2.3 PUERTO RICO — 2002: FIELD STUDIES TO RESOLVE AEROSOL PROCESSES

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1. INTRODUCTION

A number of questions remain concerning homogeneous aerosol formation by natural organics interacting with anthropogenic pollutants. For example, chlorine has been proposed as a potential oxidant in the troposphere because of its very high reactivity with a wide range of organics (Finlayson-Pitts, 1993). Indeed, sea salt aerosol in the presence of ozone has been shown to produce chlorine atoms in heterogeneous photochemical reactions under laboratory conditions (Oum et al., 1998). Whether chlorine can initiate oxidation of natural organics such as monoterpene hydrocarbons and can generate homogeneous nucleation or condensable material that contributes to aerosol loadings needs to be assessed. The nighttime reactions of ozone and nitrate radical can also result in monoterpene reactions that contribute to aerosol mass.

We are currently planning field studies in Puerto Rico to assess these aerosol issues and other atmospheric chemistry questions. Puerto Rico has a number of key features that make it very attractive for a field study of this sort. The principal feature is the island's very regular meteorology and its position in the Caribbean Sea relative to the easterly trade winds. This meteorology and the island's rectangular shape (100 x 35 miles) make it highly suitable for simplification of boundary layer conditions. In addition, the long fetch between Puerto Rico and the nearest pollution sources in Africa and southern Europe make the incoming background air relatively clean and constant. Furthermore, Puerto Rico has approximately 3.5 million people with a very well defined source region and a central area of rain forest vegetation. These features make Puerto Rico an ideal locale for assessing aerosol processes. The following sections describe specific areas of atmospheric chemistry that can be explored during the proposed field study (Puerto Rico — 2002).

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2. PROPOSED EXPERIMENTAL DESIGN

Urban- or Regional-Scale Model Testbed

Figure 1 shows a map of Puerto Rico, which approximates a rectangle 100 miles long and 35 miles wide. Puerto Rico is oriented directly along east-west lines, and its position relative to the trade winds leads to relatively constant east-to-west air flow. This means that the boundary layer wind fields for Puerto Rico will be well defined and on a scale that can be modeled with some detail. Wind speeds are typically 5-15 mph during the day and 0-5 mph during the evening hours. Wind directions are easterly over the island and northeasterly to easterly over San Juan.

San Juan is located on the northeastern section of the island. The island's approximately 3.5 million inhabitants contribute urban-plume character to the emissions in the form of motor vehicle exhaust and a well-defined set of stationary sources. Emissions from San Juan will be carried along the island. Because the maximum elevation on the island is less than 4,400 ft, the urban plume will be in the boundary layer. These factors make Puerto Rico an excellent field site for evaluation of urban- and regional-scale models.

On the eastern side of Puerto Rico, The Naval Atlantic Meteorology and Oceanography Detachment at Roosevelt Roads is a potential site for ground-based sampling of incoming background air on the eastern edge of Puerto Rico. Two forts in Old San Juan on the northeastern coast of the island could also serve as ground-based sampling sites. These forts, El Morro and San Cristóbal, are located on the western side of San Juan and are operated by the National Park Service as national monuments. Figure 2 is a photograph taken at San Cristóbal, looking toward El Morro. The winds at the forts are northeasterly, bringing background air inland.

On the eastern side of the island is El Yunque, a national forest and a source of natural hydrocarbons. Figure 3 is a photograph looking from El Yunque toward the north coast. The rain forest at El Yunque can be a site for examining the chlorine chemistry discussed in the following section. Other forests are also sources of natural hydrocarbons; the National

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Science Foundation (NSF) Arecibo Atmospheric and Radio Astronomy Station in the west central part of the island would be a very good site for sampling the air chemistry in the island plume.

With the U.S. Department of Energy (DOE) G-1 aircraft and other airborne platforms, we could examine the vertical chemistry in the plume. The reasonably constant daytime and nighttime wind fields over Puerto Rico would allow airborne platforms to follow the urban plume and assess the chemical processes and transformations in well-defined boundary conditions. All of these factors make Puerto Rico an excellent choice for potential studies of specific tropospheric chemical processes that might be key in secondary aerosol formation and oxidant production.

Chemistries Driven by Sea Salt Aerosol

As noted in the introduction, sea salt aerosol has been proposed to be a source of chlorine in the marine boundary layer (Finlayson-Pitts, 1993). Molecular chlorine photolyzes quite rapidly in the troposphere to form chlorine atoms. The chlorine atoms are highly reactive with organics, particularly natural hydrocarbons like isoprene (Ragains and Finlayson-Pitts, 1997). Monoterpenes are also quite reactive. The reaction rate of chlorine atom with isoprene is five times faster that of OH radical (Atkinson, 1997). At concentration levels of Cl and OH anticipated in marine air, Cl radical will probably be very important in initiating early morning photochemical processes, while OH will be more dominant in hydrocarbon oxidation during the middle and later hours of the day.

The Cl radical can react via addition or abstraction. In the case of abstraction, we cannot distinguish between OH and Cl chemistries. However, in the case of addition, which occurs with natural hydrocarbons like isoprene and monoterpenes, the resulting chlorinated organic compound can act as a marker for the chemistry.

Both addition and abstraction reactions lead to the formation of peroxy radicals and (for the larger organics) potentially to the formation of secondary organic aerosols. This chemistry can be examined readily in Puerto Rico. The wind speeds and surf conditions on the island generate a significant amount of sea salt aerosol that can interact with background ozone, ozone generated in the urban plume, or both to form molecular chlorine and subsequently the chlorine atom. Field efforts in Puerto Rico — 2002 will be designed to assess this type of chemistry. Sampling stations in the El Yunque forest to the east and at the NSF Arecibo facility are likely candidates for this aspect of Puerto Rico — 2002. Figure 4 is a photograph of the tropical forests surrounding the Arecibo facility.

Nighttime Chemistry

Another area of concern in the troposphere is nighttime chemistry driven by nitrate radical, NO_3. This very reactive species is produced by the reaction of NO_2 with ozone during the evening:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad [1]$$

NO_3, in turn, is in equilibrium with dinitrogen pentoxide in the troposphere:

$$NO_3 + NO_2 \leftrightarrow N_2O_5 \qquad [2]$$

Like Cl and OH, NO_3 is very electrophilic and can react with most organics by abstraction or addition (Finlayson-Pitts and Pitts, 1986). Abstraction leads to the formation of nitric acid, which can react with ammonia in the gas phase to form secondary ammonium nitrate aerosol. Addition can lead to the formation of oxygenated nitrates, which can be quite water soluble and also generate aerosol.

Nighttime chemistry of nitrate radical should occur in Puerto Rico as the plume of NO_x produced by motor vehicles is transported into the central portion of the island. The natural hydrocarbon emissions will be available for reaction, leading to these types of products. Sampling at Arecibo over several diurnal periods should allow exploration of this chemistry. The monoterpene compounds will be particularly important, because isoprene emissions are expected to decrease in the evening when stomata are closed.

Our recent work in Phoenix, Arizona, indicates that production of nitrate radical occurs in the nocturnal boundary layer at the edge of urban plumes (Gaffney et al., 2000). This phenomenon can be studied in the urban plume generated by the 3.5 million inhabitants of Puerto Rico, 1.6 million whom live in San Juan on the northeastern portion of the island.

Natural Hydrocarbon Emissions

The effects of natural hydrocarbon emissions have been found to be very important in the formation of ozone and other oxidants, and natural hydrocarbons are likely to be key species in the formation of secondary organic aerosol, as noted earlier. An outstanding modeling problem in this area is accurate assessment of natural hydrocarbon emission strengths. Puerto Rico — 2002 would be an ideal platform for testing modeling methods developed recently at

Argonne for estimating deposition and emissions (Xu and Wesely, 1999).

Argonne's approach is to use satellite data to determine leaf coverage and then to estimate isoprene and monoterpenes by modeling the system (species, distribution, emission rates, temperature and humidity dependence, etc.). The difficulty in testing this model on the U.S. continent has to do with the meteorology of the system. Isoprene and monterpenes are highly reactive, so one typically needs to look for products from the reactions on regional scales. The potential for transport of these products from a variety of different directions (i.e., source regions) makes it difficult to verify emission rates, particularly in the eastern United States. The Puerto Rican meteorology simplifies this situation. An air mass coming into the forested region is essentially totally lacking in natural hydrocarbon emissions or products. Thus, monitoring the outflow from the island by plane or examining the diurnal patterns at a series of downwind stations (Roosevelt Roads, El Yunque, Arecibo, for example) should allow us to assess both emission levels and lifetimes.

Heterogeneous Chemistry in Clouds

Another issue in secondary aerosol formation is the importance of cloud processing of soluble gases and the subsequent formation of aerosol as cloud evaporation occurs. Closely related are the chemical transformations that can occur on the surface of wet aerosols. The El Yunque National Park, where orographic clouds are formed daily, is a potential field site for exploring these processes (see Figure 3). The proposed Arecibo site, in contrast, is more likely to be affected by the urban plume from San Juan, but it also sees the frequent formation of orographic clouds. Heterogeneous chemical processing of SO_2 to form sulfate aerosols is now well established, particularly for reactions with hydrogen peroxide in wet aerosols and clouds. However, other chemical processes, including the incorporation of oxygenated and nitrated organics that are expected to have appreciable solubilities, have not been well studied. The field studies planned for Puerto Rico — 2002 will allow us to explore some of these important heterogeneous chemical reaction pathways.

Radiative Effects of Aerosols and Clouds

Aerosols and clouds can affect the radiative field of the troposphere. The scattering of radiation by aerosols has been recognized as a means of effecting cooling of the troposphere. In addition, many of the key aerosol species and dissolved aqueous pollutants can absorb longwave radiation, leading to warming (Marley et al., 1993). Indeed, as pointed out in another paper in this volume (Gaffney et al., 2000), aerosols like carbonaceous soot from fires can reduce UV-B radiation levels and subsequently decrease production of atmospheric ozone and other oxidants. These effects can be examined readily in the wintertime in Puerto Rico, because its low latitude makes UV-B levels reasonably high. Plans for the field study will include exploring opportunities for the DOE Atmospheric Radiation Measurement community to examine these types of effects and their links to climate impacts. UV-B measurements at a number of sites upwind and downwind of the San Juan region will certainly be of interest in evaluating radiative interactions of aerosols and subsequent effects on photochemical processes like ozone formation.

Boundary Layer Meteorology and Vertical Mixing

Measurements of boundary layer meteorology and vertical mixing will be very important in obtaining adequate data on the chemistry and aerosol processes of interest during Puerto Rico — 2002. The field site lends itself to addressing the interactions of a moderately complex terrain with a marine boundary layer system. Because the terrain on the island does rise to approximately 4,400 ft above the sea level, a number of key vertical mixing processes can develop, along with nocturnal boundary layer winds. These aspects of the study will be coordinated between the Environmental Meteorology Program and the Atmospheric Chemistry Program supported by the DOE Office of Biological and Environmental Research. With daytime and nighttime average wind speeds of 5-15 and 0-5 mph, respectively, the time periods for the chemistry to be examined will be 3-20 hr along the 100-mile length of Puerto Rico. Aircraft measurements will assess both downwind processes in the wake of the island and vertical influences of the meteorology on long-range transport from the island. Indeed, Puerto Rico can be thought of as a 35-mile by 100-mile megacity of 3.5 million people, and its downwind plume is certain to give insight into the effects of an urban plume on downwind regional- and global-scale chemistries.

3. INTERESTED RESEARCHERS

We will be continuing to plan for Puerto Rico — 2002 during the next two and one-half years. We invite interested participants and collaborators to contact us for further information as the field project plan develops. An Internet site will be developed in the next year and linked to the DOE Atmospheric Chemistry Program home page, located at the following Web site:

http://www.atmos.anl.gov/ACP/

A number of investigators have already indicated interest in participating in Puerto Rico — 2002. This collaborative work is expected to involve the NSF, the National Oceanic and Atmospheric Administration, the Navy, the National Park Service, and other agencies with interests in understanding aerosol processes.

The following research scientists have expressed an interest in collaborative research efforts as part of the proposed Puerto Rico — 2002 field work:

Argonne National Laboratory
- Rich Coulter
- Paul Doskey
- Jeff Gaffney
- Rao Kotamarthi
- Nancy Marley
- Marv Wesely

Battelle, Columbus
- Chester Spicer

Lawrence Berkeley National Laboratory
- Tica Novakov

National Center for Atmospheric Research
- Darrel Baumgardner
- Sasha Madronich

Pacific Northwest National Laboratory
- Carl Berkowitz
- Chris Doran
- Jerome Fast

Universidad Nacional Autonomous de Mexico, Mexico City
- Graciela Raga

University of California, Irvine
- Barbara Finlayson-Pitts

University of Chicago
- John Frederick

University of Minnesota
- Peter McMurray

University of Puerto Rico
- Oswaldo Rosario
- Brad R. Weiner

We look forward to hearing from others.

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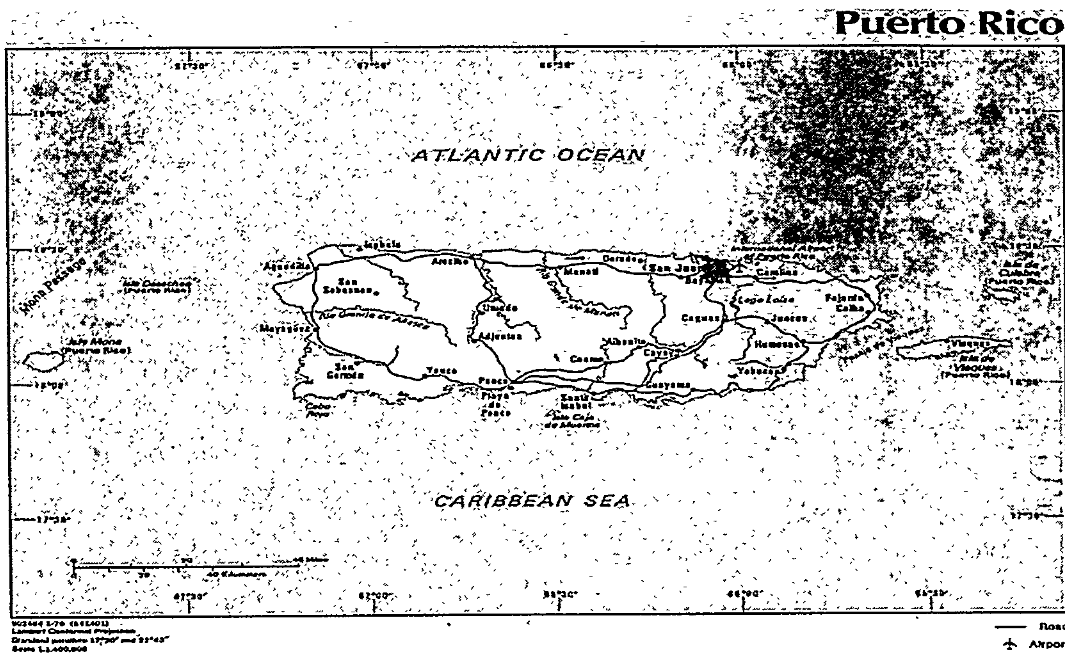

Figure. 1. Map of Puerto Rico. Arecibo National Science Foundation Radio Astronomy Station is almost directly south of Arecibo in the middle of the island.

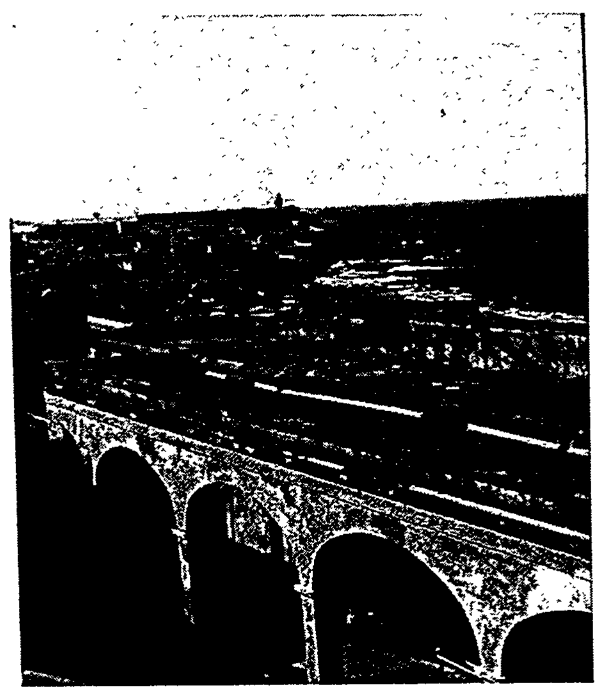

Figure 2. View of El Morro fortress from Fort San Cristobal. This site is in Old San Juan, on the northeastern end of Puerto Rico. Winds are typically northeasterly at this site (i.e., off the Atlantic Ocean).

Figure 3. Photograph of the north shore of Puerto Rico from El Yunque National Forest. Note the orographic clouds that form almost every afternoon over this rain forest.

Figure 4. Photograph of the radioastronomy facility at Arecibo. This National Science Foundation facility is located in the heart of a heavily forested area in the west central part of the island. Winds are predominantly from the east, making this an excellent potential site for addressing natural hydrocarbon anthropogenic pollutant interactions from San Juan, which is located to the northeast.