Final Workplan for National Air Toxics Monitoring Program – Community Assessments

Project Title: ***Enhanced Delaware Air Toxics Assessment Study***

Project Lead:
Joseph M. Martini
State of Delaware Department of Resources and Environmental Control
302-323-4542; joseph.martini@state.de.us

Project Partners

Murray V. Johnston
University of Delaware
302-831-8014; mvj@udel.edu

Andrey Khlystov
Duke University
919-660-5209; andrey@duke.edu

Jason K. S. Ching
NERL, U.S. EPA
919-541-4801; ching.Jason@epa.gov

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I. ABSTRACT

The Delaware Air Quality Management Section (AQMS) embarked on the Delaware Air Toxics Assessment Study (DATAS) project in early 2003 to gain a better understanding of ambient concentrations of air toxics throughout Delaware, exposure to those air toxics, and the health risks associated with that exposure based on nationally-accepted health benchmarks. DATAS is connected to Delaware's commitment to develop a comprehensive framework to address local risk. The DATAS initiative actualizes the vision of the State, Local, and Tribal (S/L/T) role in the national risk-based phase of the air toxics program. Delaware's goal has been to develop a mature air toxics monitoring network, a superior emissions inventories, and modeling capabilities to support the quantitative evaluation, characterization, and tracking of risk-based impacts.

Consistent with the goals and objectives of the Urban Air Toxics Strategy, DATAS is a tool that can be used to assist with the following activities:

- Assessing air toxics health impacts in communities other than those monitored,
- Development of air quality standards based on cumulative risk which in turn is based on national health benchmarks,
- Develop control strategies for the purpose of meeting the new standards,
- Assist the permitting process base its decisions on cumulative impacts,
- Improvement of emission inventory development, and
- Development of enhanced modeling capabilities through the use more representative upper air data.

Specifically, DATAS involves the development of a monitoring network for 2003 and a speciated 2003 air toxics emission inventory that will be integrated with ambient air quality modeling and meteorological components into a meaningful resource that can be used to accurately characterize risk, both regionally and locally. The project began in January 2003 and will continue though early 2005.

Delaware's existing toxics monitoring network has been designed using EPA Compendium Methods to measure the following pollutant categories:

- Volatile Organic Compounds (VOCs), Method TO-15a.
- Dioxins/Furans (D/F), Method TO-9a.
- Carbonyls, Method TO-11a,
- Polynuclear Aromatic Hydrocarbons (PAHs), Method TO-13a, and
- Metals, Method IO-3.5

AQMS recognizes the limitations of toxics sampling with these methods, particularly the lack of temporal and spatial resolution associated with collecting samples on media and shipping to off-site laboratories for analysis. Thus, AQMS, as part of this proposal, is proposing to use real-time, single-particle mass spectrometry to be used as an additional resource in characterizing atmospheric aerosols. The use of this technology will provide additional data necessary in identifying chemical markers for source apportionment, and thus provide information to AQMS that can be used to aid in the development of control strategies for reducing HAP impacts at the communities of interest.

Additionally, AQMS is proposing to supplement existing measurements at one monitoring site with mobile measurements of several air toxics components, providing a spatial distribution on the order of 100 meters.

Mobile monitoring will provide information on two counts. First, it will serve to provide spatial information from mobile transits, e.g., along and normal to traffic pattern, along the crosswind paths of point sources leading to the goal of characterizing the monitored data. Secondly, it will provide spatial variability information at fine scales that can be used to compare to the modeled concentration distribution function of the variability for the grid cell in which the monitor is located. This will be useful to evaluating the NERL, the so-called “Neighborhood-scale” air quality modeling paradigm described as follows: Since exposure estimates depend on concentration and dosage, both the grid model prediction of concentration, as well as the magnitude of the range of the within-grid variability becomes an important measure of risk. The US EPA Neighborhood scale modeling project is designed to provide model outputs of both gridded concentrations from its CMAQ modeling system for air toxics, as well as model outputs of the concentration distribution functions that describe the with-in grid variability. This paradigm for air toxics assumes that when significant within-grid concentration variability is known to exist, additional information on the characteristics of such distributions will be supplied to complement the grid resolved simulations from the CMAQ modeling system as inputs to risk-based population exposure models and assessments. The contribution to this variability is a result of source dispersion within grid as well as from the photochemistry from within grid transport and turbulence. Currently, a formal collaboration is in place between the State of Delaware, DNREC, EPA Region III, and EPA – NERL towards implementing the neighborhood-scale modeling approach for the State of Delaware and Philadelphia. The mobile monitoring component of this project will be invaluable toward evaluation of the spatial variability distribution predictions.

The remaining sections of this proposal detail AQMS’ proposed integration of these technologies to Delaware’s toxics monitoring program.

II. PROJECT DESCRIPTION

A. Monitoring Design:

The proposed monitoring design for the enhanced Delaware Air Toxics Assessment Study (E-DATAS) will include the following monitoring locations:

- Wilmington
- Delaware City
- Summit Bridge
- Felton (rural, background site), and
- Seaford

These sites would be used to characterize pollutant concentrations within an extended area that has relatively uniform land use with dimensions in the 0.5 to 4.0-kilometer range. Although there are no micro-scale sites defined in this project, the Delaware City site is source dominated, and therefore is also representative of a micro-scale approach. i.e., define pollutant concentrations in air volumes associated with area dimensions ranging from several meters up to about 100 meters. All stations are sited using established EPA siting guidelines.

These sites will be non-mobile stations equipped to monitor target air toxic compounds once every 6th day, for a 1-year duration. For most of the sampling, the schedule will follow the established PM10 sampling schedule. Exceptions will be noted throughout this document. Thus, most sampling will represent a 24-hour sampling period, beginning 12:01 a.m. and ending 11:59 p.m. All sampling will be performed in Eastern Standard Time. The target compound groups, identified by station are presented in Table A.1.

Table A.1 Target Compound Groups/Parameters Proposed for E-DATAS[a]

Station	VOCs TO-15a	Carbonyls TO-11a	Metals IO-3.5	Surface Meteorology	Upper-Air Meteorology	Real-Time Mass Spec.
Wilmington	X	X	X	X	X	X
Delaware City	X	X	X	X		
Summit Bridge	X	X	X			
Felton	X	X	X	X		
Seaford	X	X	X	X		

[a] *AQMS stopped PAHs on 12-31-03. PAHs are not being included as part of the E- DATAS. This stoppage is due to extremely low concentrations measured 2003 year-to-date.*

The continuation of this monitoring platform for the proposed enhanced monitoring proposal is contingent upon Region III's ability to provide uninterrupted in-kind analytical assistance for VOC's, carbonyls, and metals. Should Region III be unable to provide analytical support, sampling for these compounds will be stopped immediately.

A.1 Real-Time, Single Particle Mass Spectrometry

Single particle mass spectrometers are ideally suited to count ambient particles as a function of size and composition.[*Johnston*, 2000; *Johnston and Wexler*, 1995; *Noble and Prather*, 2000]. Because of the sheer volume of data that is collected, typically tens to hundreds of thousands of particle spectra, statistical or neural network chemo metric treatments have been employed to classify particles into a relatively small number of groups having similar spectra. These groups can then be correlated with particle size, meteorological variables, time-of-day, and known emission sources to characterize the ambient aerosol. The ionization method used in single particle mass spectrometry, laser ablation, is applicable to a wide range of particle compositions – organic and inorganic, semivolatile and refractory. Metals are particularly well suited for detection. [*Rhoads et al, 2003; Pharses et at, 2003; Lake et al, 2003*]

Metals are important trace constituents of ambient particles. Metals can serve as tracers for specific emission sources, and they may adversely affect human health.[*Fernandez et al.*, 2000; *Fernandez Espinosa et al.*, 2002] Current regulations for particulate matter are based upon total mass in a specified size range. Understanding how the number concentrations of particles containing metals change as a function of particle size, time and location may help characterize the sources of these emissions and the health effects they induce.

Elemental markers have proven to be highly useful in identifying major sources of primary urban aerosol particles. For example, selenium is nearly a unique tracer of coal combustion aerosol. Likewise vanadium and nickel are often excellent makers of oil combustion aerosol. Aerosol particles emitted from municipal incinerators typically contain up to 40% $ZnCl_2$ by mass and percent levels of Cd, Sb, and Pb, the combination of which is often a highly effective signature for this source. [*Gordon*, 1988]

Many air pollution studies have focused on the contributions of primary and secondary sources of aerosol and to what extent they comprise the total mass loading in urban and rural environments. [*Antony Chen et al.*, 2002] Both source-oriented and receptor-oriented models have been used. The accuracy and precision of these models are determined in large part by the time resolution of ambient particle measurements. This is most certainly the case for metals where concentration gradients may be steep during a diurnal cycle. Until recently, most source apportionment and receptor modeling studies relied on 12- or 24-hour integrated samples. The time resolution achieved in a field measurement is limited by the amount of sample required for analysis and the cost per analysis. In general, short sampling times are preferred as these provide for improved source attribution by preserving the dynamic variation in concentrations of atmospheric constituents and reducing the number of sources affecting an individual sample. Ideally, sampling times should be short relative to changes in wind direction, i.e., for stationary sources. AQMS is proposing to use this technology in conducting source apportionment activities, necessary to addressing HAP control strategies.

Under an umbrella agreement between the DNREC and the University of Delaware, AQMS is proposing to contract with the University of Delaware, Department of Chemistry and Biochemistry to incorporate real-time, particle-size mass spectrometry into E-DATAS. Single particle measurements will be performed with a RSMS III, a laser ablation time-of-flight mass spectrometer capable of simultaneous positive/negative ion detection. This non-routine, but proven technology, has been deployed previously at EPA sponsored Particulate Matter Supersites in Atlanta [*Rhoads et at, 2003*], Houston [*Pharses et al, 2003*], Baltimore [*Lake et al, 2003*], and Pittsburgh [*unpublished*]. The instrument will be housed in a trailer at the Wilmington site. Outside air will be sampled into the mass spectrometer inlet through one of nine orifices used to select the particle size. [*Phares et al.*, 2002] The nine orifices correspond to nine specific particle size set points between 45 and 1250 nm in diameter (ca. 45, 50, 90, 115, 140, 220, 440, 770, and 1250 nm). Measurements will be made on-site for 12 months, maximizing a sampling protocol for acquiring single particle spectra that is designed to maximize the time between laser maintenance periods without significantly compromising the robustness of the data set. Single particle spectra will be acquired at 2-hour intervals on a continuous basis. At the beginning of each sampling interval, the instrument will be cycled through the nine orifices (particle sizes). Single particle spectra will be acquired over a ca. 30-minute time period in a manner that produces roughly equal numbers of particles analyzed at each size. The particle analysis rate is typically 8 – 10 particles per minute, yielding 2880-3600 particles analyzed per day. The entire data set for a year of operation is likely to exceed 1,000,000 particles analyzed, which will be the largest such data set of its type recorded to-date.

Data collected as part of existing EPA-funded monitoring at the Wilmington site will also be analyzed with the real-time mass spectrometer data.

A.2 Mobile Measurements

AQMS has requested the University of Delaware subcontract with Duke University to perform mobile air toxics measurements. These measurements will be made at spatial scales of 100 meters near the Wilmington monitoring site. The technique is similar to the one Duke has used in the Netherlands to study spatial distribution of particulate matter in and around Amsterdam and Nijmegen (Weijers et al, 2004). For this project we will install several continuous instruments on a mini-van mobile laboratory equipped with a Global Positioning System (GPS). These instruments will measure the following components:

1. formaldehyde
2. chromium (III) and (VI)

Aerosol and gas collector (Khlystov et al., 1995) will be used to collect formaldehyde, chromium as well as other inorganic species. This instrument provides a continuous flow of dissolved aerosol and gas species that will be directed to on-line chemical detectors for formaldehyde and chromium (III) and (VI). The detectors provide a time resolution of 30 seconds. Formaldehyde will be measured using a technique described in Fan and Dasgupta (1994). Chromium (III) and (VI) will be determined using the techniques described by Ohshima et al. (1990). In one line, Cr(III) will be determined, while in the other, the sum of concentrations of Cr(III) and Cr(VI). The Cr(VI) concentration will be determined as the difference between the two lines. Aerosol particle number and size will be measured with standard Condensation Particle Counter (CPC) and Scanning Mobility Particle Sizer (SMPS). Particle number can be measured every second and particle size distribution – every 30 seconds.

Mobile measurements will be performed in the neighborhood of the monitoring station during four one-week campaigns, one each season (winter, spring, summer and fall). This will allow characterization of seasonal variability of different local sources, as well as the distribution of spatial distribution of the pollutants. Because mobile measurements are very flexible, we can adjust the driving route if necessary to study a particulate area in more detail.

A.3 Upper-Air Meteorology

AQMS is proposing to operate an upper-air acoustic sounder and multilevel tower as part of E-DATAS. The sounder and multilevel tower will be located at the Felton station, and will provide upper air meteorology during this project for use in quantifying atmospheric stability and regional transport, parameters which are not available with existing surface meteorology collection practices. Funding for the purchase and operation of this equipment will be provided by Delaware-specific sources.

B. Modeling Design

In order to assess toxic air pollutant impacts in local communities, this section presents a modeling approach to estimate annual average ambient HAP concentrations at the local communities of interest in Delaware. Although modeling is a dynamic and quite involved process, the approach described here provides a framework for reliably estimating HAP concentrations. The modeling will be performed with a 2003 projected HAPs emission inventory. This approach can be applied for 2004 projected HAPs emission inventory.

B.1 Modeling Approach

One approach to assess toxic air pollutant impacts on local communities is to perform air quality monitoring at many locations within communities. Although desirable, it is not practicable considering the number of assessment sites throughout the state and the resources that are necessary to conduct such field monitoring. Alternatively, air quality models that have been tested and evaluated over a wide range of meteorological conditions and emissions can be a resource to provide this information to local communities.

AQMS will be applying air quality models to assess health impacts from direct inhalation for both the local- and regional-scales. Local-scale modeling would be used to predict impacts for receptors located near emission sources, while the regional-scale modeling will be used for calculating impacts for distances of several kilometers up to the size of the airshed. The regional-scale modeling is necessary to simulate transport of pollutants from upwind areas that will contribute to concentrations in the local-scale area. Regional-scale modeling estimates ambient concentrations resulting from all emission sources in an area, whereas local-scale modeling gives more detailed information in the vicinity of point and area sources on a local scale.

Because the EPA-identified list of 188 HAP compounds is too comprehensive to be modeled, DATAS will model more than 33 urban HAPs for both local- and regional-scale modeling, which contribute to the majority of the health risk. The list of HAPs to be modeled will consist of the 33 urban HAPs consisting of volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs), carbonyl compounds, and metals, and also the compounds that are identified as of importance to EPA Region III states.

Regional-scale models estimate uniform concentration fields within a receptor grid of several square kilometers resulting from multiple emission sources: point, area, mobile, and biogenic. AQMS will apply and test two grid-based models for regional-scale modeling – CAMx and CMAQ (core part of Models-3). Both CAMx and Models-3 (June 2002 release) use the SAPRC-99 chemical mechanism modified to incorporate toxic chemistry. The CAMx has been traditionally applied for ozone modeling, while Models-3 represents the state-of-science model that has been developed by EPA. The mechanism designated as SAPRC-99 is a complete update of the SAPRC mechanism released in 1990. Condensed versions of the SAPRC-99 mechanism have been developed for use in air quality modeling.

B.1.1 Regional-Scale Modeling

A nested-grid approach for regional-scale modeling of meteorology and air quality will be used. The outer modeling domain (12 km x 12 km grid) will extend beyond the state boundary lines, with the inner domain (4 km x 4 km grid) centered on Delaware. The outer domain is defined based on a number of factors - the transport of pollutants from distant sources, capture of major emissions sources, reasonable turn around time of the modeling runs, etc. Figure B.1 shows the outer domain (D01) and one nested inner domain (D02) covering the entire state of Delaware, and Figure B.2 shows the inner nested modeling domain. However, if it is determined that the modeling runs for this domain definition are more demanding, we may choose a three-way nested grid modeling approach.

The regional-scale air quality models will be applied using an entire year of data for meteorology and monthly average emissions to estimate annual concentrations due to transport of pollutants from distant sources as well as background ambient air quality concentrations for the local-scale areas. The entire year of 2003 will be simulated to create high-resolution gridded meteorological data. Simulations with CAMx will be conducted using one full year of meteorology and CMAQ for selected episodes in summer and winter.

To generate the meteorological inputs for regional-scale models, AQMS propose to use two different meteorological models – CALMET and MM5. CALMET is a diagnostic model and is the simpler of the two models. It requires inputs from observational data for surface and aloft winds as well as temperature data and generates three-dimensional meteorology fields to drive air quality models. The surface and aloft data will be obtained from the National Weather Service (NWS) stations, all other surface stations and airports. For initialization of the CALMET model, all available surface stations and upper air rawinsonde stations will be used. The model performance of CALMET can also be improved by initializing it with MM5 output. MM5 is an advanced state-of-science prognostic meteorological model that solves the conservation equations to simulate winds and temperatures. CALMET will be used to generate meteorological data for CAMx and MM5 to generate data for Models-3. If resources and time permit, however, MM5 will be modeled for an entire year. The MM5 model will be initialized from the files generated by the National Climate and Environmental Prediction (NCEP) center and National Center for Atmospheric Research (NCAR). The MM5 data can be used in both CAMx and CMAQ simulations.

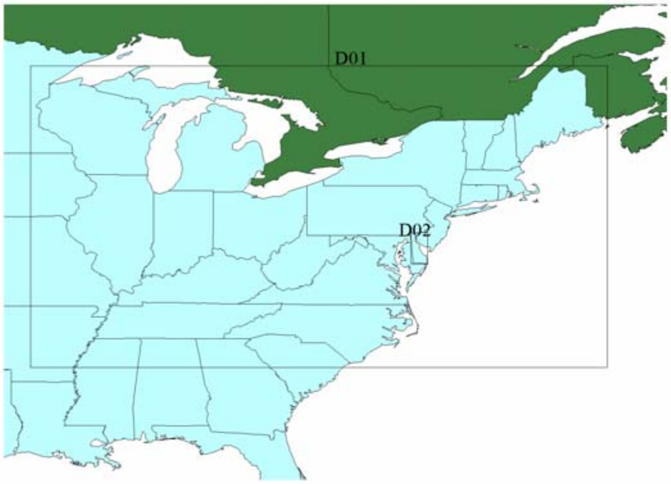


Figure B.1 Regional-scale modeling domain

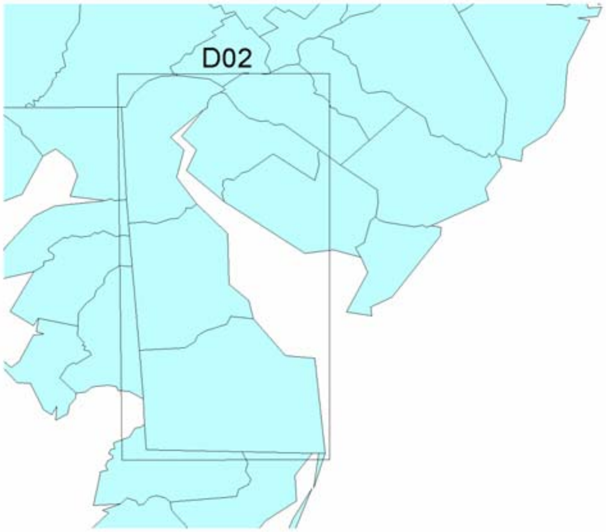


Figure B.2 Inner nested modeling domain

Boundary conditions for both regional-scale models will be determined from all available data and special modeling studies.

B.1.2 Local-scale Modeling

Local-scale models provide detailed concentration field near emission sources. AQMS recommends the use of more than one model to estimate ambient concentrations – they are ISCST, AERMOD and CALPUFF for point and area sources and CALINE for mobile sources. For the purposes of this study, local-scale study areas are chosen based on the following criteria:

- Population density,
- Roadway network,
- Industrial density,
- Location of monitoring sites, and
- Sensitive receptors such as schools, hospitals, etc.

Based on the above criteria, AQMS selected three communities in New Castle County, and one each in the Kent and Sussex Counties. Each of the domains will cover an area of approximately 10 x 10 km, and will include a network of receptors placed at 0.5 km apart. The local-scale modeling will also use a nested domain (4 x 4 km) with a finer resolution of 50 m. The local-scale modeling study will obtain meteorology data, i.e., hourly surface observations and upper air data, from local airports and on-site measurements.

B.1.3 Model Performance

Performance evaluation for each model is necessary to ensure that the models are working properly and that modeling results are reliable. Model performance will be evaluated to compare model estimates of concentrations with measured hourly concentrations for criteria pollutants, and 24-hour and annual concentrations for toxic pollutants where measurements are available. Standard statistical techniques, such as bias and gross error, will also be calculated for annual model estimates as well as for monthly and seasonal averaging times.

To evaluate the regional- and local-scale air quality models, meteorological and air quality data collected from the monitoring networks will be utilized. Although similar tests and evaluation procedures are used for regional and local-scale modeling, a greater level of resources is necessary for evaluating the regional model. The Technical Review Group (TRG) will identify the procedures to evaluate model performance for both regional- and local-scale models.

Funding for this modeling-to-monitoring exercise will be provided by Delaware-specific funds.

C. Proposed Budget

The proposed budget for this project is as follows:

The budget for E-DATAS of $265,129 for 18 months will provide support for costs associated with the operation and support for real-time mass spectrometry and mobile monitoring at/near the Wilmington site.

The details of this budget are provided in Table C.1.

Table C.1 Proposed Budget for E-DATAS

Budget Category	Estimated Cost	Comment
Personnel	$ 0.00	
Fringe Benefits	$ 0.00	
Contractual Costs • University of Delaware[a] • Duke University[b]	 $184,000 $58,432	University Cost includes: • Setup/Equipment • Monitoring
Travel	$ 0.00	
Equipment	$ 0.00	
Supplies	$ 0.00	
Other • Shelter for Mass Spec. • Site Preparation • Audit Fee	 $ 20,000 $ 2,432 $ 265	Site Preparation includes: • Electric Line • Internet Data Line • Site Excavation • Security • Phone Line
Total Direct Costs	$ 265,129	
Total Indirect Costs	$ 0.00	
Total Cost	$ 265,129	

[a] The University of Delaware budget is detailed as follows:

- $79,000 for salaries
- $39,000 for supplies and expenses (most of this is due to laser refurbishment costs during the project period)
- $35,000 for capital equipment
- $31,000 for overhead

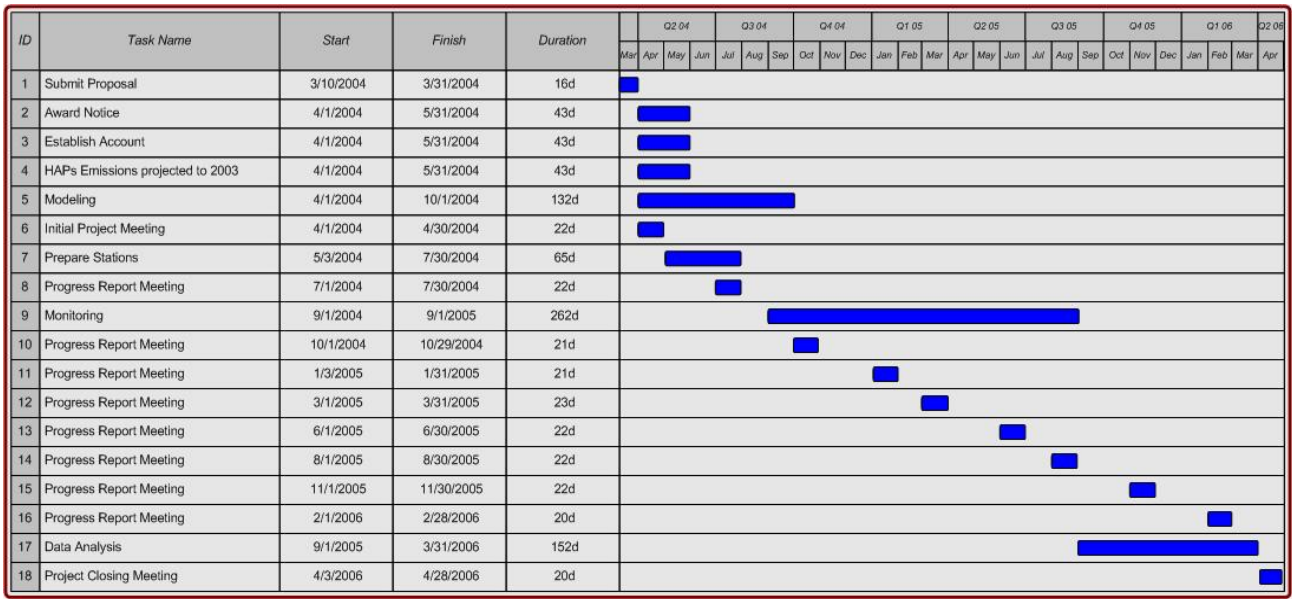
[b] Duke University budget is detailed as follows:

- $31,339 for operation of equipment
- $2,000 for supplies
- $2,800 for lodging expenses
- $20,489 Duke University administrative costs
- $1,804 fringe benefits

Proposed Timeline

The proposed AQMS timeline for E-DATAS detailed in Figure D.1

Figure D.1 Proposed Timeline for E-DATAS



ID	Task Name	Start	Finish	Duration
1	Submit Proposal	3/10/2004	3/31/2004	16d
2	Award Notice	4/1/2004	5/31/2004	43d
3	Establish Account	4/1/2004	5/31/2004	43d
4	HAPs Emissions projected to 2003	4/1/2004	5/31/2004	43d
5	Modeling	4/1/2004	10/1/2004	132d
6	Initial Project Meeting	4/1/2004	4/30/2004	22d
7	Prepare Stations	5/3/2004	7/30/2004	65d
8	Progress Report Meeting	7/1/2004	7/30/2004	22d
9	Monitoring	9/1/2004	9/1/2005	262d
10	Progress Report Meeting	10/1/2004	10/29/2004	21d
11	Progress Report Meeting	1/3/2005	1/31/2005	21d
12	Progress Report Meeting	3/1/2005	3/31/2005	23d
13	Progress Report Meeting	6/1/2005	6/30/2005	22d
14	Progress Report Meeting	8/1/2005	8/30/2005	22d
15	Progress Report Meeting	11/1/2005	11/30/2005	22d
16	Progress Report Meeting	2/1/2006	2/28/2006	20d
17	Data Analysis	9/1/2005	3/31/2006	152d
18	Project Closing Meeting	4/3/2006	4/28/2006	20d

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