Definitions

ANSI – American National Standards Insitute
ASQC – American Society for Quality Control
ASTM - American Society for Testing and Materials
CFR – Code of Federal Regulations
GIS – Geographic Information System
NIOSH – National Institute for Occupational Safety and Health
QA – Quality Assurance
QA/R-2 – EPA Quality Assurance Document
QAMP – Quality Assurance Management Plan
QAO – Tribal Quality Assurance Officer
QAPP – Quality Assurance Project Plan
QC – Quality Control
RFP – Request for Proposal
RQAO – Regional Quality Assurance Officer
SOP- Standard Operating Procedure
SOW – Statement of Work or Scope of Work
SRMT – St. Regis Mohawk Tribe
USEPA or EPA – United States Environmental Protection Agency

Introduction

The St. Regis Mohawk Tribe (SRMT), Environment Division (Division) has established a Quality Assurance Management Plan (QAMP) based on, EPA REQUIREMENTS FOR QUALITY MANAGEMENT PLANS EPA QA/R-2, United States Environmental Protection Agency, FINAL MARCH 2001.

The Division's QAMP has been designed to incorporate and reflect the U.S. Environmental Protection Agency (EPA) Quality Management Plan guidance for documenting, plans, implementation, and assessment of the effectiveness of its quality assurance and quality control operations that are applied to its environmental programs.

It also is the desire of the Division to incorporate QAMP strategies for achieving credible data while at the same time developing a system that is effective and ensures the proper stewardship of resources it receives for conducting environmental work. The QAMP is also designed to ensure that all data and information collected are of the needed and expected quality for their intended use.

The QAMP provides a description of the processes that will be utilized by the Division for ensuring that all data collected by the Tribe provides the level of confidence required for each and every environmental program or project, ultimately affecting the decisions that will be made by the Division and the Tribe. The QAMP describes the policies and procedures for ensuring that work processes, products, or services satisfy stated expectations or specifications.

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"Characterization of Benzene and Other Air Toxics in Akwesasne"

RFA NO: OAR-EMAD-05-16

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Funding Requested: $348,197.00

The Winds: Owera' shon: a

Let us give thanks to the winds of the earth. From the four directions they come, carrying the rains upon their back, and bringing change to the weather and the seasons. They deliver our words, and can be gentle as a whisper, or have the power of a hurricane. The winds fill us, and connect us to all life, and are the breath of the ancestors of life. The winds are the sacred breath of the Creator. Let us acknowledge the winds. So be it in your mind. Now our minds are as one.

BACKGROUND

Akwesasne, in the early years prior to being introduced to industrialization, was wealthy in regards to natural resources such as land for vegetation and livestock, clean rivers and streams for aquatic life and clean air for our people and wildlife to breathe. This way of life no longer exists since the settling of three major industrial plants, General Motors Central Foundry and two Alcoa Aluminum smelters.

The land that is in the St. Lawrence River Valley has greatly diminished over time with these industrial plants due to their emissions of pollution into the air. Inversions help these pollutants settle from the air onto the ground and absorb into the soil, which then leach into our water veins underground finding its way into the main river systems.

Detrimental effects are seen in each category by the path the pollutants follow through the air, soil, and water. These effects are; inhalation of dangerous vapors in the air, ingestion of dangerous compounds from eating locally organically grown vegetables and livestock from Akwesasne, and consumption of fish and other aquatic species from the rivers and streams in Akwesasne.

Almost everything affects the air: paint and solvents evaporate; air conditioners release Freon (ozone depleting substances); cars emit combustion by-products (smog) that are released into the environment; power plants supplying electricity and manufacturing plants making products release millions of tons of pollutants into the air each year.

The Akwesasne community is located in northern New York, 10 miles east of Massena, NY (Figure 1). It is situated in the northwestern most corner of Franklin County, bordered by St. Lawrence County. It is also divided by the international boundary of the United States and Canada. Approximately 7,200 Mohawks reside on the US portion of the Reserve with a total population nearing 15,000 overall.

The Akwesasne community (US portion) consists of approximately 14,600 acres, primarily unused agricultural land and wetlands. There has been a decline in agricultural activities over the years due to the negative influence of industrial emissions and pollution. The rivers had also previously provided a means of income through guide fishing, and fish marketing. Since then, industrial pollution has been responsible for the contamination of the fish, to the point that government warnings have been limiting the consumption of fish.

Project Description

It is the policy of the St. Regis Mohawk Tribe to maintain a reasonable degree of purity of Tribal Air resources, which shall be consistent with the public health and welfare and the public enjoyment. The industrial development of the reservation while protecting the flora and fauna, physical property and other natural resources, require the use of all available practical and reasonable methods to prevent and manage air pollution on the reservation.

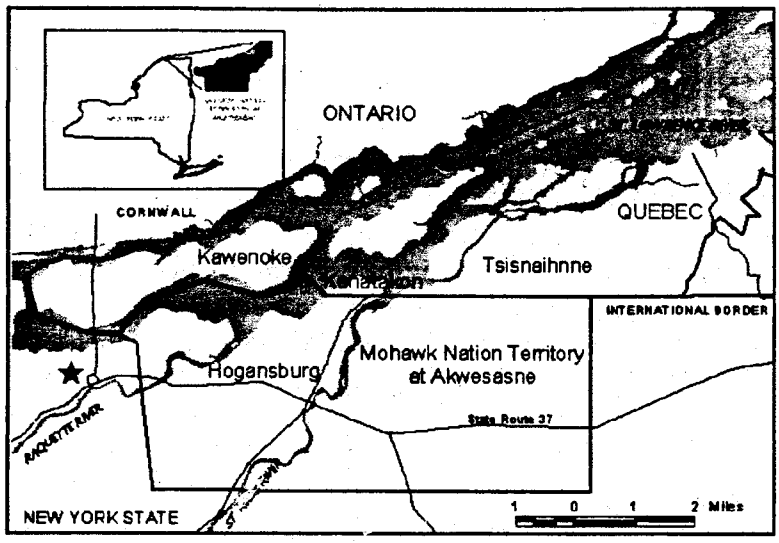

Figure 1. Map of Northern New York and Canada showing the location of the Mohawk Nation Territory at Akwesasne. Star designates the location of the ALCOA St. Lawrence Reduction Plant.

The St. Regis Mohawk Tribe's (SRMT) Air Quality Program has been in existence for 11 years. Over the years, the Program has expanded its capabilities through section 103 grants to include monitoring for criteria pollutants, indoor air education, acid rain and most recent, the development of a comprehensive Tribal Implementation Plan (TIP) for air quality. This plan outlines how the tribe plans to attain or maintain the air quality within its exterior boundaries. It is a "living document" that will be updated as new information or technology becomes available.

Immediately to the west of the border of the reservation is ALCOA's St. Lawrence Reduction Plant (Latitude: 44° 58' 55 N", Longitude: 74° 45' 08" W). According to their "Notification of Continuous Release under CERCLA §103(f)," this facility releases 29,140 pounds per year of benzene. Given the prevalence of westerly and northwesterly winds, these emissions are likely to be transported to Akwesasne on many days. Benzene is also emitted by motor vehicles and through volatilization losses from vehicle filling operations. Over the past several years Akwesasne has built up to over 15 gas stations. Exposure to benzene can also occur with the reduction in people's homes. Gasoline agricultural activities and compromised natural resources, in order to improve the economy of Akwesasne, development materialized in the way of gas stations. Over the past several years Akwesasne has built up to over 15 gas stations... There are a large number of gasoline stations. However, motor vehicle fuel also contains ethyl benzene, toluene, and xylenes. Gasoline is volatilized from vehicles in enclosed garages. There where there can also be stored gasoline for small engine operations (lawn mowers, chain saws, all terrain vehicles (ATV), and snowmobiles).

Long term exposure to benzene has been shown to cause acute myelogenous leukemia. Workers are exposed to significant amounts of benzene when working with petroleum products. Most workers come into contact with benzene through inhalation and to a much lesser extent by absorbing it through their skin when working with gasoline or solvents. Community exposure to benzene from gasoline spills or fueling stations has been documented in numerous cases.

As a specific example, the Tranguch Fuel Spill was estimated to involve the leakage of 50,000-900,000 gallons of gasoline from underground storage tanks in Hazle Township and Hazleton, Pennsylvania. As a result, it is believed that residents within the remediation area were chronically exposed to low levels of benzene since at least 1990. A total of 663 individuals representing 275 households were studied. The age-adjusted standard incidence ratios (SIRs) for the Hazle Township/Hazleton affected area was 0.82 (95% CI: 0.64-1.18) for all-site cancer and was 4.12 (95%CI: 1.12-10.55) for leukemia. These results suggest a possible association

between chronic low-level benzene exposure and increased risk for leukemia in the residents living near gasoline spills or fueling stations. (Patel 2004)

The air quality program proposes to asses the impact of benzene and other air toxics on the Akwesasne Community in conjunction with the Center for Air Resources Engineering and Science at Clarkson University. Under this project the air quality program will: a) Use the data collected to support any health effect assessments from the area,; b) Evaluate air quality models that in turn can be used for exposure assessments,; c) Develop a baseline reference frame of air quality concentrations that support estimates of community exposure and provide the basis for the longer term measuring of progress of a planned emissions strategy program,; d) characterize pollutants that are not ubiquitous, yet present local or regional concern, ; and e) Delineate local scale HAP concentration gradients that are driven by factors such as proximity to, and influence by, sources and other factors unique to our particular community.

The Center for Air Resources Engineering and Science at Clarkson University will be partnering with the Tribe for support of instrumentation for the monitoring and sample analysis and the expertise in data analysis and modeling of this project. The Tribe's Air Quality Program will be responsible for monitoring, sample/quality assurance project plans, and recruitment of individuals to participate as well as reports and budget for grant.

Project Summary

Akwesasne is located along a major state highway, state route 37, which runs directly through the territory. State Route 37 is the major artery for the North Country connecting major ports of entry to Canada as well as connecting cities and towns to the shipping industry and is heavily used by the trucking industry. The Akwesasne Mohawk Casino and other facilities attract a number of additional people to the territory and increase the volume of traffic and gasoline use. Thus, the problem is to assess the impact of the ALCOA plant on benzene concentrations across the territory relative to the ambient and personal exposure from motor vehicles and other gasoline use.

Exposure Assessment

Experimental Methods

Ambient Sampling

The United States Environmental Protection Agency (EPA) procedures TO-14a and TO-15 were established as standardized methods to clean, prepare, sample and analyze low concentrations of VOCs from air using evacuated canisters. (Ref EPA TO-14, 15) (Ref) The

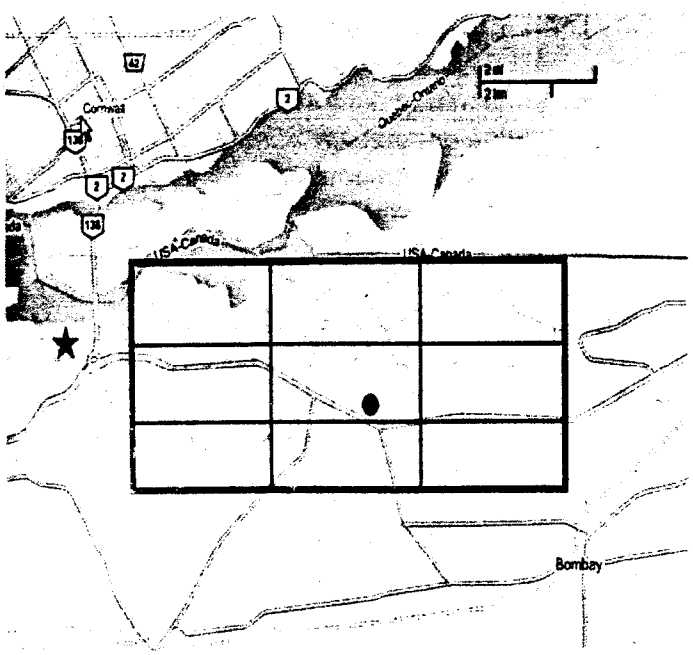

Figure 2. Map of the area showing a tentative grid array to define the locations of the measurements relative to major benzene sources. The star represents the reduction plant and the circle represents a casino.

TO-15 Method is well established for collection of low levels of volatile organic compounds at fixed sampling sites to assess the ambient exposure levels in a geographic location. The area of interest can be divided into subsections where there are expected to be gradients of concentration from west to east with increasing distance from the ALCOA aluminum plant and in either direction north or south from NY 37. We can thus use NY 37 as an approximate boundary of our sampling grids as shown in Figure 2. Sampling locations will be identified in each grid cell. The sampling plan will be to collect a 24- hour sample every sixth day for a year using an evacuated a summa canister at each sampling location. The ambient sampling program will be interactive with the developing modeling effort. As the modeling capability is developed as described below and results become available, supplemental. Supplemental sampling will be done to evaluate the modeled results. This iterative process to will allow us to characterize the exposure to benzene profile with in

Analysis

Analyses of the collected canisters will be accomplished using the TO-15 protocols and the facilities of the Center for Air Resources Engineering and Science at Clarkson University. A Thermo Electron Polaris Q GC/MS with a TRACE GC will be used to perform the analyses. It has positive and negative chemical ionization capability, a micro electron capture detector, and an ion trap mass spectrometer capable of MS/MS analyses. With this system we can perform the routine TO-15 protocol. Clarkson is in the process of obtaining the canister system and related analysis capability and will have it in place by the end of the present calendar year.

Source Sampling

To support the data analysis to permit the apportionment of benzene emitted by the point source relative to that emitted by mobile sources and related activities, source samples will be collected and analyzed. Gasoline samples will be collected periodically from multiple stations to ensure that we can account for the changing formulation of the fuel as a function of season. Headspace samples will be obtained and analyzed using comparable methods to obtain the BETX (benzene, ethyl benzene, toluene, and xylenes) components.

In addition, we will use Tedlar bags to collect a series of tailpipe samples from 10 vehicles in each season. These will include cold start and hot start as well as high speed idling as there is no available dynamometer. These samples will again be analyzed in a similar manner for their constituents with an emphasis on BETX.

Personal Sampling

A novel air sampler based on the use of a capillary flow controller connected to evacuated canisters, (300 mL, 1 L and 6 L) was designed by Rossner and coworkers (Rossner and Farant, 2004; Rossner et al., 2002; 2004). The capillary tube, used to control the flow of air, is a variation on a sharp-edge orifice flow controller. It essentially controls the velocity of the fluid (air) as a function of the properties of the fluid, tube diameter and length. Based on the geometry of the capillary, the airflow into the canisters is controlled at a very low flow rate, ~0.1 mL/min. This low sampling flow rate allows for the use of small volume canisters as personal samplers to collect benzene and other volatile organic compounds. This method allows for the collection of a whole air sampling to examine a multitude of compounds in indoor and outdoor air environments. Figure 3 presents a schematic diagram of the capillary canister. The personal capillary-canister can be used following the same TO-15 method, yet they are small enough to collect personal sample on individuals living in the Akwesasne community.

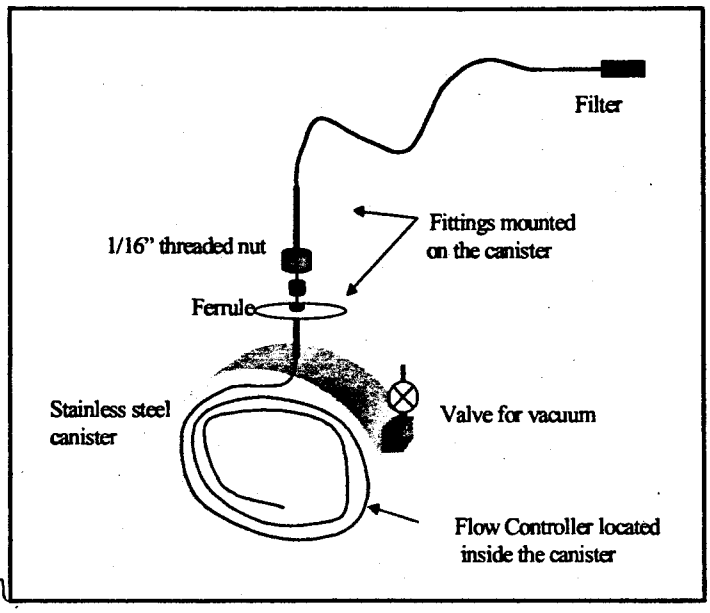

Figure 3. Capillary-Canister air sampling device. The canisters dimensions are a 300 mL stainless steel chamber 10 cm in diamter (4 inch), 2.5 cm wide (1 inch) weighing approximaetly 225 g (~8 oz).

Personal samples will be collected concurrently with the ambient on individuals working and living in Akwesasne. Volunteers will be asked to wear small 300 mL personal capillary-canisters to measure the benzene levels in the personal breathing zone of the individuals. The personal sample will be collected for 8-24 hours depending upon the individual's activity patterns. Replicate samples will be collected on the same individual to obtain a range of concentrations he or she is exposed to.

Data Analysis

Using the locally derived profiles for evaporative gasoline and tailpipe emissions to estimate the concentration of benzene present in the samples from evaporative gasoline losses and mobile source tailpipe emissions. The amount of benzene in excess of this amount will be attributed to the reduction plant. We can also use a broader spectrum of compounds measured in the source samples and EPA Chemical Mass Balance model to estimate the contributions of these two sources. Personnel at Clarkson have extensive experience in data analysis and will assist in building the capabilities for source apportionment so that it will be available for future studies.

Modeling the Impact of the Aluminum Plant

At the present time, there is limited modeling capability within the St. Regis Mohawk Tribe Environment Division and an important part of this project will be to implement this capability by modeling the benzene release from the reduction plant. MOBILE 5 and 6 have been used as part of their emissions estimations. Close interaction between the Environmental Division personnel with the Clarkson researchers will ensure that the modeling capability is developed and will be available within the Division to meet future modeling needs. A commercially available modeling system such as Breeze AEROMOD/ISC will be acquired. The measurements made in the exposure assessment can be used to evaluate several modeling approaches. Meteorological data is available from the nearby Massena airport (MSS) and the SRMT is currently installing a meteorological monitoring system on a 10 meter tower at the Environmental Division facilities. We will develop a modeling capability that will permit the

estimation of the dispersion of the three major industrial facilities to the west of the territory as well as line and area sources within the region. .

Specific Objectives

The specific objectives are:

1. Develop a QAPP and all of the associated SOPs
2. Adapt the TO-15 protocols to the specific analytical equipment at Clarkson
3. Identify the sampling locations and recruit the volunteers for the personal sampling
4. Obtain the computer models and perform modeling based on historical meteorological data
5. Conduct the monitoring program, obtain and analyze the source samples
6. Perform the preliminary data analyses and compare to the source modeling results
7. Perform integrated assessment including dispersion model and source apportionment results
8. Prepare final report and associated journal publications.

Project Estimated Time-Line

Goal: Characterize the concentration of Benzene and other air toxics within the territory of Akwesasne		
Tasks	Time Period (month) **Begin**	**End**
Objective 1: QAPP Development and Approval	1	4
Objective 2: Adapt TO-15 protocols to specific analytical systems	4	8
Objective 3: Finalize the sampling plan (locations and individuals	6	8
Objective 4: Obtain, install, and test dispersion models	6	10
Objective 5: Conduct the monitoring program including source samples.	8	20
Objective 6: Preliminary data analyses,	18	20
Objective 7: Complete the data analyses and modeling	20	23
Objective 8: Write final report and publications	22	24
Measurements for Evaluating Results: Approval of QAPP within 4 months; Demonstration of analytical capacity; Canister results for 9 samples every 6th day as well as 6-8 personal canister samples collected and analyzed monthly for one year. Capability to use the dispersion models to assess the impacts of the major industrial sources to the west of the territory.		
Indicators: BETX concentrations and long-term indicators for human health and environment such as reduced risk (quantitative).		
Efficiency: The results of this study will provide critical information to assess the importance of the industrial point source of benzene to the exposure across Akwesasne relative to motor vehicle and house specific sources. Such information will permit the development of effective and efficient plans for exposure reductions.		

Quality Assurance

The Environment Division of the St. Regis Mohawk Tribe is strongly committed to good science and EPA-approved quality assurance (QA) practices, such as the QA practices used by the New York State Department of Environmental Conservation. This commitment complements the US EPA's own emphasis given to a comprehensive and coordinated QA program.

The Quality Assurance Management Plan (QAMP) describes the Environment Division's QA program. Its objectives are to clearly delineate the Environment Division's QA policy and management structure that will be used to implement the QA strategy and the QA monitoring requirements necessary to document the reliability and validity of environmental data.

The Environment Division is committed to sufficient QA activities being conducted within the Division to insure that all environmental data generated and processed will be scientifically valid, of known precision and accuracy, of acceptable completeness, representativeness, and comparability and where appropriate, legally defensible.

The technical and administrative authority for all QA matters within the Environment Division will be assigned to the Quality Assurance Officer (QAO). The QAO will review, comment and concur on all Environment Division project plans and review data generated for interaction between EPA's Regional QA program, Environment Division programs, and other environmental monitoring agencies in QA related matters.

There shall be an effort to assure that all personnel performing tasks and functions related to data quality have the needed training and experience. Field personnel will be evaluated by their supervisors to determine training needs (Table 1.).

Table 1.

Function	Personnel	Contact Number
QA Officer	Les Benedict	518-358-5937
EPA QA Officer	Kai Tang	732-321-4364
Sampling Operations	Angela Benedict-Dunn	518-358-5937
Sampling QC	Alan Rossner	315 268-6470
Data Processing	Philip Hopke	315-268-3861
Data Validation	Philip Hopke	315-268-3861

The SRMT Environment Division has become one of the more advanced tribal environmental programs in the country due in part to the experience gained dealing with industrial pollution. The increase in communications speed and transfer capability will realize tremendous benefits to the entire community of Akwesasne and those partners working toward improving the quality of life for Native people.

Reports

The project will begin with the development of a Quality Assurance Project Plan (QAPP). Quarterly progress reports will be prepared in accordance with the grant requirements. The final report that will comprehensively describe all of the activities and results derived from this project. The report will contain information specifically related to the field sampling and analytical tasks of this work plan.

Project Management Is this relevant?

On September 19, 2000, May 25, 2001 and March 5, 2003 letters signed by the Regional Administrator for the US Environmental Protection Agency (US EPA) announced the approval for the St. Regis Mohawk Tribe's request for *Eligibility Determination for the St. Regis Mohawk Tribe for Treatment in the Same Manner as a State Under the Clean Air Act.* In the letter, the US EPA Region 2 Office of Regional Counsel (ORC) and the Division of Environmental Planning and Protection (DEPP) determined the SRMT met the criteria at 40 CFR 49.6;

(1)The applicant is an Indian Tribe recognized by the Secretary of the Interior;

(2)The Indian Tribe has a governing body carrying out substantial governmental duties and functions;

(3)The functions to be exercised by the Indian Tribe pertain to the management and protection of air resources within the exterior boundaries of the reservation or other areas within the Tribe's jurisdiction.

The Indian Tribe is reasonably expected to be capable, in the EPA Regional Administrator's judgment of carrying out the functions to be exercised in a manner consistent with the terms and purposes of the CAA and all applicable regulations.

Environmental samples collected by SRMT ED personnel include air, water, soils and biota for 68 various organic and inorganic contaminants and standard measurements. Quality Assurance Project Plans have been, or are in the process of being, developed and approved according to USEPA guidelines and requirements.

The project team consists of: (1) Angela Benedict-Dunn, SRMT; (2) Robert Phillips, SRMT; and (3) Student Intern, TBD. (34) Philip K. Hopke, Clarkson, (45) Alan Rossner, Clarkson, (56) 1.5 FTE graduate students. The team will hold regular project meetings either in person or via teleconference every two weeks throughout the project.

Biographical Information on Key Personnel

Angela Benedict-Dunn

Ms. Angela Benedict-Dunn, Air Quality Program Manger, SRMT will be the Project Manager. Ms. Benedict-Dunn will ensure that project objectives are achieved and reporting requirements are met. Additionally, Ms. Benedict-Dunn will be in charge of recruiting a student intern for the three years of the project.

Ms. Benedict-Dunn has worked for the SRMT ED for 10 years in various disciplines. Ms. Benedict-Dunn has been working for the air quality program for 6 years and the program manager for 4 years. Ms. Benedict-Dunn holds an Associate Degree in Math/Science from North Country Community College. Ms. Benedict-Dunn has managed EPA projects for the Tribe with total combined budgets of over $500,000.

Student Intern

A student intern will be recruited from the local area and will be registered as a full time student. The internship will be for 10 weeks in the summers 2006 and 2007 as well as the ability to put time in for the school breaks. The requirements of the student intern will be for environmental studies. Native preference applies in filling this position. Applicants not entitled to Native Preference will receive consideration without discrimination based on age, sex, disability or national origin.

Philip K. Hopke

Dr. Hopke, Bayard D. Clarkson Distinguished Professor and Director of the Center for Air Resources Engineering and Science at Clarkson University, has been actively studying air pollution for over 35 years. Although concentrating on particulate pollution, he has broad experience in monitoring, modeling, and data interpretation. He has developed and applied a variety of data analysis tools to air quality data and has published over 320 peer reviewed journal publications.

Alan Rossner

Dr. Rossner is an Assistant Professor of Environmental and Occupational Health and Director of the Environmental Science and Policy Program at Clarkson University. Dr. Rossner is a Certified Industrial Hygienist with an MS degree from the University of Washington and a PhD from McGill University. Dr. Rossner has extensive experience in exposure and risk assessment and monitoring for volatile organic compounds in air. His PhD work focused on the development and application of an improved personal canister system for VOC sampling and analysis.

Graduate Students

A graduate student will be recruited for the full period of the grant and a second will be hired to assist during the year of field studies. These students can be in a variety of degree programs including Chemical Engineering, Chemistry, Civil and Environmental Engineering and Environmental Engineering and Science. A special effort will be made to recruit Native Americans for these positions.

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