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SF-424
Application for Federal Assistance
Title: Analysis of Ambient Particulate Arsenic

Document Status

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IGMS Information

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Project Officer:		**PO Phone:**	
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Solicitation Information

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Opportunity Title:	Community-Scale Air Toxics Ambient Monitoring	**Competition Title:**	
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Submission Information

Submission:	Application	**Grant:**	Non-Construction
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Applicant Information

	Grants.gov	IGMS
Applicant Type:	A: State Government	State
Applicant Name:	Missouri Department of Natural Resources	Missouri Department of Natural Resources
Applicant DUNS #:	878144757	878144757
Organizational Unit:	Dept.of Natural Resources	
Sub Org Unit:	Div. of Environmental Quality	
EIN:	44-6000987	44-6000987
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Project Information

Federal Agency: EPA

CFDA:	66.034
Project Title:	Advanced Sampling and Data Analysis for Source Attribution of Ambient Particulate Arsenic and Other Air Toxics Metals in St. Louis
Project Period Start:	07/01/2007 **Project Period End:** 06/30/2009

Congressional Districts

Estimated Funding

Federal	$491,842
Applicant	$0
(For all applicants including states)	
State	$0
(For state contribution to non-state applicants)	
Local	$0
Other	$0
Program Income	$0
TOTAL	**$491,842**

Is the Application subject to review by State Executive Order 12372 Process?	Yes - Was Made Available for Review
Available for Review:	04/08/2007
Is the Applicant delinquent on any Federal Debt?	No

Authorized Representative

Key Contacts

Budget Summary

Application Attachments

Grants.gov Application:

Notifications History

BUDGET INFORMATION - Non-Construction Programs

OMB Approval No. 4040-0006
Expiration Date 04/30/2008

SECTION A - BUDGET SUMMARY

Grant Program Function or Activity (a)	Catalog of Federal Domestic Assistance Number (b)	Estimated Unobligated Funds		New or Revised Budget		
		Federal (c)	Non-Federal (d)	Federal (e)	Non-Federal (f)	Total (g)
1. 1 year - 2007/2008	66.034			$143,406.00		$143,406.00
2. 2 nd year - 2008/2009	66.034			$348,436.00		$348,436.00
3.						$0.00
4.						$0.00
5. Totals		$0.00	$0.00	$491,842.00	$0.00	$491,842.00

SECTION B - BUDGET CATEGORIES

6. Object Class Categories	GRANT PROGRAM, FUNCTION OR ACTIVITY				Total (5)
	(1) 1 year - 2007/2008	(2) 2 nd year - 2008/2009	(3)	(4)	
a. Personnel	$23,336.00	$32,893.00			$56,229.00
b. Fringe Benefits	$9,965.00	$14,045.00			$24,010.00
c. Travel	$3,831.00	$6,137.00			$9,968.00
d. Equipment	$0.00	$192,500.00			$192,500.00
e. Supplies	$3,878.00	$9,400.00			$13,278.00
f. Contractual	$6,000.00	$5,000.00			$11,000.00
g. Construction	$66,733.00	$51,045.00			$117,778.00
h. Other	$11,000.00	$11,000.00			$22,000.00
i. Total Direct Charges (*sum of 6a-6h*)	$124,743.00	$322,020.00	$0.00	$0.00	$446,763.00
j. Indirect Charges	$18,663.00	$26,416.00			$45,079.00
k. TOTALS (*sum of 6i and 6j*)	$143,406.00	$348,436.00	$0.00	$0.00	$491,842.00
7. Program Income	$0.00				$0.00

Standard From 424A (Rev. 7-97)
Prescribed by OMB Circular A-102

SECTION C - NON-FEDERAL RESOURCES				
(a) Grant Program	(b) Applicant	(c) State	(d) Other Sources	(e) TOTALS
8. 1 year - 2007/2008				$0.00
9. 2 nd year - 2008/2009				$0.00
10.				$0.00
11.				$0.00
12. TOTAL (sum of lines 8-11)	$0.00	$0.00	$0.00	$0.00

SECTION D - FORECASTED CASH NEEDS					
	Total for 1st Year	1st Quarter	2nd Quarter	3rd Quarter	4th Quarter
13. Federal	$143,406.00	$35,852.00	$35,852.00	$35,851.00	$35,851.00
14. Non-Federal	$0.00				
15. TOTAL (*sum of lines 13 and 14*)	$143,406.00	$35,852.00	$35,852.00	$35,851.00	$35,851.00

SECTION E - BUDGET ESTIMATES OF FEDERAL FUNDS NEEDED FOR BALANCE OF THE PROJECT				
(a) Grant Program	FUTURE FUNDING PERIODS (Years)			
	(b) First	(c) Second	(d) Third	(e) Fourth
16. 2nd year - 2008/2009		$348,436.00		
17.				
18.				
19.				
20. TOTAL (*sum of lines 16-19*)	$0.00	$348,436.00	$0.00	$0.00

SECTION F - OTHER BUDGET INFORMATION	
21. Direct Charges: $328,985 *	22. Indirect Charges: $45,079 * *
23. Remarks: * Budget in the construction catagory is for program specific distribution * * APCP & ESP have a different yearly percentage rate for indirect. APCP's SFY 2007 is 22.55 % and ESP's SFY 2007 is 38.67%.	

Title:	**Advanced Sampling and Data Analysis for Source Attribution of Ambient Particulate Arsenic and Other Air Toxics Metals in St. Louis**
Category:	Community-Scale Monitoring
Applicant Info:	Missouri Department of Natural Resources, Air Pollution Control Program P.O. Box 176, Jefferson City, MO 65102-0176 Contact Person – Terry Rowles -Telephone number (573) 751-4817 Fax number (573) 751-2706 E-mail address terry.rowles@dnr.mo.gov
Funding Requested:	$491,842 (total project cost, same)
Project Period:	July 1, 2007 – June 30, 2009

PROJECT DESCRIPTION

1. Background and Motivation

The St. Louis Community Air Project (CAP, 2005) featured detailed measurements of air toxics in an urban residential neighborhood. Annual-average ambient concentrations were compared to benchmarks for 1 in 100,000 increased cancer risk from a 70-year exposure sustained at the observed annual-average ambient concentration. Six hazardous air pollutants (HAPs) of concern were identified through this process (**Table 1**) and the Missouri Department of Natural Resources (MDNR) has taken a proactive approach to addressing these CAP findings. Formaldehyde exhibited the highest ambient concentrations relative to the cancer benchmarks. Thus, a second phase of measurements was commissioned which included both urban and rural integrated sampling and a UV-DOAS deployment for continuous formaldehyde measurements. Key findings from that work are also summarized in the CAP final report (CAP, 2005). The agency is next turning its attention to toxic metals, most importantly, arsenic. Table 1 also includes the eleven pollutants of concern for St. Louis identified from the 2005 Urban Air Toxics Monitoring Program (UATMP, 2006). Arsenic is one of four pollutants common to both lists (italics) and air toxic metals (underlined) account for two of the CAP pollutants of concern and three of the UATMP pollutants of concern.

Table 1. Air Toxic Pollutants of Concern (City of St. Louis)

CAP Study	2005 UATMP
o *acetaldehyde*	o *acetaldehyde*
o *arsenic*	o *arsenic*
o *benzene*	o *benzene*
o *formaldehyde*	o *formaldehyde*
o chromium(1)	o 1,3-butadiene
o "diesel exhaust"(2)	o p-dichlorobenzene
	o cadmium
	o carbon tetrachloride
	o hexaclhoro-1,3-butadiene
	o manganese
	o tetrachlorethylene

(1) Chromium not reported as pollutant of concern for 2005 UATMP due to filter contamination.
(2) "Diesel exhaust" not measured as part of the CAP study but was deemed a pollutant of concern by the stakeholder group.

Heavy metals are of significant concern as air toxics and indeed metals / metal compounds (hereafter termed "metals" for the purpose of this proposal) represent eight of the thirty-three species considered as priority pollutants in the USEPA Integrated Urban Air Toxics Strategy (64 FR 38706-38740). For the St. Louis CAP study, the annual average (2001-2003) $PM_{2.5}$ arsenic concentration was 2.0 ng/m^3 which was at the established benchmark of 2 ng/m^3 for increased cancer risk. More recent measurements show levels of arsenic similar to those observed in the CAP study but also highlight some of the challenges in both performing data reduction and understanding the true behavior of these species in the urban environment. **Table 2** summarizes the annual average arsenic concentrations for 2000 through 2006. Measurements were conducted at Arnold (a suburban site ~30 km south of the City of St. Louis central business district; CBD) Blair Street[1] (an urban site ~5 km north of the CBD), and Bonne Terre (a rural site ~85 km south of St. Louis) using $PM_{2.5}$ speciation trends network (STN) samplers. Assuming a representative MDL for arsenic of 1.46 ng/m^3 for the STN data (the MDL varies by

[1] The Blair Street site is also one of the original NATTS sites and features a battery of HAPs measurements.

sampler type and laboratory performing the XRF analysis), 50% of the 772 samples collected at Blair Street are below the MDL and only 0.6% of the samples have concentrations more than ten times the MDL. The other two $PM_{2.5}$ sites have even lower signal-to-noise and thus spatial patterns in arsenic cannot be inferred from the $PM_{2.5}$ data.

Table 2. Annual Average Arsenic Concentration[(1)], ng/m³

	PM_{10} - NATTS	$PM_{2.5}$ - STN		
	Blair St.	Blair St.	Arnold	Bonne Terre
2000	--	1.6	--	--
2001	--	2.1	2.5	--
2002	--	1.9	1.8	--
2003	2.5[(2)]	2.4	1.9	0.9
2004	1.6	2.8	2.3	1.0
2005	2.4	2.4	2.0	0.9
2006	1.0	1.7	1.5	0.9

(1) ½ MDL imputed for non-detects
(2) July – December only

Figure 1a further demonstrates the limitations of the STN data for characterizing arsenic. Both Blair St. and Arnold exhibit similar annual mean concentrations which are greater than observed at the rural site (the prevalence of samples below MDL, including non-detects, confounds a quantitative comparison). However, there are very few days with at least one site exhibiting an arsenic concentration above three times the MDL (~4.5 ng/m³) and thus relatively few days are available to examine the drivers for intraurban variability. For the few samples at least three times the MDL, there is poor correlation in concentrations between the two sites. Taken together with the urban/rural contrast data, this suggests there are significant local (urban scale) sources of arsenic.

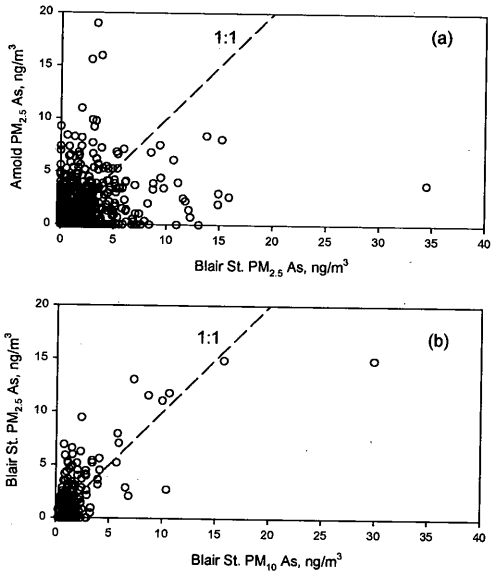

Figure 1. 24-hour integrated Arsenic concentrations: (a) $PM_{2.5}$ As at the Arnold and Blair Street sites, 2001-2006; and (b) $PM_{2.5}$ and PM_{10} As at the Blair Street site, 2003-2006.

Table 2 also lists the arsenic concentrations measured at Blair Street using a PM_{10} sampler with sampling and analysis protocols adopted for the NATTS network. This approach captures particles over a broader portion of the inhalable size range and also features much better detection limits (~0.02 ng/m³) than the conventional $PM_{2.5}$ speciation method. Virtually all of the PM_{10} arsenic concentrations are greater than ten times the MDL. Annual average concentrations for PM_{10} and $PM_{2.5}$ arsenic are similar (Table 2), and one might conclude that the day-to-day difference would merely reflect that the measurements are often near the $PM_{2.5}$ arsenic detection limit. However, **Figure 1b** shows that there is significant day-to-day variability in the relationship between $PM_{2.5}$ arsenic and PM_{10} arsenic and, disconcertingly, there are numerous days with $PM_{2.5}$ arsenic concentrations greater then three times the MDL yet with $PM_{2.5}$ arsenic much greater than the PM_{10} arsenic. This behavior cannot be explained by differences in the cutpoint curves for the samplers and is attributed to large uncertainties in the STN XRF measurements for concentrations near (within a factor of ten of) the MDL.

PM_{10} arsenic annual average concentrations measured at Blair Street are of the same order of magnitude as those measured at other NATTS sites in the US (www.epa.gov/air/data/ reports.html). However, maximum 24-hour concentrations measured at Blair Street are frequently higher than those measured at other sites. These high individual day measurements suggest that there may be localized sources whose impact is only observed at a

specific location when meteorological conditions are optimal for impacting that location. Thus, measurements at more sites using approaches with suitable detection limits will improve the characterization of ambient arsenic concentrations and provide data suitable for quantitative analysis including source apportionment.

Metal smelting operations, cement kilns, agricultural burning, and combustion engines are all sources of arsenic compounds. Other sources include tobacco smoke, wood burning (treated and untreated), gasoline, oil, coal, and use of arsenic-containing pesticides and herbicides. Multiple industrial and other area sources release small quantities of arsenic compounds that are difficult to estimate and include in existing emission inventories. The 1996 National Toxics Inventory for St. Louis City indicates an annual release of about 500 pounds of arsenic compounds, 94% from industrial sources. Ambient arsenic concentrations in the US have been modeled based on known emissions as a part of the National-Scale Air Toxics Assessment (NATA). The modeled concentration in the census tract that includes the Blair Street station is 0.25 ng/m^3 (www.epa.gov/ttn/atw/nata1999). This concentration is an order of magnitude lower than the measured concentration, suggesting that the inventory of arsenic sources may be incomplete, and suggesting that more measurement of ambient arsenic concentrations would be beneficial.

In summary –

- Ambient particulate matter arsenic has been identified as a pollutant of concern for St. Louis by both the St. Louis Community Air Project (CAP) study and the 2005 UATMP analysis.
- While $PM_{2.5}$ speciation network monitoring yields annual-average arsenic concentrations similar to annual-average PM_{10} arsenic from the air toxics program, arsenic intraurban variability at finer time scales (which could be used to infer emission source locations) cannot be determined due to the low signal-to-noise for the $PM_{2.5}$ speciation network arsenic data.
- PM_{10} arsenic from the air toxics program has high signal-to-noise (virtually all concentrations are more than ten times the MDL) and a network of such integrated measurements, complemented by additional high time resolution measurements, could be used to examine intraurban variability and identify emission source regions.

Through this proposal we seek to more comprehensively understand the temporal and spatial variability of arsenic and other air toxic metals with the use of new monitoring and data analysis methods. Our hope is to discern where and under what conditions the highest levels of certain metals are occurring, and to increase our ability to say what sources may be causing them. We are thus responsive to the "**community-scale monitoring**" category of the solicitation. This project will advance our ongoing effort to investigate and address HAPs of concern in St. Louis. It will demonstrate the use of a suite of measurement strategies towards understanding pollutant behavior on various temporal and spatial scales, and as such will serve as a national model for similar studies. It is directly responsive to the primary objective of the solicitation, "to identify and more accurately define the extent of local scale HAP impacts".

2. Project Objectives

The core objectives of the proposed project are to describe the climatology of and develop a conceptual model (including identifying sources) for ambient particle arsenic and selected other air toxics metals in the St. Louis area. The work will proceed in two phases. **Phase I** will feature a network of three PM_{10} air toxics metals sampling sites to refine our understanding of the spatial distribution of ambient particle arsenic burdens. Compared to $PM_{2.5}$ speciation monitoring this approach provides improved method detection limits due to the larger air volumes sampled. Variations in surface meteorology during sample collection still present a limitation for interpreting data from this 24-hour integrated sampling, but the spatial coverage of the network provides an opportunity to constrain the probability fields for arsenic emissions. Samples will be collected every third day for one year and analyzed by ICP-MS. **Phase II** will feature high time resolution measurements at six sites for periods of one month each. A continuous monitor such as the Cooper Environmental Xact Ambient Air Toxics Monitor (AATM) will be used to collect and analyze ambient particulate matter at high time resolution and with sufficient air volume sampled to overcome detection limit issues. Samples will be collected and analyzed with time resolution of four hours or less. High time resolution concentration data coupled with surface meteorological data will be used to infer emission source locations for arsenic and other heavy metal

compounds. Sampling will initially be conducted at the Blair Street site, with subsequent deployment locations determined based on results from Phase I and from the prior deployments during Phase II. The sampler will be housed in a trailer and can draw power from standard 110V/20A circuits, so little-to-no site preparations will be required. A key feature will be the rapid turnaround on the data to guide the deployments. While this project focuses on a characterization of arsenic climatology and source identification in the St. Louis area and is not designed to be a methods development study, both field and analytical measurement issues necessarily must be critically evaluated.

Overall project planning, field measurement, and data analysis and reporting will be conducted by the Missouri Department of Natural Resources (MDNR). Assistance with study design, Phase I chemical analysis, and source apportionment analysis will be done by Washington University in St. Louis (WUSTL). These two institutions have a sound track record of collaboration. Dr. Turner at WUSTL has performed several projects for MDNR including a $PM_{2.5}$ saturation monitoring study, $PM_{2.5}$ speciation and air toxics sampling at sites in eastern Missouri, ambient formaldehyde measurements using open-path ultraviolet differential optical absorption spectroscopy (UV-DOAS), and is currently providing technical support for $PM_{2.5}$ SIP development including development of a conceptual model for $PM_{2.5}$ over St. Louis. A contractor will provide a sampler similar to the Cooper Environmental Services (CES) Xact AATM to be used in Phase II. The contractor will also provide training of MDNR field monitoring personnel in instrument setup and operation.

Phase I – Spatially and Temporally Enhanced 24-hour Integrated Measurements

Motivation. The St. Louis area has multiple $PM_{2.5}$ speciation monitoring sites but the arsenic data quality is inadequate to probe intraurban variability and identify potential emission source locations. These goals can be addressed by deploying and operating a network of PM_{10} samplers following the NATTS/UATMP metals sampling and analysis protocols. Phase I of this project will feature one year of 1-in-3 day PM_{10} metals measurements at three sites in the St. Louis area. About 120 samples will be collected at each site and analyzed. This data set will be used to refine our understanding of ambient arsenic burdens and to narrow the probability fields for major arsenic emission source locations. For example, **Figure 2** shows conditional probability function (CPF) plots (Kim and Hopke, 2004) for PM_{10} arsenic at Blair Street and $PM_{2.5}$ arsenic at East St. Louis (the latter measurements were similar to STN network measurements, but the East St. Louis data has moderately higher signal-to-noise due to the site's close proximity to point sources with significant arsenic emissions). The East St. Louis CPF plot points towards two known arsenic emission sources – a zinc smelter and a hazardous waste incinerator. The prevailing bearing for high PM_{10} arsenic at Blair Street points towards the East St. Louis monitoring site rather the region southwest of the St. Louis site. This behavior was also observed for several $PM_{2.5}$ metals, including Zn and Cu, which have known major emission sources southwest of the East St. Louis site, and the precise bearings for the Blair Street CPF plot might be shifted because East St. Louis wind data were used in the analysis. Bearings of high arsenic also point east and northeast of the Blair Street site. Arsenic emission sources

Figure 2. Conditional probability function (CPF) plots for $PM_{2.5}$ arsenic at the St. Louis – Midwest Supersite (STL-SS, East St. Louis, IL) and PM_{10} arsenic at the City of St. Louis' Blair St. NATTS site. CPF plots constructed using top 25% of 24-hour integrated arsenic and hourly-average winds measured at East St. Louis. STL-SS and Blair data for the periods 6/01-5/03 and 7/02-12/06, respectively.

in these directions are unknown and, as discussed later in this section, CPF plots for 24-hour integrated pollutant data are subject to significant uncertainty if the time scales for plume impacts are on much shorter time scales (one to a few hours).

Ambient Sampling. 24-hour integrated PM_{10} sampling will be conducted at 1-in-3 day frequency at three sites in the St. Louis area. Sampling and analysis protocols will generally follow the NATTS air toxics procedures.[2] The approach and rationale will be fully detailed in a project QAPP. Data Quality Objectives (DQOs) and the attendant Measurement Quality Objectives (MQOs) will be developed and described in the QAPP. Quality Assurance activities will include system audits and performance audits performed by the independently-reporting MDNR Air Quality Assurance Unit (AQAU). The 1-in-3 day frequency – double the NATTS 1-in-6 day frequency – is intended to provide enough data from one year of measurements to support factor analysis and other detailed data mining approaches. One sampling site will be at Blair Street to provide a direct linkage between this relatively short-term study (one year) and the sustained NATTS measurements. The chemical analysis will be performed independently from the NATTS program; thus, the Blair Street data will provide an important quality check. The other two sites will be determined as the first task in this project using a battery of data (including TRI and other emission data and meteorological data) and analyses (e.g., pollutant roses for existing data). One site will likely be at or near the existing $PM_{2.5}$ speciation site in Arnold, since this site and Blair Street exhibit similar annual metrics for arsenic (Table 2) but poor day-to-day correlation (Figure 1a).

Elemental Analysis of Arsenic and Selected Other Air Toxics Metals

Elemental analysis of the Phase I PM_{10} filter samples will be performed by the Turner group at WUSTL for arsenic and other selected elements using ICP-MS. A shared instrument facility for faculty in the Department of Energy, Environmental & Chemical Engineering (EECE) includes an Agilent Technologies 7500ce ICP-MS purchased and installed in early 2006. Several EECE faculty have extensive experience with ICP-MS and a full-time laboratory technician oversees the day-to-day use and maintenance of the ICP-MS unit and other instruments in the shared laboratory. Arsenic quantification can be confounded by an isobaric polyatomic ion interference from argon chloride, with the chlorine originating from complex sample matrices (Brown *et al.*, 2004) or from the sample digestion reagents. However, the WUSTL ICP-MS unit is equipped with an Octopole Reaction System (ORS), also known as a collision cell, which efficiently suppresses this interference. The MDL for ICP-MS analysis of arsenic is ~0.020 ng/m^3 for PM_{10} sampling with the air toxics program protocols. Based on our analysis of existing PM_{10} arsenic data from the Blair Street site, this MDL will be sufficient to meet the DQOs and MQOs to be developed as the first step in the project planning process. Laboratory quality assurance will follow best practices including suitable frequencies of multi-point calibrations, single-point check samples, and replicate analyses. Extraction recoveries will be evaluated using a NIST SRM (e.g. urban dust), Performance evaluation will include a laboratory intercomparison (e.g. participating in the USEPA Proficiency Testing (PT) program for NATTS analytical laboratories, an analysis intercomparison with a laboratory performing well for air toxics metals in the PT program, or an analysis intercomparison with the USEPA Region 7 laboratory). Quality assurance protocols will described in detail in the project Phase I QAPP.

Data Analysis. We will perform a variety of data analyses to characterize the climatology of arsenic and other air toxics metals in St. Louis. The combination of three sites and relatively high sampling frequency will support trend analyses with substantial statistical power. Conditional probability function plots and nonparametric regression (Henry *et al.* 2002, Yu *et al.* 2004) using concentration data and surface winds will be performed to identify likely emission source locations. We will also perform source apportionment on the Blair Street PM_{10} air toxics metals data. This work will follow along two lines. First, we will determine whether the improved detection limits for the PM_{10} metals data can enhance the *$PM_{2.5}$ mass apportionment.* For example, it might be possible to tease out point source categories that were not discernible using strictly the $PM_{2.5}$ speciation data. At a minimum, the following steps will be conducted for Blair Street (and possibly for Arnold). The Turner group as part of the current MDNR-funded SIP support project has already repeated the source

[2] There might be changes in the sample extraction methodology, as recent work has demonstrated that heavy metals recovery for "hot block" acid digestion is comparable to microwave acid digestion and has certain other advantages. Any deviations from the NATTS protocol will be presented and justified in the QAPP.

apportionment by positive matrix factorization (PMF) of Lee and Hopke (2006). This apportionment serves as a methodological baseline (base case). An analysis will be conducted using the $PM_{2.5}$ STN data but including only those days for which PM_{10} air toxics metals data is also available. This will determine the stability of the PMF solution to the smaller data set size. Subsequently, an analysis will be conducted on the $PM_{2.5}$ STN data but using the PM_{10} air toxics metals data in lieu of the $PM_{2.5}$ STN data for species measured by both methods. This will demonstrate whether the use of PM_{10} air toxics data with better detection limits can improve the $PM_{2.5}$ mass source apportionment and whether it improves the apportionment of the individual metals. Second, we will perform factor analysis on the PM_{10} air toxics metals data; this is different from the aforementioned analysis which seeks to apportion the *$PM_{2.5}$ mass* in that it seeks to apportion the observed air toxics metals.

Phase II - High Time Resolution Measurements

Motivation. High time resolution measurements of air toxics metals can provide tremendous insights into their climatology and emission sources. While the Phase I project will focus on 24-hour integrated sampling and is expected to provide very useful information, it has two major limitations towards source identification and emissions quantification. First, sample collection is quite labor intensive to compile a large database for analysis. Second, even if such a database is assembled, variations in emissions and/or wind fields over the course of a day smear out what is otherwise a crisp signal. No statistical analysis can tease out the temporal features lost by time averaging. The proposed high time resolution measurements will circumvent these issues by collecting a large volume of data in a short deployment and providing data at time scales similar to the meteorological variations.

Figure 3 shows the calendar year 2004 wind rose for daily-average wind direction in East St. Louis. In this case, the data in each wind direction bin are stratified by the standard deviation of the wind direction (specifically, the Yamartino standard deviation constructed from the 5-minute winds data) rather than the wind speed. For thirteen of the sixteen wind direction bins, the wind direction standard deviation is less than 45° (blue bars) for nominally 50% or less of the time. The exception is winds from the south, which can be relatively stable throughout the day. In some cases (e.g., winds from the due west) there are no days with a narrow wind direction. This demonstrates two important aspects of the proposed study: (1) high time resolution measurements can increase the "signal-to-noise" ratio (in the sense of identifying specific emission sources) by reducing the variability inherent in sampling at a fixed receptor site with sample collection times much longer than the characteristic time for major changes in wind direction; and (2) periodically moving the receptor site allows one to capture plumes that could be completely missed by sampling at a single site (in light of the nonuniform distribution of wind directions in Figure 3). That is, given the local-scale nature of the emissions, a source immediately to the west of the East St. Louis site might be missed because the winds rarely originate from the west yet the source might be very important to ambient burdens – and thus exposures – at locations north of the emissions source in light of the prevailing winds from the south.

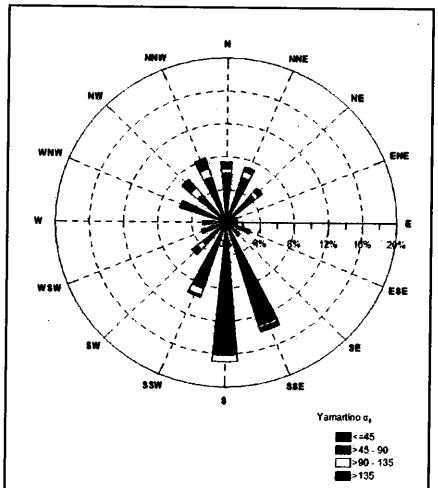

Figure 3. Wind rose of daily-average resultant vector wind direction, stratified by Yamartino standard deviation (CY2004, East St. Louis).

Figure 4 shows a six-day time series for hourly-average arsenic at the St. Louis Supersite. A University of Maryland semi-continuous elements in aerosol sampler (SEAS) was used to collect the samples with subsequent laboratory analysis by graphite furnace atomic absorption spectrometry (GFAAS). The top panel shows the hourly wind speed and direction, the middle panel shows the entire dynamic range for ambient $PM_{1.3}$ arsenic, and the bottom panel is the same data but zoomed to the bottom 10% of the dynamic range. Two very large plumes were observed during this period. The first plume corresponded to calm winds while the second plume

was coincident with light but steady winds from the southwest. The bottom panel shows two additional peaks corresponding to light but steady winds from the northwest and west, respectively. Additional SEAS data for June 2001 and November 2001 also point towards arsenic point sources to the southeast and south-southwest of the site. This example clearly demonstrates the power of high time resolution data in capturing arsenic behavior.

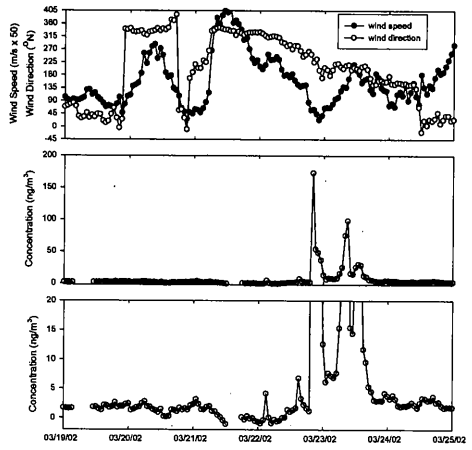

Figure 4. Six-day time series for hourly wind speed, wind direction, and $PM_{1.3}$ arsenic in East St. Louis.

Ambient Sampling. Ambient PM_{10} samples will be collected and analyzed at four-hour (or finer) time resolution using the CES Xact AATM or similar sampling and analysis instrument system. The CES Xact system consists of a modified beta attenuation monitor to collect airborne particulate matter onto a filter tape coupled with an x-ray fluorescence (XRF) analyzer to provide elemental analysis of arsenic and other metals. The instrument provides near-real time analysis results, since each spot on the filter tape is analyzed once the collection period ends. This instrument has been used as a stack monitor for metals and, in recent USEPA-funded studies, the detection limit has been improved (decreased) for the purpose of fenceline and ambient monitoring by increasing sample flow and optimizing the XRF analysis system. A detection limit as low as 0.1 ng/m^3 for arsenic can be achieved for 4-hour samples. For the Blair Street PM_{10} air toxics data, this corresponds to 99% of the 24-hour integrated concentrations being more than three times the MDL and 42% of the 24-hour integrated concentrations being more than ten times the MDL.

The sampling and analysis instrument system will be installed in a trailer than can be easily moved between sampling locations. On-site meteorology (wind speed and direction, temperature) will be collected using a short tower attached to the side of the trailer (a portable base will be used for additional support). Six deployments – each one-month in duration – will be conducted over a nine-month period. An amendment to the project QAPP will be prepared for Phase II. Quality Assurance activities will again include system and performance audits by the MDNR AQAU. There will also be measurement overlap with the Phase I integrated sampling at the Blair Street site.

Following completion of this project, the instrument system will be available for additional studies of airborne metallic species in Missouri. MDNR has a strong track record of continuing to use instruments acquired in previous EPA-funded projects, including the UV-DOAS system and a trace level carbon monoxide analyzer, both still in operation in St. Louis. Given ongoing concerns about air toxics and industrial primary emissions to ambient PM burdens (including but not limited to the St. Louis $PM_{2.5}$ nonattainment area), we anticipate this instrument system will be extensively used.

Data Analysis. We will perform a series of data analyses to interpret time-resolved data, including an effort to identify point sources or at least significantly constrain the geographic zones where such sources must be located using conditional probability plots and nonparametric regression on concentration and surface winds data. Recent work by Henry (2007) has demonstrated that nonparametric regression to yield two-dimensional fields for identifying local emission source locations can be performed on three hours data will little loss of information compared to one-hour data (in contrast, nonparametric regression performed on the 24-hour integrated data might be less insightful based on recent analysis by Henry, 2007). EPA/ORD/NERL anticipates releasing a battery of consolidated data analysis tools under the Air Pollution Transport to Receptor (APTR) platform by late 2007, and we anticipate taking advantage of these data analysis capabilities. We will also apply the multivariate pseudo-deterministic hybrid receptor model (PDRM), developed by the University of Maryland, which reconciles ambient concentrations against the products of their emission rates and atmospheric dispersion

factors for individual point sources in a receptor equation. The dispersion factors are estimated from a Gaussian plume model and used to constrain the receptor modeling solutions. In contrast to factor analysis models, this hybrid model explicitly uses knowledge of wind direction in relation to that of the known sources, as well as other plume dispersion variables, yet preserves the robustness of a least-squares fit to the ambient data. The model has been tested on time-resolved metals and SO_2 data, most notably for Tampa, FL (Park *et al.*, 2005). Given the plumy behavior of arsenic and other air toxics metals data collected at the St. Louis Supersite (Figure 4), we are confident that this approach will bring tremendous added value to characterizing both ambient levels and emission sources of air toxics metals in St. Louis.

3. Project Tasks, Deliverables and Timeline

a. **PM_{10} air toxics metals monitor siting.** MDNR and WUSTL will collaborate on finalizing the sites for 24-hour integrated PM_{10} sampling to quantify arsenic and other air toxics metals. Both existing ambient metals data (PM_{10} and $PM_{2.5}$ metals data from the Blair Street STN/NATTS site; Arnold, Alton, and Grant School (St. Louis CAP) speciation monitoring sites; and the St. Louis - Midwest Supersite in East St. Louis) and emission inventory data (including but not limited to the TRI) will be used in this assessment. *Deliverable* - a report summarizing the existing ambient and emissions inventory data will be prepared by MDNR and WUSTL, to be submitted to USEPA by the end of the first project quarter.

b. **PM_{10} air toxics metals sampling and analysis QAPP.** MDNR and WUSTL will prepare a draft QAPP for the PM_{10} air toxics metals sampling and analysis by no later than four weeks prior to commencing sampling as described in Task (c) below. Upon completion of Task (a) above (and prior to commencing sampling), this QAPP will be amended to include aspects pertaining to the monitoring sites selected. *Deliverable* - Phase I QAPP.

c. **PM_{10} air toxics metals sampling and chemical analysis (Phase I).** MDNR will conduct one year of 1-in-3 day PM_{10} sampling at three sites, commencing with the second project quarter and continuing through the fifth project quarter. MDNR will provide three PM_{10} samplers with a flow calibration inlet for these measurements. Each of the samples will be analyzed by WUSTL using ICP-MS for As, Cd, Cr, Pb, Mn, and Ni (and possibly other elements). *Deliverable* - validated data will be submitted by WUSTL to MDNR on a quarterly basis (e.g., data for second project quarter sampling will be submitted by the end of the third project quarter) for uploading to AQS.

d. **Sampler construction and testing.** A contractor will construct and deliver a turnkey unit similar to the CES Xact AATM for collecting and analyzing ambient fine particulate matter samples with four-hour time resolution. The contractor will train MDNR staff on the field operation of the unit. MDNR will install the unit in a portable shelter and test the unit for at least two full weeks prior to the first field deployment. *Deliverable* - a monitoring unit will be delivered to MDNR no later than four weeks prior to the first deployment in Task (f) below.

e. **High time resolution metals sampling and chemical analysis QAPP.** MDNR will prepare an amendment to the project QAPP for the high time resolution metals sampling and chemical analysis by no later than four weeks prior to commencing sampling as described in Task (f) below. *Deliverable* - Phase II amended QAPP.

f. **High time resolution metals sampling and chemical analysis (Phase II).** MDNR will collect and analyze four-hour PM_{10} samples for six deployments - each one month duration - over the fourth through sixth project quarters. Hourly-average wind speed and wind direction will also be measured at sites lacking on-site meteorology measurements using instruments that MDNR will provide. The first deployment will be at Blair Street. Locations for the remaining five deployments will be chosen by MDNR in consultation with WUSTL based on Phase I data and preliminary data from the initial Phase II deployments. *Deliverable* - Level 1 validated data for the entire study will be provided by no later than one quarter following the final deployment.

g. **Arsenic emissions source characterization**. Phase I and Phase II data will be analyzed to identify likely emission sources for arsenic and selected other air toxics metals. WUSTL and MDNR will perform basic trend analyses and source apportionment (e.g., factor analysis). WUSTL will apply the University of

Maryland Pseudo-Deterministic Receptor Model (PDRM) to the high time resolution data to estimate emission rates. *Deliverable* - see Task (h) below.

h. Final project report. A final project report will be prepared which describes the climatology of ambient particle arsenic (and other air toxics metals as deemed appropriate) in St. Louis. A conceptual model for ambient particle arsenic will be provided which will be based on field observations, source apportionment, and PDRM modeling. *Deliverable* - The final report will be submitted by MDNR to USEPA at the end of the project period.

4. Environmental Outputs / Outcomes

This project will support progress toward EPA Strategic Plan Goal 1, Objective 1.1, Sub-objective 1.1.2: "Reduced Risk from Toxic Air Pollutants" by collecting data and providing analysis that will improve our understanding of the level and extent of arsenic in airborne particulate matter in St. Louis.. The St. Louis area has a history of groups interested in air quality problems, e.g. St. Louis Community and Clean Air Projects and St. Louis Regional Clean Air Partnership, and a community which has obtained a level of understanding of air quality problems beyond the national average. The information obtained will be considered by MDNR and EPA as they seek to develop programs and track improvements in air quality for the area. Interested groups can assist in working with MDNR to identify ways to mitigate pollutant levels. The project can also serve as a model for similar studies in other areas.

Since the inception of the NATTS program, two metals of particular interest have been arsenic and chromium. Levels at several sites nationwide have been elevated beyond one-in-one million additional cancer risk. In the St. Louis area, monitoring for arsenic in particular has shown concentrations at levels an order of magnitude greater and more widespread than modeled in the most recent National-Scale Air Toxics Assessment (NATA). Highest impacts were predicted as localized to St. Louis City, and some areas around point sources in less populated locations, but monitoring results to date indicate increased risk to populations over a larger part of the urbanized metro area. This study will provide additional clarity to both the risk and associated sources for metals HAPs, which may be of greater concern than indicated in the NATA results for the area. Key expected outputs and outcomes include –

Outputs

- a detailed characterization of PM arsenic climatology and emission sources for St. Louis;
- data collected for this project will be placed in USEPA's Air Quality System (AQS) database;
- refinements to sampling and analysis protocols will be disseminated;
- our experience deploying and operating a state-of-art near-real-time monitor for air toxics metals will be captured in an SOP and in the final report and also disseminated at an appropriate conference or workshop;

Outcomes (short-, mid- and long-term)

- emission sources driving observed PM arsenic burdens in St . Louis will be identified (short);
- results will be communicated to key stakeholders through various forums, including but not limited to web sites operated by Missouri DNR and the St. Louis Community Air Project (short);
- applicability of a near-real-time monitor for PM trace elements will determined, with implications for both air toxics metals in particular and ambient $PM_{2.5}$ in general (short);
- emission inventories for air toxics metals can be refined using the study results, with implications to risk modeling for both St. Louis and other locations (including the NATA) (mid);
- community action to mitigate air toxics HAPs could be addressed through existing community-based organizations which address air quality issues (e.g. St. Louis CAP) (mid/long);

Plans for Tracking and Measuring Progress. Quarterly reports and frequent communication with EPA sponsors will track progress and identify any problem areas or project delays. The final project report will include a critical assessment of our success in meeting the project objectives. Specific project objectives – including hypotheses – will be defined in the QAPP. For example, there will be DQOs and MQOs, and in the latter case we will assess whether we did indeed collect data with sufficient resolution (spatial, temporal, and in terms of detectability) to characterize arsenic climatology and identify and characterize the emission sources.

The information in this report will be considered in evaluating air quality improvements as an outgrowth of controls developed for other programs, and for programs that can be considered to directly address the issues identified.

Transferability/Applicability of Outcomes to Other Locations. This project will have significant applicability to other locations: (1) identification of arsenic emissions sources in St. Louis can be used to refine arsenic emission inventories, and thus modeled risk, at other locations; (2) the intrinsic value of different data types (network of integrated samplers, versus high time resolution but relatively short duration measurements at multiple sites) will be evaluated through data analysis and the findings can be used to guide the design of cost-effective studies of air toxics metals at other locations; and (3) the use of near-real-time monitors for particulate matter air toxics metals will be evaluated with practical insights gained into the deployment and operation of such instruments.

5. Roles and Qualifications of Applicant and Partners

MDNR is the lead agency and will be responsible for project management and administration. MDNR will also conduct all field sampling, and an indepently-reporting unit of MDNR will conduct quality assurance audits of field monitoring. A subcontractor will also play a key role in this project - Washington University in St. Louis (WUSTL). WUSTL will assist with study design, provide Phase I chemical analysis, and assist with source apportionment analysis. Both organizations will play active roles in the data analysis and reporting. A contractor such as CES will provide the sampler for Phase II and will provide training to MDNR staff in operation of the sampler.

6. Biographical Information of Key Personnel

Mr. Terry Rowles is Monitoring Unit Supervisor in the Air Pollution Control Program (APCP) and will be responsible for overall project performance. Dr. Jerry Downs, Environmental Specialist, will serve as Program technical lead. Dr. Downs has been extensively involved in the NATTS implementation in St. Louis, and in analysis of air toxics and speciation monitoring data for the APCP. Celeste Koon is the Air Quality Monitoring Section Supervisor for the Environmental Services Program (ESP). She will supervise operation of PM_{10} sampling and the continuous sampling instrument. Mr. Don Gourley is the Air Quality Assurance Unit Supervisor. He will supervise quality assurance audits of field monitoring. Dr. Jay Turner is Associate Professor of Chemical Engineering at Washington University. He will be responsible for assistance with study design, Phase I chemical analysis, and assistance with data analysis, particularly with source apportionment analysis. The Turner group has extensive experience in designing and operating field sampling networks, chemical analysis of environmental samples, and performing source apportionment analysis (including work currently funded by MDNR).

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PROJECT BUDGET

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MISSOURI DEPARTMENT OF NATURAL RESOURCES (MDNR)
AIR POLLUTION CONTROL PROGRAM (APCP)
COMMUNITY-SCALE AIR TOXICS AMBIENT MONITORING
DETAILED BUDGET BREAKDOWN

	ORG 3405 MDNR/APCP (Total Project cost)	ORG 3ESP MDNR/ESP LAB (Total Project cost)	1ST YEAR PHASE I COST	2ND YEAR PHASE II COST	CATEGORY TOTALS
PERSONAL SERVICE					
APCP					
Financial grant administration (weekly grant fin. monitoring)	$1,770		$885	$885	
Program Specialist - Project manager (ES IV 2 days/month + 40 hrs reporting)	$9,118		$4,559	$4,559	
Data review, reprot (ES III 4 days/month + 80 hrs reporting	$16,278		$8,139	$8,139	
ESP					
Laboratory Personel - Air Quality Monitoring Section.		$25,963	$8,953	$17,010	
Air Quality Assurance		$3,100	$800	$2,300	
Total Personal Service			**$23,336**	**$32,893**	**$56,229**
FRINGE BENEFITS @ 42.7% for SFY 2007					
APCP	$11,600		$5,800	$5,800	
ESP		$12,410	$4,165	$8,245	
Total Fringe			**$9,965**	**$14,045**	**$24,010**
TRAVEL					
Site visits @ 24 trips to St. Louis	$6,000		$3,000	$3,000	
EPAConference/Metting in June of 2008	$1,000		$0	$1,000	
Air Quality Monitoring Section- Setting up sites, monitoring		$2,750	$750	$2,000	
Air Quality Assurance - monitoring		$218	$81	$137	
Total Travel			**$3,831**	**$6,137**	**$9,968**
OTHER					
Misc. Expense (telephone conferences,utilities)	$2,000		$1,000	$1,000	
Misc. Expense (telephone conferences,rent, utilities)		$20,000	$10,000	$10,000	
Total Other			**$11,000**	**$11,000**	**$22,000**
CONTRACTUAL					
Cooperators - contracted personnel for sample collection		$11,000	$6,000	$5,000	
Total Contractual			**$6,000**	**$5,000**	**$11,000**
SUPPLIES					
PM 10 brushless motor & filters, filters, x-ray tube,QA film strips		$13,278	$3,878	$9,400	
Total Supplies			**$3,878**	**$9,400**	**$13,278**
EQUIPMENT *					
CES Series 600 XACT Ambient Multi-Metals Monitor		$167,500	$0	$167,500	
Shelter		$25,000	$0	$25,000	
Total Equipment			**$0**	**$192,500**	**$192,500**
Total Direct Cost	**$47,766**	**$281,219**	**$58,010**	**$270,975**	**$328,985**
PROGRAM SPECIFIC DISTRIBUTION (PSD)					
Washington University	$117,778		$66,733	$51,045	
Total PSD					$117,778
APCP'S INDIRECT @ 22.55% FOR SFY 2007	$10,771				
ESP'S INDIRECT @ 38.67% FOR SFY 2007		$34,308	$18,663	$26,416	
Total Indirect					$45,079
TOTAL PROJECT COST	**$176,315**	**$315,527**	**$143,406**	**$348,436**	**$491,842**

*Note: Plan for future use of equipment is discussed on page 7 of this proposal.

ENVIRONMENTAL RESULTS PAST PERFORMANCE

Under the Performance Partnership Grant, MDNR receives Section 105 funding to operate a network of criteria pollutant monitors that report data to the EPA Air Quality System (AQS). All activities under workplans that are developed in concert with EPA Region 7 are a high priority for completion, with semi-annual reporting on progress. Items not completed or only partially completed rarely occur, but are documented in a final report to be considered for ultimate disposition. Each year, MDNR sends the SLAMS data certification letter to EPA Region 7 and OAQPS, with supporting documentation from AQS, to verify that the network was operated in accordance with 40 CFR 53 and 58 regulations, and report on any extreme episodes. MDNR also receives Section 103 grant funds from EPA to operate a network of federal reference method (FRM), continuous, and speciation $PM_{2.5}$ samplers. Data from these samplers is validated by MDNR and then uploaded to AQS. Compliance with the $PM_{2.5}$ National Ambient Air Quality Standard is monitored annually. Additional $PM_{2.5}$ speciation and continuous $PM_{2.5}$ monitoring has been a part of this sampling, with data also reported to AQS. Lastly, MDNR has received Section 103 funds from EPA, through a series of grants and amendments, for the St. Louis Community Air Project (CAP), described in the introduction to this proposal, which included air toxics monitoring at multiple sites in St. Louis. As the project evolved, it included operation of the Blair Street Station in St. Louis as a NATTS site and also included evaluation of a continuous formaldehyde analyzer and trace level carbon monoxide analyzer. Progress has been reported to EPA by frequent informal communication and in periodic progress reports. Final Reports of the results and conclusions have been submitted annually with data uploading to AQS.

PROGRAMMATIC CAPABILITY

Under the Performance Partnership Grant, criteria pollutant monitoring data has been submitted since the 1970's. Completion of workplan items are a high priority, and we are often in contact with Region 7 regarding management and operation of the sampling network. Staff training and attendance at meetings in which key monitoring issues have been a topic have been maintained. MDNR's $PM_{2.5}$ monitoring network has operated successfully since its inception in 1999. The network has been modified as needed to adapt to new regulations, such as the recent lowering of the 24-hour standard, and new technology, such as continuous and speciation sampling methods. Beyond this, $PM_{2.5}$ speciation and continuous data have been invaluable in preparing the State Implementation Plan for the St. Louis nonattainment area. Our ability to maintain this monitoring effectively has allowed us to improve attainment demonstration model performance and more clearly apportion source influences. We are confident that this work will provide a greatly improved Plan. Data completeness, a measure of network reliability, has always been very high, over 90%. Quarterly reporting commitments and the annual data certification have never been late.

Data completeness has also been high for CAP and NATTS monitoring. Results have been documented in several technical reports, and NATTS data have been included in annual UATMP reports. CAP results were a significant part of the efforts of the local Partnership Committee of government, business, and residents to improve St. Louis air quality.