

	Waste Disposal (Burning)	0.002	0.002	0.002	0.000	0.001	0.001	0.002	0.002	0.001	**0.011**
Mobile	Heavy Duty Diesel	0.042	0.015	0.003	0.003	0.007	0.007	0.024	0.006	0.005	**0.112**
	Heavy Duty Gasoline	0.001	0.001	0.000	0.000	0.000	0.000	0.001	0.000	0.000	**0.005**
	Light Duty Diesel	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	**0.002**
	Light Duty Gasoline	0.059	0.042	0.009	0.008	0.021	0.030	0.068	0.012	0.018	**0.266**
	Motorcycles (MC)	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	**0.002**
Point	External Combustion Boilers	0.001	0.009	0.000	0.000	0.003	0.000	0.002	0.004	0.000	**0.020**
	Industrial Processes	0.085	0.174	0.008	0.008	0.003	0.030	0.048	0.047	0.008	**0.411**
	Internal Combustion Engines	0.010	0.050	0.000	0.001	0.008	0.001	0.023	0.010	0.001	**0.105**
	Waste Disposal	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	**0.002**
Total		**1.254**	**1.169**	**0.281**	**0.242**	**0.367**	**0.461**	**1.138**	**0.338**	**0.558**	**5.809**

Table 8. UFP emission factors by source category.

Source Category	$PM_{0.1}$ emission factor	Emission factor units	References	Notes
LDGV				
- Low emission vehicles (LEV)	51.2	μg/km	Robert et al., 2007a	Emission rates based on chassis dynamometer tests using the federal test procedure (FTP). Tests were also performed using the unified cycle (UC) and correction cycle (CC) driving cycles.
- Three-way catalyst (TWC)	121.4	μg/km		
- Oxidation catalyst (OC)	2,501.7	μg/km		
- Non-catalyst (NC)	2,115.0	μg/km		
- Smoker	9,564.5	μg/km		
- Light-duty truck/SUV	101.0	μg/km		
HDDV				
- HDDV1	318.3	mg/km	Robert et al., 2007b	Emission rates based on chassis dynamometer tests using ARB's heavy heavy-duty diesel truck (HHDDT) driving cycle.
- HDDV2	28.7	mg/km		
- HDDV3	25.3	mg/km		
- HDDV4	23.7	mg/km		
- HDDV5	57.7	mg/km		
- HDDV6	72.1	mg/km		
Biomass burning				
- Pine	0.58	g/kg	Kleeman et al., 2008	Wood samples collected at Cal Tech between 1995 and 1997; rice straw samples collected at EPA's National Risk Management Research Laboratory in 2002.
- California oak	0.38	g/kg		
- East coast oak	0.34	g/kg		
- Eucalyptus	0.59	g/kg		
- Rice straw	0.09	g/kg		

Cigarettes	0.07	mg/cigarette	Kleeman et al., 2008	Samples collected at Cal Tech between 1995 and 1997.
Meat charbroiling	0.18	g/kg	Kleeman et al., 2008	Samples collected at Cal Tech between 1995 and 1997.
Industrial boiler (oil fired)	6.1	μg/kJ	Hildemann et al., 1991	Emission rate based on mass distribution of aerosol emissions from a midsize industrial boiler burning no. 2 fuel oil.

References

Bay Area Air Quality Management District (2010) Ultrafine Particulate Matter Study in the San Francisco Bay Area. Part I: Study Plan, August.

Cass G.R., Hughes L.A., Bhave P., Kleeman M.J., Allen J.O., and Salmon L.G. (2000) The chemical composition of atmospheric ultrafine particles. *Philosophical Transactions of the Royal Society of London Series a-Mathematical Physical and Engineering Sciences* **358** (1775), 2581-2592.

Electric Power Research Institute (2002) Technical documentation for the Community Multiscale Air Quality Model of Aerosol Dynamics, Reaction, Ionization, and Dissolution (CMAQ-MADRID), November.

Hildemann L.M., Markowski G.R., Jones M.C., and Cass G.R. (1991) Submicrometer aerosol mass distribution of emissions from boilers, fireplaces, automobiles, diesel trucks, and meat-cooking operations. *Aerosol Sci. Technol.* **14**, 138-152.

Jacobson M.Z. (1997) Development and application of a new air pollution modeling system - II. Aerosol model structure and design. *Atmos. Environ.* **31**, 131-144.

Kleeman M.J., Robert M.A., Riddle S.G., Jakober C.A., and Hannigan M. (2007) Source Apportionment of Fine and Ultrafine Particles in California. Prepared for the California Air Resources Board, August.

Kleeman M.J., Robert M.A., Riddle S.G., Fine P.M., Hays M.D., Schauer J.J., and Hannigan M.P. (2008) Size distribution of trace organic species emitted from biomass combustion and meat charbroiling. *Atmos. Environ.* **42**, 3059-2075.

Pun B., Karamchandani P., Vijayaraghavan K., Chen, S., and Seigneur C. (2005) Models-3/Community Multiscale Air Quality Model (CMAQ) User's Guide to Alternative Modules: Model of Aerosol Dynamics, Reaction, Ionization, and Dissolution (MADRID), Mercury (Hg), and Advanced Plume Treatment (APT). Prepared by Atmospheric & Environmental Research, Inc. for the Electric Power Research Institute, January.

Robert M.A., VanBergen, S., Kleeman M.J., Jakober C.A. (2007a) Size and composition distributions of particulate matter emissions: Part 1 – light-duty gasoline vehicles. *J. Air Waste Manage. Assoc.* **57**, 1414-1428.

Robert M.A., Kleeman M.J., Jakober C.A. (2007b) Size and composition distributions of particulate matter emissions: Part 2 – heavy-duty diesel vehicles. *J. Air Waste Manage. Assoc.* **57**, 1429-1438.

Zhang Y., Liu P., Liu X., Pun B., Seigneur C., Jacobson M.Z., Wang W. (2010) Fine scale modeling of wintertime aerosol mass, number, and size distributions in central California. *J. Geophysical Research* **115,** D15207, doi:10.1029/2009JD012950.