REVIEW OF U. S. ENVIRONMENTAL PROTECTION AGENCY
ATMOSPHERIC SCIENCES RESEARCH LABORATORY
DRY DEPOSITION AND MATERIALS EFFECTS PROGRAMS

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I

INTRODUCTION

1.1 Panel Mission and Responsibilities

The panel's mandate was to review two U.S. Environmental Protection Agency - Atmospheric Sciences Research Laboratory (EPA-ASRL) programs: (a) Dry Deposition (Task Group D) and (b) Materials Effects (Task Group G). Both efforts are part of the National Acid Precipitation Assessment Program (NAPAP). The specific tasks reviewed are listed in Table 1.

The projects and the associated tasks were to be reviewed from the standpoint of:

(1) objectives and technical approach, including quality assurance and quality control;

(2) outputs planned;

(3) the relationship of the outputs to the goals of the Agency; and

(4) the usefulness of the overall programs to the scientific community and/or public welfare.

In attempting to meet this mandate, the panel has not only commented on the individual tasks listed in Table 1, but has also considered their relationship to the broader goals of the Agency, i.e., development of a dry deposition

Table 1

Descriptions of Tasks Reviewed

Dry Deposition - Task Group D

Task	Contractor/Agency	Task No.
Parameterization of Pollutant Deposition Velocities	Argonne	1452
Development and Evaluation of Variance Method	Argonne	1452
Development and Application of Similarity/Heat Budget Method	NOAA	3014
Development and Application of Eddy Accumulator	In-House	3016
ASRL Concentration Monitor	In-House	4037
Development of a Sized Particle Collection System	(RFP)	5059
Research Site Operation and Methods Evaluation	Argonne/NOAA	1452/3014
Evaluation of a Research Watershed	NOAA	3014

Materials Effects - Task Group G

Task	Contractor/Agency	Task No.
Field Studies - Structural Materials (Metals)	BOMines	3024
Field Studies - Non-Metallics	Northrop	4059
Field Studies - Acid Rain Simulator	Northrop	3175
Field Studies - Site Monitoring	Various	3114
Field Studies - Aerometric Data Base	CSC	4062
Chamber Studies - Chemistry of Acid Precipitation Materials Effects	Northrop	3174
New Projects - Initial Effects on Painted Wood Substrates		
Effects on Concrete and Masonry Structures		
Effects on Roofing Asphalt Shingles		
Evaluation of Corrosion Monitor at Exposure Sites		

network and estimation of economic damage attributable to acid deposition.

1.2 Materials Reviewed

The panel has reviewed the information and materials made available in scheduled presentations, draft manuscripts reporting results, interagency agreements, project descriptors, and the most recent peer reviews of both programs. It has visited the chamber facilities of the on-site contractor and the RTP field test site. At its request, a conference call was made to Bruce Hicks to discuss the status of the NOAA deposition velocity parameterization project deemed critical to the concentration monitoring approach.

The panel especially appreciated the willingness of ASRL to arrange unscheduled meetings at short notice. These additional meetings, which were requested by the panel to augment the review process, provided important information and enabled a more thorough review.

II

DRY DEPOSITION MEASUREMENT PROGRAM - Task Group D

2.1 Background

The ultimate objective of the dry deposition program of Task Group D is to determine dry deposition to surfaces throughout the United States and to monitor future trends. The dry deposition measurement program of ASRL has several broad components directed at meeting this objective, namely

(a) Research on micrometeorological methods for determining dry deposition influences (the so-called "direct" methods);

(b) Determination of dry deposition velocities over various natural land surfaces;

(c) Development of a method to monitor atmospheric concentrations of the chemical species of greatest interest in dry deposition;

(d) Operation of three field sites for dry deposition measurement research; and

(e) Evaluation of the utility of a research watershed for estimating dry deposition.

The relationships among these tasks are shown in the diagram in Figure 1.

A major conclusion of research to date is that direct measurement of dry deposition is difficult, and is not

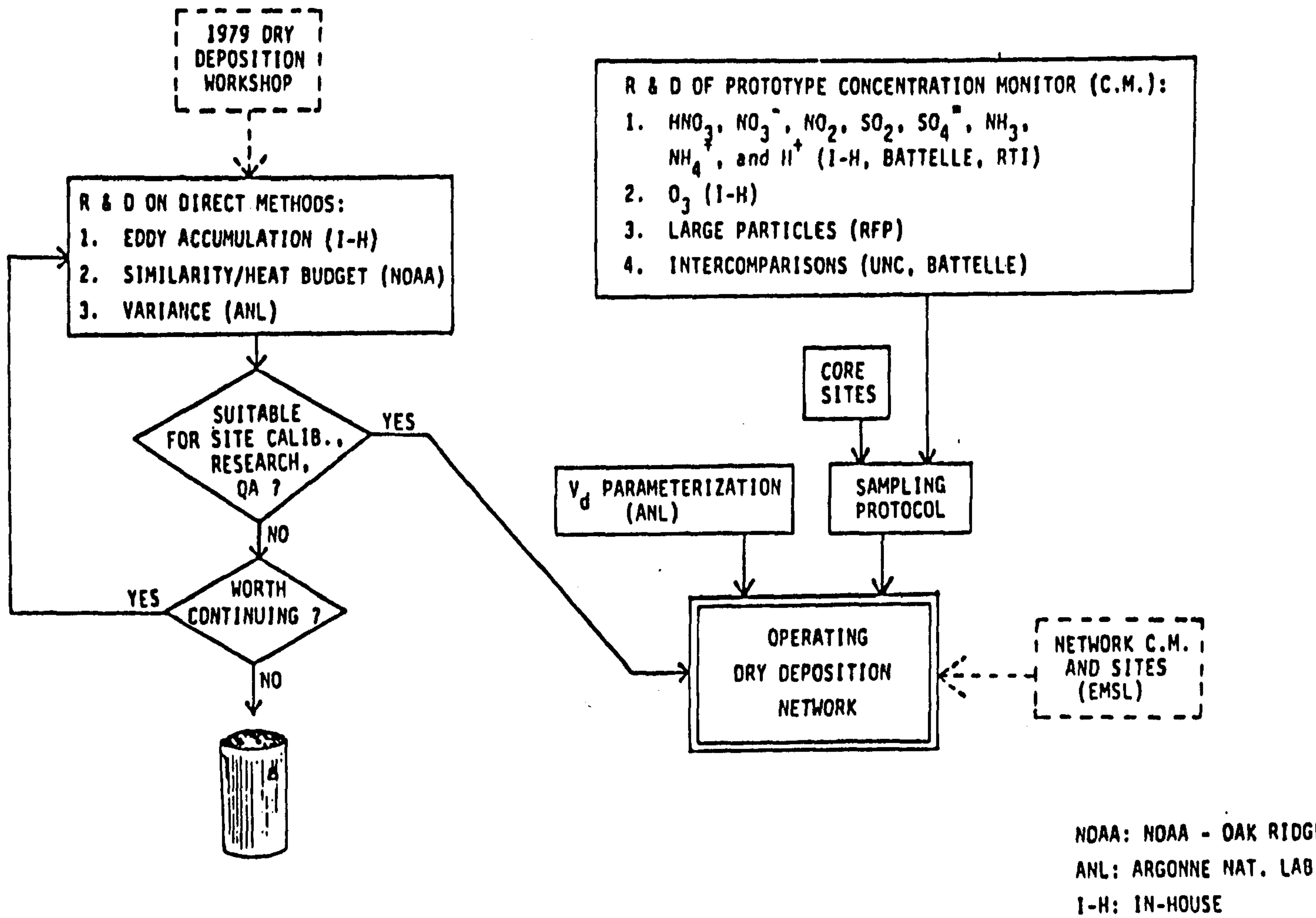

Figure 1. Schematic Representation of the Components of the ASRL Dry Deposition Measurement Program

practical with current technology in a large surveillance network. An alternate approach appears to be estimation of dry deposition flux from measurements of the pollutant concentrations and deposition velocities. Components (b) and (c) above address the two variables required for such an "indirect" method, where concentrations would be measured and the deposition velocity, V_d, would be estimated by interpolation or extension of measurements that have been made at a variety of research sites. In a separate program, the Atmospheric Turbulence and Diffusion Laboratory of NOAA is developing the methodology for estimating V_d at sites where measurements are not available.

Component (a) is concerned with development of methods that could be used in the field for deposition flux research and for validating the estimates of the indirect method. Component (d) deals with operating three field sites where basic measurements of deposition flux can be made and the indirect methods can be tested.

An alternative method for determining dry deposition fluxes is being evaluated under component (e). Here, ASRL is exploring the feasibility of direct determination of dry deposition from the difference between measured wet deposition input to a watershed and measured groundwater and stream fluxes out of the watershed.

This section reviews the various tasks that comprise these components and evaluates their design and execution from the perspectives of the program goals. In addition, because the intended use of the methods is in a national dry deposition trends network, we discuss briefly some issues raised by our review that have relevance for the implementation of that network.

2.2 Task Reviews

2.2.1 Parameterization of Pollutant Deposition Velocities

The objective of this task is to express deposition velocities for each of several pollutant species as functions of atmospheric conditions and surface conditions. Various types of surfaces will be considered, including cropland and deciduous forests in different seasons. The eddy correlation method will be used to measure V_d, while meteorological data and surface characteristics will be assessed simultaneously. Such information will be used to develop the desired expressions.

This is an important task, since the link between meteorology/surface observations and deposition velocities is not well understood. However, the project description is unclear as to the details of the parameterization. The description implies that some form of mathematical model will be developed. However, ASRL responses to reviewers' questions indicated that no such models will be developed as part of this particular task. Rather, the parameterizations will consist of tables listing deposition velocities for various atmospheric and surface conditions.

The panel feels that more explicit definitions of project tasks are needed, with clear statements of the methods to be employed and the expected deliverables. Despite problems with the project description, the panel feels that parameterized listings of the deposition velocities are worthwhile, and that the project is important to the goals of Task Group D and should continue.

2.2.2 Development and Evaluation of Methods to Measure Deposition Fluxes

2.2.2.1 Variance Method. Measurement of dry deposition flux by the variance method may be more appealing than other techniques if the method can be developed. The primary advantage is that the necessary measurements have resolution times which are slightly relaxed compared with those needed for eddy correlation. Pollutant monitors with time responses of 3-5 seconds, rather than <1 second as needed for eddy correlation, may thus be usable. The method was recommended for further development by the 1979 Dry Deposition Workshop.

Initial results of this study of the variance method indicate that ozone fluxes determined by this method agree reasonably well with those determined by eddy correlation when the former method is based on water vapor fluxes. Agreement is poorer when heat fluxes are used, possibly due to greater sensitivity to the upwind fetch. Since fast-response humidity sensors are expensive, and require considerable maintenance, the variance method may be useful primarily as a research tool. Initial work by the contractor appears promising, and so continued work on the project is worthwhile, even if the major utility of the method is currently limited to the realm of research and special studies.

2.2.2.2 Similarity/Heat Budget. Dry deposition measurement by the similarity/heat budget (S/HB) method offers the advantage that absolute turbulent fluxes need not be measured. As a result, the method is less site-specific than some of the other techniques. The time-response requirements are similar to those of the variance method. According to presentations made to the committee, ozone is the only pollutant for which the S/HB method has been successfully applied. However, the method is potentially applicable for estimating the deposition of fine particles.

This investigation of the S/HB method is in its early stages of development. The technique appears to be worth exploring, and continued funding is recommended.

2.2.2.3 Eddy Accumulation Method. This method was developed in an attempt to overcome the problems of measuring small concentrations of certain pollutants over short time scales. The eddy accumulation method permits the species of interest to be collected over extended time periods in two separate samples: one is activated by upward-moving air and the other by downward-moving air. The net flux to the surface is inferred from the difference of upward and downward fluxes.

An eddy accumulator has been built in-house by ASRL and tested in the field. Unfortunately, data reported to the panel from initial experiments involving water vapor transport did not give reliable flux data. It is not known whether the poor results were caused by data acquisition problems or by fundamental difficulties with the method.

The panel feels that work should continue despite the disappointing initial results. The project is relatively inexpensive, and although considerable additional development work may be needed, the method offers promise as a technique for pollutants which cannot be measured in real-time.

2.2.2.4 Overall Evaluation of Direct Methods Research. Based on work conducted over the past few years, it appears that none of the micrometeorological methods discussed in this report (variance, similarity/heat budget, and eddy accumulation) are likely to be useful for routine monitoring of dry deposition by unskilled personnel. Nevertheless, development of the methods for use in site calibration, quality assurance, and research purposes justifies continued work as planned by ASRL.

2.2.3 ASRL Concentration Monitor

2.2.3.1 Development and Evaluation of the ASRL Concentration Monitor. In order to measure atmospheric concentrations of the gaseous and particulate species that are of greatest interest for acidic dry deposition, ASRL has developed a prototype device for the collection of samples of these species. The design criteria for the sampler include that it be usable reliably in a network to measure mean day-time and night-time values of these species over about one week periods with 15% or better accuracy and precision. It is desired that analysis of the samples be by the same methods used for wet deposition, for maximum comparability.

The development of this device appears to be proceeding well. The basic design, including that of a transition flow reactor, is well thought out and seems sound. Many of the collection techniques for gaseous and particulate species are based on accepted methods.

The test results shown to us for gaseous HNO_3, NH_3, $SO_2$and NO_2 and for particulate $SO_4^=$, NO_3^-, and NH_4^+ give confidence that the basic design is sound and that the ±15% precision goal can be met. We were not shown data that demonstrate whether the accuracy specification is being met for all of these parameters.

The sampler should be tested under a variety of sampling and shipping temperatures, with realistic intervals between sampling and sample analysis, to give further confidence in its accuracy and precision under conditions representative of network operation. Simultaneous sampling for oxidants and NO_x should demonstrate whether or not the NO to NO_2 ratio is altered as O_3 is absorbed.

The planned improvements to the device to permit sampling of H_2O_2 and O_3 and for improved collection of HNO_3 should be developed and tested. As discussed below, there is an urgent need for this sampler for several purposes. Therefore, even while the above improvements are being developed in the laboratory, we recommend that several such samplers should be deployed in the field to provide an operational field evaluation before commitments are made for permanent deployment.

The sampler does not yet have the capability of measuring, or has not been tested for, other species of interest to NAPAP, namely HCl, HCO_3^-, Ca^{++}, PO_4^{3-}, Na^+, Mg^{++}, organic acids, and trace elements. Although it should ultimately measure as many of these as practical, these species are generally of less interest than those which it already measures, or for which a sampling capability is being planned. Therefore, we strongly recommend that deployment of this sampler should not await development or verification of the capability to measure these additional species.

2.2.3.2 Development of a Sized Particle Collection System. A procurement request is being processed for development of a method for sampling particles larger than 2 µm aerodynamic diameter with the concentration monitor described above. The concentration monitor includes a cyclone that excludes particles larger than 2 µm; the procurement proposes modification to permit sampling in two additional size ranges -- 2-10 µm and >10 µm.

The panel feels that an effort to measure 2-10 µm particles has merit and should be pursued. However, we seriously question the merit of collecting the larger particles by use of the airborne concentration monitor and feel that the resources that would be devoted to this purpose should be used elsewhere. The reasons for our recommendation are numerous, and range from fundamental questions about the scientific merit and validity of such sampling to questions about the likelihood that such large particle sampling can be accomplished at a cost that is reasonable relative to its benefits.

Specifically, we point out that the deposition velocity of such larger particles varies greatly with particle size. Consequently, the range of sizes >10 µm must consist of several narrow ranges if the measurements are to have any meaning for dry deposition characterization. An inlet that can sample particles >10 µm and that maintains the same sampling characteristics over a wide range of wind speeds would be relatively expensive to develop and test. Finally, the possibility of gravitational deposition of the larger particles in the flow channels of the concentration monitor and its transition flow reactor has to be considered.

We recommend that the resources available be devoted to the 2-10 µm collector. That collector will sample enough of the coarse mode of ambient aerosol to identify whether it plays a meaningful role in acid deposition. If research using the 2-10 µm collector indicates that coarse particles do play a major role, then it might be appropriate to undertake the more difficult task of measuring particles larger than 10 µm. The issue of >10 µm particle deposition may best be approached through the use of surrogate surfaces (see Section 2.4.3).

2.2.4 Research Site Operation and Method Evaluation

Research (core) sites are necessary for the measurement of parameters to determine dry deposition flux, to field test the concentration monitoring techniques, to intercompare methods of different theoretical basis, and to gain experience applicable to the development of the larger National Trends Network (NTN). Three sites are now operational: Argonne (funded through ANL), Oak Ridge, and Penn State (funded through NOAA). Additional measurements are being taken at cooperative sites at Champaign-Urbana (flat site of uniform surface), West Point (flat site of broken vegetation), and Whiteface Mountain (uniform vegetation on variable terrain).

One of the planned outputs of the effort at the research sites is a manual for site planning and development of NTN sites. While the choice of sites involves many considerations, the need for a scientific basis for the decision is critical. A poorly chosen site will provide little useful data, be expensive, and erode confidence in the ability to quantify the dry flux. It is important, in the initial NTN site selection process, to make use of the expertise gained from the research site studies.

The choice of the three main research sites has been well made, with careful consideration of the research design. The initial emphasis is on uniform sites (the easiest micrometeorological situation) of differing surface/vegetation type, with extension to non-uniform surfaces and variable terrain. The time-integrated concentration monitoring techniques are being intercompared with standard, realtime monitors as available. The usefulness of a 12-hour (day-night) sampling protocol is being tested, as well as the concentration monitor system in general.

The concentration measurement and flux parameterization protocols have thus far been addressing O_3, SO_2, HNO_3, NO_2 and particulate matter. To meet the EPA goals, additional species are needed. Hydrogen chloride, ammonia, nitrate aerosol, sulfate aerosol, and aerosol acidity have all been previously identified as components of the net acid flux which needed to be quantified. The alkaline components, large particles and ammonia, have received a lower priority than the acid species. However, both acids and bases are needed to determine a net acid flux, and thus should be considered in the design of research site operations.

This effort is directed toward quantifying the dry flux, which could be of magnitude equal to that of the wet deposition. The uncertainties have been improved, but the limiting factor is still the estimation of the dry deposition velocity (V_d). There is a concern that effects of meteorological/surface characteristics may be insufficiently understood to estimate V_d precisely. This is especially true for the surface wetness parameter. Its role is not well documented and field verification of surface moisture measurements is needed. However, these weaknesses have been anticipated, and an iterative improvement of the V_d estimation process is part of the long-term research. Improvements are expected in the routines used to estimate V from the meteorological parameters as well as the surface characteristics and the concentration parameter measurements.

The EPA goal is to estimate the dry flux over large areas. However, the actual geographical areas over which the concentration monitor is applicable are variable from region to region, and are largely unknown. These will need to be better understood for the NTN sites.

The dry flux measurement sites have added utility for other Task Groups. While the research sites are designed for method testing and protocol development, future monitoring sites should be cost-effective in their location. In particular, dry deposition monitoring in the RTP area should be directly coordinated with the materials effects studies. A co-location of research activities between Groups D & G in RTP, North Carolina would be desirable.

With respect to the usefulness of concentration measurements and V estimations, it is uncertain what can be expected as to sensitivity and precision. The concentration measurement approach is anticipated to be accurate within ±15% or better, and the V accuracy under the most ideal site conditions currently ranges from ±30% for SO to ±100% for fine particulate matter. These values imply significant uncertainty in the final deposition flux estiunavoidable. Improvements are needed to quantify the flux within ±30% for all the above species which are important to the net dry deposition acidity.

2.2.5 Evaluation of a Research Watershed

A preliminary field study of the feasibility of using mass balance over a watershed (Penn State) to quantify the wet and dry fluxes is near completion. The mass balance approach is well founded, but a precision better than that for the dry flux methods seems unlikely. This approach would not have a general applicability.

The advantage of a watershed is that it provides a check on the calculated dry flux and the measured wet flux. It may be useful as an indirect confirmation of dry flux measurements. However, since a watershed covers a larger and less uniform area than the expected area of representativeness for the dry flux sites, the results may not be directly comparable.

The uncertainties associated with a watershed study are large, and feasibility should be demonstrated before future expenditures are made.

2.3 Proposed 30-Site Deposition Network

EPA/EMSL intends to deploy a nationwide network (NTN) to measure trends in both dry and wet deposition. The initial deployment of 30 sites is to take place in the next two years, or so. Although this network is not the responsibility of ASRL, several of the ASRL activities have bearing on the implementation of such monitoring, and therefore we have taken the liberty of noting these cross-laboratory implications.

The tentative plans for the 30 sites include equipping each site initially with a monitor for O_3, a device that samples ambient concentrations of key species of interest to acidic deposition, and meteorological instruments. The sites will not monitor dry deposition, but rather dry deposition will be estimated using a concentration x V_d method currently under development by the NOAA Atmospheric Turbulence and Diffusion Laboratory (NOAA/ATDL).

Consequently, the quality of the trend data generated by the network depends strongly on the quality of the concentration measurements and the deposition velocity estimates. Several methods could be considered for the concentration measurements, including the ASRL Concentration Monitor, whose accuracy for the major species of interest is likely to come close to the ±15% goal set as a design criterion. The accuracy of the deposition velocity estimates is likely to be poorer, however, and it could be much poorer unless careful attention is paid to the design of the network.

Bruce Hicks, the Director of NOAA/ATDL, indicated to the panel that the methodology they are developing for estimating deposition velocity is highly preliminary. It has only been tested against measurements at a few locations and only for SO_2, O_3, and HNO_3 (and, with much uncertainty, to NO_2); it has not yet been applied to particles. If the parametric method, at its present state of development, were to be applied at an ideal site (one with topographic and vegetative uniformity for at least 1 Km around the measurement location) with properties similar to those of the research sites, Hicks estimates that weekly average deposition velocities would be accurate within ±30% for O_3 and SO_2 (and, possibly NO_2) within ±50% for HNO_3 and ±100% (rough estimate) for particles.

Hicks indicated that he was uncomfortable with use of the ATDL method without considerable further development and evaluation. He indicated that he had not been approached concerning a site selection and measurement approach appropriate for use with the parametric method.

It is clear that the success of the trends network depends largely on reasonably accurate estimates of deposition velocity. This places a sizeable responsibility on ATDL for development of a suitable method for estimating the deposition velocity. Major political decisions may ultimately be made based on findings that depend on that method.

This situation concerns the panel from two perspectives:

(1) There appears to be little communication between ASRL and ATDL, and EMSL and ATDL, concerning the deposition velocity method. Yet, both ASRL and EMSL are undertaking projects under the assumption that such a model will soon be available.

(2) The selection of sites by EMSL for the 30-site network is likely to be severely constrained by the limitations of the deposition velocity estimating method. EMSL needs to consider these constraints in the network design. If it cannot perform its task within acceptable accuracy limits under these constraints, then it will have to deploy sites at locations that will provide lower accuracy (and hope the estimating method will improve in the future). Alternatively, it will have to delay the deployment of monitors until the estimating method imposes fewer constraints. In either case, acquisition of acceptably accurate and complete dry deposition data would be delayed.

Considering these factors, the panel strongly recommends that efforts be made to increase the level of technical interaction between ASRL, EMSL, and ATDL on issues related to dry deposition monitoring. Regular meetings to review plans and progress are essential to insure the highest possible probability of acquiring meaningful data from the initial 30-site network.

The panel also recommends that the capabilities of other qualified organizations be sought to assist development of deposition velocity estimation methods. The crucial role of the dry deposition velocity in obtaining flux estimates for the 30-site network requires that a considerable effort be devoted to parameterization of V_d .

The overall efforts should be peer reviewed by experts to maximize the chances of developing a viable method which is of use to NAPAP.

2.4 General Comments

2.4.1 Management Team/Project Staff

Overall, the panel feels that the ASRL management team represents a competent and motivated group of individuals. The presentations were reasonably well prepared. The panel is pleased that ASRL has been candid and frank concerning perceived weaknesses in their program. All ASRL members with whom the panel interacted were receptive to the critical evaluation being provided, and appeared to be genuinely interested in obtaining feedback from the panel to help improve their work. Similarly, the in-house technical staff and external contractors appeared to be competent in the areas being addressed.

2.4.2 Integration of Tasks to Achieve Program Objectives

The panel recognized the difficulties in coordinating programs such as those in Task Group D. However, there are a number of areas in which efforts toward better coordination would be beneficial.

The manner in which the written material sent to panel members was prepared is indicative of less-than-optimal organization. For example, the in-house projects on the concentration monitor and eddy accumulator were summarized by inclusion of one manuscript each, although the bibliographies of both papers listed additional manuscripts authored by ASRL personnel which were relevant to the program objectives. The project descriptors for the external contracts were incomplete in some cases and provided little of the technical information needed for proper evaluation. Without the scheduled presentations to the panel by ASRL members, as well as the unscheduled meetings with opportunities for additional questions, it would have been difficult to evaluate the program. The panel feels that the written material submitted for advance review should have provided enough information to allow a reasonably thorough evaluation by individual panel members prior to the meeting.

Several specific instances of coordination problems were apparent. For example, field measurements in the Materials Effects Program (Task Group G) have been proceeding without accurate aerosol NO_3^- or HNO_3 monitoring, in spite of development of an appropriate sensor by ASRL (This is discussed in section 3.2.1.4.).

It would be especially useful for ASRL members to have a better understanding of the deposition velocity parameterizations being developed by NOAA, since the success of the ASRL efforts depend, to a great extent, on the success of these parameterizations.

2.4.3 Related Research: Surrogate Surface Methods

Despite the sizeable research efforts at developing micrometeorological methods, no funding is provided to investigate surrogate surfaces. The reason for this is probably historical: there have been sizeable expenditures for acquiring NADP dustfall bucket data over the past several years, which are now believed to have little meaning. This unproductive use of resources has apparently prejudiced the feelings of many individuals researching dry deposition against the use of any surrogate surface.

However, there is a growing body of evidence that suggests surrogate surfaces may provide an inexpensive means of acquiring direct dry deposition data applicable to the goals of Task Group D. For example, several gaseous species are removed efficiently by surfaces whose aerodynamic resistance controls overall dry deposition. A surrogate surface which reacts readily with these species may provide direct estimates of the fluxes. An example is the use of nylon surfaces to absorb HNO_3. As another example, deposition of large particles (greatly influenced by sedimentation) may be easiest to measure with surrogate surfaces rather than with airborne concentration measurements; the latter requires accurate knowledge of the size distribution to estimate fluxes, and sampling such large particles is difficult.

The panel recommends that research be initiated in surrogate surface development. It should provide new techniques for reliably and inexpensively measuring dry deposition of some species.

2.4.4 Program Strengths and Weaknesses

The primary strengths of the program relate to the competence of the personnel (in-house and external contractors), and the facilities available for conducting the work. The objectives of the program are reasonably clear and progress is being made toward achieving the objectives in a way which will be of use to NAPAP.

The primary weaknesses of the program concern lack of coordination in certain respects. Better communication is needed among the external contractors, and between the contractors and ASRL. Improved communication between Task Groups is also needed.

2.5 Recommendations (In Approximate Order of Priority)

The recommendations that follow represent issues of high priority discussed in detail and in context in this portion of the report. In some cases, a single recommendation synthesizes individual recommendations made for several tasks. In addition to those given below, a number of significant other recommendations appear in the general discussion.

- Technical interaction between ASRL, EMSL and NOAA/

ATDL on issues related to dry deposition monitoring and the proposed 30-site National Trends Network should be increased, perhaps with regular semi-annual meetings.

- The capabilities of several qualified organizations should be sought to assist development of deposition velocity estimations. The overall efforts in this area should be reviewed periodically by a panel of experts from the international scientific community.

- Research in micrometeorological methods for dry deposition measurement appears to be worthwhile and should continue.

- Spatial scales, over which the dry flux determinations and concentration monitoring are representative, need to be identified.

- The accuracy and precision of the ASRL Concentration Monitor should be evaluated over the range of conditions likely to be encountered in actual network operations.

- Research into developing surrogate surfaces for routine monitoring should be initiated. Particular emphasis should involve surrogate surface design for assessing fluxes of reactive gases, and of large particles which may play a role in neutralizing depositing acids.

- The collection of >10 μm airborne particles by the ASRL Concentration Monitor is unlikely to be useful, and should not be pursued.

- Additional emphasis needs to be put on determining the flux of alkaline species to determine a net acid dry flux.

III

MATERIALS EFFECTS PROGRAM - TASK GROUP G

3.1 Background

The ASRL program, Effect of Acid Deposition on Materials, conducted for NAPAP, is primarily concerned with those materials of construction deemed to be of broad economic significance. They are listed as: galvanized steel, weathering steel, exterior household paints, maintenance paints, automotive finishes, asphalt roofing shingles, and concrete/cement.

The Materials Effects Program in ASRL is expected to develop damage functions for these materials to differentiate between the normal expected weathering and accelerated weathering attributable to wet and dry deposition. These damage functions, the primary output of the program, are to be provided to Task Group I (Assessments) of NAPAP to permit comprehensive cost-benefit analysis of acid deposition controls on materials damage effects.

Two related materials programs are the Gaseous Air Pollutants (GAP) program of ASRL and the materials effects research on stone and marble deterioration by the

National Park Service (NPS). While the efforts of the former are to a degree integrated with the ASRL effort, that of the NPS appears not to be.

3.2 Task Reviews

3.2.1 Field Studies

3.2.1.1 Structural Materials-Metals (Task 3024). Damage functions for seven metallic materials are being developed from exposure data collected at five field sites. The corrosion rates of the panels will be correlated with data on weather, air pollutants and rain chemistry, all of which are being recorded simultaneously with the exposure data. The seven materials are representative of the most common metals in the inventory. In our opinion, additional metals need not be considered at the present time.

The four sites at which measurements are now being made are typical of rural (North Carolina and New York), surburban (New Jersey) and urban (District of Columbia) environments with low to medium concentrations of sulfur dioxide. The opening of a fifth site in Steubenville, Ohio, is a much needed extension of the program to cover industrial environments with high concentrations of sulfur dioxide. It would be desirable to open one more exposure site preferrably downstream from a combined urban/industrial area.

The exposure racks at the North Carolina, New York and New Jersey sites are installed in open areas with natural ground cover. The weathering racks at the District of Columbia and Ohio sites are located on the roofs of buildings, subjecting the specimens to the heat radiation from the asphalt roofs and emissions from roof top vents. This creates microenvironments not typical of the macroenvironments, particularly with regard to the formation of dew. The researchers should modify the exposure conditions in a manner that eliminates the microenvironment effects. Microenvironments are also being created below the transparent covers that shelter the weathering racks against rainfall at the North Carolina site. These racks should, accordingly, be modified.

Exposure times of one month are too short for meaningful studies of the effect of weather and pollution. The researchers did well to end these tests. The three-month, one-year, and three-year exposure times are suitable for studying the seasonal and short-term effects of atmospheric constituents. We understand that longer exposures may not be feasible under the time constraints of this project. However, we strongly recommend the initiation of long-term exposures. Most buildings and bridges last more than 50 years. Damage functions cannot be reliably extrapolated from 3 to 50 years. If the number of specimens from the same batch is limited, some replicate three-month or one-year exposure tests could be converted to long-term exposure tests.

The simultaneous acquisition of corrosion, weather, and air pollution data is valuable. A successful correlation of two sets may yield, perhaps for the first time in the United States, the functions needed to estimate, over a large geographical area the corrosion damage to metals from acid deposition. The researchers should, without delay, begin to correlate the exposure data with the weather and air pollution data, so as to identify the significant variables at an early stage of the program. An understanding of the phenomena would allow, if needed, adjustments in the experimental program.

We were not given an indication of the approach that will be used to construct damage functions. As a word of caution, we would like to emphasize that multivariate regression analysis describes the data within the range of the variables tested, but it is not a substitute for a mathematical model founded on an understanding of the physical-chemical mechanisms. The weight loss data must be carefully examined and interpreted in terms of the weather and air pollution data and the results of the microanalysis of the corrosion products. The development of damage functions should begin at once.

3.2.1.2 Non-Metallics. Analogous to the task on metallic materials, Section 3.2.1.1, the objective of this task is to derive damage functions for exterior paints by conducting field exposure studies. The intent is to characterize the paint film damage in terms of erosion of the film, its surface chemistry, and changes in surface reflectance. The damage will be related to the meteorological, pollution, and rain chemistry data that are being simultaneously monitored.

The approach raises questions with regard to the time of exposure, type of substrate, and development of damage functions. Three years may not be sufficient to significantly damage the paint film, especially when that coating is applied on a passive substrate such as the stainless steel panels being used in this study. For example, the service life of paint coatings on highway bridges fabricated from carbon structural steel varies from about eight years in the moist and chloride-contaminated microenvironments that occur in the Northeast and Midwest to about 30 years in the dry environments in the southwestern states. The researchers face, in this task, a problem similar to that in the field study of metals, namely, of having to derive damage functions from short-term exposures and extrapolating the results to long-term service life. Longer exposures are needed.

Our second comment relates to the type of substrate on which the paint coating is applied. In our opinion, the paints should be tested in combination with a realistic substrate. We agree with the Paint Workshop's recommendation to test a paint system on hot-rolled steel substrate. Advice on the choice of a suitable paint for hot-rolled steel should be sought from specialists, such as the staff of the Michigan Department of Transportation, Lansing, Michigan, who are the leaders in the qualification of commercial paint systems. The proposed tests of latex paint applied on western red cedar are discussed in Section 3.2.3.1.

The third comment relates to the measurement of damage. As noted in the Paint Workshop's recommendations, failure is to be assessed visually in terms of blistering, lack of adhesion, substrate rusting, and rust spots on the film. We foresee difficulties in relating such visual observations to weather and air pollution data, and quantifying them in damage functions for a given paint/substrate system.

We recognize that the paint industry may traditionally have exposed samples at a 90^0 angle from the horizontal. However, the choice of the vertical exposure for testing the paints in this task, as compared to the 30^0 exposure of the bare metallic samples (Section 3.2.1.1), introduces one additional variable, without providing any advantages. Furthermore, a slanted surface may be better for studying the effect of acid deposition.

We recommend that the researchers carefully review their current plan for testing and analysis before they continue with the field studies.

3.2.1.3 Acid Rain Simulator. The objective of the study is to quantify separately the effects of wet and dry acid deposition on steels and household paints exposed to ambient weathering. Three conditions are being studied: (1) dry only; (2) dry and ambient wet (4.5 pH average at RTP for rain); and (3) dry and controlled wet (5.6 pH spray).

It is well known that rain washing of pollutants off the surfaces of weathering steel structures helps the steel develop a protective oxide coating. Based on this experience, one would, for example, expect higher corrosion rates for weathering steel exposed to the "dry only" condition, and lower corrosion rates when skyward-facing surfaces are rinsed by the rain or the controlled spray. The other materials being tested may behave in a similar manner. Dry deposition will likely be the controlling factor, with rinsing being beneficial. The effect of the average 1.1 pH unit difference between the rain and the spray water could be masked by the generally beneficial effect of rinsing. The expected results may lead to the incorrect conclusion that the dry deposition is damaging to the materials, the wet deposition is beneficial, and the pH of the rain is not a factor.

The interpretation of the results needs to consider conditions not modeled by the experiments. For example, rain water collecting on horizontal and poorly drained surfaces in actual structures can increase the effect of acid deposition.

This experiment is elaborate and expensive. We recommend not placing a simulator at the Steubenville site until the researchers have fully characterized the results from the RTP site and understood the significance of the findings. Snowfall adds an uncertainty to the planned exposures at the Steubenville site that needs to be resolved. The pH of the rinsing water at the RTP site should be periodically checked.

3.2.1.4 Site Monitoring. Air quality and meteorology are being monitored at all five of the exposure sites. Local agencies perform the measurements at three of the sites, with the primary purpose of the measurements being other than the materials effects program. ASRL is supporting the measurements at the Newcomb, New York, and Research Triangle Park, North Carolina, sites.

Each site measures SO_2, NO_x, and O_3 continuously.

Dichotomous samplers, specially modified to collect samples over a one-week period, collect fine and coarse fractions of PM-10 particulate matter. These filters are analyzed for mass, elements (by XRF), and $SO_4^=$ and NO_3^- (by ion chromatography). Total suspended particulates are also measured similarly. Monthly-averaged rain samples are analyzed for pH and various ions. Meteorology (wind speed and direction, temperature, relative humidity, precipitation rate, and solar radiation) are measured continuously. It is expected that all of these variables play a role in the deposition of acidic material to the exposed samples.

The monitoring sites lack the ability to measure gaseous nitric acid and the nitrate analyses of the dichotomous samples do not properly reflect particulate nitrate because of volatilization of some of the material on the filters. We recommend adding a sampling method that properly characterizes NO_3^- and HNO_3 at all sites; the ASRL Concentration Monitor would serve this need.

Relative humidity is measured by hair hygrographs that are calibrated infrequently. Such instruments are known to easily change calibration. We recommend, as a minimum, that their calibration be checked weekly by comparison with a psychrometer. Installation of a more reliable humidity recording system would be preferable. Although we recognize that such systems are expensive, they are compatible with electronic recording of the data, which would reduce the costs of handling and reducing recording charts.

Quality assurance procedures for the aerometric monitoring at the sites appear to be uneven. The sites operated by local agencies comply with EPA QA procedures for monitoring, which are focused at concentration levels near ambient air quality standards. The systems and performance audits that will be performed for the sites are desirable, and the planned calibrations at low concentration levels are absolutely necessary. We hope that these calibrations will be repeated at regular intervals.

3.2.1.5 Aerometric Data Base The compilation of the aerometric data into a data base that is suited for analysis is absolutely necessary for the success of the exposure program. The aerometric data base management task appears to be accomplishing this successfully.

However, the data base would be most effective if it were designed for use with the data analysis procedures planned for the program. We did not see that a plan for data analysis had been formulated, or that the data base design had been adapted to such a plan. This is a serious shortcoming of the materials exposure program that is discussed in greater detail in Section 3.3.3 below.

There did not appear to be a procedure for applying calibration factors to data, which may become necessary. A desirable feature of the data base is the ability to flag data that deserve special attention because of poor quality, need for special calibration, or other factors. We hope that this feature will be utilized.

3.2.2 Chamber Studies

The panel strongly supports the chamber study effort. Most significant is the growing interest in characterization of corrosion layers, mass balances, and reaction kinetics. This represents a marked strengthening of the ASRL materials programs which in the past relied too heavily on regression analysis of simple weight loss data. It is important to recognize that the determination of reaction mechanisms is essential to the development of mitigative strategies and to the assignment, with confidence, of the proportions of damage attributable to wet and dry deposition. It does not appear that the group has expertise in corrosion mechanisms, or has sought the advice of appropriate experts. An understanding of corrosion mechanisms will be essential, not only to interpretation of the data obtained in chamber studies, but also for the interpretation of field exposure data. For example, the reversal in corrosion rates observed for Cor-Ten A and 110 copper exposed at the Washington, DC and RTP sites is possibly due to microenvironmental influences on reaction kinetics and mechanisms. Yet, no attempt has been made to explain these data from a mechanistic viewpoint.

3.2.3 New Projects (FY 86)

Four new projects with total support level of $500,000 were described briefly. Two involved the extension of materials effects studies to new areas, namely concrete and masonry structures and asphalt roofing shingles. A third proposed an expansion of the non-metallic study to investigate initial effects on paint films on wood substrates. The fourth encompassed placement of corrosion rate monitors developed under the GAP program at the five field exposure sites.

3.2.3.1 Initial Effects on Painted Wood Substrates.

The proposed extension of the painted surface study to include wood substrates, chamber studies, initial effects, and the mechanism of paint film failure is based, in part, on the recommendations of the recent workshop on exterior paints held at RTP. This use of industry expertise in a cost-effective manner is to be commended.

Only a brief outline was given of the proposed work. The panel is concerned that the substantial complexities introduced by the new substrate (wood) will unduly complicate the chamber study of paint films. Similarly, the experimental designs for the FTIR and thermometric studies are not yet defined. It is recommended that the initial effort be directed toward the development of experimental protocols and test methods. Field exposure of paint films on wood substrates is considered premature.

Consideration should be given to the workshop observations that: (1) historical field exposure data may provide the best means of determining actual service life, and (2) damage measurement techniques should correlate with painting frequency.

3.2.3.2 Effects on Concrete and Masonry Structures. The extensive use and wide distribution of concrete structures suggests that this material be investigated for possible acid deposition effects. However, the well-known role of chloride ion in the decay of reinforcing steel and the strongly alkaline nature of the concrete matrix suggests that a relatively small proportion of observed damage may be associated with acid deposition. Since substantial research and use experience are available, it is recommended that a workshop be conducted at RTP to review the state of concrete structure use experience and damage mechanism research prior to initiation of the laboratory study (Phase I), or the field survey involving core sampling of existing structures (Phase II).

3.2.3.3 Effects on Roofing Asphalt Shingles. Asphalt roofing shingles complete the list of construction materials of economic significance under consideration by EPA. Some sense of service life cycles and failure mechanisms is required before initiation of laboratory and field investigations. It appears appropriate to limit the effort for FY 86 to the initial literature survey (Phase I).

3.2.3.4 Evaluation of Corrosion Monitor at Exposure Sites. The panel was informed of the proposal to evaluate corrosion monitors developed under the GAP program at materials exposure sites. As noted in the 1984 review of the GAP Materials Damage Program, the response of the corrosion monitor to atmospheric pollution and meterological variables is not yet fully understood. It is not obvious that this device will prove useful in the proposed task of comparing short-term effects for the diverse materials, e.g., steel, concrete, limestone, marble, paint films, and asphalt, either in place or eventually to be placed at the field exposure sites.

3.3 General Comments

3.3.1 Management Team/Project Staff

The management and project staff team has demonstrated initiative, industry, and the ability to work together effectively. They have made good use of the workshop on paint damages to obtain guidance in an unfamiliar area.

The 1983 review panel for this project observed that "the smog chamber studies may soon lead to questions of corrosion mechanisms, a field with many experts." It is disappointing that no effort has been made to follow their recommendation that contact soon be made with such experts to obtain guidance and to assure the success of the studies.

3.3.2 Integration of Tasks to Achieve Program Objectives

The stated goal of this program is to "develop materials damage functions that partition effects of wet and dry deposition for use by Task Group I, Assessment, to develop a cost benefit model." The panel believes that inadequate attention has been paid to the uncertainties associated with the use of damage functions derived from short-term field exposure or chamber studies in the development of the cost benefit model (Figure 2) that will be used to conduct an economic assessment of acid deposition damage and to prepare an acid deposition control strategy. This issue is documented in the following section.

3.3.3 Relationship Between Field Studies, Chamber Studies and Damage Functions

For results from controlled chamber studies to be related to field studies and interpreted as damage

COST BENEFIT MODEL

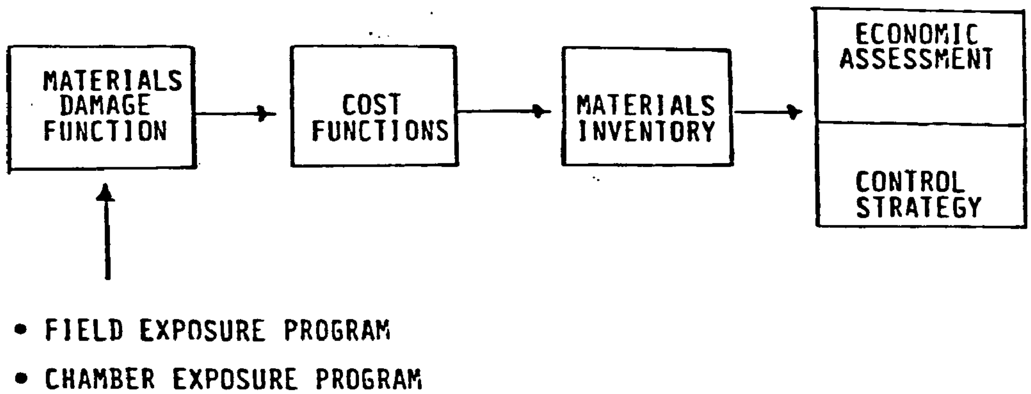

Figure 2. Task Group G Effects on Materials and Cultural Resources

functions, physical-chemical mechanisms must be proposed. The models are tested statistically, and best fits of coefficients determined. The hypothesis is well developed before the use of statistical methods. The variety of possible mechanisms and environmental conditions make engineering approximations appropriate for the simplification of the damage functions, but experimental design must be more than empirical measurements with regression relationships. Otherwise, the response is known only over the range of test conditions and cannot be extropolated to new environmental conditions.

Once a model is proposed and tested, the uncertainty in each bit of data must be carried through to the final step of the determination of the damage function. The propagation of errors must be determined for the final results. The standard deviation among replicate samples is not adequate for the interpretation of overall uncertainty.

In the chamber studies, concentrations have been measured for air species and metal and anion corrosion products. A mass balance approach is being considered. In practice, the small differences in relatively large numbers makes the comparison of material lost with corrosion products leached impractical. Once the products are collected, linear relationships are considered between product species. Non-linear relationships (e.g., pH controls of solubility) have not been considered/have not been used, and measurements of carbonates (a corrosion anion product) have not been made. Approximate linearity may exist between many species, making it difficult to determine the mechanism or cause of damage. This can be partially alleviated by the use of more controls. However, it is doubtful synergistic effects will be understood without an experimental design based on the test of specific physical-chemical mechanisms. Even the transport mechanism, such as thermophoretic effects in the dew condensation system, as compared to the real world, should be reconsidered.

With the limitations of the understanding of the chamber study results, the interpretation of the field studies becomes phenomenological. The damage functions for metals could be determined from the short-term chamber study results. Expansion of the testing in the chamber studies is needed to generate damage functions.

In the environmental conditions with the most rapid corrosion, the surface resistance to the deposition velocity should be determined. This parameter could be related to the field studies, even with variable meteorological conditions.

The main concern in the link between chamber studies, field experiments, and damage functions is that the damage is a long-term process, yet the best data for the damage function will be based on short-term studies. Considerations of long-term mechanisms and failures become crucial. Long-term studies are needed, either under NAPAP or air quality funding sources.

3.3.4 Related Research

The visit to the RTP field exposure site demonstrated the substantial commitment of the National Park Service (NPS) to field exposure studies for marble and limestone. These materials should be considered for parallel chamber studies under the direction of the Materials Effects Program under review since the NPS has neither the resources (smog chamber and associated hardware) nor the expertise necessary to conduct such work.

3.3.5 Program Strengths

The selected experimental designs are being performed well. The chamber studies are well controlled. ASTM standard exposure procedures are followed. The results are reproducible. The right metals have been chosen for study. The simultaneous measurement of air quality in the field appears excellent, with the exception of the omission of HNO_3.

3.3.6 Program Limitations

The materials effects program suffers from the inherent limitation of studying long-term processes over a relatively short time. This is recognized and may not be avoidable.

There is some question of representativeness. Standard methods have been used for reproducibility, but there is a concern that precipitation acidity effects will be largest on materials which collect/retain precipitation. The orientation of test specimens minimizes contact with wet precipitation and its effects.

In particular, snow has not been addressed. Its importance to material damage in terms of snow melt is unknown, but deserves consideration.

The major limitation is in the characterization of the mechanism of corrosion. While overall rates are empirically determined, the mechanism is still unknown. With the high covariance of the depositions of chemical species, the agent of corrosion is obscured.

An overall plan is needed to determine damage functions from the field and chamber measurements.

3.3.7 Quality Assurance and Quality Control

Quality assurance and quality control are an integral part of all environmental research. The researchers have a healthy appreciation of the limitations of specific analytical procedures. They have made commendable efforts at upgrading the QA for continuous monitors used in the field and laboratory studies.

A few limitations were noted. The metal measurements need to be confirmed by using split samples, and the method of standard additions to the liquid samples. Hydrogen peroxide is currently not considered in the corrosion modeling of condensation on metals for lack of a method of good quality assurance. This needs to be rectified to provide a measure of oxidants. Samples are not routinely subjected to a complete anion and cation balance, a standard QA technique which also provides useful information about acidity. Similarly, aerosol measurements do not determine ammonium or acidity and instead focus on nitrates, sulfates, and elements by XRF. All chemical determination techniques should be tested for quality assurance by either cross calibration with an alternate technique, or internal consistency between measurements with respect to mass, charge, or conductivity for a percentage of the samples.

3.4 Recommendations (In Approximate Order of Priority)

The recommendations that follow represent issues of high priority discussed in detail and in context in the body of this portion of the report. In some cases, a single recommendation synthesizes individual recommendations made for several tasks. In addition to those given below, a number of significant other recommendations appear in the general discussion.

- Study of physical-chemical mechanisms for corrosion should be incorporated into the research design, and carried through to the damage functions.

- A plan needs to be developed for the analysis of exposure data, and the development of damage functions.

- The aerometric monitoring at the materials exposure sites should be augmented to include nitric acid and proper measurement of particulate nitrate. The ASRL Concentration Monitor could satisfy this need.

- A series of workshops is recommended for obtaining guidance for the proposed new efforts in paint films on wood substrates, asphalt roofing shingles, and concrete before field exposure and laboratory studies are initiated.

- A modification of the field exposure program to extend measurements to long-term exposures should be initiated. Placement of a second acid rain simulator at the Steubenville site should be delayed until the results from the RTP prototype are characterized and understood.

- Propagation of errors should be carried through the testing.

- Effects of snow and irregular surface geometry should be considered.

APPENDIX A

AGENDA - PEER REVIEW OF THE ACID DEPOSITION, DRY DEPOSITION, AND MATERIAL DAMAGE PROGRAM

A G E N D A

Peer Review of the Acid Deposition Dry Deposition
And Materials Damage Program
April 23 - 25, 1985

TIME	TOPIC	SPEAKER
Tuesday, April 23	(Raleigh Inn - Raleigh, NC)	
8:00 - 8:15	Opening Session Welcome	C. Coley
	Peer Review Program Orientation ASRL Peer Review Coordinator (Closed Session)	R. Patterson
8:15 - 8:30 a.m.	Coffee and Donuts in Meeting Room	
	DRY DEPOSITION MEASUREMENT PROGRAM	
8:30 - 8:35 a.m.	Session Called to Order	R. Patterson
8:35 - 8:45 a.m.	Dry Deposition Measurement Overview	K. Knapp
8:45 - 9:20 a.m.	Direct Dry Deposition Methods Extramural Projects In-house Project	 T. Ellestad R. Speer
9:20 - 10:15 a.m.	Concentration Monitor Projects	K. Knapp
10:15 - 10:30 a.m.	B R E A K	
10:30 - 11:00 a.m.	Core Sites and Deposition Velocity Parameterization	T. Ellestad
11:00 - 11:30 a.m.	Questions and Discussion	
11:30 - 1:00 p.m.	L U N C H	
1:00 - 1:15 p.m.	Overview of Materials Effect Research Program	J. Spence
	MATERIALS FIELD EXPOSURE PROGRAM	
1:15 - 2:00 p.m.	Structural Materials	D. Flinn, BOM
2:00 - 2:30 p.m.	Deterioration of Non-Metallics	J. Spence
2:30 - 3:00 p.m.	Acid Rain Simulator	E. Edney, NSI
3:00 - 3:15 p.m.	B R E A K	

TIME	TOPIC	SPEAKER
Tuesday, April 23 (cont.)		
3:15 - 3:45 p.m.	Site Monitoring	J. Spence
3:45 - 4:15 p.m.	Data Base Management	J. Graham, CSC
4:15 - 5:00 p.m.	Questions & Discussion	
5:00 p.m. - Until	Reviewer Debriefing with Dr. Alfred H. Ellison, Director, ASRL (M-303)	Closed Session
Wednesday, April 24, 1985	(Research Triangle Park, NC and Raleigh Inn, Raleigh, NC)	
	Materials Chamber Exposure Program	
8:30 - 9:30 a.m.	Chemistry of Acid Precipitation Effects on Materials (EPA: M-303)	E. Edney
9:30 - 10:00 a.m.	New Projects	J. Spence
	Site Visit - Materials Exposure	
10:00 - 11:00 a.m.	Visit Exposure Chambers	E. Edney D. Stiles, NSI
	Site Visit - Dry Deposition	
11:00 - 12:00 p.m.	Measurement Methods (ERC Annex)	K. Knapp
12:00 - 1:30 p.m.	L U N C H (NIEHS) National Institute of Environmental Health Sciences Cafeteria	
1:30 - 2:30 p.m.	Telephone Call to Bruce Hicks	
2:30 -	Return to Hotel	
	Executive Session	Closed Session
Thursday, April 25, 1985	(Research Triangle Park)	
8:30 a.m. -	Executive Session (EPA/D-102)	Closed Session

APPENDIX B

EPA-ASRL PEER REVIEW PANEL

REVIEW PANEL
ACID RAIN (TASK GROUPS D & G) PROGRAM
April 23 - 25, 1985

Name:	Norbert S. Baer, Chairman Professor of Conservation
Work Address:	New York University 14 East 78th Street New York, New York 10021 212-772-5846
Area(s) of expertise:	Materials damage effects, preservation of cultural property
Name:	Pedro Albrecht
Work Address:	Department of Civil Engineering University of Maryland College Park, Maryland 20742 301-454-5228
Area(s) of expertise:	Atmospheric corrosion of structural steels
Name:	Cliff I. Davidson Associate Professor of Civil Engineering and Public Policy
Work Address:	Carnegie-Mellon University Pittsburgh, Pennsylvania 15213 412-578-2951
Area(s) of expertise:	Aerosol deposition, trace elements characterization and human exposure, historical air pollution trends
Name:	Howard M. Liljestrand Assistant Professor
Work Adress:	Civil Engineering, Environmental Engineering Group 8.6 ECJ University of Texas Austin, Texas 78712-1076 512-471-5602
Area(s) of expertise:	Acid-base deposition mechanism-tracers of acid/bases and receptor models, wet & dry deposition mechanism of aerosols and gases, reactions upon deposition to materials, box models of the atmosphere, kinetic models related to aerosol and acid producation.
Name:	Ivar H. Tombach Vice President, Environmental Programs
Work Address:	Aero Vironment, Inc. 825 Myrtle Avenue Monrovia, California 91016 818-357-9983
Area(s) of expertise:	Visibility, aerosol physics, fluid mechanics

APPENDIX C

PROCESS EVALUATION REPORTS

ATMOSPHERIC SCIENCES RESEARCH LABORATORY
PEER REVIEW

Process Evaluation Results for the Dry Deposition and Materials Effects Program

The Atmospheric Sciences Research Laboratory (ASRL) of the U.S. Environmental Protection Agency convened a panel of scientific experts on April 23-25, 1985, to review the Dry Deposition and Material Effects Program. The panel consisted of five scientists. These reviewers were asked to evaluate the process involved in preparing and implementing this review. This report presents their opinions of the process for this specific meeting.

The evaluation instrument was designed to assess the following aspects of the process: (1) Preview Materials; (2) Process and Logistical Information; and (3) the Review Meeting. A section was also provided for reviewers to give their comments and recommendations. The reviewers were instructed to respond to 15 items by circling numbers from 1 to 5 (with 1 representing poor; 2-fair; 3-good; 4-very good; and 5-excellent).

Only three of the five panel members have submitted a process evaluation form. Overall, the reviewers' evaluation of the peer review process was positive. Most of the areas in the instrument generated "very good" and "good" ratings. Only two items were rated fair. One panel member rated the utility of the preview materials for outside reviewers as fair, commenting that they were incomplete. The adequacy of time for review panel executive sessions also received one fair rating because the commenting panel member felt more time was needed. None of the reviewers rated any item as "poor". Table 1 presents a summary of the reviewers' ratings, as well as their specific comments and recommendations.

Table 1

Review Categories	Number of Reviewers Rating Each Item				
	Poor	Fair	Good	Very Good	Excellent
Preview Materials					
1. Written Quality			1	2	
2. Technical Quality			2	1	
3. Utility for Outside Reviewer		1*		2	
4. Adequacy of Time Available to Preview		1	4	7	
Process and Logistical Information					
5. Meeting Purpose			1	1	1
6. Scheduling of Meeting: Agenda/Format			1	1	1
7. Reviewer Responsibilities: Time/Preparation Requirement			1	1	1
8. Overall Peer Review Process			1	1	1
9. Timeliness of Meeting Notification			3		
10. Timeliness of Logistical Information			1	1	1
Review Meeting					
11. Adequacy of Time for Discussion With EPA Staff			2		1
12. Adequacy of Time for Executive Session		1**		2	
13. Quality and Utility of Presentations			1	2	
14. Quality and Utility of Materials Disseminated			2		1
15. Support Services and Activities				1	2***
TOTALS		2	17	17	9

* "incomplete"

** "need more time"

*** "very good support by Research and Evaluation Associates Staff"

Reviewers' Comments

"The lion's share of the useful review materials were distributed after our arrival at RTP, or during (or after) presentations. This made preparation of a first draft review report (as suggested in the introductions) impossible."

"The support by the Research and Evaluation Associates staff was excellent. The hotel facilities were poorly managed by the hotel. The lodging was OK, though."

"The time needed to prepare a coherent report is somewhat more than the time we were given, even though most of us gave up a good portion of the night's sleep to get this job done."

"The only weakness in the review process is the time constraint on Review Panel Discussion as the report is written. That a highly responsible committee averaged 4-5 hours sleep, essentially skipped dinner (24), skipped breakfast and lunch (25) during the period Wednesday (24) 3 PM thru departure, Thursday (25) 3 PM and still had but little time to discuss the completed draft report indicated to this reviewer that the schedule is a bit tight."

Reviewers' Recommendations

"I would not eliminate any aspect of the review process but would suggest that a later departure (session closing time) be scheduled for the last day. I think we all agreed that one wants the best posible draft submitted at the time of adjustment, rather than a weak draft to be upgraded later."

APPENDIX D

ASRL RESPONSES TO REVIEWERS' COMMENTS

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ATMOSPHERIC SCIENCES RESEARCH LABORATORY
RESEARCH TRIANGLE PARK
NORTH CAROLINA 27711

MEMORANDUM

DATE: July 8, 1985

SUBJECT: Response to Peer Review Comments on Materials Effect Program

FROM: John Spence, Project Manager

TO: Ron Patterson
Technical Planning and Review Office

THRU: William Wilson
Acting Director, EMCD

Reviewers' Comment	ASRL Investigators Response
1. "The researchers should modify the exposure conditions in a manner that eliminates the microenvironment effects. Microenvironments are also being created below the transparent covers that shelter the weathering racks against rainfall at the North Carolina site. These racks should, accordingly, be modified." (p. 29)	Meteorological instrumentation have been installed adjacent to the material exposure racks at the DC and Ohio sites in an attempt to measure the microenvironment associated on the roof. Air sampling is also taken at roof top at both sites. In addition to these measurements, a corrosion monitoring device (developed under GAP), which is an excellent time-of-wetness sensor, is proposed for installation at all material exposure sites in FY86. The transparent covers installed by BOM are considered experimental devices that will likely be modified during the study. The BOM has developed the covering device to insure consistent corrosion of samples under the device.
2. "We understand that longer exposures may not be feasible under the time constraints of this project. However, we strongly recommend the initiation of long-term exposures." (p. 29)	Under the NAPAP, the maximum exposure time of materials is likely 3 to 5 years. Longer exposure periods (10-20 years) are not possible within the existing NAPAP.
3. "The researchers should, without delay, begin to correlate the exposure data with the	We agree. Correlation studies are planned in FY86. The main problem which could delay these studies is

weather and air pollution data, so as to identify the significant variables at an early stage of the program. An understanding of the phenomena would allow, if needed, adjustments in the experimental program." (p. 30)

the computerization and validation of the aerometric data base.

4. "We were not given an indication of the approach that will be used to construct damage functions. As a word of caution, we would like to emphasize that multivariate regression analysis describes the data within the range of the variables tested, but is is not a substitute for a mathematical model founded on an understanding of the physical-chemical mechanisms. (p. 30)

Chamber exposures of materials and the analysis corrosion products of field exposed materials will provide insight into the physical-chemical mechanisms of degradation. This information will support the development of damage functions via multivariate regression analysis of field exposure data.

5. "The researchers face, in this task, a problem similar to that in the field study of metals, namely, of having to derive damage functions from short-term exposures and extrapolating the results to long-term service life. Longer exposures are needed." (p. 31)

In the non-metallics program, exposures beyond 3-years are planned. This was apparently missed in the review.

6. "Advice on the choice of a suitable paint for hot-rolled steel should be sought from specialists, such as the staff of the Michigan Department of Transportation, Lansing, Michigan, who are the leaders in the qualification of commercial paint systems. The proposed tests of latex paint applied on western red cedar are discussed in Section 3.2.3.1." (p. 32)

We agree. Test panels of an alkyd on hot-rolled steel are being prepared by the Steel Structures Painting Council for exposure at the materials sites in FY86. This study will be coordinated with other exposure programs of the alkyd paint that the Steel Structures Painting Council is sponsoring.

An Interagency Agreement (IAG) with the Forest Products Laboratory is planned for late FY85. This IAG will involve laboratory testing of latex paints applied on western red cedar.

7. "We foresee difficulties in relating such visual observations to weather and air pollution data, and quantifying them in damage functions for a given paint/substrate system." (p. 32)

The main problem with visual inspection of the field exposure alkyd paints is the time it takes to see film failure (substrate rusting). The visual observations using color photographic standards according to ASTM procedures will be used. In conjunction with the field exposures, chamber exposures of the alkyd paints are planned for FY86 to assess early film failure under controlled pollutant environments. This study will investigate the use of thermography and other techniques to detect early film failure.

8. "We recognize that the paint industry may traditionally have exposed samples at a 90° angle from the horizontal. However, the choice of the vertical exposure for testing the paints in this task, as compared to the 30° exposure of the bare metallic samples (Section 3.2.1.1), introduces one additional variable, without providing any advantages. Furthermore, a slanted surface may be better for studying the effect of acid deposition." (p. 32)

All of the painted panels are exposed at 90° in accordance with ASTM D 1006-73. If painted wood substrates are incorporated into the field exposure program, panels will likely be exposed at the vertical and horizontal positions.

9. "This experiment is elaborate and expensive. We recommend not placing a simulator at the Steubenville site until the researchers have fully characterized the results from the RTP site and understood the significance of the findings. Snowfall adds an uncertainty to the planned exposures at the Steubenville site that needs to be resolved. The pH of the rinsing water at the RTP site should be periodically checked." (p. 34)

The placement of a mobile covering device at the Steubenville site is scheduled for FY85 and should not be delayed. The decision to place mobile covering devices with simulated rain at the RTP and Steubenville sites is based on a two-year study of metals and coatings using a covering device at the RTP exposure site. The Steubenville site has considerably higher SO_2 levels than the RTP site. The covering devices at both locations will be used to separate the effects of dry deposition (SO_2) and clean rain (pH 5.6) on materials degradation.

This information is needed for the FY87 and FY89 assessment reports.

10. "The monitoring sites lack the ability to measure gaseous nitric acid and the nitrate analyses of the dichotomous samples do not properly reflect particulate nitrate because of volatilization of some of the material on the filters. We recommend adding a sampling method that properly characterizes NO_3^- and HNO_3 at all sites; the ASRL Concentration Monitor would serve this need." (p. 35)	We agree. A request has been made to Task Group D to consider placement of dry deposition monitors including measurement of nitric acid, at each of the materials exposure sites in FY86.
11. "Relative humidity is measured by hair hygrographs that are calibrated infrequently. Such instruments are known to easily change calibration. We recommend, as a minimum, that their calibration be checked weekly by comparison with a psychrometer." (p. 35)	Only the Newcomb site uses the hair hygrograph to measure relative humidity. Plans are to replace this unit in FY85.
12. "The systems and performance audits that will be performed for the sites are desirable, and the planned calibrations at low concentration levels are absolutely necessary." (p. 36)	In addition to the regular calibrations and audits perfomed at the sites, a complete system's and performance audit of air monitoring and meteorological instrumentation is planned at least once a year.
13. "We did not see that a plan for data analysis had been formulated, or that the data base design had been adapted to such a plan," (p. 36)	The aerometric data base is being computerized in standard SAROAD format for use by various organizations, NPS, USGS, ANL, BOM, EPA, etc. who are involved in exposure of materials at the sites. Each of these organizations will use this data base to develop damage functions. This project will not develop a plan for analysis of their materials damage data.
14. "It does not appear that the group has expertise in corrosion mechanisms, or has sought the advice of appropriate experts." (p. 37)	The review panel fails to acknowledge the corrosion expertise of F. Haynie, who has published extensively on pollutant induced corrosion, and D. Flinn, S. Kramer and J. Carter at the BOM,

which is recognized as a leading government laboratory on metallic corrosion.

15. "Yet, no attempt has been made to explain these data from a mechanistic viewpoint." (p. 38)

No interpretation of the corrosion data was presented because this phase of study is planned for FY86 when validated aerometric data and 3-year corrosion data are available.

16. "It is recommended that the initial effort be directed toward the development of experimental protocols and test methods. Field exposure of paint films on wood substrates is considered premature." (p. 39)

We agree. A joint research program involving the exposure of painted wood substrates in controlled environmental chambers is being planned by EPA and USDA Forest Products Laboratory.

17. "Since substantial research and use experience are available, it is recommended that a workshop be conducted at RTP to review the state of concrete structure use experience and damage mechanism research prior to initiation of the laboratory study (Phase I), or the field survey involving core sampling of existing structures (Phase II)." (p. 39)

We agree.

18. "It appears appropriate to limit the effort for FY86 to the initial literature survey (Phase I)." (p. 40)

We agree.

19. "It is not obvious that this device will prove useful in the proposed task of comparing short-term effects for the diverse materials, e.g., steel, concrete, limestone, marble, paint films, and asphalt, either in place or eventually to be placed at the field exposure sites." (p. 40)

The evaluation of the corrosion monitor by ASRL was not presented because the work is within the GAP program. Based on the results of the lab and field test of this device, it is our recommendation to incorporate the corrosion monitor into the field exposure study.

20. "The panel believes that inadequate attention has been

The uncertainties associated with the development of the damage functions, paid to the uncertainties associated with the use of damage functions derived from short-term field exposure." (p. 41)

particularly the uncertainty of the regression coefficients, will be available to the users - the Assessment Program (Task Group I).

21. "With the limitations of the understanding of the chamber study results, the interpretation of the field studies becomes phenomenological. The damage functions for metals could be determined from the short-term chamber study results. Expansion of the testing in the chamber studies is needed to generate damage functions." (p. 44)

We agree. (However, see responses number 4 and 23.)

22. "The visit tothe RTP field exposure site demonstrated the substantial commitment of the National Park Service (NPS) to field exposure studies for marble and limetsone. These materials should be considered for parallel chamber studies under the direction of the Materials Effects Program under review since the NPS has neither the resources (smog chamber and associated hardware) nor the expertise necessary to conduct such work." (p. 45)

We agree.

23. "The major limitation is in the characterization of the mechanism of corrosion. While overall rates are empirically determined, the mechanism is still unknown. With the high covariance of the depositions of chemical species, the agent of corrosion is obscured." (p. 46)

The chamber studies are providing insight into the role wet and dry acid deposition play in the corrosion of materials. Deposition velocities, soluble corrosion products, etc. will provide insight into the mechanism of corrosion. However, a detailed characterization of the mechanism of corrosion for all materials being studied is beyond the funds available to this program.

We have attempted to respond to the list of recommendations (p. 48) as they appeared within the report. As we have discussed, the covering device to be installed at Steubenville, Ohio should be completed in FY85. The covering devices at RTP and Steubenville will be used to resolve the effects of dry deposition of SO_2 on materials within the timeframe of the NAPAP. The effects of snow, ice, fog, etc. are not being addressed in this program because of the limitation of resources. We agree that irregular surfaced materials should be included in this study. We are proposing to include irregular shaped materials as well as field weathered materials as part of our chamber program in FY86.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ATMOSPHERIC SCIENCES RESEARCH LABORATORY
RESEARCH TRIANGLE PARK
NORTH CAROLINA 27711

DATE: July 8, 1985

SUBJECT: Response to Peer Reviewers Comments on Dry Deposition Program

FROM: Kenneth T. Knapp
Project Manager, Dry Deposition Project

TO: Mr. Ronald Patterson
Technical Planning and Review Office

Reviewers' Comment	ASRL Investigators Response
1. "However, the project description is unclear as to the details of the parameterization." (p. 7)	The PO is revising the project description of task 1452 on the IAG with Argonne.
2. The ASRL concentration monitor, "the sampler should be tested under a variety of sampling and shipping temperatures, with realistic intervals between sampling and sample analysis,..." "...several such samplers should be deployed in the field to provide an operational field evaluation before commitments are made for permanent development." (p. 12)	ASRL ran a short field test of 7 week-long test then turned the systems over to EMSL who is now doing the recommended evaluation.
3. "The sampler does not yet have the capability of measuring, or has not been tested for, other species of interest to NAPAP, namely HCL, HCO^{-}_{3}, ..." (p. 12)	The ASRL CM (sampler) collects particles that can be analyzed for these species. However, neither time nor funding has permitted the development of these measurements at this time. While of interest to NAPAP, they are low priorities.
4. "However, we seriously question the merit of collecting the larger particles by use of the airborne concentration monitor and feel that the resources that would be devoted to this purpose should be used elsewhere." (p. 13)	I do not agree with the panels assessment of the merit of collecting particles larger than 10µm. In fact, several good proposed approaches were received in the proposals for this RFP. In the RFP. we gave a 3 to 1 priority to the smaller 2 to 10 µm particles but felt that if it were possible we should start the research for the greater than 10 µm particles as soon as possible.

5. "The issue >10μm particle deposition may best be approached through the us of surrogate surfaces." (p.14)

In the 1979 workshop on dry deposition, many of the attendee felt that there was no good evidences that surrogate surfaces is a usable approach, thus it was given a low priority. We are not working on this since NOAA is funding research in this area. We will withhold judgement of the merit of this approach until the NOAA work is completed

6. "One of the planned outputs of the research sites in a manual for site planning and development of NTN sites." "A poorly chosen site will provide little useful data, ..." (p.15)

While we donot disagree with this, the output is not one of ASRL-EPA but a NOAA/ATDL output funded by NOAA. Choosing the NTN sites is an EMSL/EPA function not ASRL.

7. "To meet the EPA goals, additional species are needed. Hydrogen chloride, ammonia..."

We intend to go after these but have had to prioritize the pollutants by NAPAP needs, research time available and funding.

8. "a co-location of research activities between Groups D & G in RTP, North Carolina would be desireable." (p.17)

This is being worked on by EMSL and John Spence (PM Group G).

9. "(1) There appears to be little communication between ASRL and ATDL, and EMSL and ATDL, concerning the deposition velocity method." "...interaction between ASRL, EMSL and ATDL on issues related to dry deposition monitoring. Regular meetings to review plans and projects are essential..." (p. 21)

While the Vd project is a NOAA funded ATDL/NOAA project, Bruce Hicks (ATDL) has kept ASRL informed. I don't know the extent of the communication between ATDL and EMSL. I agree that some regular meeting is a good idea. We have had several such meetings.

10. "The panel also recommends that the capabilities of other qualified organizations be sought to assist development of deposition velocity estimation methods." (p. 21)

We are not in a position to recommend this since it is a NOAA assignment. We will be a part of the vigorous review of the method.

11. "The panel recommends that research be initiated in surrogate surface development." (p. 25)

As stated in response to number 5, this is a low priority approach of questionable application and we feel that the NOAA support is sufficient at this time.

APPENDIX E

REVIEW OF THE PANEL REPORT AND RESPONSES BY THE LABORATORY DIRECTOR

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ATMOSPHERIC SCIENCES RESEARCH LABORATORY
RESEARCH TRIANGLE PARK
NORTH CAROLINA 27711

DATE: July 24, 1985

SUBJECT: Review of ASRL Responses to the Dry Deposition and Material Damage Peer Review

FROM: Jack H. Shreffler JHS
Deputy Director, ASRL (MD-59)

TO: Ron K. Patterson
Peer Review Coordinator, TPRO, ASRL (MD-59)

THROUGH: Alfred H. Ellison
Director, ASRL (MD-59)

I have read the report of the peer reviewers on the Dry Deposition and Material Effects Programs at ASRL based on the review held April 23-25, 1985. I have also read the ASRL project managers responses to the various recommendations and criticisms contained in the review report. There were some misunderstandings about the latitude available to ASRL in choosing methods, time lines, or budgets and about the exact responsibilities vis-a-vis other laboratories or agencies in NAPAP. Generally, the responses are complete and relevant, although some further questions are highlighted below. By copy of this memorandum I am instructing project managers to take some additional action.

Dry Deposition

The reviewers were complimentary and highly supportive of the systematic approach taken to assessing a number of dry deposition methods. A strong recommendation was made to increase the interaction and communication between ASRL, EMSL, and ATDT on issues related to dry deposition monitoring. Ken Knapp should take every opportunity to increase the interaction and should be able to demonstrate the positive effects of that effort in the future.

Material Effects

The peer reviewers praised the management and project staff as having demonstrated initiative, industry, and the ability to work together. There was strong support for the chamber studies. Field studies were also supported with some reservations concerning methods. The response prepared by John Spence is complete in addressing all reviewer criticisms, although there are two areas that I believe could use further elaboration. John should prepare a follow-up memorandum for the report.

First, the response to comment 1 (Spence memo) seems to skirt an important issue. The microenvironment may require a rather complex set of instruments for characterization. Measuring only on the building top or under the canopy will not answer the real question: What is the difference between the site and a nearby representative location?

Second, the reviewers several times mention study of corrosion mechanisms as a missing element (e.g., comments 14, 15, 23). Perhaps the response to 23 is getting close, but I think there should be some elaboration on what "insights" will be provided and how that differs from a "detailed characterization of the mechanism."

In a conversation with John, I was told that agreements with comments 17 and 18 mean those actions will be taken.

cc: K. Knapp
J. Spence

APPENDIX F

CLARIFICATION COMMENTS BY ASRL

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ATMOSPHERIC SCIENCES RESEARCH LABORATORY
RESEARCH TRIANGLE PARK
NORTH CAROLINA 27711

MEMORANDUM

DATE: July 30, 1985

SUBJECT: Clarification of ASRL Response to Material Damage Peer Review

FROM: William E. Wilson
Acting Director, EMCD

TO: Jack Shreffler
Deputy Director, ASRL

Microenvironments (#1)

There were two questions raised regarding microenvironments. One has to do with the stationary covering device used by the Bureau of Mines. Measurements have shown a higher relative humidity under the shelter and the Bureau of Mines plans to modify the covering device so that temperature and relative humidity will not be different. The second question referred to the increased temperature at rooftop sites due to absorption of light by asphalt roofs. The reviewers recommended that "the researchers should modify the exposure conditions in a manner that eliminates the microenvironment effects." At one site the roof is covered with a light colored gravel which should reduce the temperature over that of a black asphalt roof. We will investigate the possibility of covering the black asphalt at the other site with light colored rock.

We must emphasize, however, two factors. One, in deriving damage functions the important considerations are that the environment to which the specimens are exposed is adequately measured, not that it is characteristic of any specific exposure condition, and that an adequate range of exposure conditions are included in the set of exposure sites. Therefore, we do not believe that the fact that the rooftop environment is different from a ground level enviornment will reduce the accuracy or value of the resulting damage functions. However, since the time-of-wetness is important we investigate the possibility of modifying the one rooftop site that might have the time-of-wetness lowered by the asphalt roof. The second fact is that because of financial restraints we must install our exposure racks at pre-existing sites. Due to security problems many urban sites are placed on roofs.

At one site a rooftop vent will be extended to a sufficient height so that the emissions will not impact the specimens during most wind conditions. The buildings, a library and an office building are not expected to generate emissions of significant concern.

Mechanisms (#23)

The reviewers emphasized the need to determine the mechanisms of damage in order to develop damage functions which could reliably apportion damage to specific pollutants and which could be used to predict damage under a variety of environmental conditions. We agree with the reviewers. We have been making some progress in persuading NADAP to accept this viewpoint but still do not have sufficient funds to implement an adequate mechanistic study. We feel that the analysis of corrosion on the specimen surface and products in dew and rain runoff from both field and laboratory samples will provide a useful data base for research into damage mechanisms. We will use the reviewers comments in the next round of program planning in an effort to obtain funds to add research on mechanisms to the program.