# Grand Rapids, Wisconsin
# Wood Smoke Monitoring Case-Study

## Work Plan

Principle Investigator:
David C. Snyder, Ph.D.
Assistant Professor
Department of Chemistry
University of Wisconsin-Stevens Point
dasnyder@uwsp.edu

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The University of Wisconsin-Stevens Point

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# 3 Introduction

Epidemiological evidence has clearly demonstrated a relationship between exposure to particulate air pollution and adverse human health consequences, particularly in individuals who have underdeveloped, weakened, or otherwise compromised lung function or immune systems[1-3]. Acute exposure to high levels of particulate matter (PM) has been shown to increase the prevalence of hospital admissions, morbidity, and mortality due to cardiovascular disease[4-6]. Recent research into the causal relationships between exposures to particulate air pollution and adverse health impacts has suggested that inhalation of fine particles can trigger an inflammatory response that may be exacerbated by the presence of heavy metals and oxygenated organic compounds contained in these particles[7-9].

Biomass burning can be an important contributor to fine particulate concentrations (PM2.5) at local, regional, and global scales and can be a significant source of organic compounds. The Urban Organics Study, conducted in 2004 – 2005, concluded that biomass burning contributed as much as 15 to 25 percent of the organic carbon (OC) observed at five sites in the Upper Midwest (see http://www.ladco.org/reports/rpo/monitoring/urban_organics_study_integration_final_report_sti_uw.pdf for details). A more recent study documented both the spatial and temporal distribution of organic carbon attributable to biomass burning. The Upper Midwest Biomass Burning Impact Study ascertained that the contribution of biomass smoke to organic carbon observed across rural and urban sites was between 7 and 12 percent during the summer months and between 16 and 28 percent at these same sites during the winter heating season (see http://www.ladco.org/reports/rpo/monitoring/final_biomass_burning_study.pdf for details). The findings of this study suggest that residential wood burning is an important contributor to local scale PM2.5 and fine particulate organic carbon concentrations observed during winter months in the Midwestern United States. In addition to being an important contributor to organic carbon concentrations, biomass burning can be a significant source of water-soluble, oxygenated organic compounds[10,11] and polynuclear aromatic compounds (PAHs) that may contribute to the adverse health consequences associated with exposure to particulate air pollution[12].

Emissions from residential wood burning in suburban and rural areas have not been extensively studied. However, due to the highly localized nature of such emissions, wood smoke from fireplaces and outdoor wood-fired boilers (OWBs) may represent one of the most significant sources of acute exposure to fine particulate matter in rural areas during the winter months, and information regarding the impact that these sources have on air quality and human health is of interest to suburban and rural communities.

The primary goals of this project are to determine the impact of wood smoke emissions on air quality in the town of Grand Rapids, WI. The study is being conducted with the consent and cooperation of the Grand Rapids Town Board. Key questions to be answered by the project are:

1. What are the wintertime concentrations of fine particulate matter (PM2.5) in the Grand Rapids area, and how do PM2.5 concentrations vary spatially and temporally?

2. What are the important sources of PM2.5 observed during periods of high fine particulate concentrations, and what is the impact of wood smoke on PM2.5 levels observed during these episodes?

These questions will be answered by the following measurement and analysis objectives:

- Collect real-time measurements of PM2.5 mass at three sites in the Town of Grand Rapids, WI during a 90-day period from December 2011 to February 2012 in order to identify pollution episodes and assess general air quality

- Collect daily particulate samples at one more monitoring locations during the study period.

- Analyze selected samples for wood smoke markers and other source markers to ascertain the impact of wood smoke on air quality.

- Collect high time-resolved meteorological measurements (wind speed/direction) in order discriminate between local point sources of wood smoke and regional wood smoke impacts

The results of this work will be used to determine what actions could be taken to improve air quality during the primary heating season in Grand Rapids, WI.

# 4 Technical Approach

The project will consist of the collection of daily fine particulate matter (PM2.5) samples and real-time air quality and meteorological data at three fixed monitoring sites in the town of Grand Rapids, WI over a contiguous period of approximately 90 days. In addition to the fixed sites, a mobile monitoring regime will be established to collect real-time PM2.5 mass data during selected periods in locations throughout the Grand Rapids area. Chemical analysis of PM2.5 samples will follow sample collection and will include mass, elemental carbon and organic carbon (ECOC), sulfate, nitrate, water-soluble organic carbon (WSOC), and levoglucosan, an organic molecular marker for biomass smoke, and a suite of organic molecular markers (a full list of markers and their sources is given in Section 6 of this document). Real-time nephelometric (light-scattering) measurements of PM2.5 mass will be collected at all three fixed sites, and light-

absorption measurements of PM2.5 Black Carbon (BC) will be obtained at the designated primary monitoring site.

## 4.1 Work Plan and Quality Assurance Project Plan

This work plan was prepared in accordance with the requirements of the Lake Michigan Air Director's Consortium (LADCO) and the United States Environmental Protections Agency (USEPA). The QAPP was prepared as a separate document by the project team.

## 4.2 Objectives and Measurements

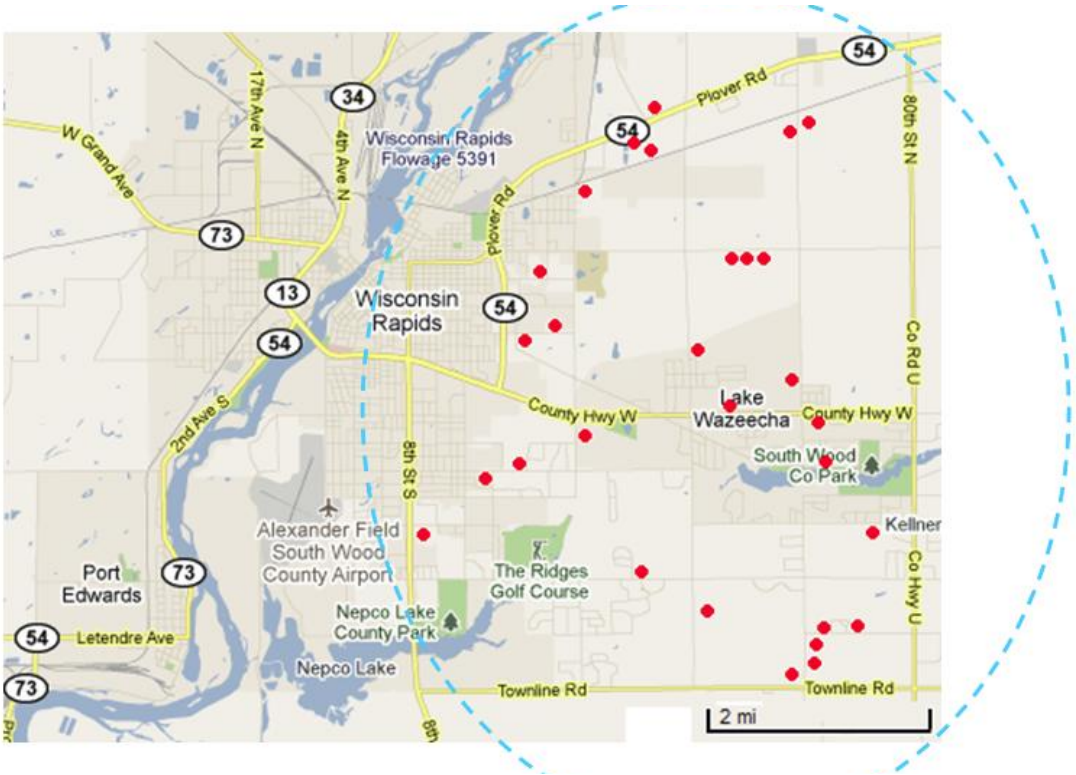
The primary objective of this work is to generate a database of chemical and meteorological data that can be used to quantify the impact of biomass smoke on local air quality in Grand Rapids, WI. Specifically, the study will focus on generating quantitative information concerning the impact of residential outdoor wood-fired boilers (OWBs), and other biomass smoke sources, on the levels of fine particulate matter (PM2.5) observed during the primary heating season in Grand Rapids. A second objective of the study is to generate quantitative information on the spatial and temporal concentrations of PM2.5 in Grand Rapids, WI and to identify the most significant sources of PM2.5 observed during elevated pollution episodes, with the understanding that this information would be used in a non-regulatory manner to suggest actions that could be taken to mitigate such episodes. The final objective of this work is to provide undergraduate students attending the University of Wisconsin-Stevens Point with opportunities to participate in scientific inquiry and to communicate and disseminate scientific findings to both the general public and the scientific community.

## 4.3 Sample Collection and Measurements

### 4.3.1 Fixed-Site Monitoring and Sample Collection

Daily PM2.5 samples and real-time PM2.5 data will be collected at a primary fixed site (designated as site "A"), and real-time data will be collected at two, secondary sites (designated as sites "B" and "C"). A summary of the proposed deployment of instruments and samplers is provided in Table 1a. Maps of the fixed sites and mobile monitoring routes are shown on the following pages.

**Figure 1:** Town of Grand Rapids, WI – Known OWB units




* The dashed blue line roughly denotes the Town of Grand Rapids.

**Figure 2**: Locations of Fixed Monitoring Sites

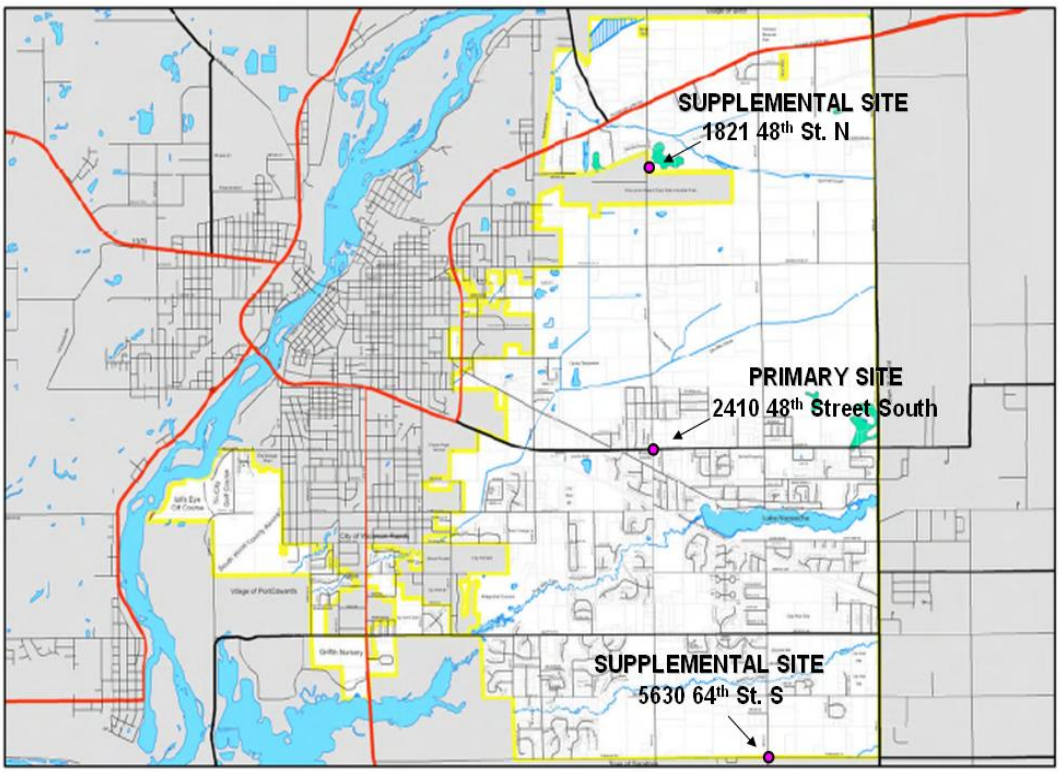


Table 1a: Summary of Instrument and Sampler Deployment

| Instrument/Sampler | Primary Site "A" | Secondary Site "B" | Secondary Site "C" |
|---|---|---|---|
| | *Measurement Frequency* | | |
| DataRAM DR4 | Continuous | Continuous | Continuous |
| Wood Smoke Kit | Continuous | Continuous | Continuous |
| FRM Sampler | Daily | - | - |
| Speciation Sampler | Daily | - | - |
| Med. Vol. Samplers | Daily | - | - |
| Beta Atten. Monitor | Continuous | - | - |
| Aethalometer | Continuous | - | - |
| Meteorological Station | Continuous | Continuous | Continuous |

Table 1b: Summary of Measurements

| Measurement | Analytical Method | Primary Site "A" | Secondary Site "B" | Secondary Site "C" |
|---|---|---|---|---|
| | | *Measurement Frequency* | | |
| PM2.5 Mass | Light Scattering | Continuous | Continuous | Continuous |
| PM2.5 Mass | Beta Attenuation | Continuous | - | - |
| PM2.5 Mass | Gravimetric | Daily | - | - |
| PM2.5 BC | Light Absorption | Continuous | - | - |
| Wind Speed/Direction | Sonic Anemometer | Continuous | Continuous | Continuous |
| PM2.5 WSOC | TOC by adaption of Standard Method 5310C | Daily | - | - |
| PM2.5 ECOC | Laboratory Based NIOSH method 5040 | Event Based | - | - |
| PM2.5 Sulfate/Nitrate | Ion Chromatography | Event Based | - | - |
| PM2.5 Levoglucosan | Solvent Extraction GCMS | Event Based | - | - |
| PM2.5 Organic Molecular Markers | Solvent Extraction GCMS | Event Based | - | - |

### 4.3.2 Mobile Monitoring

The objectives of the proposed mobile monitoring effort are to enhance the spatial resolution of air quality data collected during the study and to provide a means to more fully investigate the impact of localized wood smoke on air quality during high particle pollution events. Mobile monitoring will be conducted using a vehicle equipped with a Thermo Scientific pDR-1500 personal DataRAM, a PM2.5 size-selective inlet, a data-logging GPS receiver, and a laptop computer. The pDR-1500, which is identical to the instruments that will be deployed at the three fixed sites, will be used to measure fine particle (PM2.5) concentrations during mobile operations.

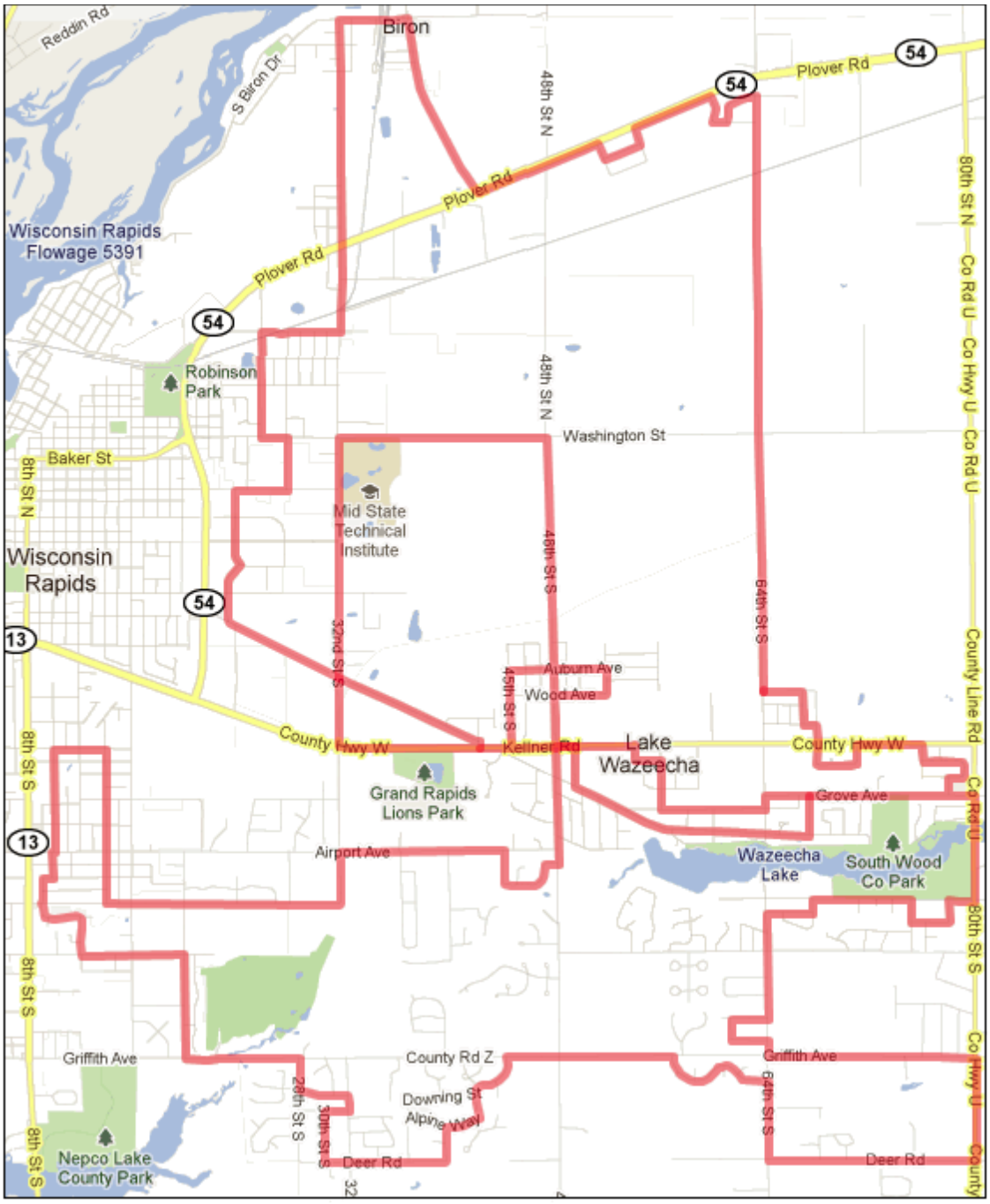
Spatially resolved PM2.5 measurements will be collected during evening hours across a pre-determined set of routes through and around the Town of Grand Rapids, and monitoring periods will include both week-days and week-ends. Routes will include residential areas south of Kellner Rd./ Highway W where the highest concentration of OWBs have been noted but will also include agricultural areas to the north and east of the principle study site located at 2410 48$^{th}$ Street South.

The UWSP team will also be prepared to deploy the mobile monitoring vehicle in response to any high particle pollution events observed during the study. Real-time PM2.5 BC concentrations will be used to identify any prolonged periods of haze or wood smoke that might merit further investigation. Mobile operations will take place from January 2$^{nd}$ – 20$^{th}$, 2012; however, the UWSP team will be prepared to deploy in response to high particle events at any time during the study period (Dec. 2011 – February 2012). Eight to ten evenings are proposed, each consisting of 3 – 4 hours of monitoring (e.g. 8 PM – 12 AM). Monitoring will coincide with scheduled fixed site visits (initially planned for M, W, F, and Sa/Su), the scheduling of which may depend on weather and road conditions.

Each mobile monitoring period will begin and end at the primary study site (2410 48$^{th}$ Street South), and the mobile pDR-1500 will collect data at the primary site for a minimum of 20 minutes before the start of operations in order to provide inter-comparison data with the fixed-site pDR-1500. UWSP will also conduct some limited mobile monitoring prior to the start of the mobile monitoring period in order to collect comparison data during low wood smoke periods and to develop its mobile monitoring capabilities.

The attached driving route was shared with (and approved by) the Grand Rapids Town Board.

**Figure 3:** Mobile Monitoring Routes



## 4.4 Project Personnel

The objectives and tasks outlined in this proposal will be accomplished under the direction of Dr. David Snyder, who currently serves as an Assistant Professor in the Department of Chemistry at the University of Wisconsin-Stevens Point. Operation and maintenance of fixed monitoring sites, collection of samples and data, and mobile monitoring operations will be accomplished by undergraduate students from the University of Wisconsin-Stevens Point under the direct supervision of Professor Snyder. Students will be trained in all aspects of instrument and sampler operations including instrument calibration, sample handling and storage, sampler operation and programming, data storage, and quality control and quality assurance (QA/QC) procedures specific to the project. Specific QA/QC procedures will be outlined in the QAPP.

## 4.5 Real-Time and Integrated Filter-Based Measurements.

Real-time data will be collected continuously throughout the monitoring period at all three study sites as outlined in Table 1a. 24-hr filter-based samples will be collected daily at the primary monitoring site. Two (2) filters will be collected each day at the primary site – one (1) quartz fiber filter for use in levoglucosan and ECOC measurements and one (1) Teflon filter for use in PM2.5 mass and WSOC measurements.

### 4.5.1 24-hr Averaged PM2.5 Mass

Daily measurements of PM2.5 mass will be made by collecting fine particulate matter onto pre-weighed, 47 mm Teflon filters using a R&P Model 2025 Sequential Sampler (i.e. FRM sampler). Sample filters will subsequently be weighed in order to provide a measurement of 24-hr averaged PM2.5 mass. Samples will be handled and analyzed in accordance with the Federal Reference Method for PM2.5.

24-hr averaged mass measurements will provide additional QA/QC checks on real-time mass measurements made at the primary monitoring site and can be used to identify candidate samples for more detailed chemical analysis.

### 4.5.2 24-hr Averaged PM2.5 Water-Soluble Organic Carbon (WSOC)

Teflon filters collected via the FRM sampler will be leached in Milli-Q water and analyzed for water-soluble organic carbon using Standard Method 5310C. 24-hr averaged concentration of WSOC will be obtained for each day during the project and will be used to provide a measure of the daily variability of biomass smoke during the stud. WSOC concentrations will be compared to organic carbon (OC) attributed to biomass smoke by

the organic molecular marker levoglucosan in order to ascertain if WSOC is an effective tracer for biomass smoke at the primary Grand Rapids Monitoring site.

### 4.5.3 24-hr Averaged PM2.5 Levoglucosan

Selected PM2.5 samples collected on 90 mm quartz-fiber filters using a URG 3000B medium volume sampler will be analyzed for levoglucosan via solvent extraction gas-chromatography/mass spectroscopy (GCMS). Levoglusan measurements will provide a positive indicator of the presence of biomass smoke and can be used to estimate the contribution of biomass smoke to organic matter contained in PM2.5.

Selection of samples for levoglucosan will be made in consultation with LADCO. The current budget provides for up to 30 samples to be analyzed.

### 4.5.4 24-hr Average PM2.5 Organic Molecular Markers (OMM)

Selected PM2.5 samples collected on 90 mm quartz-fiber filters using a URG 3000B medium volume sampler will be analyzed for organic molecular markers via solvent extraction gas-chromatography/mass spectroscopy (GCMS). OMM measurements will be used to model the sources of organic carbon in fine particulate matter via a chemical mass balance model (CMB). The CMB model will be used to determine the relative contribution of biomass smoke to organic matter contained in PM2.5.

Selection of samples for OMM will be made in consultation with LADCO. The current budget allows for up to 7 samples to be analyzed.

### 4.5.5 24-hr Averaged PM2.5 Elemental Carbon and Organic Carbon (ECOC)

Selected PM2.5 samples collected on 90 mm quartz-fiber filters using a URG 3000B medium volume sampler will subsequently be analyzed for ECOC via a laboratory-based NIOSH method 5040.

ECOC measurements will be made on samples that have been analyzed for levoglucosan or OMM in order to provide a basis for determining the contribution of biomass smoke to organic carbon.

### 4.5.6 24-hr Averaged PM2.5 Sulfate and Nitrate

Selected PM2.5 samples collected on 47 mm nylon filters using a Met-One Super Sequential Aerosol Speciation Sampler (S/SASS) will be analyzed for sulfate and nitrate

by ion chromatography. Samples analyzed will coincide with those analyzed for levoglucosan and organic molecular markers, and together with the CMB model, will be used to in a mass-closure model as a basis for estimating the overall contribution of wood smoke to PM2.5 mass. The current budget allows for up to 36 samples to be analyzed.

### 4.5.7 Real-Time PM2.5 Mass (DataRAM)

Continuous measurements of PM2.5 mass will be provided at all three monitoring sites by a DataRAM DR-4000 nephelometer (Thermo Anderson, Smyrna, GA). The DataRAMs will be used to provide high time-resolved mass measurements that may be used to identify plume impacts.

Note: the DataRAM can be configured to collect particulate samples for laboratory analysis.

### 4.5.8 Real-Time PM2.5 Mass (Beta-Attenuation Monitor)

Additional real-time measurements of PM2.5 mass will be obtained at the primary monitoring site using a portable beta-attenuation monitor (E-BAM, Met One Instrumets, Grants Pass, OR). The E-BAM will also provide wind speed and direction data.

The use of the E-BAM at the primary site will provide redundancy in case the primary PM2.5 monitor (DataRAM or portable nephelometer contained in the NESCAUM wood smoke kit) should fail. Additionally, the E-BAM data will be used for QA/QC purposes at the primary site.

### 4.5.9 Real-Time PM2.5 Black Carbon (BC)

Real-time measurements of PM2.5 black carbon (BC) will be made at the primary monitoring site using a two-channel Aethalometer (Model AE22, Magee Scientific, Berkeley, CA). A comparison of the data reported by the two channels of the Aethalometer (light attenuation measured at 880 nm and 370nm) will be used to identify plume impacts from sources of biomass smoke.

### 4.5.10 NESCAUM Wood Smoke Kit

Additional real-time PM2.5 mass data and wind speed/direction data will be provided at the primary site and the supplemental sites by a wood smoke monitoring kit developed by NESCAUM. The version of the kit to be utilized for this study will consist of a portable nephelometer (pDR1500 PM monitor, Thermo Anderson, Smyrna, GA) and a sonic anemometer for measuring wind speed/direction.

## 4.6 Data Validation, Analysis, and Database Preparation

### 4.6.1 Data Validation and Verification

All data collected by UW-Stevens Point during the course of the study will be reviewed internally prior to release for internal or external analysis. Integral parts of our quality assurance approach include: field blanks, analytical and procedural blanks, calibration standards, spiked samples, standard reference materials, and unique sample IDs for data chain of custody. Specific review and validation procedures are outline in the QAPP and are briefly summarized here.

1. Analysis of filter-based samples will not commence until at least 30 days of samples have been collected, including collection of field, trip, and storage blanks.

2. All blanks, calibration curves, calibration checks, and standard additions to sample matrices must meet the quality assurance standards set forth in the QAPP. If failures occur, steps will be taken to determine the source of any errors or contamination and, if necessary, samples will be re-analyzed once the errors have been corrected.

3. Integrated filter-based measurements will be checked to ensure that they fall within the range of the standards used for calibration of the appropriate analytical instrument. Samples that fall below the detection limit for a given analytical method will be marked in the database as "below MDL". Samples that lie above the range of the calibration curve will be reanalyzed after the instrument has been re-calibrated to a greater concentration range. Any sample whose analyte concentration lies above the maximum detection limit will be re-analyzed after the sample has been appropriately diluted or divided.

4. Where possible, data will be checked for consistency through comparison of co-located measurements. Specific to this study, real-time PM2.5 mass data will be checked against co-located real-time and filter based measurements and real-time BC data will be compared with filter-based EC data.

5. Measurement statistics (max, min, mean, standard deviation) generated during this work will be compared against data published in peer-reviewed literature or data reported directly to LADCO, NESCAUM, or USFS as a means of providing further data validation.

### 4.6.2 Data Analysis

UW-Stevens Point will focus its data analysis efforts on the following objectives.

1. Determination of the efficacy of WSOC as a low-cost wood smoke tracer at the primary monitoring site through the inter-comparison of WSOC and levoglucosan measurements, EC/BC and EC/OC ratios, and 24-hr averaged PM2.5 mass, OC, and BC

2. Source apportionment of organic carbon using chemical mass balance models (CMB). Primary source contributions to PM2.5 organic carbon will determined using a molecular marker approach in which contributions are determined from the effective-variance least squares linear regression of the product of the source-contributions and concentrations of a set of organic molecular markers[13]. Calculations of source contributions will be accomplished using a software package (EPA-CMB v.8.2) available from the United States Environmental Protection Agency. Specific markers used in this analysis include, EC, C28-C34 n-alkanes, levoglucosan, 17α(H)-22,29,30-trisnorhopane, 17ß(H)-21α(H)-30-norhopane, 17α(H)-21ß(H)-hopane, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, indeno(1,2,3-cd)pyrene, benzo(ghi)perylene, and picene.

3. Estimation of the contribution of wood smoke to PM2.5 mass using a mass closure model. For this analysis, the contribution of wood smoke will be determined by assuming that aerosol observed at the primary study site is composed of ammonium sulfate, ammonium nitrate, organic carbon, and elemental carbon.

4. Verification of mass calibration factors used by the various nephelometers deployed during the study

5. Inter-comparison of co-located measurements for QA/QC purposes

### 4.6.3 Database Preparation

A database of study information will be prepared and will include the following information and data.

1. Detailed site visit information including sampling activity, observed weather conditions, sampler and instrument calibration data, and other general observations

2. Sampler operation information including sampling times and dates, flow rates, internal temperature and humidity

3. Results of laboratory analysis (mass, EC/OC, Levoglucosan, OMM, WSOC) including instrumentally determined extract concentrations, sample flow rates, sample flow volumes, blank concentrations, calibration data, and blank-corrected 24-hr averaged atmospheric mass concentrations

4. Real-time data (PM2.5 mass, wind speed/direction, PM2.5 BC) including time stamps, reported concentrations, flow rates, internal instrument conditions, calibration data

5. Inter-comparison results for co-located measurements

6. Geographic information system (GIS) data for mobile monitoring data

## 4.7 **Reporting**

Results of data collection, verification, and validation will be submitted in the form of a database as outlined in section 4.6.3. Results of data analysis efforts will be detailed in a final report, which will include key findings and recommendations for future work. Specific questions to be answered will include:

1. Is WSOC an effective tracer for biomass smoke during the primary heating season in North-Central Wisconsin?

2. How do the various methods for measuring PM2.5 mass compare during high/low wood smoke events?

3. What is the contribution of wood smoke to organic carbon observed in Grand Rapids, WI?

4. What is the relative contribution of wood smoke to overall PM2.5 mass in Grand Rapids, WI?

# 5 Schedule and Deliverables

The period of performance for this project will be from mid August 2011 to June 2012. The following assumptions have been made regarding the project in order to develop the schedule.

- 90 days of monitoring and sample collection, beginning December 1, 2011 and concluding on February 28, 2012.
- Identification of target samples for levoglucosan and OMM analysis within four weeks of the completion of the monitoring effort
- Completion of levoglucosan/ECOC/OMM and WSOC measurements within two months of the completion of the monitoring effort

Table 2 below summarizes the proposed schedule of activities and submission of deliverables by task as indicated in the QAPP. For written reports, one electronic copy and ten paper copies will be produced. The final report will include an executive summary. UW-Stevens Point will provide high-quality and professionally written reports for this project in the form of reproducible, copy-ready masters and electronic Microsoft Word and Adobe PDF files. A final electronic version of the project data base will delivered to LADCO as a Microsoft Excel file, and all data will be included in written form as appendices to the final written report. Preliminary data will be furnished to LADCO upon request, and verified and validated data sets will be made available to LADCO to facilitate data analysis as such data sets become available.

Table 2: Schedule of Activities and Deliverables by Task

| **Task(s)** | **Deliverable(s)** | **Due Date** |
|---|---|---|
| Tasks 1: Site set-up | Brief progress report | November, 2011 |
| Tasks 1: Monitoring and sample collection | Brief bi-weekly progress reports, measurements | December, 2011 – February, 2012 |
| Task 3: Database generation (real-time PM2.5 mass, meterology, and BC) | Validated and verified data sets | March, 2012 |
| Task 2: Chemical analysis (PM2.5 mass, WSOC) | Validated and verified data sets | March - April, 2012 |
| Task 2: Chemical analysis (selection of samples for levoglucosan, OMM, ECOC) | Conference calls | March - April, 2012 |
| Task 2: Chemical analysis (levoglucosan, ECOC, OMM) | Validated and verified data sets | April - May, 2012 |
| Task 4: Database generation and final report | Final database, final written report | June, 2012 |

# 6 Management Plan

Tasks outlined in the QAPP will be managed by Dr. Snyder. Filter preparation, organic molecular marker analysis, levoglucosan, and PM2.5 mass measurements will be accomplished with the assistance of the Wisconsin State Laboratory of Hygiene (see http://www.slh.wisc.edu/ for more information on the Wisconsin State Lab of Hygiene which operates as a part of the University of Wisconsin-Madison). WSOC analysis will be accomplished with the assistance of the Water Science and Engineering Lab (WSEL) at the University of Wisconsin-Madison.

Dr. Snyder will be responsible for training all site operators, for the shipping and custody of all samples, the generation of the project data base, the analysis of samples, data analysis as outlined in section 4.6.2 of this work plan, and generation of the final report. UW-Stevens Point meets USEPA contract requirements, and all information and data will be delivered in the public domain.

# 7 References

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