

State of California
AIR RESOURCES BOARD

Resolution 06-6

January 26, 2006

Agenda Item No.: 06-1-1

WHEREAS, the Air Resources Board has been directed to carry out an effective research program in conjunction with its efforts to combat air pollution, pursuant to Health and Safety Code sections 39700 through 39705;

WHEREAS, a research proposal, number 2602-250, entitled "Impact of Reactive Halogen Species on the Air Quality in California Coastal Areas," has been submitted by the University of California, Los Angeles;

WHEREAS, the Research Division staff has reviewed and recommended this proposal for approval; and

WHEREAS, the Research Screening Committee has reviewed and recommends for funding:

Proposal Number 2602-250 entitled "Impact of Reactive Halogen Species on the Air Quality in California Coastal Areas", submitted by the University of California, Los Angeles, for a total amount not to exceed \$300,000.

NOW, THEREFORE BE IT RESOLVED, that the Air Resources Board, pursuant to the authority granted by Health and Safety Code section 39703, hereby accepts the recommendation of the Research Screening Committee and approves the following:

Proposal Number 2602-250 entitled "Impact of Reactive Halogen Species on the Air Quality in California Coastal Areas", submitted by the University of California, Los Angeles, for a total amount not to exceed \$300,000.

BE IT FURTHER RESOLVED, that the Executive Officer is hereby authorized to initiate administrative procedures and execute all necessary documents and contracts for the research effort proposed herein, and as described in Attachment A, in an amount not to exceed \$300,000.

I hereby certify that the above is a true
and correct copy of Resolution 06-6, as
adopted by the Air Resources Board.

Lori Andreoni, Clerk of the Board

ATTACHMENT A

“Impact of Reactive Halogen Species on the Air Quality in California Coastal Areas”

Background

Free radical species drive the atmospheric reactions that produce ozone and other pollutants. The hydroxyl radical (OH) and peroxy radicals (HO₂ and RO₂) dominate the daytime chemistry and the nitrate radical, NO₃, dominates the nighttime chemistry. Current airshed models are built on the chemistry of these radicals. Recent observations indicate that an additional set of radical species – reactive halogen species (RHS - halogen atoms and halogen oxides) – may also play an important role in ozone and particulate matter (PM) chemistry in urban coastal environments. In spite of their possible importance, no measurements of these species have been made along the coast of California. The proposed project will address this poorly understood chemistry by bringing together four uniquely qualified research groups to conduct atmospheric observations of RHS and associated compounds at a suitable site near the South Coast Air Basin.

Objective

There are three primary objectives of this research project. The first objective is to measure atmospheric concentrations of RHS and their precursors upwind of a coastal city in California. Specifically, the first measurements on the California coast of reactive halogen species (ClO, BrO, IO, OIO), precursors of RHS (Cl₂, Br₂, I₂) and several unique reaction products of chlorine + VOC chemistry will be obtained. The second objective is to estimate the impact of observed halogen concentrations on urban coastal air quality, in particular on ozone, NO_x and PM. A simple chemical box model approach is proposed to determine the impact of RHS on dominant photochemical pathways in an urban environment; these results will be compared with previous model results for the air basin. The third objective is to evaluate the sources of RHS through an analysis of the observations. The origin and behavior of RHS in the coastal troposphere will be investigated through correlation analysis of RHS concentrations, meteorological parameters, single particle composition, and path-integrated concentrations of several other trace gases.

Methods

A wide variety of instruments will be deployed for this project. Long-Path Differential Optical Absorption Spectroscopy (LP-DOAS) will be operated by the UCLA group and will measure concentrations of halogen oxides and molecular iodine (and several other species, e.g. O₃, NO₂, HCHO, NO₃) with a five minute time resolution; Multi-Axis DOAS will measure the vertical distribution of these gases. In-situ Gas Chromatography/Mass Spectrometry (GC/MS) will be utilized by the Washington State University group to measure hydrocarbons and unique products from halogen + VOC reactions, such as 4-chloroacetaldehyde from the reaction of 1,3-butadiene with Cl atoms in the presence of NO. Atmospheric Pressure Ionization Mass Spectrometry (API-MS) will be used by the Battelle group to measure molecular halogens; 5-10 species can be measured with a one minute time resolution. Electron microscopy (TEM and SEM) and electron/ion probe

techniques (CCSEM/EDX, TOFSIMS) will be employed by the Pacific Northwest National Laboratory group to analyze particle morphology, internal particle structure, and individual particle elemental composition. Supporting instruments will provide measurements of NO, CO, NO₂, O₃, (and other gas-phase species), actinic flux, aerosol size distribution, and meteorological parameters (wind speed, wind direction, T, RH). In summary, a unique comprehensive data set on halogen species, aerosols, and important trace gases will be collected for this project.

Expected Results

The expected results from this work are a greatly improved understanding of coastal RHS chemistry that can be used by the Board to assess the impact of RHS on urban coastal air quality and to help determine whether RHS chemistry should be included in airshed models.

Significance to the Board

The proposed measurements would add a tremendous wealth of scientific information concerning ambient concentrations, origins and influence on pollutant formation of RHS. This information is fundamental to correctly modeling the formation of ozone and secondary aerosols, and hence to assess various strategies for air pollution controls in coastal areas.

Contractor:

University of California, Los Angeles

Contract Period:

36 Months

Basis for Indirect Cost Rate:

The State and the UC system have agreed to a ten percent indirect cost rate.

Cofunding:

The Coordinating Research Council is considering contributing \$150,000 to the cost of this study.

Principal Investigator (PI):

Professor Jochen Stutz

Contract Amount:

\$300,000

Past Experience with this Principal Investigator:

Dr. Stutz is the head of a laser spectroscopy laboratory that contains several state-of-the-art Differential Optical Absorption Spectroscopy (DOAS) instruments for high-sensitivity investigations of many trace atmospheric species. He is a recognized leader in observations of radicals and their precursors in the open atmosphere by spectroscopic techniques.

Prior Research Division Funding to UCLA:

Year	2005	2004	2003
Funding	\$0	\$1,939,750	\$0

BUDGET SUMMARY

University of California, Los Angeles

“Impact of Reactive Halogen Species on the Air Quality in California Coastal Areas”

DIRECT COSTS AND BENEFITS

1.	Labor and Employee Fringe Benefits	\$ 60,602
2.	Subcontractors*	\$189,077 ¹
3.	Equipment	\$ 0
4.	Travel and Subsistence	\$ 600
5.	Electronic Data Processing	\$ 900
6.	Reproduction/Publication	\$ 300
7.	Mail and Phone	\$ 765
8.	Supplies	\$ 300
9.	Analyses	\$ 0
10.	Miscellaneous	<u>\$ 32,981²</u>
	Total Direct Costs	\$ 285,525

INDIRECT COSTS

1.	Overhead	\$ 14,475
2.	General and Administrative Expenses	\$ 0
3.	Other Indirect Costs	\$ 0
4.	Fee or Profit	<u>\$ 0</u>
	Total Indirect Costs	<u>\$ 14,475</u>

TOTAL PROJECT COSTS

\$300,000

¹ These costs are associated with work to be performed by two groups: Dr. Thomas Jobson, Washington State University, and Dr. Chet Spicer, Battelle Memorial Institute. Dr. Jobson's group will measure selected VOCs, and Cl and Br containing VOC oxidation products once every hour using gas chromatography/mass spectroscopy. Dr. Spicer's group will measure molecular halogens using atmospheric pressure chemical ionization (APCI) tandem mass spectrometry (MS/MS). In addition to these field measurements, each group will reduce data, analyze and interpret data, and contribute to manuscripts and the Final Report. The majority of costs are for labor, with a minor component for materials and supplies and field campaign equipment use.

² All costs associated with logistics for the three week field study are included in this category. As the PI, Jochen Stutz, UCLA, will act as the coordinator of groups and disburser of funds for this element of the project. The field campaign costs include: general setup of equipment (transportation of equipment, rental of laboratory space, purchase of misc. setup materials); lodging and food for UCLA, WSU, and Battelle; and consumables (Xe-arc lamps, gases, aerosol sampling grids (TEM), and shipment of sampling grids).

Attachment 1

SUBCONTRACTORS' BUDGET SUMMARY

Subcontractor: Battelle Memorial Institute

Description of subcontractor's responsibility: Dr. Spicer's group will carry out measurements of molecular halogens using an APCI/MS/MS instrument, analyze and interpret data, and contribute toward manuscripts and the Final Report. These expenses include:

DIRECT COSTS AND BENEFITS

1.	Labor and Employee Fringe Benefits	\$ 26,751	
2.	Subcontractors	\$ 0	
3.	Equipment	\$ 0	
4.	Travel and Subsistence	\$ 0	
5.	Electronic Data Processing	\$ 0	
6.	Reproduction/Publication	\$ 0	
7.	Mail and Phone	\$ 0	
8.	Supplies	\$ 0	
9.	Analyses	\$ 0	
10.	Miscellaneous	<u>\$ 15,895</u>	
	Total Direct Costs		\$ 42,646

INDIRECT COSTS

1.	Overhead	\$ 56,445	
2.	General and Administrative Expenses	\$ 0	
3.	Other Indirect Costs	\$ 0	
4.	Fee or Profit	<u>\$ 7,927</u>	
	Total Indirect Costs		<u>\$ 64,372</u>

TOTAL PROJECT COSTS \$107,018

SUBCONTRACTORS' BUDGET SUMMARY

Subcontractor: Washington State University

Description of subcontractor's responsibility: Dr. Jobson's group will carry out measurements of selected VOCs, and Cl- and Br-containing VOC oxidation products using an in-situ GC/MS instrument. In addition, Dr. Jobson's group will operate particle counters and particle collectors, analyze and interpret data, and contribute toward manuscripts and the Final Report. These expenses include:

DIRECT COSTS AND BENEFITS

1.	Labor and Employee Fringe Benefits	\$56,131
2.	Subcontractors	\$ 0
3.	Equipment	\$ 0
4.	Travel and Subsistence	\$ 0
5.	Electronic Data Processing	\$ 0
6.	Reproduction/Publication	\$ 0
7.	Mail and Phone	\$ 0
8.	Supplies	\$ 2,500
9.	Analyses	\$ 0
10.	Miscellaneous	<u>\$ 0</u>
Total Direct Costs		\$ 58,631

INDIRECT COSTS

1.	Overhead	\$23,428
2.	General and Administrative Expenses	\$ 0
3.	Other Indirect Costs	\$ 0
4.	Fee or Profit	<u>\$ 0</u>
Total Indirect Costs		<u>\$ 23,428</u>

<u>TOTAL PROJECT COSTS</u>	<u>\$ 82,059</u>
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