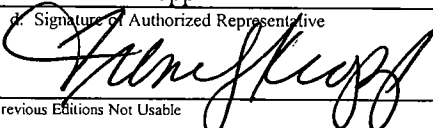


**APPLICATION FOR
FEDERAL ASSISTANCE**

1. TYPE OF SUBMISSION Application <input type="checkbox"/> Construction <input checked="" type="checkbox"/> Non-Construction		Preapplication <input type="checkbox"/> Construction <input type="checkbox"/> Non-Construction	2. DATE SUBMITTED	Applicant Identifier
			3. DATE RECEIVED BY STATE	State Application Identifier
			4. DATE RECEIVED BY FEDERAL AGENCY	Federal Identifier
5. APPLICANT INFORMATION				
Legal Name: NJ Department of Environmental Protection			Organizational Unit: Division of Science Research and Technology	
Address (give city, county, state, and zip code): Department of Environmental Protection PO-420 Trenton, NJ 08625			Name and telephone number of the person to be contacted on matters involving this application (give area code) Linda J. Bonanno, Ph.D., (609) 984-9480	
6. EMPLOYER IDENTIFICATION (EIN): / DUNS# 21-6000928 / 60-741-5197			7. TYPE OF APPLICANT: (enter appropriate letter here) <u>A</u> A. State H. Independent School District B. County I. State Controlled Institution of Higher Learning C. Municipal J. Private University D. Township K. Indian Tribe E. Interstate L. Individual F. Intermunicipal M. Profit Organization G. Special District N. Other (Specify): _____	
8. TYPE OF APPLICATION: <input checked="" type="checkbox"/> New <input type="checkbox"/> Continuation <input type="checkbox"/> Revision : If Revision, enter appropriate letter(s) in box(es): A. Increase Award B. Decrease Award C. Increase Duration D. Decrease Duration Other Specify: _____				
10. CATALOG OF FEDERAL DOMESTIC ASSISTANCE NUMBER: <u>66 . 034</u> TITLE: Surveys, Studies, Investigations			9. NAME OF FEDERAL AGENCY: USEPA	
12. AREAS AFFECTED BY PROJECT (cities, counties, states, etc.): State			DESCRIPTIVE TITLE OF APPLICANT'S PROJECT: Development and Optimization of a Sampling and Analytical Method to Measure Hexavalent Chromium in Ambient Air	
13. PROPOSED PROJECT:		14. CONGRESSIONAL DISTRICT OF:		
Start Date 10/5/05	End Date 9/7/05	a. Applicant: 12	b. Project	
15. Estimated Funding:		16. IS APPLICATION SUBJECT TO REVIEW BY STATE EXECUTIVE ORDER 12372 PROCESS? a. YES. THIS PREAPPLICATION/APPLICATION WAS MADE AVAILABLE TO THE STATE EXECUTIVE ORDER 12372 PROCESSES FOR REVIEW ON DATE _____ b. NO. <input type="checkbox"/> PROGRAM IS NOT COVERED BY E.O. 12372 <input type="checkbox"/> OR PROGRAM HAS NOT BEEN SELECTED BY STATE FOR REVIEW		
a. Federal	\$174,349.00			
b. Applicant				
c. State	\$64,108.00			
d. Local				
e. Other				
f. Program Income				
g. TOTAL	\$238,457.00	17. IS THE APPLICANT DELINQUENT ON ANY FEDERAL DEBT? <input type="checkbox"/> Yes If "Yes" attach an explanation. <input checked="" type="checkbox"/> No		
18. TO THE BEST OF MY KNOWLEDGE AND BELIEF. ALL DATA IN THIS APPLICATION/PREAPPLICATION ARE TRUE AND CORRECT, THE DOCUMENT HAS BEEN DULY AUTHORIZED BY THE GOVERNING BODY OF THE APPLICANT AND THE APPLICANT WILL COMPLY WITH THE ATTACHED ASSURANCES IF THE ASSISTANCE IS AWARDED.				
a. Typed Name of Authorized Representative Irene S. Kropp		b. Title: Assistant Commissioner		c. Telephone Number (609) 292-2916
d. Signature of Authorized Representative 				e. Date Signed 8/17/05

Previous Editions Not Usable

2. Narrative Workplan

- a. Project Title:** Development and Optimization of a Sampling and Analytical Method to Measure Hexavalent Chromium in Ambient Air
- b. Category:** Methods Development
- c. Applicant Information:**
- Organization: New Jersey Department of Environmental Protection
Address: Division of Science, Research and Technology
PO Box 409
Trenton, NJ 08625-0409
- Contact Person: Linda J. Bonanno, Ph.D.
Phone: (609) 984-9480
Fax: (609) 292-7340
Email Address: linda.bonanno@dep.state.nj.us
- d. Funding Requested:** \$174,349
- e. Total Project Cost:** \$238,457 (includes \$19,108 for in-kind salaries from NJDEP, \$25,000 for personnel and chemicals from UCAMPP, \$20,000 for personnel and instrumentation time from EOHSI, NIEHS analytical center).
- f. Project Period:** October 2005 through September 2007
- g. Project Description:**

1. Detailed Project Summary:

The overall goal of this proposed study is to develop a reliable, sensitive sampling and analytical method to measure hexavalent chromium [Cr(VI)] in ambient air. We discovered during our pilot work on the Urban Community Air Toxics Monitoring Project, Paterson City, NJ (UCAMPP), that there are many sampling and analytical artifacts which can influence the measured concentration of Cr(VI) in ambient air. The main objectives of this study are to: 1) optimize the Ion Chromatography-Inductively Coupled Plasma Mass Spectrometry (IC/ICPMS) method for Cr(VI) analysis, e.g., lower the detection limit to the one in a million risk level i.e., 0.083 ng/m³; 2) characterize sampling and analytical artifacts that can impact the measured concentration of Cr(VI) in ambient air, e.g., stability of Cr(VI) during sampling, storage and extraction; 3) characterize the effect of environmental conditions on Cr(VI) stability during sampling, e.g., aerosol type and composition, pH, relative humidity (RH), temperature (T), ozone (O₃), sulfur dioxide (SO₂) and nitrogen dioxide (NO₂) in our Controlled Environment Facility (CEF), which is a stainless steel chamber designed for controlled human exposure studies at the Environmental and Occupational Health Sciences Institute (EOHSI); and 4) test our method under various real world environmental conditions. A secondary objective is to develop a method that can quantitatively determine total and water soluble Cr(VI) in ambient air particles. The results obtained from the proposed study will enrich the United States Environmental Protection Agency (USEPA) Air Monitoring method database, and contribute to the national and local ambient air monitoring, exposure and risk assessment for Cr(VI).

Previous work has found that Cr(VI) is associated with fine particles (Kimbrough, 1999). The Cr(VI) measurement method includes: collecting PM_{2.5} on a filter matrix, extracting the filter in a certain pH solution (to be determined by this study) by ultrasonification, and analyzing the extract for Cr(VI), both total and soluble forms, and trivalent chromium [Cr(III)] by Ion Chromatography-Inductively Coupled Plasma Mass Spectrometry (IC/ICPMS). The New Jersey Department of Environmental Protection (NJDEP) and EOHSI partnership on this proposed project has three major benefits: 1) the expertise of the EOHSI team on Cr(VI) speciation; 2) having a CEF to test the developed method under various conditions in a controlled setting; and 3) New Jersey has both point sources of Cr(VI) and chromate laden waste sites where we can field test this method. The specific aims of this work are detailed below.

Specific Aim 1: Optimize an Ion Chromatography-Inductively Coupled Plasma Mass Spectrometry (IC/ICPMS) Method for Cr(VI) Analysis and Lower the Detection Limit to 0.083 ng/m³.

Cr(VI) is recognized as a pulmonary carcinogen by the International Agency for Research on Cancer and the US Toxicology Program (Barceloux, 1999). Cr(VI) compounds have been enlisted as one of the 188 hazardous air pollutants (HAPs) in the 1990 Clean Air Act, as one of the 33 urban air toxics HAPs and one of the 18 core HAPs by the USEPA (USPEA, 2004). The accurate determination and appropriate detection limit for risk assessment of Cr(VI) is critical to remedial actions and the health and safety of the public. Current Cr(VI) sampling and analytical methods, documented in the EPA Air Method Database, include the National Institute for

Occupational Safety and Health (NIOSH) Method 7600 and Method 7604. These methods were designed for occupational exposure monitoring, which may not be suitable for ambient air monitoring. The detection limits of NIOSH Method 7600 and 7604 are at $\mu\text{g}/\text{m}^3$ to mg/m^3 level (operating range is $1 \mu\text{g}/\text{m}^3$ to $5 \text{mg}/\text{m}^3$ for NIOSH Method 7600, and $10 \mu\text{g}/\text{m}^3$ to $4 \text{mg}/\text{m}^3$ for NIOSH Method 7604), which are not sensitive enough to measure pg/m^3 – ng/m^3 level of ambient airborne Cr(VI) due to their relatively insensitive detection methods (visible absorption spectrophotometry for Method 7600 and conductivity detection for Method 7604).

ICPMS is a newly developed analytical method with the advantage of high sensitivity and low interferences. The ICPMS method is significantly more sensitive than colorimetric quantification protocols (Buckley, 2003). It can also provide isotope information using EPA Method 6800, Elemental and Speciated Isotope Dilution Mass Spectrometry (EIDMS and SIDMS methods). Although this method is listed in the test methods for soil and solid wastes, EPA Method 6800 can be regarded as a universal method for metal measurements in aerosols, soils and solid waste extraction solutions. The principal behind Method 6800 is to use enriched stable isotopes to label each chemical species in a spike. The spike is used to monitor the change each species undergoes during these processes. Specifically, if a spike is created where all of the Cr(VI) is ^{53}Cr , then any $^{53}\text{Cr}(\text{III})$ should be proportional to the amount of Cr that was reduced after the spike was added. Conversely if the spike contains $^{50}\text{Cr}(\text{III})$ then any $^{50}\text{Cr}(\text{VI})$ discovered during the analysis should represent oxidation of the Cr(III) already present in the sample.

Being able to monitor these changes requires both the means to separate the two Cr species from one another as well as the capability to measure the isotope ratios of each species. The separation technique we propose for this research is ion chromatography and the isotopes will be measured by ICPMS. We have also used ion chromatography coupled to ICPMS to measure chromium in dust samples from Jersey City (Freeman et al. 2000). Dr. Buckley's group (from EOHHSI) has used these speciation techniques to measure chromium species in matrices including synthetic gastric juice, soils, water, foods and mineral supplements (Buckley et al. 2005). Dr. Buckley's group is currently funded to demonstrate the efficacy of method 6800 to monitor for chromium species inter-conversion in some NJ waste soils (NJDEP contract #SR05-029). In this proposed work, Cr(VI) and Cr(III) will be separated by IC and quantified by ICPMS. Laboratory experiments will be conducted to optimize the analytical conditions to achieve the best separation of Cr(VI) and Cr(III), as well as resolution from other possible contaminants. The separation of Cr(VI) and Cr(III) will enhance our ability to determine Cr(VI) and the inter-conversion between Cr(VI) and Cr(III). The analytical conditions for IC will be tested for different column types (anion vs. cation exchange column) and eluent solutions (HNO_3 , NaOH or Na_2SO_4). This work will improve analytical sensitivity, minimize the analytical interferences, and validate USEPA Method 6800.

This work will be completed during the 2nd and 3rd quarter of year 1 of the project period.

Specific Aim 2: Characterize Sampling and Analytical Artifacts that can Impact the Measured Concentration of Cr(VI) in Ambient Air.

A. Stability During Sampling:

A mutual conversion, i.e., a sampling artifact, can occur between Cr(VI) and Cr(III) during the sampling process. However, this sampling artifact has not been fully investigated. We will use three of the four isotopes of chromium for this work: ^{50}Cr , ^{52}Cr , and ^{53}Cr , which have a natural abundance of 4.31%, 83.76%, and 9.55% respectively. Isotope enriched standard solutions will be used to quantify the inter-conversion between Cr(VI) and Cr(III) during sampling. A ^{50}Cr enriched Cr(III) standard solution and a ^{53}Cr enriched Cr(VI) standard solution will be spiked simultaneously on each filter type. Since chromium can only convert between different oxidation states (III and VI) and not different isotopes (^{50}Cr , ^{52}Cr , and ^{53}Cr) during sampling, the artificial add-in isotope enriched standard spikes will enable us to quantify the inter-conversion of Cr(VI) and Cr(III) when Cr(VI) and Cr(III) are simultaneously measured and monitored at ^{50}Cr , ^{52}Cr and ^{53}Cr during ICPMS analysis.

Sampling artifacts will be evaluated under different environmental conditions (i.e., aerosol type and composition, pH, T, RH, O_3 , SO_2 and NO_2) in our CEF. O_3 , SO_2 and NO_2 were selected because previous research suggested that O_3 can oxidize Cr(III) to Cr(VI), SO_2 can reduce Cr(VI) to Cr(III), and SO_2 and NO_2 may alter the pH of the aerosols and therefore promote the conversion of Cr(VI) to Cr(III) during sampling process (Seigneur, 1995).

The stability of Cr(VI) will be tested on different types of filters as well as on different types of particles. The filter types include cellulosic filters, Polyvinyl Chloride (PVC) filters, Quartz Fiber Filters (QFF), and Teflon filters. These filters are commonly used for Cr(VI) measurement. The particle types include primary diesel

particles, secondary aerosols, and soil particles. While testing, air containing O₃, NO₂, or SO₂, will be pulled through a blank filter spiked with both Cr(III) and Cr(VI) isotope and a filter with pre-collected particles with spiked Cr(III) and Cr(VI) isotopes for 24 hours to examine the loss of Cr(VI) during sampling process. Primary diesel emission particles and secondary aerosols will be generated in the CEF. Standard reference material for soil will be used for these tests.

The high concentrations of O₃ (120 ppb), SO₂ (140 ppb), and NO₂ (53 ppb) that are often found in ambient air will be tested first (Cooper, 1994). If the impact of these compounds on the Cr(VI) stability is significant, further tests at lower concentrations, e.g., EPA ambient criteria levels, will be done. The range of temperature to be tested is from 10° to 35°C and RH will be from 10 to 95%. Field testing described in Aim 3 during winter will allow us to test at even lower temperatures.

We will also test the stability of Cr(VI) during sampling using a pre-treated filter. Given the properties of PVC, QFF and Teflon filters, only cellulose filter will be tested for this condition. The filter will be pre-treated with basic solutions, such as NaHCO₃, NH₄OH and NaOH, as suggested by previous studies as well as our ongoing research (Boiano, 2000; Vitale, 1997; Sheehan, 1992). The results from the pretreated cellulose filters will be compared to the non-pretreated cellulose filters, and whether the pretreatment can prevent Cr(VI) from converting will be evaluated.

B. Investigate the Stability of Cr(VI) after Sampling:

The inter-conversion between Cr(III) and Cr(VI) can also occur after sampling, e.g., during sample storage and extraction. Isotope enriched Cr(III) and Cr(VI) will be spiked on filters (both blank filters and filters with pre-collected particles). Filters will be extracted at designated time intervals (e.g., 0, 1, 2, 7, 14, 30 days) and analyzed immediately after extraction. The after-sampling stability of Cr(VI) on a filter will be evaluated by monitoring Cr(VI) and Cr(III) simultaneously at ⁵⁰Cr, ⁵²Cr and ⁵³Cr during ICPMS analysis.

C. Investigate the Effect of pH on Cr(VI) Stability During Extraction:

Previous studies show that pH value is a key factor affecting the Cr(VI) stability during sampling and extraction (Li, 2002; Boiano, 2000; Vitale, 1997; Sheehan, 1992). Cr(VI) is expected to be stable at weak basic conditions. Basic solutions, such as NaHCO₃, Na₂CO₃ and phosphate buffers, have been used to extract filter samples for Cr(VI) analysis in previous studies (Boiano, 2000; Vitale, 1997). However, Cr(III) tended to convert to Cr(VI) during the basic condition based on our preliminary tests. Second, some basic buffer solutions can interfere with Cr(VI) analysis using ICPMS. For example, ¹²C (carbon atom with the atomic weight of 12) in the NaHCO₃/Na₂CO₃ buffer can react with argon, the ICPMS auxiliary and nebulizer gas, to form ⁴⁰Ar¹²C ion pair, which will interfere with the detection of Cr(VI) monitored at atomic weight 52. In addition, our preliminary experiment during the UCAMPP study showed that Cr(III) tends to precipitate with the basic conditions and the conversion is not reversible. The formation of the Cr(III) precipitation limits our ability to measure Cr(III) and the inter-conversion between Cr(VI) and Cr(III) using the SIDMS method. However, both Cr(VI) and Cr(III) were observed stable at weak acidic conditions and no precipitation occurred. Therefore, buffers with different pH values from basic to acidic, including NaHCO₃/Na₂CO₃, NH₄OH, and K₂HPO₄/KH₂PO₄, HNO₃, and H₃BO₃, will be tested as extraction solvents in this study. After extraction, samples will be analyzed immediately, and the inter-conversion between Cr(VI) and Cr(III) will be quantified by measuring Cr(VI) and Cr(III) at ⁵⁰Cr, ⁵²Cr and ⁵³Cr simultaneously.

This work will be completed during the 3rd and 4th quarter of year 1 of the project period.

D. Improve Extraction Efficiency:

High extraction efficiency is required for Cr(VI) measurements due to its low concentration in the atmosphere. Extraction efficiency will be determined by measuring spiked Cr(VI) on particles collected on a filter using water as well as buffer solutions with different pHs, from acidic to basic. The duration of ultrasonification will be tested to obtain the highest extraction efficiency. The buffer solutions described above will be tested and the one that can stabilize Cr(VI) on filter medium and in sample extract, provide the highest extraction efficiency, and does not affect IC/ICPMS separation and quantification, will be selected for future filter preparation and sample processing.

This work will be completed during the 3rd and 4th quarter of year 1 of the project period.

Specific Aim 3: Field Evaluation of the Developed Method.

The developed method will be field-evaluated at a minimum of two locations having different aerosol composition, i.e., one dominated by mobile source emissions and one dominated by industrial sources. Given the concern of the catalytic property of As, Fe, V, and Mn, the effect of those elements on Cr(VI) sampling artifacts will be evaluated. Selected trace elements will be analyzed by ICPMS at EOHSI. New Jersey has a history of chromate contaminated waste sites and hosts a number of facilities which have the potential to emit Cr(IV), such as hard chrome electroplaters. We will select locations, which not only have different aerosol compositions, but are also located near sources where we would expect to measure Cr(VI). A minimum of 6 samples at each location will be collected, 3 on a selected winter day (low O₃ season) and 3 on a selected summer day (high O₃ season). Cr(VI) concentration, precision and recovery will be reported.

This work will be completed during the 4th quarter of year 1 and the 2nd quarter of year 2 of the project period.

In addition, PM₁₀ samples for Cr(VI) analysis are also being collected in Paterson City during the UCAMPP study, which will collect samples between October 2005 and September 2006. The cost of sample collection and analysis for UCAMPP has already been funded and will provide additional no-cost resources to this proposed study.

Secondary Objective: Exploratory Study of the Speciation of Cr(VI).

Airborne Cr(VI) is a general name for both soluble and insoluble forms of hexavalent chromium in the ambient air. The toxicity of soluble and insoluble Cr(VI) is expected to be different due to their different solubilities (Barceloux, 1999). Cr(VI) presents as K₂Cr₂O₇ (water soluble form) and PbCr₂O₇ (water insoluble form) in ambient air (Kimbrough, 1999). However, it is not clear whether measured Cr(VI) represents water soluble, insoluble or total Cr(VI) in ambient air. A previous study claimed both soluble and insoluble Cr(VI) were extracted at pH = 12 by NaOH solutions (James, 1995). Others claimed that soluble Cr(VI) was extracted by carbonate salts at pH = 8 (Boiano, 2000). NIOSH Method 9101 (Chromium, Hexavalent, in Settled Dust Samples) provides a practical guideline for soluble Cr(VI) extraction. However, those methods cannot be directly applied to our method development because they use different detection techniques.

In this proposed study standard Cr(VI) solutions (K₂Cr₂O₇) and insoluble powders (PbCr₂O₇ and BaCr₂O₇) will be spiked on a filter. The spiked filter will be extracted with the buffer solution that has been selected from Specific Aim 2. The insoluble fraction will be extracted subsequently with buffer solutions with different pH values. The extraction procedures and the recovery of both soluble and insoluble Cr(VI) will be determined and reported.

This work will be completed during the 4th quarter of year 1 and 1st quarter of year 2 of the project period.

Data Analysis:

During method development, at least three experiments will be performed under each condition, and the relative standard deviation (%RSD) between the three tests must be less than 15%.

Scatter plots and regression analyses (linear and nonlinear) will be performed on the IC/ICPMS condition optimization part. The response/recovery of Cr(VI) and Cr(III) will be plotted against different chromatography and ICPMS conditions. The condition corresponding to the highest response/recovery will be selected. The optimal Cr(VI) extraction efficiency will also be found this way.

During the investigation of the Cr(VI) sampling artifacts, descriptive analysis and regression analysis will be used to evaluate the Cr(VI) recovery verses different environmental conditions. Analysis of variance (ANOVA) will be performed to compare the Cr(VI) recovery on the different types of filters. A t-test will be conducted to evaluate the difference between pretreated cellulose filters and non-pretreated cellulose filters. The effect of pH values on the extraction efficiency will also be explored in this manner.

ANOVA will be performed to compare the stability of Cr(VI) under basic, neutral and acidic conditions after sampling. Kinetic curves will fit the degradation of Cr(VI) on filters or in solutions with different pH values. The degradation rate of Cr(VI) under each condition will be calculated based on the simulation.

During CEF and field evaluations, the recovery of Cr(VI) will be regressed on ambient O₃, SO₂, and NO₂ concentrations and other trace element concentrations. ANOVA will be performed to compare the recovery of Cr(VI) during high and low O₃ seasons. Basic statistics from field sampling, such as mean and standard deviation of Cr(VI) will also be calculated and reported.

This work will be completed during the 2nd quarter of year 1 and the 4th quarter year 2 of the project period.

2. Work Products:

A final report to USEPA will be submitted at the end of the project period. Standard Operating Procedures will be included in the final report. This work will be completed in the 4th quarter of year 2 of the project period. Articles will be submitted to peer reviewed journals for publication.

3. Benefits to the Public:

This proposed research will benefit the public by providing a reliable and sensitive method for measuring Cr(VI) in ambient air. It is important to have a reliable method, which can differentiate between Cr(VI) and Cr(III), because Cr(VI) is a potent human carcinogen, and Cr(III) is an essential trace element. Presently, USEPA has assigned 34% of total chromium as hexavalent chromium. This percentage may grossly under or overestimate the amount of Cr(VI) and therefore the risk associated with chromium. It is also expected that the toxicity of insoluble and soluble Cr(VI) is different (Barcelous, 1999).

4. Applicability of Project Outcomes:

The methods for accurately measuring concentrations of Cr(VI) in ambient air are important to the analytical, health, regulatory and industrial communities.

5. Tracking/ Measuring Plan to Achieve Environmental Outcomes (specified in Section 1):

The development of sensitive and reliable sampling and analytical methods which measure Cr(VI) in ambient air will assist state agencies and local communities to identify and profile sources of air toxics, help to characterize the extent of local-scale air toxics problems, and track air toxics risk reduction activities.

The proposed timeline is presented in Table 1:

Table 1. Proposed Timeline

<u>Objectives</u>	<u>Year 1</u>				<u>Year 2</u>			
	<u>Q1</u>	<u>Q2</u>	<u>Q3</u>	<u>Q4</u>	<u>Q1</u>	<u>Q2</u>	<u>Q3</u>	<u>Q4</u>
Contract Executed	√	√						
Order Supplies	√							
IC/ICPMS condition		√	√					
During-sampling stability			√	√				
After-sampling stability			√	√				
Extraction efficiency			√	√				
Cr(VI) speciation				√	√			
Field evaluation					√	√	√	
Data analysis		√	√	√	√	√	√	√
Final report								√
Publications								√

6. Evaluation of Project Success:

The most important evaluation of the project's success will be the ability to: 1) obtain the 0.083 $\eta\text{g}/\text{m}^3$ detection limit; 2) recover 80% of the known concentration; 3) achieve stability through sampling and analysis; and 4) characterize the impact of co-pollutants.

7. Roles of Project Applicant and Partners:

Linda J. Bonanno, Ph.D., NJDEP, will be the project manager for this proposed study. Her responsibilities include overall project management, identifying and coordinating sites for the field studies, overseeing study

design, quality assurance and progress by requiring quarterly reports from EOHSI, reviewing and editing the final report to USEPA and publications and coordinating efforts between this proposed study and UCAMPP.

Charlie Pietarinen, NJDEP, will consult on all aspects of the methods development with special emphasis on monitoring. Mr. Pietarinen's experience and contacts with other scientists in the monitoring and analytical fields is invaluable for gauging the progress of the proposed study, and communicating findings to other scientists investigating Cr(VI) method development, as well as to interested parties at organizations such as the USEPA and Northeast States for Coordinated Air Use Management (NESCAUM).

Zhuhua (Tina) Fan, Ph.D., EOHSI, will be the Principal Investigator for this project. She will take the overall responsibility for the project coordination and the successful execution of the project at EOHSI. She will work closely with Dr. Bonanno and other co-investigators for the study design and implementation. She will be responsible for evaluation of the quality of all collected data generated in the proposed study and be responsible for preparation of annual reports and publications.

Qingyu Meng, Ph.D., EOHSI, with the support from Drs. Fan and Buckley, will design and implement the lab and field tests, supervise graduate students on daily basis to conduct the field and lab experiments, conduct data analysis, and assist in preparation of annual report and publications.

Brian Buckley, Ph.D. EOHSI, will provide technical guidance for the study design and project execution, especially analytical method development, QA/QC plan, and assist in preparation of reports and publications.

8. Biographical Information of Key Personnel:

Linda J. Bonanno, Ph.D., is a Research Scientist with the Division of Science, Research and Technology of NJDEP. She earned a joint doctoral degree in Environmental Science and Public Health from Rutgers University and the University of Medicine and Dentistry of New Jersey. Dr. Bonanno has worked on sample analyses and data management for the National Human Exposure Assessment Survey (NHEXAS) study, field sampling for the Hudson County Chromium Study, supervised air sampling for the Particle Exposures of High-Risk Subpopulations study in NY, NY, and is the Principle Investigator for the Urban Community Air Toxics Monitoring Project, Paterson City, NJ (UCAMPP) and the Asthma Outreach and Education Initiative in Camden Waterfront South. She also has experience in monitoring indoor air contamination. Her present areas of research include air toxics, human health, cumulative risk assessment and data management/analyses.

Charlie Pietarinen is Chief of the Bureau of Air Monitoring (BAM) with the NJDEP. Mr. Pietarinen received a BS degree in Biology from Valparaiso University and has over 25 years experience in air pollution including air toxics monitoring. BAM's program includes routine monitoring for criteria pollutants, air toxics and acid deposition. BAM is responsible for data acquisition, quality assurance, data reporting, special purpose monitoring projects and the oversight of third party monitoring projects. BAM operates and maintains over 25 continuous air monitoring stations and over 20 particulate sampling locations. Under Mr. Pietarinen's direction, four comprehensive air toxics monitoring sites have been established. He has extensive knowledge of ambient air monitoring instrumentation and practices and is the NJDEP's principal liaison with the USEPA and other parties on air monitoring issues.

Zhuhua (Tina) Fan, Ph.D., is an Assistant Professor in the Department of Environmental and Occupational Medicine at the University of Medicine and Dentistry of New Jersey. Her expertise is in air pollution, method development for air sampling and analyses, exposure measurement and assessment, atmospheric chemistry, and health risk assessment. She has conducted research on the development of an analytical method to measure cations and anions in acid rain and underground water from an oil field by ion chromatography, development and evaluation of USEPA standard methods to measure organic Hazardous Air Pollutants from different sources, and development of sampling devices to measure personal exposures to PAHs and carbonyls. She has also conducted research to investigate community exposure to air toxics and potential health effects.

Qingyu Meng, Ph.D., is a Research Teaching Specialist in the Department of Environmental and Occupational Medicine at the University of Medicine and Dentistry of New Jersey. His expertise is in personal exposure to PM

and air toxics, exposure modeling, environmental statistics and environmental analytical chemistry. He developed sample digestion and ICPMS analysis protocols for trace elements during the Relationship of Indoor, Outdoor and Personal Air study. He is developing Cr(VI) measurement method for the UCAMPP study. He also participates in field air sampling for other ongoing projects.

Brian Buckley, Ph.D., is an Analytical Chemist and is the Executive Director of Laboratories at EOHSI. Currently he is specializing in spectroscopic, mass spectrometric and chromatographic methods development for analysis of environmental contaminants and their metabolites. His research group has specialized in synthetic biofluid extractions for estimating bioavailability and human health risks of heavy metals, ultra-trace metals quantification and metal speciation by chromatography coupled to plasma mass spectrometry. He currently has methods to speciate Hg, As, and Cr.

9. Additional information to Address Ranking Factors in Section V.

A. Background about Cr(VI) as one of the HAPs:

Chromium exists in the ambient air primarily in the trivalent and hexavalent states (Kimbrough, 1999). Cr(III) is considered to be essential to humans in trace concentrations. In contrast, the Cr(VI) is recognized as a pulmonary carcinogen by the International Agency for Research on Cancer and the US Toxicology Program (Barceloux, 1999). Occupational exposure to airborne Cr(VI) has been associated with an increased risk of lung and nasal cancer (Crump, 2003). Toxicological studies have found pathways through which airborne Cr(VI) sabotages normal body functions (Crump, 2003). As a result, Cr(VI) compounds have been enlisted as one of the 188 hazardous air pollutants (HAPs) in the 1990 Clean Air Act, as one of the 33 urban air toxics HAPs and one of the 18 core HAPs by the U.S. Environmental Protection Agency (USEPA, 2004).

Cr(VI) compounds have been clearly defined as one of the national cancer risk drivers in the Air Toxics Component of the National Ambient Air Monitoring Strategy and contribute significantly to the national cancer risk. Results generated from the National Air Toxics Assessment (NATA) show that more than 35,000,000 people have risk levels from Cr(VI) inhalation that are higher than the 1 in a million risk level, 3,600,000 people have higher than 10 in a million risk level, and 110,000 people have higher than 100 in a million risk level. NATA also discovered significant local risks for many communities nationwide. To identify the populations at risk and protect public health, a sensitive and reliable air sampling and analytical technique for Cr(VI) measurement is essential to measure Cr(VI) at or below its one in a million cancer risk threshold (0.083 ng/m³).

B. Current and Ongoing Measurement Methods for Cr(VI):

Current Cr(VI) sampling and analytical methods documented in the EPA Air Method Database include the National Institute for Occupational Safety and Health (NIOSH) Method 7600 and Method 7604. These methods were designed for occupational exposure monitoring, and are not suitable for ambient air monitoring. The specific limitations of current methods are discussed below.

First, current methods are not sensitive enough for monitoring of Cr(VI) in ambient air. Cr(VI) concentrations during occupational exposures could be hundreds and thousands of times higher than environmental levels. The detection limits of NIOSH Method 7600 and 7604 are at $\mu\text{g}/\text{m}^3$ to mg/m^3 levels (operating range is $1 \mu\text{g}/\text{m}^3$ to $5 \text{mg}/\text{m}^3$ for NIOSH Method 7600, and $10 \mu\text{g}/\text{m}^3$ to $4 \text{mg}/\text{m}^3$ for NIOSH Method 7604), and are not sensitive enough to measure pg/m^3 – ng/m^3 level of ambient airborne Cr(VI) due to their relatively insensitive detection methods (visible absorption spectrophotometry for Method 7600 and conductivity detection for Method 7604). Other methods are also available for occupational inhalation exposure measurement of Cr(VI), such as NIOSH Method 7605 (UV detection), NIOSH Method 7703 (visible spectrophotometry), Occupational Safety and Health Administration (OSHA) Method 215 (UV detection) and OSHA Method 103 (differential pulse polarography). The problem of insensitivity is also associated with these methods; therefore, they cannot be applied for Cr(VI) monitoring in ambient air.

Second, current sampling methods may not capture the sampling artifacts that may occur under different environmental sampling conditions. Research has shown that Cr(III) and Cr(VI) may interconvert during sampling and sample processing (storage and extraction) (Buckley, 2005; Li, 2002; Boiano, 2000; Vitale, 1997; Sheehan, 1992), which may bias Cr(VI) measurement. The degree of the inter-conversion is expected to be affected by the sampling duration, temperature, relative humidity, aerosol pH, and the concentration of ozone, SO₂, and NO₂. These parameters can be quite different between occupational settings and ambient conditions. For

example, the sampling duration for Cr(VI) occupational exposure measurement ranges from a couple of hours to ten hours, which is much shorter than the 24-hr ambient air monitoring time. Also, occupational exposures to Cr(VI) usually occur indoors, where T, RH, aerosol type and composition, pH, and the concentration of O₃, SO₂, and NO₂ can be quite different from outdoors. Therefore, sampling artifacts can be different between occupational exposure sampling and ambient air monitoring.

A few studies have explored the stability of Cr(VI) during sample storage and extraction (after-sampling stability) (Li, 2002; Sheehan, 1992); however, no studies have been conducted to evaluate the stability of Cr(VI) during 24 hour ambient air monitoring [the conversion of Cr(VI) to Cr(III) during sampling, or the sampling artifacts associated with conversion and stability of Cr(VI)]. Alkaline pre-treated filters were used to stabilize Cr(VI) during sampling in some studies, but, to our best knowledge, neither controlled experiments nor field evaluations have been conducted to date which evaluate the performance of those approaches (ERG, 2005; Sheehan, 1992). Therefore, the issue of Cr(VI) sampling artifact is still unknown.

Third, current Cr(VI) measurement methods cannot distinguish between soluble and insoluble Cr(VI), and the "concentration of Cr(VI)" has not been clearly defined. Cr(VI) exists in particulate matter in both soluble and insoluble forms (Kimbrough, 1999). K₂Cr₂O₇ is the major soluble form of Cr(VI) and the insoluble form of Cr(VI) is represented by PbCr₂O₇ and BaCr₂O₇ (Kimbrough, 1999). Airborne Cr(VI) is a general name for both soluble and insoluble forms of hexavalent chromium in ambient air. The toxicity of soluble and insoluble Cr(VI) is expected to be different due to their different solubilities (Barceloux, 1999). The solubility of Cr(VI) is expected to affect its toxicity (Barceloux, 1999) and therefore the risk of exposure to Cr(VI). It has been shown that soluble and insoluble Cr(VI) can be separated using basic extraction solutions at different pH values (Ashley, 2001; James, 1995). However, these findings have not been evaluated during Cr(VI) ambient air monitoring. The speciation of Cr(VI) will help EPA to conduct more accurate studies on Cr(VI) exposure and risk assessment and to refine criteria for Cr(VI) in ambient air.

A method, which is being developed by the Environmental Research Group (ERG), is reported sensitive enough to measure Cr(VI) as low as 0.029 ng/m³ using an IC/Colorimetry approach (ERG, 2005). However, the sampling artifact and speciation of Cr(VI) has not been investigated; Cr(III) cannot be measured by this method; and the impact of different ambient conditions, such as aerosol type and PH, O₃ concentration, has not been fully field-evaluated.

3. Detailed Budget:

Development and Optimization of a Sampling and Analytical Method to Measure Hexavalent Chromium in Ambient Air							
Personnel	Role	Appt.	Effort	Base	Year 01	Year 02	Total
Z. Fan, Ph.D.	PI	12	10%	\$73,973	\$7,397	\$7,619	\$15,016
Q. Meng, Ph.D.	co-I	12	30%	\$43,800	\$13,140	\$13,534	\$26,674
To Be Named	Graduate Student	12	100%	\$23,000	\$23,000	\$23,690	\$46,690
Total Personnel:					\$43,537	\$44,843	\$88,380
Fringe:							
Faculty and Staff @34.25% Year 01; increased by 1% in Year 02					\$7,034	\$7,456	\$14,490
Graduate Student @ 7.65%					\$1,760	\$1,812	\$3,572
Total Fringe:					\$8,794	\$9,268	\$18,062
Travel:							
Local travel (sample collections)					\$0	\$2,000	\$2,000
Presentation at Conference @ \$1500 Per Individual*					\$0	\$1,500	\$1,500
Total Travel:					\$0	\$3,500	\$3,500
Supplies:							
Filters					\$1,000	\$500	\$1,500
Cr Isotope enriched solutions					\$2,000	\$2,000	\$4,000
Chemicals (Cr standard, acid, base, etc.)					\$1,000	\$1,000	\$2,000
CEF facility					\$2,000	\$0	\$2,000
Sampling pumps and supplies					\$2,500	\$500	\$3,000
Office supplies					\$500	\$500	\$1,000
Lab supplies					\$1,000	\$1,000	\$2,000
Total Supplies:					\$10,000	\$5,500	\$15,500
Other Expenses:							
Telephone					\$500	\$500	\$1,000
Publications					\$0	\$1,000	\$1,000
Total Other:					\$500	\$1,500	\$2,000
Subcontract:							
Rutgers University*-refer to the Rutgers Subcontract sheet.					\$15,851	\$15,017	\$30,868
Total Subcontract:					\$15,851	\$15,017	\$30,868
Direct Costs					\$78,682	\$79,628	\$158,310
Indirect Costs @ 10%					\$7,868	\$6,671	\$14,539
Total Costs Method Development					\$86,550	\$86,299	\$172,849

Travel to Conference for Dr. Linda J. Bonanno

\$ 1,500

TOTAL FUNDS REQUESTED FROM USEPA

\$174,349

Subcontract to Rutgers University

Personnel	Role	Appt.	Effort	Base	Year 01	Year 02	Total
Brian Buckley	co-I	12	5%	\$96,757	\$4,838	\$4,983	\$9,821
Fringe: 32.5% Year 01 increased by 1% in Year 02					\$1,572	\$1,669	\$3,241
Supplies IC/ICPMS instrument supplies					\$8,000	\$7,000	\$15,000
Direct Costs					\$14,410	\$13,652	\$28,062
Indirect Costs @ 10%					\$1,441	\$1,365	\$2,806
Total Costs					\$15,851	\$15,017	\$30,868

4. Quality Assurance Narrative:

The NJDEP has an approved general quality assurance plan on file with the USEPA. The NJDEP will submit a QA/QC plan that is specific to this proposed method development to the USEPA before the project starts. During the sampling and extraction method development, 15% lab blanks and duplicates will be conducted. The acceptable Relative Standard Deviation (RSD) for replicate samples must be less than 15%. During the IC/ICPMS analysis, a quality assurance sample will be analyzed before and after five real samples are analyzed. If the quality control sample was not within +/- 20% of the certified value for target elements the instrument will be recalibrated and the batch reanalyzed. Once the NJDEP has been notified of the grant award, we will complete our Quality Management Plan and Quality Assurance Plan and forward them to the USEPA.

References:

- Ashley K, Andrews RN, Cavazos L, et al. Ultrasonic extraction as a sample preparation technique for elemental analysis by atomic spectrometry. *Journal of analytical atomic spectrometry*, 2001, 16, 1147-1153.
- Barceloux, DG. Chromium. *Clinical Toxicology*, 1999, 37(2), 173-194.
- Boiano JM, Wallace ME, Sieber WK, et al. Comparison of three sampling and analytical methods for the determination of airborne hexavalent chromium. *Journal of Environmental Monitoring*, 2000, 2, 329-333.
- Buckley B, Johnson W, Fischer E, et al. Measurement of Heavy Metals in Biological and Environmental Matrices Using Microwave Extraction, Inductively Coupled Plasma Mass Spectrometry and Ion Chromatography for Assessing Potential Risk to Human Health. (Chinese) *Journal of Environmental and Occupational Medicine*, 2003, 20(6), 418-421.
- Buckley B, Johnson W, Tu Q, et al. Are There Alternatives to 6800? "To Label or Not To Label? That is the Question", National Environmental Monitoring Conference, July 26th, 2005.
- Cooper CD, Alley FC. *Air pollution control: a design approach*. Waveland Press, Inc. Prospect Heights, IL, 1994.
- Crump C, Crump K, Hack E, et al. Dose-response and risk assessment of airborne hexavalent chromium and lung cancer mortality. *Risk Analysis*, 2003, 23(6), 1147-1163.
- Eastern Research Group, Collection and analysis of hexavalent chromium in ambient air. Presented at the AWMA 98th annual conference, Minneapolis, MN., June 2005.
- Freeman NCG, Lioy PJ, Stern AH. Reduction in residential chromium following site remediation. *Journal of the Air & Waste Management Association*, 2000, 50, 948-953.
- James BR, Petura JC, Vitale RJ, et al. Hexavalent chromium extraction from soils: a comparison of five methods. *Environmental Science & Technology*, 1995, 29, 2377-2381.
- Kimbrough DE, Cohen Y, Winer AM, et al. A critical assessment of chromium in the environment. *Critical Reviews in Environmental Science and Technology*, 1999, 29(1), 1-46.
- Li Y, Pradhan NK, Foley R, Low GKC. Selective determination of airborne hexavalent chromium using inductively coupled plasma mass spectrometry. *Talanta*, 2002, 57, 1143-1153.
- Seigneur C, Constantinou E. Chemical kinetic mechanism for atmospheric chromium. *Environmental Science & Technology*, 1995, 29(1), 222-231.
- Sheehan P, Rick R, Ripple S, et al. Field evaluation of a sampling and analytical method for environmental levels of airborne hexavalent chromium. *American Industrial Hygiene Association Journal*, 1992, 53(1), 57-68.
- USEPA. *National Monitoring Strategy: Air Toxics Component*. USEPA, 2004.
- Vitale RJ, Mussoline GR, Rinehimer, KA. Environmental monitoring of chromium in air, soil and water. *Regulatory toxicology and Pharmacology*, 1997, 26, S80-S85.