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Emission Characterization and Emission Inventories for the 21st Century

The anticipated needs of the air quality management community and the associated air quality modeling tools will require greater resolution of emissions on various temporal and spatial scales as well as on the physical and chemical properties of the emission species.^{1,2} Thus, we look to utilize state-of-the-art source monitoring techniques to improve the characterization of emissions.

These enhanced emission data can be used in air quality models to develop cost-effective air quality management processes to address the air quality issues of the 21st Century. More accurate emissions will improve the credibility of air quality model predictions. Adding the improvement of the emissions (spatial) variation across the grid model domain will further improve the credibility of the model-predicted exposure location to reactive pollutant concentrations. Finally, the temporal variation in the release of emissions also improves model prediction confidence due to the attempt to better match photochemical precursor emissions with the diurnal variation in solar strength. Hence, we address not only the improvement in emissions accuracy in general, but improvement of the spatial and temporal characterization.

Figure 1 illustrates the distribution of important emissions species across the major source categories for criteria air pollutants, and mercury, considered a hazardous air pollutant. The uncertainty in the emission estimates varies by source category, but all need improvement. We are most concerned about the uncertainties in the emission inventory which could affect the decisions about control strategies or policies. Therefore, we have focused on the measurement technologies which could improve characterization of electricity generating units, mobile sources, industrial sources, and natural sources.³



Major Constituents (2007), thousands of short tons

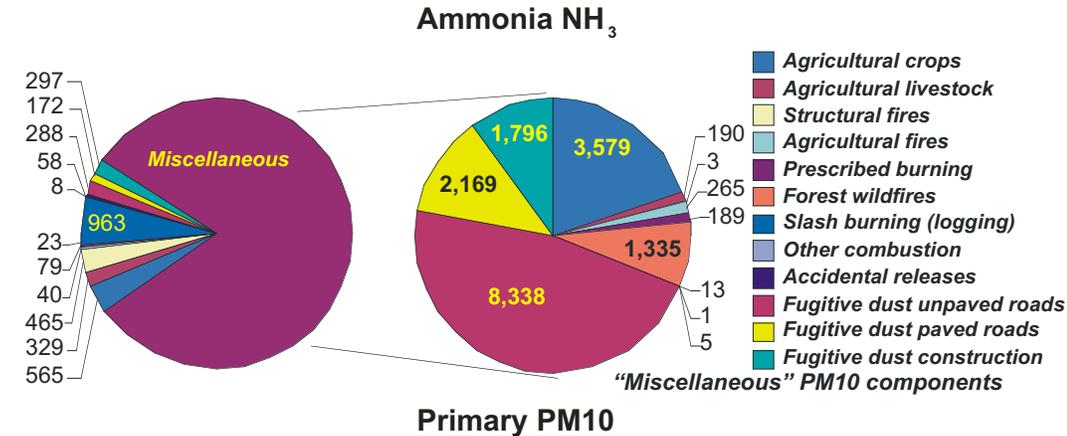
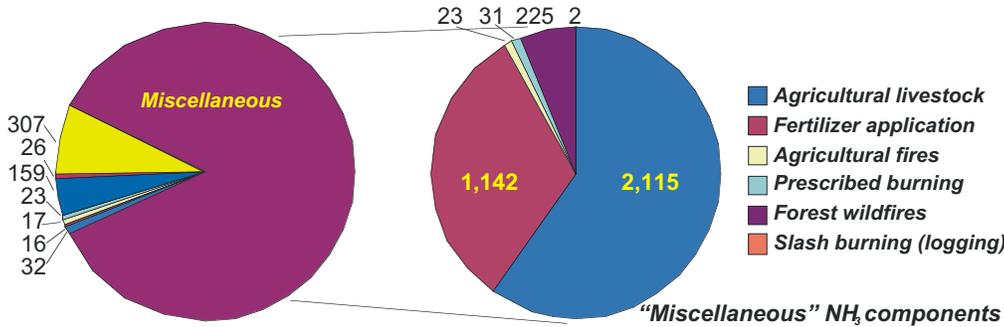
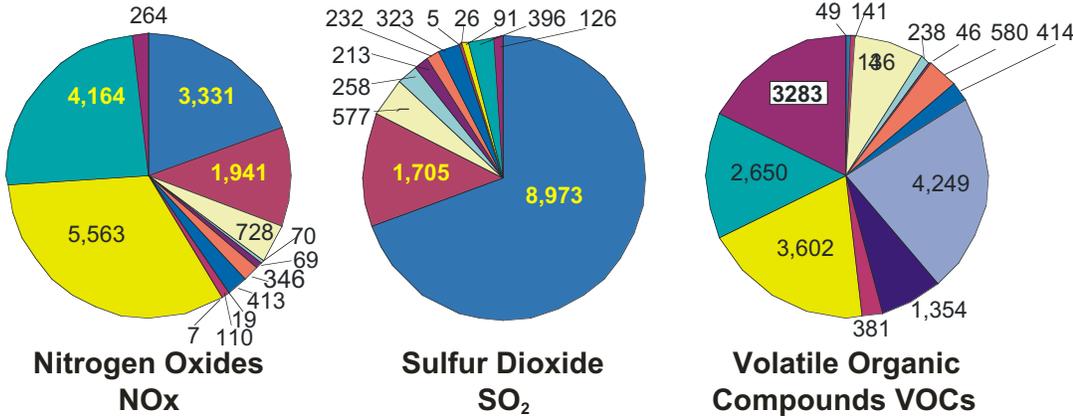
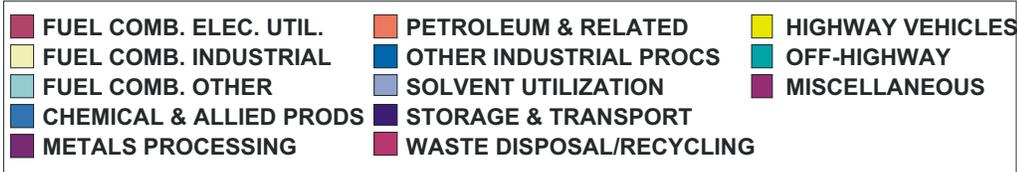


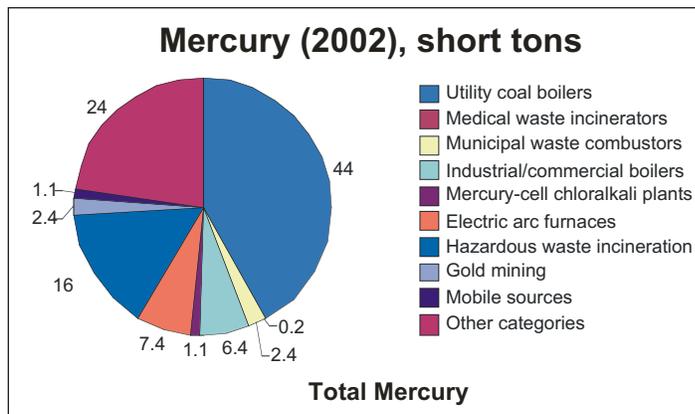
Figure 1. Major constituents (2007). United States national emissions inventories for point and area sources of oxides of nitrogen (NO_x), sulfur dioxide (SO₂), volatile organic compounds (VOCs), ammonia (NH₃), and particulate matter with effective aerodynamic diameter less than 10 micrometers (PM₁₀). Units: thousands of standard tons per year. Color legend at top of figure refers to primary segments of each emitted component, shown in the top row and the left chart in the second and third rows. The right chart in the second and third rows are the expanded "Miscellaneous" sectors for ammonia and PM₁₀ respectively, and their associated legends. All figures and legends are from Reference 4 EPA 2009a National Emissions Inventory Air Pollutant Emissions Trends Data. Top row charts are for datum year 2008, main charts in second and third rows for 2007, and miscellaneous charts for 2002.

Electricity Generating Units

The major importance of this sector to air quality management activities has resulted in emissions from electricity generating units generally being the best characterized source category. Continuous oxides of sulfur and nitrogen (SO_x, NO_x), and carbon

monoxide (CO) emission source monitoring data are available on an hourly basis with latitude and longitude locations, along with stack height and plume rise information. There are accuracy and precision indicators for the monitoring instruments as well. Characterization of these pollutants from

Figure 2. Mercury emissions, 2005. United States national emissions inventory for point and area sources of total mercury (sum of divalent, elemental, and particulate-bound mercury estimates). Units: standard tons per year. Source: Reference 5. EPA 2009b. 2005 National Emissions Inventory Data and Documentation.



sources requires customizing many different model inputs to reflect local conditions. The models estimate emissions which are then spatially and temporally apportioned for grid-based air quality modeling according to activity using a surrogate such as population or roadway surveillance data. Better apportionment can be achieved using a local travel demand model and truck model applications. These provide

electric generating units sets the current standard for pollutant characterization for other source categories.

speeds, volume, activity and location according to roadway and time.

Testing and development of continuous monitors for particulate matter emissions from electric generating units is also underway. In addition, mercury monitors have been introduced to U.S. coal-fired power plants. As of May 2009, approximately 800 purchases of atomic fluorescence (dry) or sorbent trap (wet) monitors have occurred, and approximately one-fourth of these are believed to be installed, calibrated, and operating in stack flue gas environments. Additional deployment of these measurement technologies will further improve the characterization of electricity generating units.

Mobile Sources

The mobile source emissions inventory is comprised of on-road vehicles that range from motorcycles to eighteen-wheel tractor-trailers and non-road equipment as well as vehicles that range from lawnmowers to commercial jet aircraft.

Currently, on- and off-road mobile source emissions are predicted using models developed from emissions testing and other data. The accuracy of the predictions is dependent on the testing data accuracy and the subsequent parameterization to reflect real world conditions. New modeling methods for on-road vehicles are promising because they depict emissions as a function of “driving mode” and are based on data measured on-the-road by portable emissions measurement systems rather than emissions depicted according to the driving cycle followed by a vehicle driven on a laboratory dynamometer.

Inventory development for on- and off-road mobile

The apportionment of emissions can be validated using the results of corroborative data or analyses. These can derive from independently performed studies such as emissions testing, and “top-down” methods such as receptor modeling, grid model source attribution applications, tunnel studies, or inventory versus ambient measurement comparisons.

Ambient profiles of volatile organic compounds (VOC) and PM species may be used in top-down analyses to validate the inventory, but accurate on- and off-road VOC and PM speciation profiles from testing must be also be available. Hence, there is a future measurement need to enable correlation of measured ambient particle-size *and* particle- and gas-phase speciation with corresponding fast response measurements at the tailpipe. More measurements are needed in the ambient and in-use vehicle testing. More development of mobile source activity data is also critical on two levels—to best represent emissions, and to best represent the emissions through temporal and spatial allocation.

Future technology measurement methods are not the remedy to emissions inventory reconciliation, however. The concern remains of testing the correct combination of vehicles to represent the inventory average. This concern is well-founded as some on-road vehicles are not accurately represented in the inventory because the vehicles are poorly maintained and are non-complying (i.e. the 10 percent of the on-road fleet that is responsible for over 50 percent of the on-road emissions.)⁶ These “high emitters” are difficult to find and subsequent

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voluntary access to the vehicle for testing is usually denied. Therefore, portable Remote Sensing Detector (RSD) technology is used to characterize the high emitters in the inventory.⁷ Continued RSD program use can improve the spatial and temporal distribution of high emitter emissions in the emissions inventory. Nonetheless, utilization of state-of-the-art and innovative measurement techniques could significantly improve the basis for emission models for mobile sources.

Industrial Sources

Improving the characterization of the emissions from the industrial sector requires improving temporal, spatial, and species resolution. The technology to accomplish this mission is generally available, but collection and quality assurance of the necessary activity and emission data can be very expensive. This dilemma is illustrated by focusing on the petrochemical industry which is one of the most difficult sectors to quantify accurately because the emissions are from various processes. The emission sources are not only conventional stacks but also

tanks, cooling towers, wastewater treatment systems, flares, valves, and flanges from which fugitive emissions originate. These emissions occur under normal operating conditions as well as during startup, shut-down, and malfunction situations. Emissions from some of these sources may not be correctly characterized in the current emissions inventories. For example, one study estimated that the ethene emissions from petrochemical plants in Houston in 2006 were lower than estimates derived through field measurements by a factor of ten.⁸

Efforts to improve emissions characterization should be matched to the nature of the suspected cause of the emissions inventory discrepancy—requiring some insight. The cause of discrepancies may fall into one or more of the following general categories: unknown and unaccounted sources; known but previously unaccounted sources; known but under-accounted sources; or uncertainties with respect to speciation.

Developing insights into these issues might be

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achieved using improved and innovative monitoring techniques, such as the infrared camera, ultraviolet differential optical absorption spectroscopy, fourier transform infrared, light detection and ranging and solar occultation flux technologies. However, such techniques are costly and will only be helpful in better characterizing emissions if they are used in studies that are designed to match the nature of the suspected cause of the emissions inventory discrepancy and the operating and physical configuration of the emissions source. In addition, the necessary activity data as well as emission characterization information will be required at the appropriate temporal and spatial resolution to satisfy the requirements of future air quality modeling and assessment activities.

Natural Sources

Important natural and quasi-natural sources include: VOCs from vegetation; PM and its precursors from wildland fires; nitric oxide (NO) from lightning; mechanically-disturbed and wind-blown geogenic dust from agriculture, construction, and mobile sources; and ammonia from agricultural-related activities. With emissions varying from widespread to highly localized spatial scales, and with the temporal scale similarly ranging from sporadic to highly regular, traditional monitoring methods are challenged to provide quantitative information on the spatial and temporal variability of these sources. Two non-traditional monitoring methods for improving estimates include satellite imagery and micrometeorological flux measurements.

Data from satellites are beginning to be used to build emission inventories as well as to constrain and evaluate emission inventories from a top-down perspective. Vertical atmospheric columns of chemical composition are being derived from satellite data for compounds such as formaldehyde, carbon and nitrogen dioxide (CO₂, NO₂). Formaldehyde has proven an especially useful surrogate for constraining the isoprene emissions inventory which is overwhelmingly dominated by vegetation. The temporal variability of satellite-derived NO₂ columns has been analyzed to study the effectiveness of the NO_x SIP call in reducing emissions from combustion sources in the U.S. and in

detecting natural sources of NO from soils and lightning.⁹

Challenges of inventorying fire emissions include identifying and acquiring dispersed sources of fire activity data, using evolving models that characterize fuel loading, relying on uncertain emission factors, and relying on uncertain methods to represent fire emission sources. Satellite imagery can and is assisting in this effort by providing information on burn signatures, fire intensity, and plume heights. For example, the recently launched CALIPSO platform (www.calipso.larc.nasa.gov) is beginning to yield three-dimensional images of smoke plumes and early results suggest that these data may improve estimates of tropospheric injection heights for large wildfires.

Assessment of actual contributions of smoke emissions from various biomass burning management practices to PM and ozone levels, visibility, and reactive nitrogen (deposition) mass, retrospectively can only be done by developing receptor/hybrid models for an integrated assessment. This is because the knowledge of emitted gas and particle species and aerosol chemistry formation processes required to successfully exercise deterministic models for the apportionment of organic aerosols or other chemical species is not currently available and will not be in the foreseeable future (10-year time frame).

Development of a receptor/ hybrid model will require a number of field programs to measure the appropriate tracer species and chemical and physical characteristics of both primary and secondary aerosols and gases as a function of fire and fuel type. The technology to cost-effectively and quantitatively measure many of these species has already been developed. The receptor/hybrid modeling approach must be further developed to combine these measurements with conservative and/or chemical dispersion model predictions. The goals of this analysis are to: 1) separate biomass-burning-related carbonaceous material and gases from all other sources; 2) apportion the biomass-burning-related aerosols retrospectively to various fire classification types such as wildland, prescribed,

agricultural, and residential smoke emissions; and 3) estimate ranges of air quality impacts of various source types at five- and ten-year future time scales.

About 85 percent of ammonia emissions come from agricultural-related activities. In critical reviews of emissions from animal feeding operations, EPA and the National Academy of Sciences have recommended that additional measurements be collected to support process-based and mass-balance models to estimate emissions. The spatially- dispersed and temporally-variant nature of these emissions will require the exploration of non-traditional techniques like long path laser monitoring.

Micrometeorological flux measurements, which combine measurements of atmospheric turbulence and gas/aerosol concentrations, can be used to capture the source and sink terms and to help in building and/or evaluating process-based algorithms for estimating emission rates. Compounds particularly amenable to flux measurements include mercury, ammonia, and biogenic VOCs.

Critical Issues: Inventory Projections and Uncertainty Quantification

Current emissions inventories often serve as the basis to project future inventories using population and economic growth indicators. Uncertainties in these projections are exacerbated when technology and fuel use changes are projected forward in time. For mobile sources, economic and urban growth model results affect vehicle fleet activity and emissions projections. Therefore, economic growth models also require the highest scrutiny possible. Additional

focus is needed in the future to ensure that emissions projections are based on the appropriate data to ensure that the best representation of spatial, temporal, and species allocation is achieved.

Uncertainty indicators of emission estimates are needed to prioritize the application of limited resources for improving emission characterization. In addition, uncertainty indicators are needed to provide confidence in decisions about control strategies and policies. Improving the current situation for characterizing the uncertainty of emission estimates will be a particular challenge since accurately quantifying the uncertainty may require substantial additional resources and methods development.¹

Summary

To meet the expectations of users of emission inventories in the 21st Century, the emissions community will need greater temporal, spatial, and species resolution of emissions from all source categories than have been measured in the past. The community can only achieve this by utilizing the currently available technologies as well as developing more cost-effective emission monitoring techniques to enhance the characterization of emissions from all source categories. This will require development and utilization of innovative techniques to characterize emissions. Characterization of the uncertainty in emission estimates will also present significant challenges and these efforts will require investments from all entities—government, industry, academia, and the public. **em**

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