RESEARCH PRE-PROPOSAL to the ENVIRONMENTAL PROTECTION AGENCY Minority Institutions Research Support Program

# THE CHARACTERIZATION OF AIRBORNE PARTICULATES AND THEIR TOXIC PROPERTIES IN A PETROLEUM-PETROCHEMICAL INDUSTRIAL ENVIRONMENT

Submitted by:

INSTITUTE FOR ENERGY, ENVIRONMENT, AND BIOMEDICAL SCIENCES (IEEBS)

Catholic University of Puerto Rico



in collaboration with

CENTER FOR ENERGY AND ENVIRONMENT RESEARCH
University of Puerto Rico
THE FOSSIL FUELS RESEARCH PROGRAM

UPR . DOE

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JUNE 1979

Fresident, CUPR

President, UPR

Director, CEER

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# THE CHARACTERIZATION OF AIRBORNE PARTICULATES AND THEIR TOXIC PROPERTIES IN A PETROLEUM-PETROCHEMICAL INDUSTRIAL ENVIRONMENT

### Abstract

Selected hydrocarbons, and other air contaminants in particulate matter in a heavily industrialized site in tropical Puerto Rico will be isolated, identified, and characterized, by various chromatographic and spectrometric means. Special effort will be dedicated to establish the size distribution of airborne particulates and to identify the nitrogen and sulfur containing polycyclic aromatic heterocompounds, volatile hydrocarbons and potentially toxic trace elements. Associated mutagenic and teratogenic effects of selected fractions will be studied in an effort to define some toxic properties of help in predicting potential hazards concerning human health. Knowledge of composition and size distribution of particulate material, chemical transformation of pollutants and its associated toxicological effects will support biomedical studies in Puerto Rico dealing with a very wide spectrum of personal discomfort and illness. Of particular significance to the study is the fact that (1) major industrial plants in the south coast petroleum-petrochemical complex have reduced operations or closed down temporarily. This could help establish the impact of their respective operations in the overall quality of the region airborne particulates; and (2) current efforts to obtain a dispensation from

having low sulfur content fuel oils on the basis that no further cost to human well-being and environmental health will occur could turn out to be detrimental to the air quality of the region.

### Biographical Sketch of Key Personnel

Juan J. Rigau, Ph.D., Project Director
Center for Energy and Environment Research, University of
Puerto Rico
Institute for Energy, Environment and Biomedical Sciences,
Catholic University of Puerto Rico

Richard R. Eckert, Ph.D., Principal Investigator Institute for Energy, Environment and Biomedical Sciences, Catholic University of Puerto Rico

Arnaldo Carrasquillo, Ph.D., Principal Investigator Institute for Energy, Environment and Biomedical Sciences, Catholic University of Puerto Rico

Gabriel A. Infante, Ph.D., Principal Investigator Institute for Energy, Environment and Biomedical Sciences, Catholic University of Puerto Rico

Hilda López López, Ph.D., Principal Investigator Center for Energy and Environment Research and Medical Sciences Campus, University of Puerto Rico

José A. Carrasco, Ph.D., Principal Investigator Center for Energy and Environment Research and Medical Sciences Campus, University of Puerto Rico

### RESUME

Juan J. Rigau, B.Sc., M.Sc.,

University of Puerto Rico; Ph.D.,
Wayne State University; Head Fossil
Fuels Research, Director, Project 60,
Biodegradation of Organic Sulfur Compounds in High Sulfur Crude Oils, and
Project 48, Biodegradation of Hydrocarbons in Venezuelan Extra-Heavy Crude
Oils. Research interests in sulfur
chemistry in petroleum, petroleum and
coal biodegradation, fossil fuels composition, and environmental impacts of
fossil fuels utilization. Secondary
interests on energy and environment
policy formulation, high volume applications of sulfur and solar energy.

Previous position:

Director, Office of Petroleum Fuels
Affairs, Office of the Governor, 19731976; Energy and Environment Consultant
to the Economic Development Administration, 1969-1973; Research Fellow, Sulfur
Chemistry exploratory research, Wayne
State University, 1965-1969; Research
Assistant, Puerto Rico Nuclear Center
1960-1965.

Collateral Interests:

Consultant to several institutions of higher education; former member "Senior Energy Advisory Committee", CEER, former president College of Chemists of Puerto Rico; Member Sigma XI, Phi Lambda Upsilon, Who's Who in Government, ACS, College of Chemists. Has published over ten papers in referee journals and made extensive oral presentations in his research fields of interest.

### BRIEF CURRICULUM VITAE

### Richard R. Eckert

Age: 36 years

Marital Status: Married, 1 daughter

PhD., University of Kansas, Kansas, Physics, 1971

M.S., University of Kansas, Kansas, Physics, 1966

B.S., Case Institute of Technology, Cleveland, Physics, 1964 (Honors)

Position: Professor of Physics, Catholic University of Puerto Rico
1978 - to date

Tenure granted in 1976

Associate Professor - 1973-1978, CUPR

Assistant Professor - 1971-1973, UCPR

Publications - About 15 papers in the areas of Physics, air pollution and computer models.

Richard Eckert, 1979, "Particulate Contamination in Puerto Rico The Physics Teacher 11, 32-32.

Presentations: About 20 oral presentations in the same fields.

Services: President, Puerto Rico Chapter of American Association of Physics Teachers, 1978-1979.

Principal Investigator for NIH-MBS Grant No. 3-S06-RR-08067-08S1, Atmospheric Particulate as a Public Health Hazard

Catholic University representative on the Puerto Rico Council of Higher Education, Accreditation Committee for Electronic Data Processing Colleges.

### BRIEF CURRICULUM VITAE

### Arnaldo Carrasquillo

Birth Date: December 7, 1937 Place: Santa Isabel, P.R. U.S. Citizen

### Education

Ph.D. Organic Chemistry, Ohio State University, Columbus, 1971 M.S. Organic Chemistry, University of Puerto Rico, Rio Piedras, 1966 B.S. Organic Chemistry, University of Puerto Rico, Rio Piedras, 1959

### Positions:

Professor of Chemistry, Catholic University of PR, 1978 - to date Tenure granted in 1976 Biomedical Research Program Director, 1976-1978, CUPR Associate Professor, CUPR, 1973-1978 Assistant Professor, CUPR, 1971-1973

### Honors

President, Puerto Rico Section, American Chemical Society

### Research Areas

Organic Chemistry, Natural Products Chemistry, Photochemistry, Environmental Chemistry

### Research Grants:

Biomedical Research Grant from MBS Program, U.S. National Institute of Health.

### Publications:

About ten (10) publications in Organic Chemistry

### Oral Presentations:

About thirty (30) oral presentations in the same areas.

### BRIEF CURRICULUM VITAE

### Gabriel A. Infante

Birth Date: November 3, 1945

Place: Havana, Cuba

Citizenship: United States

Address: Department of Chemistry

Catholic University of PR

Ponce, PR 00731

Tel. (809) 844-4150 Ext. 242

### Education:

B.S. Chemistry, 1967, Catholic University of P.R.

M.S. Chemistry, 1969, University of Puerto Rico, Mayaguez

PhD. Chemistry, 1973, Texas A&M University, Texas

Post-Doctoral, Radiation Chemistry, 1974, Carnegie Mellon University, Pittsburg

### Honors

Undergraduate: Medals Analytical, Organic Physical and Industrial Chemistry

Graduate: Graduate Outstanding Award, Texas A&M University, 1973

Professional: Outstanding Educator of America, 1975

Who's Who of South and South West, 1976

Chairman American Chemical Society, Puerto Rico, 1977

General Chairman, IX Caribbean Chemical Conference, December 1977

Chairman Advisory Committee on Chemistry 1977-1978

Positions: Associate Professor with Tenure, Department of Chemistry

Catholic University of Puerto Rico, 1976 - to date

Director Biomedical Research Program

Catholic University of Puerto Rico, 1978 - to date

Associate Scientist, Center for Energy and Environment Research.

### Research Areas

Radiation Chemistry, Cancer Research, Micellar Chemistry, Environment Chemistry and Pollution.

### Research Grants

Biomedical Research Support Grant from MBS Program and National Cancer Institute, U.S. National Institute of Health

U.S. Energy Office throught the Puerto Rico Center for Energy and Environment Research.

### Publications

About forty (40) publications in scientific journals mainly in the areas of Radiation Chemistry, Micellar Chemistry and Pollution

About sixty (60) oral presentations in scientific meetings and conferences in the same areas described above.

### RESU'LE

Hilda Ibpez-Lopez, B.Sc., M.Sc., Ph.D.

- University of Puerto Rico; Assistant Professor, Department of Anatomy, School of Medicine, University of Puerto Rico. Primary area of interest on Embryology, Histology, and Embryotoxic effects of environmental pollutants. Secondary interest on Endocrinology of Reproduction.

Previous position:

Associate Professor, School of Medicine, Catholic University of P.R., 1977-1978 while on leave of absence from the University of Puerto Rico; Assistant Professor, School of Medicine, University of P.R., 1976-; Instructor, University of P.R., 1965-1975; Research Assistant, University of P.R., 1964-1965.

Collateral interests:

Director of the Embryology and the Musculo-skeletal courses of Human Biology I for Medical Students; Director of the Histology course for Dental Students; Thesis Advisor of graduate students in the Department of Biology, University of P.R.; Thesis Advisor of graduate students in the Department of Anatomy, School of Medicine, University of P.R.; Member of. the Human Biology I Committee: Member of the Cardiorespiratory, and the Renal and Urogenital Sub-Committees of Human Biology I; Member of Beta, Beta, Beta Honorary Society. worked in three investigations (in preparation for publication) and made several oral presentations in her research findings on cytological changes in the pars distales of the hypophysis of anoline lizards under various conditions.

### RESUME

José A. Carrasco-Canales, B.Sc., M.T., M.S, Ph.D., Assistant Professor, Department of Microbiology and

partment of Microbiology and Medical Zoology, School of Medicine, University of Puerto Rico. Primary area of interest, Mycology, Molecular genetics and Mutagenicity of Carcinogens on Bacteria. Secondary interest on Microbial Physiology and Immunology.

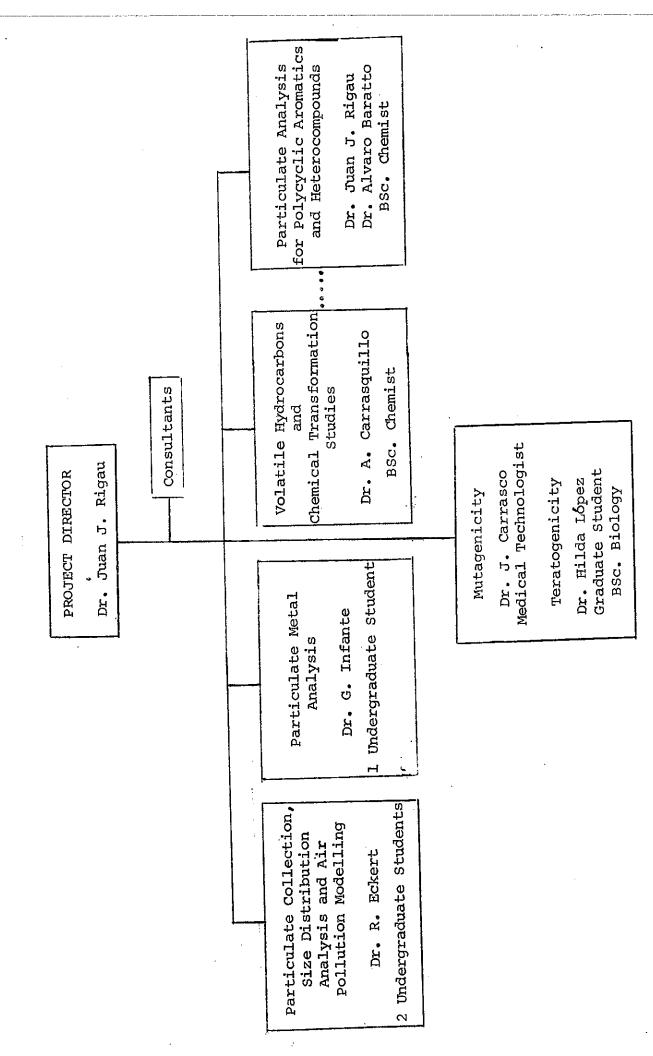
Previous Position:

Instructor in Microbiology, Dept. of Microbiology, School of Medicine of the University of Puerto Rico 1963-1974; Assistant in Mycology, Dept. of Microbiology, School of Medicine of the University of Puerto Rico 1962-1963.

Collateral Interests:

Director of the Infectious Diseases Block for 2nd year Medical Students, Member of the Human Biclogy II Committee. Member of the Promotions Committee for 2nd year Medical Students, Member of the Award's Committee of the University of Puerto Rico School of Medicine. Has worked on investigations in Mycology and Molecular genetics leading to four publications and one more in progress.

THE CHARACTERIZATION OF AIRBORNE PARTICULATES AND THEIR TOXIC PROPERTIES IN A PETROLEUM-PETROCHEMICAL ENVIRONMENT



### 1. Objective of this Project

This proposal attempts to develop an interdisciplinary cooperative program involving the recently created Institute for Energy,
Environment, and Biomedical Sciences of the Catholic University of
Puerto Rico and the Center for Energy and Environment Research of
the University of Puerto Rico to carry out the following objectives:

### a. Principal objectives

- Initiate a systematic effort to characterize potentially toxic trace elements and organic constituents (especially sulfur and nitrogen derivatives) downwind and upwind the neighborhood of a petroleum-petrochemical complex.
- 2. Correlate the structure of the molecules detected with their possible mutagenic and teratogenic effects. Extracts from particulate matter of various sizes will be obtained and evaluated for biological activity.
- 3. Improve our knowledge of sources of toxic substances by studying airborne particulate composition with an orientation to establish (a) if the particulate matter in the south coast industrial complex is responsible for impacting the atmosphere from neighboring cities downwind from the complex and (b) if the particules bearing these contaminants are small enough to be deposited efficiently in human lungs.

### b. Subordinate objectives

- Study the transformation of individual reactive chemicals and that of their primary conversion products by exposing them to filtered air from the region of interest and/or to specific major contaminants.
- 2. Employ air pollution computer simulation methods to correlate the chemical nature of the contaminants with the prevailing meterology of the region.
- 3. Conduct research in areas remote from immediate sources of pollution to provide background values in areas directly unaffected by point source emissions.
- 4. Train research scientists and students in environmental health research by developing an interdisciplinary research program to increase our knowledge of toxic substances in the environment.

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### c. Statement of Problem

In the last three decades, Puerto Rico has experienced a mihighly significant economic development, based on the industrial,
sector (Appendix I, Table I). A considerable number of industries
are established annually. They exploit petroleum derivatives
both as raw material and as energy sources directly and indirectly (Appendix I, Table III) and generate environmental impacts of concern to the general population. Appendix I, Figure la shows
some chemical considerations relevant to the sulfur and nitrogenes
derivatives present in crude oil. Knowledge of crude oil composisition is necessary to better understand the complexity of the
stack emissions in a refining-petrochemical complex.

Both with respect to point and area sources, the industrial areas comprising the Cataño and Guayanilla-Peñuelas municipalities (Appendix I, Figure 2) bears the brunt of the pollutants emitted in Puerto Rico. Therefore, because of its vicinity to Catholic University of Puerto Rico research facilities, and the fact that the petroleum-petrochemical complex has been the subject of numerous citizens complaints because of its emitted pollutants, we have selected the Guayanilla-Peñuelas area as the subject of this proposal with a long range objective of studying other sites and the effects of air pollutants on human health in Puerto Rico. Figure 1 shows some major air pollution related issues.

South coast residents living close to or downwind from the Guayanilla-Peñuelas industrial site are potentially exposed to

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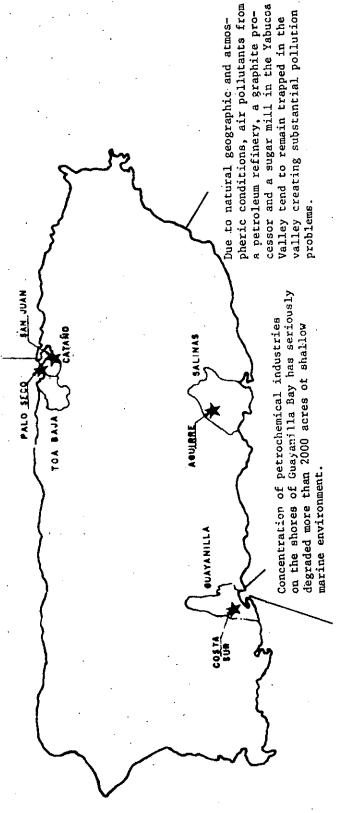
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Figure 1

MAJOR AIR POLLUTION RELATED ISSUES AND

# LOCATION OF MAJOR POWER PLANTS IN PUERTO RICO

residents in a civil suit. EQB data reports discharges of phenol, oil and grease, ammonia, sulfates and chromium above permitted levels. Cataño, a highly industrialized area, has won the dubious distinction of being the most polluted area in Puerto Rico. Gulf Oil Co. officials in Cataño admitted violations of the waste discharges permit issued by the federal Environmental Protection Agency, confirming charges made by



Thlorine gas escapes from PPG Industries stemming irom power failures have injured local residents. The plants effluents into surrounding bodies of water, including Guaynilla Bay, affect the community of fishermen nearby. Both problems are a source of continuous friction between the residents of the area and the plant.

# RECENT ISSUES:

- Coal operated power plant and its related environmental impacts.
- Reassessment of the sulfur content fuel burned in industry and the Costa Sur power plant in Guayanilla without further cost to human well-being and environmental health.

most all industrial emissions generated at the complex. In this zone, we find the huge 1,156,000 KW Costa Sur thermoelectric unit and the rather impressive chemical and refining complexes of CORCO, Union Carbide, and the PPG Industries chloro-alkali plant (Appendix I Table IV). A thermoelectric (1,396,000 KW) and combined cycle units can be found in the Aguirre (Salinas) area (Table I). Total population at the representative south coast municipalities of Guánica, Yauco, Guayanilla, Peñuelas, Ponce, Juana Díaz, Santa Isabel, Salinas, and Guayama in 1976 was 412,230 with a population density of (per square mile).

In general, the major pollutants of concern in the GuayanillaPeñuelas area, are those associated with fossil fuel combustion (Appendix I, Table II) and those related to petroleum-petrochemical operations (Appendix I, Fugure 3). Production and subsequent reactivity or degradation of the constituents of these emissions in combination with particular meterological conditions has led to photochemical oxidants, chemical carcinogens, and particulate materials. These particles are heterogeneous in size, shape, chemical contents, etc., depending on the type of process and other parameters. All the polynuclear aromatic hydrocarbons (PAH) are contained in the particulate emissions and some of them are the most potent carcinogens known.

The pollution attributed to particulate matter which contains the carcinogenic PAH was estimated at 88,123 tons in 1970 which were generated in the Guayanilla-Peñuelas area.

TABLE 1. DAILY FUEL CONSUMPTION BY PLANT

Plant		Dependable Capacity (KW)	Aver Maximum Fuel Sulfur Content (%)	Average Daily 1) Fuel Consumption (Bbls/day)
2	860 G			
		×		
Costa Sur		1,156,000	L.O 3)	20,332
San Juan		522,000	1.5	8,416
Palo Seco		758,000	2.5	13,096
Aguirre		1,396,000 2)	2.5	15,307
		1		

1) For natural year 1976.

Steam turbines of combined cycle units not included (200,000KW). 2) On April 2, 1979, the Water Resources Authority (the local utility) asked to be allowed to burn two percent sulfur fuels and is looking for a permanent ammendment to air quality regulations, due for an update July 1. 3)

Source: Puerto Rico Energy Office

The damages associated with air pollution include the costs associated with damage to human health, the costs of pollutionrelated cleaning and maintenance activities, the costs of inhibited growth and destruction of plant and animal life, and the reduction in property values. 3-4 For instance, SO2, an acidic, corrosive, poisonous gas produced almost entirely by the burning of fuel containing sulfur as an impurity can cause temporary or permanent injury to the respiratory system. When particulate matter is inhaled with adsorbed sulfur dioxide, health damage may increase significantly. Sulfur dioxide can irritate the upper respiratory tract. Carried into the lungs on particles, it can injure delicate tissue. 5 It has been known that some of the mechanisms for the transformation of sulfur dioxide to sulfate, involve homogeneous, photochemical, gas phase conversion to particles. Other mechanisms involve heterogeneous reactions in liquid droplets or in liquid films on the surfaces of solid particles. It is entirely possible that more than one of these mechanisms may contribute concurrently to the conversion of sulfur dioxide to sulfate in the atmosphere. 6

On the other hand, hydrocarbons represent unburned and wasted fuel. Normally, the gaseous hydrocarbons at concentrations found in the atmosphere are not toxic, but they are a major pollutant because of their role in forming photochemical smog. Particulate matter, derived from fuel combustion such as power plants (Appendix, Table II) and automobiles, containing metallic, polynuclear aromatic hydro-

carbons, sulfurated, nitrogenated, and oxygenated substances which have been shown to exhibit carcinogenic and co-carcinogenic properties 7-8 in experimental animals and have been associated with the incidence of various types of cancer in man. Although great efforts are underway to study the isolation, identification, and reactivity of these compounds in other parts of the world, very little or no information is available for Puerto Rico.

Guayanilla's air, containing one of the highest pollution levels in Puerto Rico, is the source of numerous resident complaints of pollution related health problems, and two medical studies have found evidence to back their allegations. 9-11 In Guayanilla, residential neighborhoods lie several miles downwind from a highly integrated petroleum-petrochemical complex with the combined smokestacks of PPG, the Commonwealth Oil Refining Co., Union Carbide, Water Resources Authority of Puerto Rico power plants, and other factories. Residents of different neighborhoods, including Villa del Rio, the Guayanilla beach, and Magas, have banded together in the past three years to form anti-pollution committees.

Size-distribution of elements and organic compounds in particulates has considerable significance in terms of environmental health.

11a-11c It has been found that it is from small particles which contaminants are most effectively extracted into the human bloodstream.

11a Thus particles less than about lam in equivalent aerodynamic diameter deposit predominantly in the alveolar regions of

the lung where the absorption efficiency for most trace elements is 60 to 80 percent. Larger particles, on the other hand, deposit in the nasal, pharyngeal, and bronchial regions of the respiratory system and are removed by cilial action to the stomach where absorption efficiency is commonly only 5 to 15 percent for most trace The lung constitutes then the major gateway to the bloodstream for toxic elements that are present in airborne particles. More recent results illustrate that over 90% of polycyclic aromatic hydrocarbons is found on the particles smaller than 3 mm and that about 75% of the benzo (A) pyrene and 85% of the coronene are associated with particles of aerodynamic diameter less than 0.26 µm. 11C Almost one half of the total mass of both polynuclear hydrocarbons are associated with aerosols in a very narrow size range (0.075 - $0.12 \, \mu m)$ The available evidence suggests that polynuclear aromatic hydrocarbons contribute mainly to the smaller size particles having a high probability of being adsorbed in the pulmonary region of the respiratory tract.

A recent Health Department Report 10 found that more than 30 percent of all patients admitted into emergency rooms in Cataño and Guayanilla during 1975 and 1976 suffered from pollution-related ailments (e.g., asthma, allergy, irritation and broncho-pulmonary diseases). In relatively pollution-free Luquillo and Naguabo, however, only ten percent of the cases were linked to pollution. Furthermore, the study alleged to have found a correlation between cancer deaths and polluted areas. Southern coastal plain vital statistics are

shown in Appendix I, Table 4.

Tomás Morales Cardona, a biophysicist and professor at the University of Puerto Rico Medical School, measured the lung capacity of 454 residents of Cataño and found that more than five percent of them had an obstructive respiratory disease, such as asthma, bronchitis or emphysema, and 50 percent suffered from problems in their upper respiratory system such as allergies, nasal problems, and sore throats. 11,12 In similar tests on 397, residents of Santa Isabel, only one person, 0.25 percent, was found with a lung disease. Morales, who carried out similar tests in Guayanilla, told us he will finish analyzing his data in the next few months.

The Environmental Quality Board (EQB) is now asking the federal government to designate Guayanilla and Cataño as "Central regions" under the Clear Air Act. This designation would prohibit any more air polluting industries from coming in. The EQB is now in the process of validating the air pollution dispersion model to determine whether compliance plans due June 30, 1979 will be strict enough to bring Guayanilla within the federal standard, or whether further actions will have to be taken. In 1972 the Environmental Quality Board (EQB) prohibited the use and sale of fuel oil anywhere on the island containing more than 2.0 percent sulfur after April, 1973. Although other levels in other areas are higher, a figure of one percent was set on fuel burned in Guayanilla. More

recently, on April 2, 1979 the Water Resources Authority (WRA) asked to be allowed to burn two percent sulfur fuel. CORCO and other industries in the area are asking for only 1.5 percent sulfur. They argue that even if the closed PPG, Oxochem and Puerto Rico Olefins plants become active again no increased health hazard will occur.

In Guayanilla, EQB has eight intermittent monitors, four to measure particulates and four for sulfur dioxide, which give a reading every six days. It also records data from eight Water Resources Authority sulfur dioxide monitors which operate continuously. The intermittent samples, which give only about 50 readings in a year, are statistically valid, but may miss many of the highs in pollution levels, which vary widely between different days and different hours of the day. Today there exists a better understanding of the process of environmental assessment (Appendix I, Figure 1b) and the influence of heavy fuel oil composition and boiler conditions on particulate emissions has been reported. 13

Atmospheric contamination depends on a host of factors, the most pertinent being the type, quantity, and location of the emission source and the particular atmospheric patterns capable of displacing and diluting the gaseous and particulate pollutants. The diluting effect is produced by weather conditions, temperature, wind direction, and velocity, humidity, and rainfall, etc. Precipitation helps in ridding the air of solid impurities depositing them on pastures, rivers, lakes, etc. Some of the contaminants

are dissolved, some mechanically flushed down by condensation of water vapor; and still some photochemically interact to form photocxidants as end products.

Finally, the predicted particulate and sulfur dioxide concentration for 1978 and 1985 are shown herein (Appendix I, Tables VI-VII, and Figure 6). The predicted particulate air quality levels for both 1978 and 1985 were found to exceed the primary particulate standards (75 mg/m<sup>3</sup> annual geometric mean) in the following Air Quality Maintenance Areas (AQMAS):

- San Juan

- Cuayanilla

- Ponce (1985 only)

- Mayaguez

- Dorado

- Guánica (1985 only)

The sulfur dioxide standard (80 mg/m<sup>3</sup> annual arithmethic mean) was also found to be exceeded both in 1978 and 1985 in several AQMAS.

- San Juan

- Guayama (1985 only)

- Guayanilla

- Yabucoa (1985 only)

- Dorado (1985 only)

These results show an indication of the seriousness of our environmental problem, however, any interpretation of ambient level measurements and air quality trends must consider the serious limitations of present data-collection practices; more importantly, in Puerto Rico, up to now there has been no efforts (with the exception of isolated measurements on total particulates and trace metals) oriented to generate badly needed information on reactive volatile hydrocarbons, polycyclic aromatic hydrocarbons, metals, or photochemical oxidants.

To help solve this crucial lack of environmentally significant information, work will be conducted by researchers of the Institute for Energy, Environment and Biomedical Sciences of Catholic University of Puerto Rico in collaboration with the Fossil Fuel Research Program of the Center for Energy and Environment Research, in an attempt to elucidate for the first time some of the chemical and biological aspects of pollution in the Guayanilla-Peñuelas area. Clearly, this study is badly needed to support preventive medical care programs in Puerto Rico. (Appendix I, Figure 4 and 5)

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This proposal attempts to:

- 1. Improve our knowledge of the chemical composition of the volatile hydrocarbons and the acidic, basic, nuetral, and polar fractions isolated from airborne particulates in the neighborhood of a petroleum-petrochemical environment. This is necessary to obtain a better understanding of the potential health hazards associated with transport and penetration of particulates into the respiratory system.
- 2. Measure both the size distributions and chemical composition of particles in ambient air, in order to understand the sources, and the behavior of airborne particulates in the atmosphere. Observations on size distributions of trace elements and/or key organics in particulates, if sufficiently distinctive, could be used as a means of source identification if data on size distributions of particles from specific types of sources were available.
- 3. Correlate toxic properties such as mutagenic and teratogenic effects with the chemical composition of selected test fractions.

The proposed research will be of significance also to:

1. Cancer epidemiology studies underway at the Center for Energy and Environment Research of the University of Puerto Rico as well as field, clinical, toxicological or laboratory investigations to be undertaken at Catholic University of Puerto Rico's recently created Institute for Energy, Environment and Biomedical Sciences.

- Help initiate work toward establishing a damage function for the Guayanilla-Peñuelas area. Catholic University of Puerto Rico researchers are currently planning studies oriented to characterize the nature and magnitude of the population at risk affected by given levels of pollutants.
- 3. Strengthen the infrastructure for compositional studies related to the atmospheric emissions arising from coal or coal-oil slurries combustion power plants. These fossil fuels are alternatives presently under the active consideration of our government energy policy makers. Studies on the nature of air emissions will affect decisions regarding control techniques before or after combustion.
- 4. Provide public officials with an effective data base for efficiently allocating limited resources among the many conflicting demands for pollution control and other aspects of the social welfare.
- Act as a vehicle for the training of environmental health scientists and for continuing mission oriented research at Catholic University of Puerto Rico and the Center for Energy and Environment Research.

### 3. Work Plan

### a. Research Approach

### 1. <u>Background</u>

Although the reactive hydrocarbons have been fully recognized in the last two decades as having an important role in the photochemical reactions of air pollutants, the techniques for the isolation and quantitation of the ambient hydrocarbons, because of their sub-ppm concentration and complex mixture, only recently have started to be reported in detail. For example: the earliest description of atmospheric hydrocarbons was made by Eggersten and Nelsen in 1958. 22 A procedure for trapping large volumes of air and some data for atmospheric analyses were A monitor of the  $\mathbf{C}_2$  to  $\mathbf{C}_7$  aliphatic hydrocarbons in the Los Angeles atmosphere was then presented by Beligan. The individual analysis of  $C_{8}$  - $C_{18}$  hydrocarbons in Paris was made by Raymond and Guiochon. 24 Auto exhaust was demonstrated as a common source for most of the individual aliphatic and aromatic hydrocarbon species in the atmosphere. 25 Louw, Richards and Faure have described a versatile GC method for the determination of  $C_1$   $-C_{13}$  volatile organic compounds in city air and applied it to the identification of more than 200 volatile organics occuring in the air of three large South African cities. 25a Identification of the volatile compounds

in city atmosphere has been accomplished by others employing the more powerful GC/MS technique. 25b, 25c

Altshuller and Bufalini 26a have reviewed the hydrocarbon photooxidation mechanisms covered in the literature through 1964. More recently, Altshuller has reviewed 26b the formation and removal of SO, and oxidants from the at-The review describes the transport and chemical transformations of organics, nitrogen oxides, and ozone, and the conversion of sulfur dioxide to sulfates and the transport of these species. Stephens and co-workers 27 reported rates of reaction of aliphatic hydrocarbons in the ultra-violet irradiation of atmospheric samples. However, Altshuller and co-workers cited that the acetylene reaction is undetectable and butanes react very slowly with natural sunlight. Also, the report shows that no marked synergistic effects on rates of hydrocarbon reaction were observed in comparing the irradiation of these complex atmospheric hydrocarbon mixtures with the laboratory irradiations of single hydrocarbons with nitrogen oxides.

In addition to the light hydrocarbons and heterocompounds, the polynuclear aromatics are frequently found in the dust-fall of polluted atmospheres. 29,11b,11c However, no data is available on these potentially carcinogenic compounds in this island.

The composition of polynuclear aromatics extracted from airborne particulates will obviously be dependent on the extraction and purification procedure involved and could also depend on the size distribution of airborne particles. Recent reports, have shown the presence (Table II) of a number of sulfur containing heterocyclics, 30 aza-arenes, 31 and polycyclics with partially saturated rings. 32

Compositional studies on particulates are of great environmental concern because of a wide environmental distribution of particulates obtained from various combustion processes, and the potent mutagenicity of a number of compounds adsorbed on particulates such as certain polycyclic aromatic hydrocarbons (PAH). (Figure 2)

Aza-arenes formed as trace pollutants by the incomplete combustion of N-containing organic matter have been found in the basic fraction of New York City's suspended particulate matter. 31

Aza-arenes, with the exception of neutral indole and carbazole homologs, are found in the basic organic fraction of suspended particulate matter. Although, in general, this fraction only constitutes a small percentage (0.5 - 3%) of the organic matter, <sup>33</sup> bioassay data have shown the basic fraction to be carcinogenic to infant mice when administered subcutaneously. <sup>34</sup>

## SELECTED HETEROCOMPOUNDS AND POLYNUCLEAR AROMATIC HYDROCARBONS IN AIRBORNE PARTICULATE MATTER

Benzo (f) isoquinoline	pyrene	Benzo (def) naphtho- penzothiophene <sup>8</sup> , b	N N Benzo (h) quinoline
Acridine	e general de la companya de la comp		; i.
dibenzothiophene	benzo (a) dibenzothiphene		
		benzo (e) pyrene	benzo (/) quinoline
phenanthrene	benzo (ghi) fluoranthene	benzo (a) pyrene	phenanthridine
anthracene			
anunacene	cyclopenta (cd) pyrene	perylens	benzo (a) anthracene- 5,6 - quinone
H <sub>2</sub> C			
4H-cyclopenta ( <i>def</i> ) – phenanthrene	benz (a) anthracene	Indeno (1,2,3-cd) pyrene	Ö dibenzo (b, def) chrysene -5, 6- quinone
fluoranthene	chrysene	9,10 - anthraquinone	li C Denzo (a) pyrane -6, 12- quinone

The benzene extractable compounds from airborne particulate matter from a residential area were separated into neutral, acidic and basic substrates. The the neutral fraction, saturated aliphatic hydrocarbons, polynuclear aromatic hydrocarbons and polar oxygenated substances were identified. The acidic fraction consisted mainly of a homologue series of fatty acids and aromatic carboxylic acids, some of them with hydroxy substitution. The basic fraction consisted of the nitrogen containing anologues of the important polyaromatic hydrocarbons present in the neutral fraction.

Pierce and Katz<sup>35</sup> have described a method for the analysis of polycyclic quinones derived from polynuclear aromatic hydrocartons. 9,10 -Anthra-quinone, benzo (q) pyrene - 6,12 - quinone, benzo (q) pyrene - 1,6 - quinone, benzo (q) pyrene - 3,6 - quinone and dibenzo (b,def) chrysene - 7,14 - quinone were identified in samples of suspended particulate matter collected in Toronto, Ont.

The carcinogenic activity of a particular compound is very dependent on its structure. Shape, size, electronic, and steric factors; all seem to be important. For example, the addition of alkyl, substituent groups in different positions on the ring of certain PAH, can either have an activating or deactivating influence. 36-37 Similarly, the

substitution of a sulfur for an ethylene group in a ring, may increase or decrease the carcinogenic activity of that particular compound. 38

Since pyrogenesis of PAH is strongly dependent on the combustion conditions, the content of PAH sampled in an industrial area, is a composite of the emissions from various points and mobil sources. For that reason, it is reasonable to expect PAH to differ quantitatively and qualitatively among different cities and even locations within each city. Those considerations, coupled with the recent identification of many sulfur containing polycyclics in air particulate matter, <sup>39</sup> indicates that information about polycyclic heterocompounds must be included in studies concerning the environmental hazards of petroleum related industrial operations.

Finally, the composition and size distribution of particulate material in the atmosphere has been under investigation for several years. The aerosol in the atmosphere consists of substances of various origin, such as soil, ocean, organic material and gases. After production the aerosol is mixed and further modified as it ages. This includes mixing of aerosols of different origin, coagulation to form new particles, adsorption of gases, chemical reactions within the particles, mainly in the presence of liquid water and dry

and wet removal. A detailed explanation of some properties of aerosols is described by Jaenicke. 38a

Since several organosulfur compounds have been detected in atmospheric particulate matter the problem arises whether, besides oxidation to sulfate, SO, might also react with other However, the concentration of various sulfurcontaining compounds is small and it appears that they might come from exhaust gases and stack emissions, rather than through combination of SO, with organic compounds from various sources. (Will be interesting to see if when the Puerto Rico Olefins, Inc. plant start operations the concentrations of organo-sulfur compounds in particulates increases correspondingly). It is also reported that by equilibrating particulate matter with SO2, sulfonic acid derivatives are formed, The formation of these compounds seems to be of minor importance in the conversion phenomena of SO<sub>2</sub>. 38C its importance in enhancing the toxic effects of these particles cannot be discarded at this moment. Since the concentration of pollutant aerosols with respect to particle size is important in the evaluation of their atmospheric transport and penetration into the respiratory system several studies have been conducted utilizing high and low volume cascade impactors. 39a-39j

High volume cascade impactors are most useful in applications when aerosol mass loadings are very low and large volumes must be sampled to provide significantly weighable or analyzable mass on all stages. 39d They can also be used in high mass load atmospheric environments to collect short term samples. Various workers have reported 38d-38e however, that high volume ()20 ft 3 min-1, or > 0.6 m min-1) impactors very often experience particle bounce effects which result in a displacement of the larger particles mass to smaller size stages. The particle bouncing is believed to be due to the inability of dry solid particles to adhere to dry impaction surfaces. Instead of impacting, the particle recoils off the surface, and is carried to succesively smaller particle stages. There is considerable evidence that this error can be minimized by the application of an adhesive humecant to the impaction stages. 38e In addition many impactors now in use sample air at the rate of about 1-2 m<sup>3</sup>/hrs., so that in a 24 hour sampling period only about 10-50  $\mu$ g of any one element will be present, distributed over several collection surfaces. Consequently higher sensitive analytical techniques must be used. 39d In order to collect enough particles for chemical analysis, especially if organic compounds are of interest, sampling times of 4-9

days may be necessary, according to degree of air pollution and weather conditions.

Recent investigations <sup>39a-39j</sup> on composition and size distribution of in-stack particulate material at coalfired power plants has revealed three broad classes of enrichment factor (EF) distributions for particulates.

Most elements show little, if any, enrichment (compared to the input coal) as a function of particle size; several of the more volatile, toxic trace elements do exhibit increased enrichments on the smaller particles; and two elements, Fe and Ce, had decreasing enrichments with decreasing particle size.

Potentially toxic metals and organic compounds will be analyzed and results compared with those found in other areas. For instance, elements for which EF>>1 are referred to as "enriched" elements, and to determine their origins, we must find sources whose particles have equal or greater EF's. 391

# 2. Description of Specific Research Plan

A detailed analysis of organic and metallic pollutants entails the techniques of sampling, extraction, separation and characterization. These techniques will be described separately in their experimental sequence.

- 1. Characterization of Hydrocarbons and Metals.
- A. <u>Sampling and size-distribution measures</u>—In order to obtain meaningful representation data, sampling locations are very important. The data obtained must be statistically related to different variables such as: source, meterological conditions, time-of-day, etc. The sampling locations will be categorized according to the predominant nature of the area (e.g., power plants, industrial, freeways or residentials). The sample will be collected based on the results obtained from simulation runs employing the Environmental Quality Board's computer model. Proper communication with the EQB already exists.

size distribution of particulate material will be established by aerodynamic sizing of airborne particulates using a five stage Sierra impactor. Proper sampling times will be established as needed. Also, sampling of of particulate matter will be carried out utilizing high volume samplers with glass fiber filters. The glass fiber filter will be used to analyze for total inorganic pollutants, particularly lead, mercury, iron, vanadium

and nickel. The metal analysis as a function of particulate size distribution will supplement work currently conducted at Catholic University on metals in particulates. Calibration methods for high-volume samples will be used according to the techniques described in the literature.

either cryogenic collectors, 40 of gas samples, adsorption of the organic components in the air 41 on a high surface adsorbent or by means of the method of Louw, Richard and Faure using Mylar plastic bags for small samples and a charcoal sampler for large samples. This will be followed by a contamination free transfer of the sample to a flame ionization detector gas chromatograph or one with a specific flame photometric detector. The cryogenic collection requires small volumes (0.1 - 0.5 liters) of air samples while the adsorption method may require an air flow rate of approximately 4 liters/min. The detectable concentrations by the cryogenic and adsorption methods are 10<sup>-8</sup> gm/liter and 10<sup>-10</sup> gm/liter, respectively.

### B. Analysis

a. <u>Extraction</u> - Extraction of organic compounds such as polynuclear aromatic hydrocarbons will be accomplished by solid-liquid<sup>45</sup> or liquid-liquid<sup>46</sup> extraction. Initial liquid/solid extraction with ether will

be followed by a variety of common solvents such as benzene, cyclohexane, chloroform, benzene/methanol, etc. 42 Ether may turn out to be a convenient solvent, because the loss of sample material during the evaporation of the extracts is reduced as compared to other higher boiling solvents. 42a All extractions will be done in semi-darkness and precautions 47 will be taken to ensure the uniform treatment of each sample and extract. After extraction, the solvents will be carefully evaporated in the dark at room temperature under reduced pressure.

b. <u>Separation</u> - Separation techniques for extracted compounds from particulate matter could include gelpermeation, 48-48a column chromatography 46-49-50 thin-layer chromatography, 49-51-54-55 vapor phase preparative chromatography, 50 glass capillary gas chromatography 50a and high pressure liquid chromatography (HPLC). 10 In particular, a generalized approach (used intensely in our own laboratories) for the liquid chromatographic analysis of very complex hydrocarbon mixtures will be tried in this work. As in crude oil analysis, the fractionation of particulate extracts into saturates, aromatics and polars (mostly nitrogen and oxygen containing polar compounds) will be desirable. Further separation of the aromatics and polars will be performed followed by col-

lection of given peaks or groups of peaks followed by reinjection into a different and convenient HPLC column or into a GC or GC/MS system. The HPLC approach (Figure 3) will be supplemented by a modification of the procedure of Haines and Thompson 53a (Figure 4). This will generate conveniently separated fractions for further detailed analysis.

column chromatography, and preparative gas chromatography will be used also as supplementary techniques when separating and collecting individual components as needed. Various GC column packings will be explored in this work. Some suggested ones presented in the Supelco literature on hydrocarbon and polycyclic aromatic hydrocarbons have been found very useful in our current work on petroleum composition and biodegradation. Other suggested ones based on the literature and our own experience will be explored. For instance, high-temperature gas chromatograms could be run on a gas chromatograph with stainless steel column packed with 3% Dexsil 300 on 80/100 mesh chromosorb W or a support-coated open tubular column (SCOT) silicone DC-550 column, 25a-25d temperature programmed.

Since mass spectra of isomeric compounds show little difference, prior chromatographic resolution is necessary

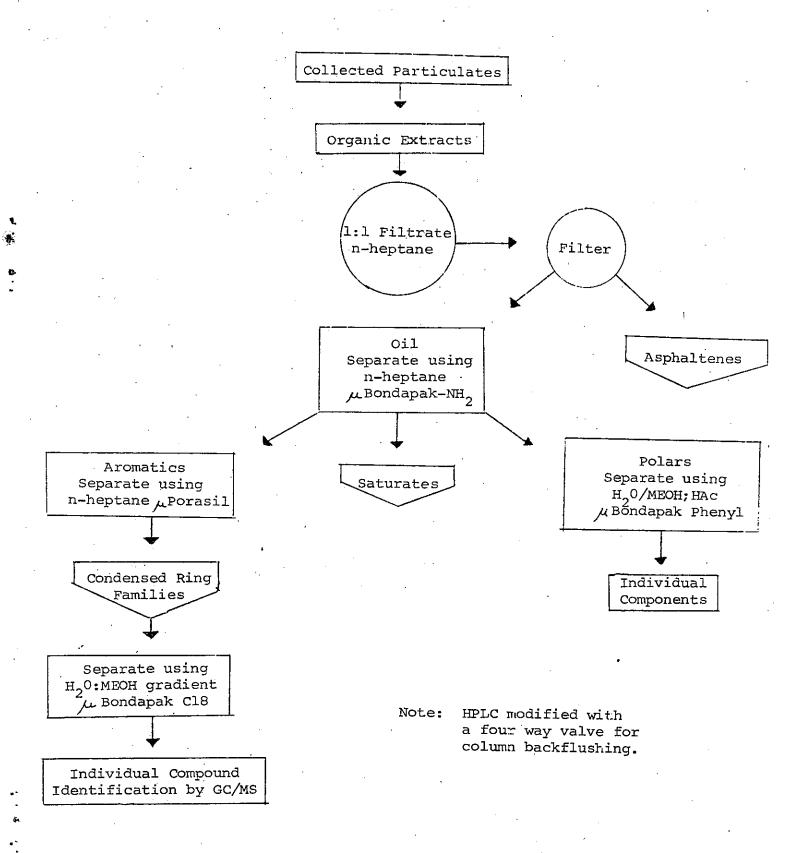


Figure 3: High Performance Liquid Chromatography Suggested Separation Scheme.

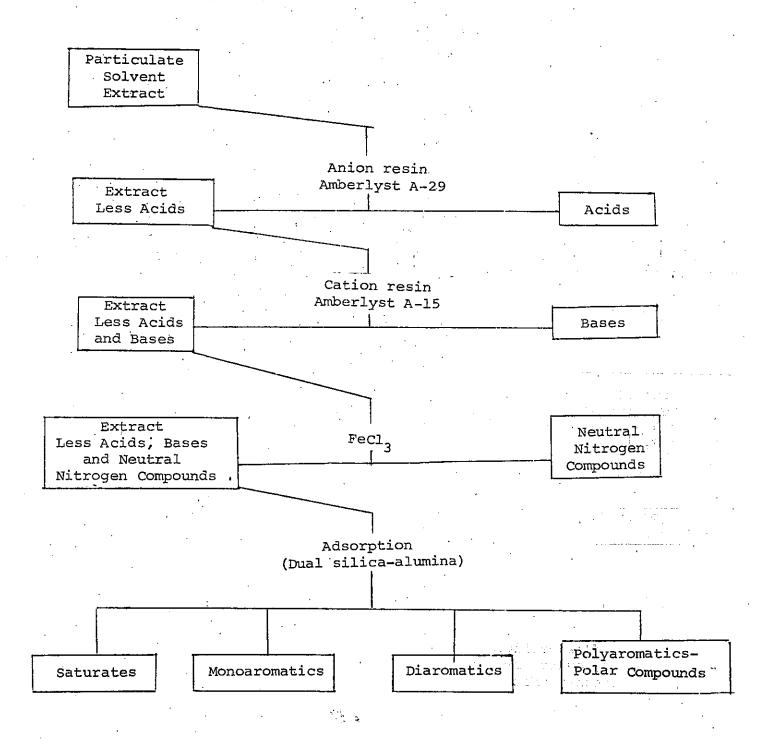


FIGURE 4: Outline of Separation Scheme for Organics in Airborne Particulates Extracts.

for their identification. Inert glass-high-resolution capillary columns in such analysis will be desirable.

59-60 Since glass capillary and convential gas chromatographic separations and HPLC techniques will be widely utilized in this work as major identification tools, they will be further described in the following section. The retention time of 20 common compounds and the properties pertinent to the chromatogram are shown in Table II.

<u>Characterization</u> - Gaseous and light hydrocarbons in the part per-billion range will be characterized by flame-ionization gas chromatography. 61 Specific sulfur detectors will also be used in this work. 61a For reliable sulfur analysis using a flame photometric detector the column should posess high resolution properties, since large amounts of hydrocarbon are known to quench the emission of small quantities of sulfur compounds when eluted simultaneously. A micro-coulometric detector will be employed if necessary. Current work in our labs is finding very useful the use of a microcoulometric detector for the analysis of benzo and dibenzothiophene derivatives in petroleum. A system involving pyrolysis-GC-Microcoulometer as reported by Drushel will be employed 61b plore the presence of sulfur containing families of benzothiophene, dibenzothiophenes, etc.

Table II.

# DATA FOR POLYCYCLICS

	- 1	•				-	
	Compound	Carcinogenic	Relative Retention	Mol			Scla conon.
엙	\	activity	Time (Pyrene)	Vol wt	Mp. C	Resolution	mg/mi
m	Fluorene		0.345	165.22	116-117		(1) e
7	9-Fluorenone		0.579	180,19	98		0.40
က	Phenanthrene	ļ	0.612	178.23	101		0.10
4	Anthracene		0.625	178.23	216.2	C. 634	5.10
เก	Acridine	ļ	0.665	179.21	111		0.125
လ	Carbazole	1	0.720	167.21	247		0.135
7	Fluoranthene	-	0.948	202.26	111		0.10
ω	Pyrene	·	1.000	252,25	149.	•	0.18
თ	11H-Benzo(a)fluorene		1.068	216.29	189-190		0.14
10	11H-Benzo(b)fluorene	!	1.101	216.29	209-210,5	0.9126	0.12
Н	Bonzo(c)pnenanthrene	+ 4- +	1.255	22.8.25	ထ		•
11	Benz (a) anthracene	+	1.274	228,29	162	62.7	9,12
II	Triphenylene	<b>i</b>	1.281	228,29	196.5	2	•
12	Chrysene	+	1.284	228.29	254		0.14
6). mi	Naphthacene	ŧ	1.304	228,29	357		0.06
14	Benzo(k)fluoranthene	1	1.552	252.32	217		0.10
15	Benzo( )pyrene	+ 1.	1,639	252.32	175-177	0.590	0.09
9	Jonzo(e) gyrene	(a) + (b) +	1.660	252,32	178	1.214	0.13
17	Perylene	0 (1) 0 (1) 1 0 (2)	1.689	252,32	273-274		0.13
18	Dibenz (a,h,)anthracene		2,223	278,35	269.70	:: ,	0.12
19	Benzo (ghi) perylene	eras A	2,346.	276.34	277-279	- \ - \ - \ - \ - \ - \ - \ - \ - \ - \	0.12
20	7H-Dibenzo(c.g.)carbazole	+ + + + + + + + + + + + + + + + + + +	<b>7.</b> 450	267	157-158		0.10
	5 (c) (c) (d)		-	·		an N	
Source	Scurce: D.A. Lene, H. K. Woe, and M.	. Kotz . Anal. O	hem <u>45</u> . 1776 (1973)	ଦ୍ରପ୍ରକ୍ର ୧୯	tomorise Towns		itiána Nov
	).	2 4	. (	1			

columns with graphitized carbon black could be used for gas chromatographic separations of hydrocarbons. Expical retention times for a variety of hydrocarbons are included for reference purposes (Table III). Porous-layer open tubular columns using graphitized thermal carbon black show high selectivity for geometrical isomers, and allow difficult separations at temperatures lower than with dexsil columns. By changing the nature or the concentration of the stationary phase, a range of selectivities may be obtained from that of the pure graphitized thermal black support to that of the pure liquid stationary phase. Several other standard support materials will be employed during the gas chromatographic separation procedures.

High pressure liquid chromatography (HPLC) has many distinct advantages over other forms of chromatography. 52 Resolution of isomers is equivalent to gas chromatography with a greater number of theoretical plates (ea. 5,000). Unlike gas chromatography, there is no requirement for volatility or thermal stability. It is only necessary that the compounds be soluble in some solvent-aqueous or organic. The efficiency of this technique, with its superior utility for the study of labile reactive molecules, has made the study of chemical carcinogenesis and the

analysis of complex hydrocarbon mixtures more approachable than previously envisioned. Analysis of the eluate fractions from chromatography will be achieved if necessary by a combination of ultraviolet, fluorescence, infrared, nuclear magnetic resonance and mass spectrometry.

Mass spectrometry will be used to identify complex samples (e.g., sulfur-containing and nitrogen containing polycyclics and polycyclic aromatic hydrocarbons in par-This instrument will be directly interfaced ticulates). with a gas chromatograph with computerized data acquisition and used in conjunction with HPLC and column chromatography (CC) 64 separated fractions. The ancillary techniques allow for the separation and characterization of individual components simultaneously. With the aid of reference compounds unique structural formulae could be assigned for some basic ring systems and standard addition will be performed to determine the concentration range by integrating the mass spectrometer output. Although, confirmation of the identities of many of the PAH reported in the literature was accomplished by comparison of GC retention times with those of acquired standards, the accumulations of many more standard compounds will be necessary to provide the positive identification of all compounds.

Table III RETENTION TIMES ON GRAPHITIZED CARBON BLACK

Column: 30ft, 0:125 inch OD stainless steel Packing: 0:4% SE-30 on GCB-2 Conditions: 30ml/min nitrogen at 150°C, isothermal

HYDROCARDON	RR	SHB*	<u>C#</u>
Isopentane	0.519	0.78	5
Cyclopentane	0.54		5
Cyclopentane	0.602	0.61	5
n-peniane	1. <b>0</b> 00		5
Cyclohexane	1.245		6
2, 2 dimethylbutane	1.31	1.10	. 6
Methyleyelopentane	1.38	•	6
2, 3 dimethyl butane	1.743		6
1-methyleyelopentane	1.93		6
3-methyl pentane	2.04	2.20	6
3-methyl-cis-2-pentane	2.17		6
Benzene	2.21	2.14	. 6
3-methyl-trans-2-pentane	2.26		6
2-nicthyl-2- pentane	2.28	2. 22	6
Cis-2·hexene	2.31	2.31	6
1-hexene	2.32	2.33	6
4, 4-dimethyl-trans-pentene-2	2.51		7
2, 3, 3-trimethyl-a-butane	2.58		7
trans-2-hexene	2.68	2.69	6
3,3-dimethylpentane-1	2.72		7
4,4-dimothylpentene-1	2.86	•	7
1-cis-2-dimethyleyclopentane 2, 3-dimethylbutne-2	3.26		7
2, 2-dimethylpentane	3, 41	3. 36	6
Methylcyclohexane	3.44		7
2, 4-dinethylpentane	3.63		7
3-ethyl-cis-pentane	<b>3.</b> 98 .	4.22	7
2, 4, 4-trimethylpentane-1	4.29	•	7
2, 2-directly -trans-3-hexene	5.81		8
Cis-2-heptene	6.95		8
Iso-octane (2, 2, 4 TMP)	7.13 7.24	7.04	7
Trans-2-heptene	8.40	7.94	8
n-heptane		0.00	7
Toluene	8.98 9.08	9.20	7
2, 5-directhyl-trans-3-hexene		9.14	7
	9, 99		8
Ethyl henzene Octone-1	1 <b>8.</b> 85		8
	1 <b>9.</b> 59	<b>2</b> 1.33	. 8
Ethyl benzene	18.85	21.33	8
Octone-1	19.59	21.33	8
Cumene	27.0		8
n-octane	27.82	27.50	8
stryrene	36		8
m-xylene	38.9		8.
p-xylone	43.1		8
o-xy)cne	43. 1		8
n-propylbenzene	49.1		9
a-methyl styrene	68.8		9
m-ethyl toluene	71.8		8
p-ethyl toluene	77.8		9
o-ethyl toluene	80.9		9

SHB\* refors to W. Schneider, H. Bruderreck and I. HalasZ Anal. Chem. 36, No. 8, 1533, July 1864 reporting their work using capillary columns.

Ultraviolet-visible absorption spectroscopy could also be employed in the identification and determination of polynuclear hydrocarbons; this affords the advantage that the wave length maximum of a compound is independent of the presence of other compounds (if sufficiently diluted).

Nuclear magnetic resonance spectroscopy on occasions could be employed for the determination of specific methyl-aromatic hydrocarbon mixtures of structurally similar compounds. 39,65 The identification of these carcinogens could be made on the basis of relative chemical shifts, methyl chemical shift at infinite dilution and peak multiplicity information.

Atomic absorption spectrometry will be used for quantitative metal analysis. Details of the procedure are discussed in Walsh et al. <sup>38f</sup> Briefly, a portion of each sample filter is low temperature ashed, the residue is dissolved in HF and HNO<sub>3</sub>, and the solution is diluted for direct injection elemental analysis using a Perkin Elmer Model 503A atomic absorption spectrophotometer with a Model 2100 heated graphite analyzer. Preliminary analysis will be performed by means of an optical emission spectrograph.

2. Chemical Transformations of Reactive Pollutants in the Presence of Hydrocarbons or other Local Contaminants.

Recently, Pitts and collaborators have reported that polycyclic aromatic hydrocarbons adsorbed in glass fiber filter paper are activated as shown by the Ames mutagenic test when exposed to filtered air. The authors isolated strongly mutagenic substances including the nitro derivatives. This suggests a simple way to study some transformations of reactive atmospheric pollutants present in the industrial sector of Guayanilla-Peñuelas. The adsorbed samples will be selected from the manufactured basic petrochemicals and other industrial products of the area (e.g., Appendix I, Fig. 3 and Table IV).

General Procedure - Atmospheric reactions involving basic petrochemical intermediates will be studied submitting them to the following procedure:

- 1. Selected contaminants will be allowed to interact with the atmosphere under existing conditions in the neighborhood of a petroleum petrochemical complex.
- 2. The isolated contaminant material will be tested for (a) mutagenic activity and (b) the presence of transformation products.
- 3. The results will be compared with control experiments.

4. The biological activity and/or the nature of the new components will be studied further.

The reactions will be promoted by mixing high volumes of atmospheric air with the contaminant under study. High boiling contaminants will be studied by treating a glass fiber hi-vol filter with it and using a modified high volume sampler to pull air through it. Volatile contaminants will be injected to the mainstream of air and the reaction products trapped in a cold trap.

In these experiments, the atmospheric air composition may be altered by filtration, drying and/or addition of other components to simulate a typical condition such as when a large emission of an industrial substance escapes to the environment (e.g., chlorine, reactive olefins ...)

The treated contaminants will be extracted, tested for biological activity, and analyzed for the presence of new components by modern analytical techniques.

The above simple experiments will help in understanding possible effects of variations inair flow patterns, chemical and physical changes, in general, the interaction of meterological and chemical and physical processes under conditions of extreme complexity as those encountered in heavy industrial complexes. The data generated will also help in defining those pollutants capable of remaining in the air for long periods of time.

### Air Pollution Models

The power plant model is one of two gaussian type models employed by the Environmental Quality Board of Puerto Rico capable of a dispersion analysis. It computes maximum quantities of SO, for different stacks based on fuel sulfur content. model considers not all emission sources-only point sources are used as a model, input emissions from area sources are ignored. The model does consider terrain features by adjusting the effective plume height based on local topography. In general, the power plant model and the Air Quality Display Model (AQDM) will be helpful in estimating the impact on the ambient air of sources emitting particulates and sulfur dioxide. Specific sampling sites will be selected with the aid offered by these planning and regulatory tools.

# Metereological Considerations 14

Puerto Rico, located between 18 00' and 18 30'.

North latitude, has a maritime tropical climate except at some of the higher interior locations. This climate is characterized by small diurnal and seasonal temperature changes, high humidity, persistence of the northeast trade wind, and convective cloud types.

The mean annual temperature at Ponce, for example, is 71.1 F. The mean daily maximum temperature is 88.1 F, while the mean daily minimum temperature is 69.4 F, a diurnal variation of 18.7 F.

Relative humidities are generally high in this climatic zone, being over 80% half the time.

Although poorly understood, the importance of the meteorological parameters discussed above in air pollution control is not denied. Temperature and humidity (and solar radiation also) affect the mechanisms of oxidation and hydration and the rate of chemical and toxicological modification. These factors may operate in two ways to affect the amount of harmful pollutants: first, by acceleration of the physicochemical change which may lead to reduced or increased toxicity; and, second, by washout by rain.

Once generated, most pollutants become airborne and it is, of course, the local wind direction which determines where these airborne wastes will go.

Puerto Rico is situated in the region of the trade winds which is one of the most steady and persistent wind regions on earch. In these regions, the wind blows from easterly directions most of the time;

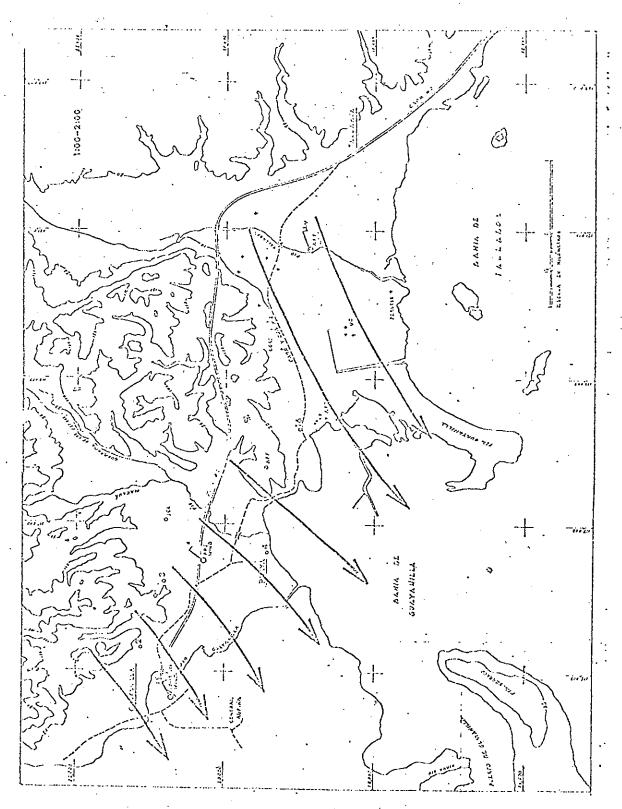
westerly winds are rare. Wind roses for three metereological stations in the Guayanilla area are shown in Figure 5.

Wind conditions at the surface in the coastal areas, can differ greatly from those at 5,000 feet due to effects introduced by the terrain, and in particular, by the diurnal oscillations produced by the land and sea breeze (Figs. 5-7). These two factors are the most crucial considerations in determining the behavior of air contaminants released to the atmosphere in a coastal area.

The stability of the atmosphere and the induced effects upon horizontal and vertical fluctuations of the wind determine the horizontal and vertical dispersion of the airborne material. Wind speed, of course, is important in this respect, not only because of mechanically induced turbulence, but also because of the functional relationship between the vertical gradients of wind and speed and temperature.

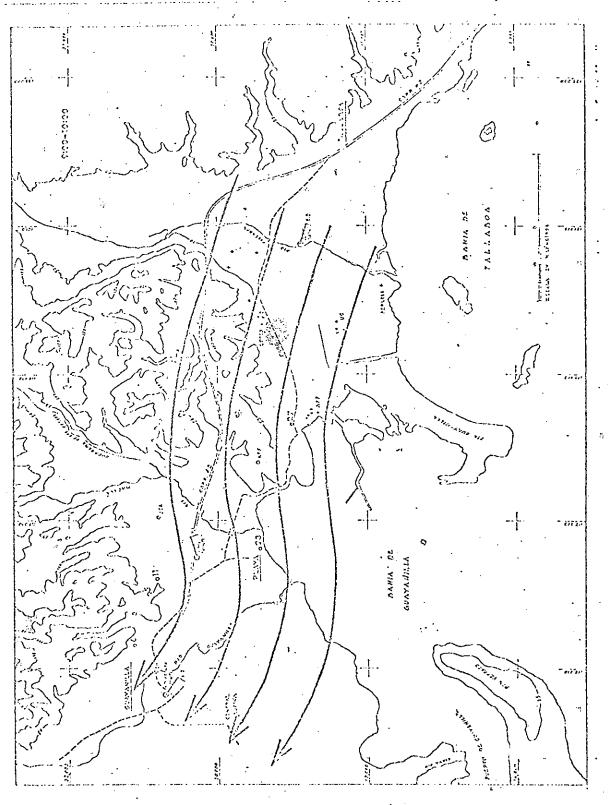
In general, the three most important parameters for the practical determination of the transport and diffusion of airborne material: wind speed, wind direction, and vertical stability will be considered in analyzing the results of this work. Wind rose and other metereological information for Guayanilla

has been recently generated by the EQB<sup>69</sup> as a result of a contract arrangement with the old Office of Petroleum Fuels Affairs now the Puerto Rico Energy Office (Figure 8). This work was performed during the tenure of Juan J. Rigau as executive director.

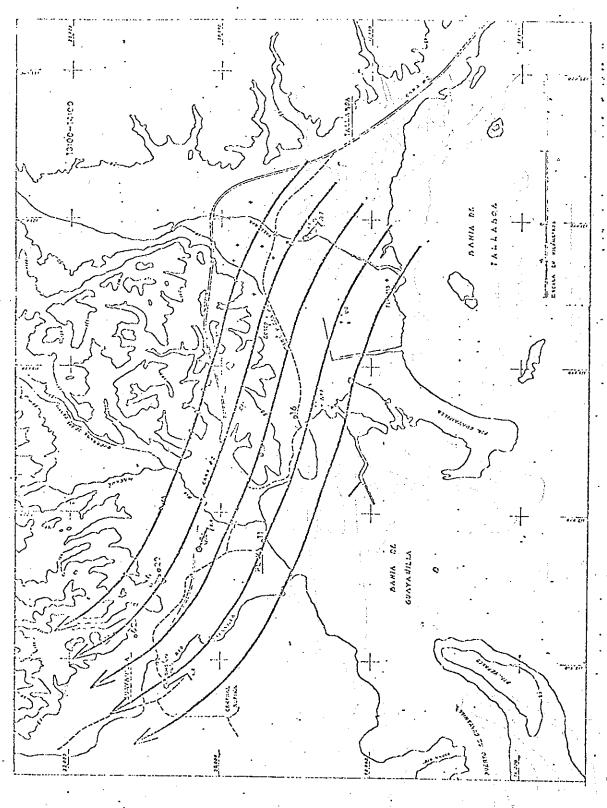


Source: Environmental Quality Board (EQB) Fig

Figure 5

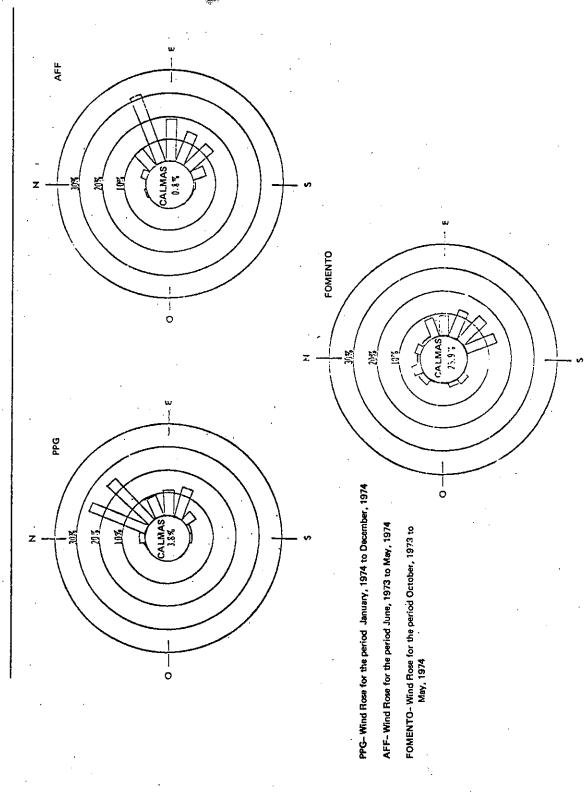


Source: Environmental Quality Board (EQB)



Source: Environmental Quality\_Board (EQB)

Figure 8: WIND ROSES FOR THE THREE METEREOLOGICAL STATIONS LOCATED IN GUAYANILLA



Source: Office of Petroleum Fuels Affairs, 1976

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### Mutagenicity and Teratogenicity of Airborne Pollutants

This proposal will also establish whether or not selected airborne particulate extracts (in total particulate and/or specific size ranges) and/or its chemical transformation products are identified as mutagenic to certain strains of bacteria and teratogenic to mammalian organisms. Annually, significant amounts of several thousands of toxic chemicals from the petroleum-petrochemical industrial complex and power plant operations, are thrown into the environment, none of which have been tested for mutagenicity or teratogenicity.

### A. Ame's Mutagenicity Test

### 1. Background

The Ame's mutagenicity test is the method of choice among the assays utilizing bacteria. A series of specific strains of Salmonella typhimurium were developed by Ames which are noted for their sensitivity to mutagenic agents in the area of the genome regulating histidine synthesis. The Salmonella typhimurium strains are auxotrophic for histidine production so that when inoculated into minimal media where this aminoacid is absent they can not grow. If the bacteria are mixed with a mutagenic agent, a potential carcinogen, it may cause back mutations in that part of the genome and reinstate the ability to

synthesize histidine. Therefore colonies of these prototrophic organisms will appear on the minimal media thus indicating that the substance tested exhibits mutagenic properties.

Some substances do not present mutagenic activity directly, but may acquire this property when processed by the cellular enzyme systems which convert them to active agents. Therefore any compound showing no direct mutagenicity is re-tested using a liver microsomal preparation (S-9 mixture) and the bacteria. This procedure allows for metabolic processing rendering them as active carcinogens. Once any of the tests has given positive results a quantitative test will be performed again but using different amounts of the tested mutagen, to determine its potency as a mutagenic agent. 67a-67f.

- 2. Methodology
   (Work scheme as actually run in our laboratory)
- a. Particulate organic samples will be solubilized in an appropriate solvent such as: ethyl alcohol, acetone, dioxane or DMSO. (Diagram 1)
  - b. Direct Spot Test: Screening
    - i. The 4 tester strains of <u>Salmonella typhimu-ruim</u> (TA-98, TA-100, TA-1535, TA-1537) are grown separately overnight in nutrient broth.

ii. A portion of 0.1 ml of bacterial growth is mixed with 2 mls. of molten agar, overlaid on minimal media and allowed to solidify. This is done in triplicate for each strain per substance to be assayed.

iii. A sample of 10 \( \rho \). I of the solubilized agent is placed on the center of each plate so that as it diffuses it will establish a range of concentration. In this way there will be a place of optimal concentration for mutagenesis to occur. Controls will be both negative, plates having no carcinogen added, and positive, plates to which mutagenic agents known to affect each specific strain will be added.

iv. The plates are incubated for 72 hrs. at 37°C. Colonies that appear in test plates are counted and compared to negative controls. An increase in at least two fold the number of revertands is considered positive.

- c. Quantitative: plate incorporation assay.
  - i. Without microsomes (S-9 mixture):
    - 1. Test will be carried out as above but utilizing a series of concentrations of each

- substance giving a positive result (0.2,
- 2, 20 and 500/kg per plate) added to the molten agar and mixed with the bacteria.
- 2. There should be a dose-response curve for the agent corroborating the original results and determining the "potency" of the agent.

# ii. With microsomia (S-9 mixture)

- 1. The test will be utilized for substance giving negative results on the screening test.
- 2. The procedure is like the one outlined above but a microsome fraction will be added to the molten agar (45 C), bacteria and carcinogen mixture.
- Positive and negative controls are also carried in this assay.
- 4. Results are determined by counting the number of revertant colonies after 72 hr. incubation as compared to negative control plates.

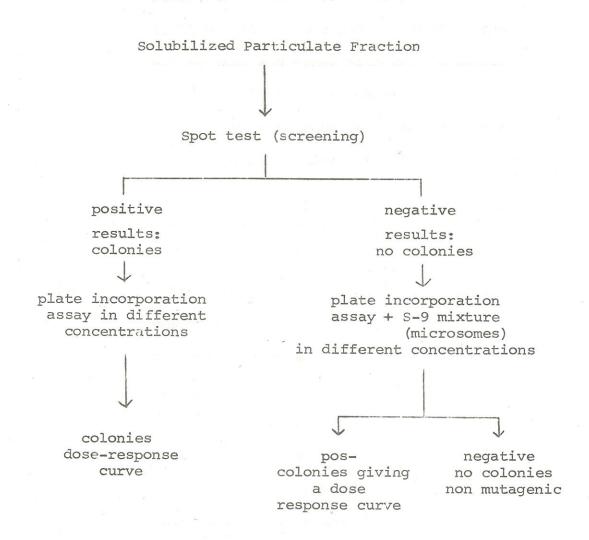


Diagram 1: Ames Mutagenicity Test Procedure.

## B. Teratogenicity Test

### 1. Background

Recently sulfur containing aromatic hydrocarbons have been detected in airborne particulates and refinery wastewaters, making toxicity test of substances present in emissions and discharges to the environment necessary when the human exposure to those substances is significantly increasing.

In addition, it is known that the effect of certain noxious chemicals in the normal environment of the human organism may lead to congenital malformations in man. The study of teratogenic effects has been included in procedures laid down for toxicological evaluation of most medical substances. However, teratogenicity is only one example of embryotoxic effects, some of which are long-term or even very long-term. The importance of prenatal toxicology goes far beyond any particular field of therapy. It must be seriously considered in the context of the wide field of occupational exposure as well as in the context of any neighborhood exposed to the transport and transformation of primary pollutants.

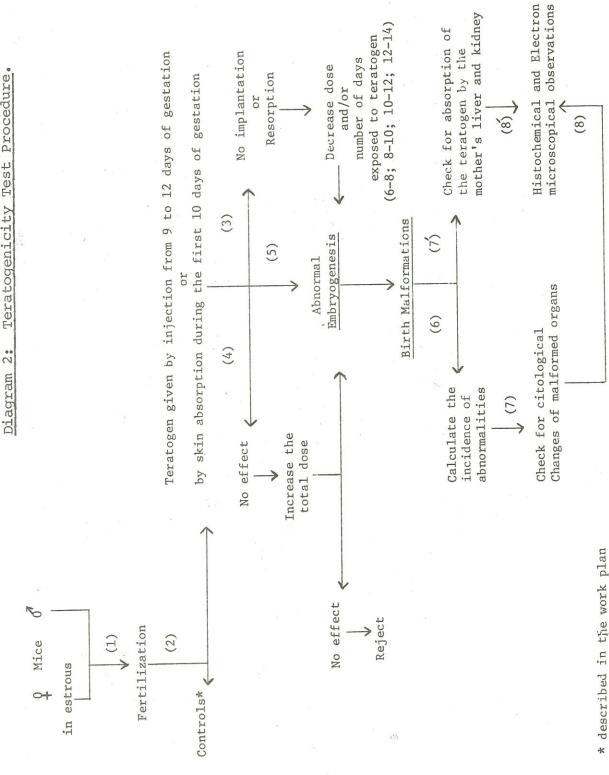
To the best of our knowledge only one chemical agent in the nature of an environmental contaminant or pollutant has been established as embryotoxic in man, namely, methyl mercury which causes both prenatal and postnatal toxicity 70-72 in the form of minamata disease.

For the detection of possible teratogens in samples of fractions of different size of airborne particulate matter in areas near energy producing plants the following procedures will be followed. It is important to observe that these procedures are currently being used in our laboratory testing benzothiophene as a possible teratogen. (Diagram 2)

Methodology (Work scheme as practiced in our laboratory)

Unmated female mice weighing 30 g or more and in the estrous phase of the cycle will be caged with males at 10:00P.M. Those mice observed in copulation will be isolated and considered zero days pregnant (see step 1 of Diagram 2). Some strains will be used in others to compare the susceptibility to the teratogen. They are maintained in individual cages, fed a diet of Purina Chow and water ad libitum.

Experimental groups of pregnant mice will be weighed and treated with intraperitoneal injections of appropriate doses of the testing samples of fractions of airborne particulate matter. The initial dose of the teratogenic sample will be the acute, single LD50 for mature mice. Ten pregnant mice of 9-12 days of gestation will receive this



dose (see Step 2). Injection is made with a 21-gauge needle into the right lower quadrant of the abdominal cavity. Others will be treated with the sample by absorption via the skin. A small portion of the skin of the hindlegs will be shaved and 0.015 ml of the sample is dispensed over the naked skin twice a day during the first ten days of gestation (see Step 2). Samples are dissolved in distilled water. Insoluble ones will be dissolved in dimethyl sulfoxide (DMSO).

On the eighteenth day of gestation, the day prior to expected littering for controls, the mice are anesthetized with ether and the abdomen is opened. The uteri of control and treated mice are carefully examined. The total number of living and dead fetuses and implantation sites is regarded as the total number of conceptuses. Viable embryos will be weighed and examined grossly. Abdomens will be opened and stored in 10 per cent neutral formalin or Bauin's solution to be studied later. Some will be exiscerated, stored in 95 percent ethanol, and later cleared and strained for study of the osseous skeleton.

If all of the fetuses have been resorbed leaving only residual implantation sites in surviving pregnant animals, further studies are pursued (see Step 3).

Many chemicals at doses causing resorption at the time of implantation if given on one of the following 3 to 4 days allow fetuses to survive showing developmental abnormalities at sacrifice on the eighteenth day of gestation. Since implantation in the uterine mucosa is at about the end of the fifth and beginning of the sixth day, groups of ten pregnant mice will receive the initial dose of sample fractions of particulate matter which will be tested for teratogenicity from days 6-8, 8-10, 10-12, and 12-14 of gestation respectively. By the fourteenth day of gestation, the fetuses can survive much higher doses, and for this reason we are not going beyond that gestational age.

Groups of ten pregnant mice in each category of gestational days will serve as controls, receiving injections of distilled water or DMSO, as well as similar groups of controls will be exposed to absorption of distilled water or DMSO by the skin.

In the case that no effect of the testing sample is found, and no malformations are present in the offspring, the dose of the testing teratogen must be increased (step 4). If after doing this no effect is found it will be rejected as a possible teratogen.

However, if birth malformations are present in the offspring of one or more of these groups of experimental pregnant mice (steps 3-5) as a result of abnormal embryogenesis caused by the testing teratogen, the following procedures will be followed (see steps 6-8).

All those groups which give positive results will be repeated for confirmation. Then, the incidence of abnormalities or malformations will be calculated for each one of the testing samples of fractions of airborne particulate matter (step 6). Also, the litter LD50 and the teratogenic range below litter LD50 will be calculated for each sample.

In order to study the malformations, the fetuses will be subjected to free-hand razor blade sectioning technique <sup>75</sup> which permits a gross study of all the organs and systems of the fetuses. After doing this, a citological study of each one of the malformed organs or systems will be done using histochemical and electron-microscopical observations (steps 7-8). Besides, for the confirmation of the absorption of the testing teratogen by the mother's organism, is is necessary to do citological studies of the liver and the kidney of all experimental pregnant mice which give rise to abnormal

fetuses, and compare them with those organs of the control pregnant mice (steps 7'-8').

## 3. Rationale for Selected Approach

This proposal covers an extremely important area of preventive environmental health. First, since no previous study of this nature has ever been attempted in Puerto Rico, our intent was to integrate the best resources available at Catholic University of Puerto Rico and the University of Puerto Rico. Operational costs to develop an inherently expensive research project will be minimum by pooling re-This is an important factor if the experience generated in this project is to be applied later to other heavily polluted and densely populated areas like Cataño on the north coast of the island. Catholic University took the initiative to investigate the Guayanilla-Peñuelas area because of its close vicinity to the sector, a key element when field work and detailed knowledge of the area is involved; and to jointly develop it with CEER because of their detailed knowledge of the petroleum-petrochemical industry, petroleum composition, the availability of trained personnel and good lab facilities.

Second, a multidisciplinary approach was followed in the design of the plan of work in order to generate data with a system perspective of the problem. This will increase our opportunities to help not only in defining the existing conditions in the south coast industrial complex,

but also in communicating our results effectively to the Commonwealth of Puerto Rico regulatory agencies and the Governor's Office.

Third, we feel that it is important that the researchers associated with the project are professionally qualified and recognized as objective, and non-partisan. This is essential every time solutions to sensitive and important problems are involved; and

Fourth, we selected this project because we are convinced of the need to explore areas of biomedical interest associated to the process of energy consumption and production. This will facilitate integration into the field of various groups already interested, planning and/or conducting research work at the basic sciences departments of our two major Schools of Medicine.

## 4. Unusual Features,

- a. One of the most unusual features of the proposed work is that this proposal probably represents the only opportunity that Puerto Rico will get in a long time to come to explore under a professional perspective the problems associated with the emissions of particulate matter in a heavily industrialized sector. In particular, problems associated with the emissions to the atmosphere in a fully integrated petroleum-petrochemical complex and future ones if a selection is made on a proposed coal-operated power plant.
- b. The South Coast Complex currently has shut-down three of its major plants: The Puerto Rico Olefins, Hercor Chemicals, and PPG, all producers of very reactive pollutants. This highly unusual circumstance will permit us to assess the impact of their respective emissions in the aggregate of contaminants available for characterization. This ofcourse, is an important and unique event that could bring knowledge of great importance to the United States Environmental Protection Agency in its efforts to harmonize economic development and environmental degradation. It is envisioned that in the course of next year those plants will again be operating. So, this is an opportunity that should not be passed.

c. As previously expressed this work constitutes a multidisciplinary effort involving researchers from various backgrounds that are in position to induce themselves a multiplier effect by promoting additional research in their respective institutions.

## b. Methods of procedure, analysis and evaluation

Experimental procedures and analysis have been described in detail in the corresponding sections of the plan of work. Evaluation process will try to tie closely the findings of the work with current regulatory issues of interest to government, industry and, the academic sectors. Project management should also try to establish the implications of the work to future designs of industrial complexes and relevance to base line studies particularly if a decision on the proposed coal-power plant is finally taken.

Close supervision of all phases of the work will be maintained throughout project development in order to keep all principal investigators aware of the progress made by the different groups. Monthly meetings of all project personnel will serve to exchange views, help solve problems and revise the plan of action.

SCHEDULE OF ACCOMPLISHMENTS

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Month After Grant Award

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- Particulate Collection, Size-Distribution Analysis and Air Pollution Modelling. Site selection for particulate sampling. B
  - Modification and calibration of cascade impactor.
    - Estimate collection times, sample particulates and conduct sizedistribution.
      - Simulation runs using the EQB's Air pollution model.
- Correlation between pollution levels point sources and metereology.
- Particulate Metal Analysis. ပံ
- for atomic absorption and optical Sample collection and preparation emission spectrography analyses.
- Metal analysis in total particulate matter.
- Metal analysis by size distribution of airborne particulates.
  - Statistical evaluation of data.
- formation studies. å
- Volatile Hydrocarbons and Chemical trans-Sample Collection

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# Major Activities Description

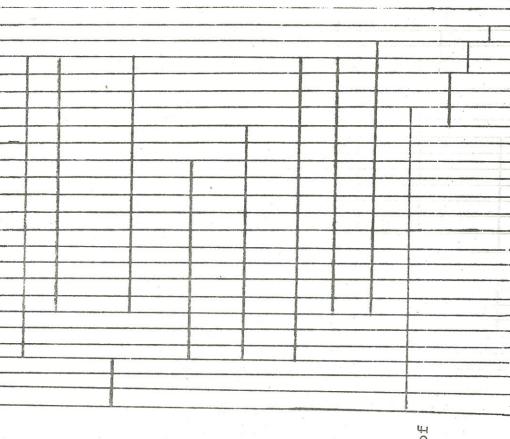
Month After Grant Award

4.

- Quantification of selected indi-Separation and characterization. vidual compounds.
  - test for chemical transformation Hi-vol sampler modification and studies.
    - Chemical transformation studies. Particulate Analysis For Polycyclic Aromatics and Heterocompounds. 5.

H

- Sample collection. -
- basic, neutral, polar aromatics). selected fractions (e.g., acid, Extraction and separation of
  - aromatics and heterocompounds in Characterization of polycyclic total particulates.
    - Analysis for selected PAH's and or heterocompounds.
- Quantification of selected individual compounds 5
- Mutagenicity. Fi
- Testing of samples. 0
- Determination of the mutagenicity of selected fractions. 2
  - Statistical analysis e, 4,
    - Writing of report.



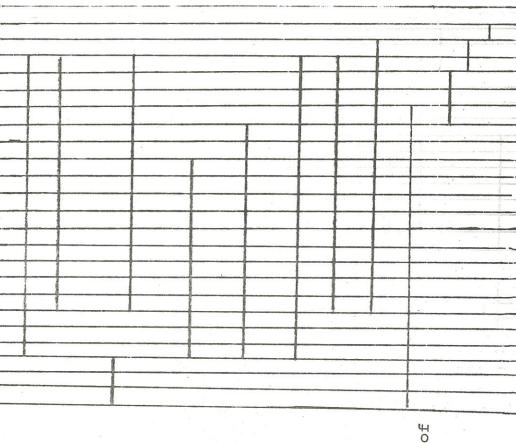
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Month After Grant Award

- Quantification of selected indi-Separation and characterization. vidual compounds. 2.0
  - test for chemical transformation Hi-vol sampler modification and studies. 4.
    - Chemical transformation studies. Particulate Analysis For Polycyclic 5°

F

- Aromatics and Heterocompounds.
  - Sample collection. 7°
- basic, neutral, polar aromatics). selected fractions (e.g., acid, Extraction and separation of
  - aromatics and heterocompounds in Characterization of polycyclic total particulates. e
- Analysis for selected PAH's and or heterocompounds. 40
- Quantification of selected individual compounds 5.
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- Testing of samples. -
- Determination of the mutagenicity of selected fractions.
  - Statistical analysis
    - Writing of report.

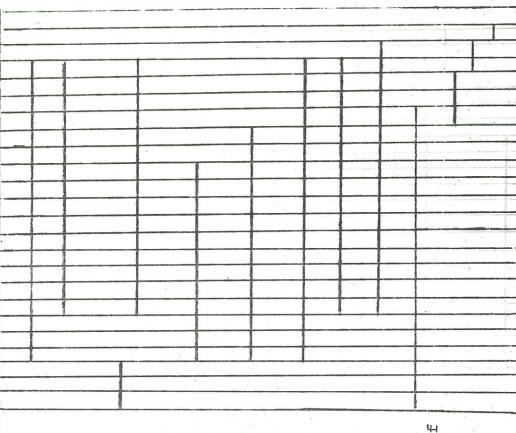


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Major Activities Description

Month After Grant Award

- Separation and characterization. 2.0
  - Quantification of selected individual compounds.
    - test for chemical transformation Hi-vol sampler modification and studies.
- Chemical transformation studies. 5
- Particulate Analysis For Polycyclic Aromatics and Heterocompounds. E I
  - Sample collection.
- basic, neutral, polar aromatics) selected fractions (e.g., acid, Extraction and separation of
- aromatics and heterocompounds in Characterization of polycyclic total particulates.
- Analysis for selected PAH's and/ or heterocompounds.
  - Quantification of selected individual compounds 5
- Mutagenicity. 더
- Testing of samples. -
- Determination of the mutagenicity of selected fractions.
  - e m
- Statistical analysis Writing of report.



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Major Activities Description

Month After Grant Award

Teratogenicity

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Animal breeding.

Determination of embriotoxicity of selected test fractions.

Calculation of incidence of selected

Histochemical and electronmicroscopical observations of malformed organs. abnormalities.

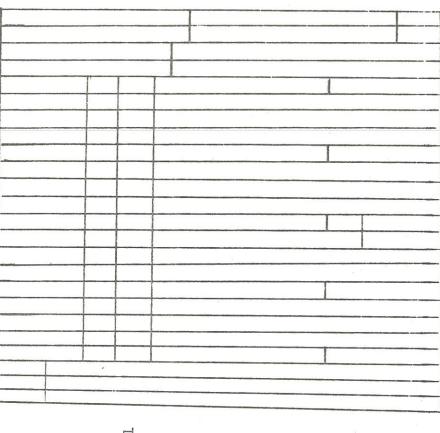
Analysis of results. ° °

Writing of final report.

periodically in the evaluation of all pertinent experimental results covered under (Statistical analysis will be conducted this project) Quarterly reports for internal progress evaluation and feedback. H

Annual progress report. . H

Submit final report. b



- d. Personnel Responsibility for each part of the Work Plan.
  - 1. Project Director (Dr. Juan J. Rigau) (50%) The director is responsible for the overall administrative and scientific aspects of the project. He will coordinate the different groups and collaborate in the extraction separation, and characterization of polycyclic aromatic hydrocarbons particularly sulfur containing polycyclics and will correlate the data generated under this program with other research and analytical efforts conducted at the Center for Energy and Environment Research, the Department of Health and the Environmental Quality Board of Puerto Rico.
  - 2. Principal Investigator (Dr. Gabriel Infante) (25%) This investigator will be in charge of the metal analysis
    in particulates. His participation will also include collaboration in the separation, characterization, and quantitation associated with chemical transformations of reactive
    pollutants in the presence of local air contaminants.
  - 3. Principal Investigator (Dr. Arnaldo Carrasquillo) (25%)
    This investigator will be in charge of determining chemical transformations of environmental airborne pollutants and the analysis of volatile hydrocarbons. He will also collaborate in the characterization of nitrogen containing polycyclic aromatic hydrocarbons.

carry out continuous extractions and other routine analysis of samples obtained from the field.

- 8. Two B.S. Undergraduate Students Students from the Physics Department will conduct research assigned by the principal investigator. They will operate the apparatus needed to sample particulates and collaborate in the running of the air pollution model.
- 9. <u>B.Sc. Undergraduate Student</u> will conduct research assigned by the principal investigator. A student from the Chemistry Department, he will conduct the metal analysis in particulates and other associated tasks.
- 10. Principal Investigator (Dr. Hilda López) (40%) will be in charge of the teratogenic tests and supervision of graduate students of the Department of Anatomy, UPR Medical School (e.g., Mr. Calixto Soto; MSc., a graduate student, will be doing teratogenic tests as part of his thesis work for the Ph.D. degree. He will devote 100% of his time to this project).
- 11. BSc. in Biology (100%) will be in charge of the preparation of the histological sections and animal care and feeding.
- 12. Principal Investigator (Dr. José A. Carrasco) (40%) He will be in charge of the Ames Mutagenicity Assay and supervision of graduate students from the Department of Microbiology, UPR, Medical School.

- 13. Medical Technologist (100%) will conduct work on the Ames test under the supervision of a well trained technician currently doing the Ames assay in our lab.
- 14. <u>Utility Man</u> will take care of animals, cleaning of cages and lab ware in the mutagenicity and teratogenicity laboratories.

## e. Facilities and Equipment Presently Available.

## Catholic University of Puerto Rico

To support energy and environment research programs at Catholic University of Puerto Rico, the Administration has created an Institute for Energy, Environment and Bio-Medical Sciences. The laboratory facilities will be finished this summer and are located at the Medical School (See Appendix II for diagram. This concept will prove highly beneficial to the development of interdisciplinary research work in collaboration with undergraduate and graduate students and professors of the College of Sciences and the Medical School. Equipment available for this project includes chemical and biological hoods, two research gas chromatographs, colorimeters, high vacuum line facilities, thin-layer chromatography apparatus, ultracentrifuges, soxhlet extraction apparatus, and six high volume samplers. Major laboratory equipment available to the Institute from other on Campus facilities include infrared and ultraviolet spectrophotometers, Turner fluorometer, nuclear magnetic resonance spectrometer, atomic absorption, etc. For that reason, only the equipment judged to be indispensable for this work is requested under this proposal.

## Center for Energy and Environment Research

Research facilities at the Center for Energy and Environment Research are the typical ones encountered in an institution dedicated to solar energy research, terrestial, marine, and human ecology. The Fossil Fuels Research Program of the Division of Environmental Health and Impact has developed a research effort covering the microbial degradation of high sulfur crude oils. Equipment available for the separation and characterization of petroleum fractions includes two research gas chromatographs with flame photometric and flame ionization detectors with glass capillary column capabilities, a HPLC instrument with UV and differential refractometer detectors and a back flush four way valve attachment, TLC, IR and UV spectrophotometers. Well equipped microbiology laboratories are available as part of the facilities of the the Fossil Fuel Program and Medical School, UPR. A Hewlett Packard Model 5985A quadruple mass spectrometer with on line gas chromatography-computer capabilities and dual chemical/electron ionization source is abailable to our program under special arrangement from the Horse Racing Commision Laboratory. They charge us for materials and a percentage of the maintenance and service contract depending on time demand on the instrument. Animal room, electron microscopy facilities, compound microscopes, and some cages are available as part of the facilities for the teratogenic work.

## 4. Budget Schedule

The project director and principal investigators are active participants in the energy-environment programs started at the Institute for Energy, Environment and Biomedical Sciences of Catholic University of Puerto Rico and the Center for Energy and Environment Research. Both research oriented organizations support their respective academic faculties to which they serve in addition to the island of Puerto Rico in helping develop energy and environment research programs.

The proposed budget includes compensatory time for their research involvement in the proposed project. Salary is estimated based on the percentage of time that will be dedicated to project development using their yearly salary as a base.

SCIENTIFIC PERSONNEL	TIME DEVOTED	ED	1979-80	1980-81
Name and Position				
Juan J. Rigau, Senior Scientist I and Project Director (CEER and CUPR)	20%		15,000	15,000
Richard Eckard, Principal Investigator and Professor of Physics (CUPR)	25%		4,700	4,700
Gabriel Infante, Principal Investigator				
and Associate Professor of Chemistry (CUPR)	25%		4,400	4,400
Arnaldo Carrasquillo, Principal Investigator and Professor of Chemistry (CUPR)	25%		4,700	4,700
Alvaro Baratto, Scientist I (CEER and CUPR)	20%		7,200	7,200
José Carrasco, Principal Investigator and Assistant Professor of Microbiology (CEER)	40%		9,200	9,200
Hilda López, Principal Investigator and Assistant Professor of Anatomy (CEER)	40%		9,200	9,200
			54,400	54,400

TECHNICAL PERSONNEL	TIME DEVOTED	1979-80	1980-81
(2) BSc. Chemists (CEER and CUPR)	100%	15,600	15,600
(1) BSc. Biologist (CEER)	100%	7,800	7,800
(1) Medical Technologist (CEER)	100%	10,800	10,800
<ul><li>(1) Graduate Student (CEER)</li><li>(Department of Anatomy, UPR, Medical School)</li></ul>	*	4,200	4,200
(3) Undergraduate Students (CUPR)	* *	7,920	7,920
(1) Secretary (CEER)	100%	6,600	009"9
(1) Utility Man (CEER)	* *	2,880	2,880
0.3	Sub-Total	55,800	55,800
Gross Salary Fringe Benefits (20%) Christmas Bonus (4%) (Legislated by Local Law)		110,200 22,400 1,800	110,200 22,400 1,800
II.	Total	134,400	134,400

Salary based on \$350/month on a minimum of 20 hrs./week research involvement.

<sup>\*\*</sup> Salary based on \$3.00/hr., 15 hrs./week during the period of August-May and 35 hrs./week during the summer.

<sup>\*\*\*</sup> Salary based on 20 hrs./week at \$3.00/hr.

## Operating Budget Outlay:

82,530 1,000 10,000

85,493 1,000

10,000

134,400

134,400

1980-81

1979-80

Curomatographic adsorbents, GC/MS recorder paper, solvents, reference chemicals for quantitation, mice food, embedding medium, stains, petri-dishes, etc.)

8,000	235,930	408
44,585	275,478	511,
	Grand Total	Total Budget

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(d) Consultants
(Dr. William H. Zoller, Department of Chemistry,

David Pastor, University of Puerto Rico, Humacao Campus, University of Maryland, College Park, Md. and Professor Zoller is well known for his work on particulate analyanalysis-particulate sizing and computer modelling. will be assisting the project in the areas of metal zing and Mr. Pastor is the applied mathematician developed the Commonwealth Air Pollution Model

3 Model 235 Sierra high-volume cascade impactors Particulate Sampling Metal and Organic Analysis Equipment (e)

(Sierra Instruments, Carmel Valley, California) \$6,000 served a warning that under Note: A compromise was made in selecting the Sierra sample particulate matter for the organic and metal analysis. Walsh et al<sup>38f</sup> served a warning that und impactor because of its capacity to collect enough

1,000	500	2,000	
2,000	4,500	4,000	

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high humidity in the coastal sampling area we bespecified by its stated operational characterisbouncing error does not appear to be significant ticle size distribution will be confirmed by uscellulose fiber impaction surfaces may not proping a modified cascade impactor as used by W.H. when sampling marine aerosols. Because of the erly collect ambient aerosol size fractions as Zoller in Maryland. (Zoller has agreed to be a tics. However, they found that the potential certain conditions, the Sierra impactor with lieve the bouncing error will be minimal. consultant to this project).

W.

2 Waters Associates Inc., HPLC Bondapak col-umns.	Fluorescent Detector for HPLC.	Grafite Furnace for Atomic Absorption.	Atomic absorption lamps to supplement current ones.	Replacement equipment for air sampling (Hi-vol samples) and modification for the chemical transformation experiments.
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Mutagenicity and Teratogenicity	Petri-dish Filler.	Petri-dish Stacker.		Airmar cayes and scands.	Tissue Processor.	Tissue Embedding Center.	Sharnener		
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Computer time will be covered by the participating institutions. Indirect expenses will be divided between Catholic University of Puerto Rico and the Center for Energy and Environment Research, University of Puerto Rico, based on their respective direct involvements. H<sub>2</sub> Notes:

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### APPENDIX I

- 1. Table I: Socio-Economic and Energy Indicators in Selected Fiscal Years Terminating on June 30.
- 2. Table II: Fuel Used by the Puerto Rico Water Resources Authority for Power Generation.
- 3. Table III: Puerto Rico Petroleum Flow Pattern and Relation of Energy Used and Lost in the Process Calendar Year 1976 in thousand Barrels.
- 4. Figure la: Chemical Configurations Related to Sulfur and Ni-67 trogen Derivatives in Fuel Oil.
- 5. Figure 1b: Components of Environmental Assessment.
- 6. Figure 2: Municipalities, Standard Metropolitan Statistical Areas, and Selected Places.
- 7. Figure 3: Existing Refining and Petrochemical Industry 1975.
- 8. Table IV: Petrochemical Production in U.S. and Puerto Rico.
- 9. Table V: Southern Coastal Plain Vital Statistics.
- 10. Figure 4: Incidence Rates for Ten Common Primary Sites Puerto Rico 1975.
- 11. Figure 5: Trend of Incidence of Lung Cancer Puerto Rico 1974.
- 12. Table VI: 1978 Projected Air Quality Levels Annual Arithmetic Mean.
- 13. Table VII: 1985 Projected Air Quality Levels Annual Arithmetic Mean.
- 14. Figure 6: Predicted Particulate Air Quality Annual Average-Area Sources Only 1975-75.

## APPENDIX II

Diagram of Catholic University of Puerto Rico Institute for Energy, Environment and Biomedical Sciences Facilities.

## APPENDIX III

 Letter of the President Catholic University of Puerto Rico to the Executive Director (now President) of the Environmental Quality Board of Puerto Rico and the corresponding answer.

## APPENDIX IV

Curriculum Vitae Project Director and Principal Investigators.

APPENDIX I

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Figure 3:

EXISTING REFINING AND PETROCHEMICAL INDUSTRY-1973

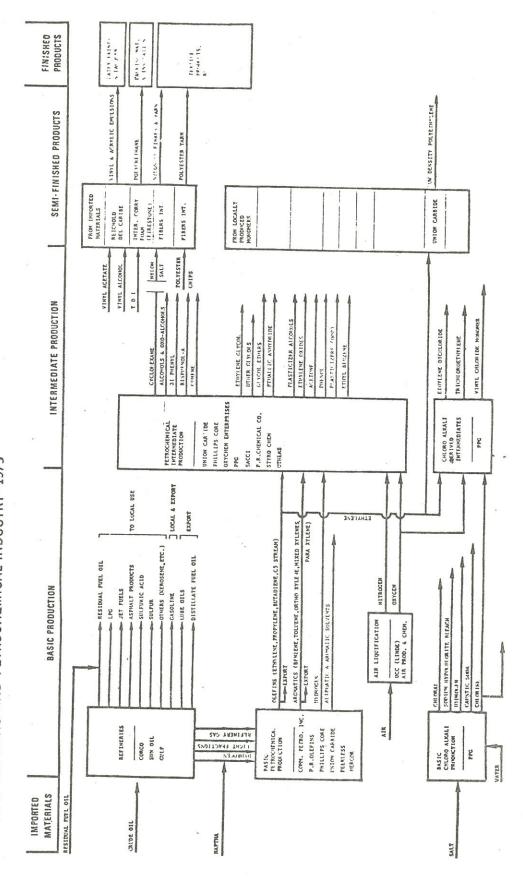


TABLE IV: PLTROCHEMICAL PRODUCTION IN U.S. & PUERTO RICO  $^{1}$ 

1775 M lbs.   22,329 M lbs.   10,060 M lbs.   10,060 M lbs.   10,060 M lbs.   3,644 M lbs.   260 M gal.   3,644 M lbs.   3,644 M lbs.   3,474 M lbs.   3,474 M lbs.   2,013 M lbs.   2,00 M lbs.   2,250 M lbs.   2,25	Product	Production (1973)	United States	%U.S. Preduction
1775 M lbs. 22,329 M lbs			110aact1011 (13/3)	Irom Fuerto Fico (1976)
1050 M lbs. 10,060 M lbs. 9.  260 M gal. 1,458 M gal. 17.  87 M gal. 818 M gal. 7.  137 M gal. 1,068 M gal. 7.  299 M lbs. 2,013 M lbs. 10.  1036 M lbs. 3,474 M lbs. 29.  500 M lbs. 5,351 M lbs. 8.  200 M lbs. 2,250 M lbs. 8.  200 M lbs. 2,354 M lbs. 9.  200 M lbs. 2,354 M lbs. 2,354 M lbs. 2,354 M lbs. 2,354 M lbs. 3.	Ethylene	$\geq$	2	C
360 M lbs. 3,644 M lbs. 9. 260 M gal. 1,458 M gal. 17. 87 M gal. 818 M gal. 7. 137 M gal. 1,068 M gal. 7. 299 M lbs. 2,013 M lbs. 14. 450 M lbs. 3,474 M lbs. 29. 500 M lbs. 5,351 M lbs. 8. 200 M lbs. 2,250 M lbs. 8. 200 M lbs. 2,250 M lbs. 8. 200 M lbs. 2,175 M lbs. 9. 20 M lbs. 2,175 M lbs. 2.	Propylene			m
360 M lbs. 3,644 M lbs. 9. 260 M gal. 1,458 M gal. 17. 87 M gal. 818 M gal. 7. 137 M gal. 1,068 M gal. 7. 299 M lbs. 2,013 M lbs. 14. 450 M lbs. 3,474 M lbs. 29. 500 M lbs. 5,351 M lbs. 89. 84 M gal. 2,250 M lbs. 8. 84 M gal. 2,354 M lbs. 8. 20 M lbs. 2,250 M lbs. 89. 84 M gal. 2,354 M lbs. 8.	D::+: 2:::(	<u> </u>	JOO MIE	I
260 M gal. 1,458 M gal. 17. 87 M gal. 60 M gal. 7. 137 M gal. 1,068 M gal. 7. 299 M lbs. 2,013 M lbs. 14. 450 M lbs. 3,474 M lbs. 29. 500 M lbs. 5,351 M lbs. 84 M gal. 2,354 M lbs. 82 3.35 M lbs. 82 3.35 M lbs. 84 M gal. 2,354 M lbs. 87 M lbs. 87 M lbs. 20 M lbs. 87 M lbs. 20 M lbs. 2,175 M lbs. 20 M lbs. 2,175 M lbs. 20 M lbs. 2,175	Butadlene	$\geq$	644 M	•
87 M gal. 849 M gal. 7. 137 M gal. 1,068 M gal. 7. 299 M lbs. 2,013 M lbs. 10. 1036 M lbs. 3,474 M lbs. 29. 200 M lbs. 5,351 M lbs. 8.440 M lbs. 20.0 M lbs. 2,250 M lbs. 8.440 M lbs. 2,354 M lbs. 20 M lbs. 2,354 M lbs. 2,354 M lbs. 3.3 m lbs. 2,175 M l	Benzene	60 M	$\geq$	17.8
60 M gal. 818 M gal. 7.  137 M gal. 1,068 M gal. 2,013 M lbs. 14.  450 M lbs. 3,474 M lbs. 29.  500 M lbs. 5,351 M lbs. 84 M gal. 2,250 M lbs. 8.354 M lbs. 8.350 M lbs. 8.354 M lbs. 8.350 M lbs. 8.350 M lbs. 2,354 M lbs. 2,354 M lbs. 20 M lbs. 2,00 M lbs. 2,	Toluene	$\geq$	Z 6	
137 M gal. 1,068 M gal. 299 M lbs. 2,013 M lbs. 14. 450 M lbs. 4,167 M lbs. 10. 500 M lbs. 5,351 M lbs. 9. 84 M gal. 2,354 M lbs. 8. 310 M lbs. 8,440 M lbs. 3.20 M lbs. 20 M lbs. 2,354 M lbs. 3.30 M lbs. 3.70 M lbs. 3.70 M lbs. 3.70 M lbs. 5,354 M lbs. 2,901 M lbs.	Mixed xylene	$\geq$	$\geq$	•
299 M lbs. 2,013 M lbs. 14. 450 M lbs. 4,167 M lbs. 10. 1036 M lbs. 3,474 M lbs. 29. 200 M lbs. 2,250 M lbs. 8.44 M gal. 2,354 M lbs. 20.0 M lbs. 2,354 M lbs. 20.0 M lbs. 2,354 M lbs. 20.0 M lbs. 2,175 M lbs. 2,901 M lbs. 2,90	Ortho xylene	$\geq$	$\geq$	•
450 M lbs. 4,167 M lbs. 10.  1036 M lbs. 3,474 M lbs. 29.  500 M lbs. 2,250 M lbs. 8.44 M gal. 2,354 M lbs. 23.0 M lbs. 2,354 M lbs. 20 M lbs. 2,175 M lbs. 20 M lbs. 2,175 M lbs. 2,100 M	Para xylene	99 M	$\geq$	14 9
reol 1036 M lbs. 3,474 M lbs. 29. 29. 200 M lbs. 2,250 M lbs. 2,354 M lbs. 8.440 M lbs. 20 M lbs. 2,175 M lbs. 20 M lbs. 2,175 M lbs. 2	Xylene oxide	50 M	M 291	
ide 500 M lbs. 5,351 M lbs. 9. 200 M lbs. 2,250 M lbs. 8.1 lene 84 M gal. 2,354 M lbs lene 310 M lbs. 8,440 M lbs. 3. 20 M lbs. 2,175 M lbs. 0.	Ethylene glycol	$\geq$	174 M	
e 84 M gal. 2,250 M lbs. 8.  lene 310 M lbs. 8,440 M lbs. 3.  20 M lbs. 2,175 M lbs. 0.  ber 75 M lbs. 2,901 M lbs. 2.	Vinyl Chloride	$\geq$	351 M	. 0
e 84 M gal. 2,354 M lbs. — 1ene 310 M lbs. 8,440 M lbs. 3. 20 M lbs. 2,175 M lbs. 0. ber 75 M lbs. 2,901 M lbs. 2.	Phenol	$\geq$	250 M	
lene 310 M lbs. 8,440 M lbs. 3. 20 M lbs. 2,175 M lbs. 0. 2,901 M lbs. 2.901 M lbs.	Cyclohexane	$\sum$	354 M	٠.
20 M lbs. 2,175 M lbs. 0.	'len	$\mathbb{Z}$	440 M	3.7
75 M lbs. 2,901 M lbs. 2.	Nylon Fiber	$\geq$	175 M	•
	Polyester Fiber	M lb	901 M	2 (2)

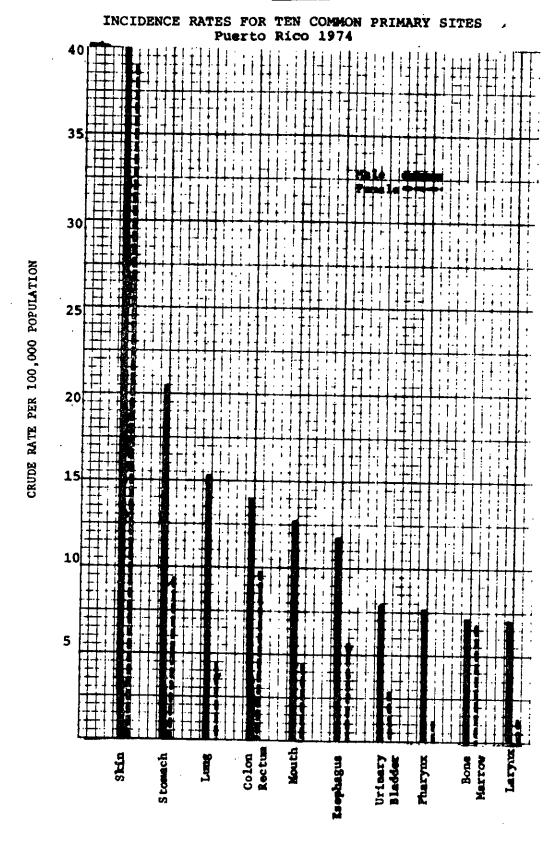
1/Report to Congress on Petrochemicals Office of Economic Impact Federal Energy Administration

TABLE V: SOUTHERN COASTAL PLATN VITAL STATISTICS

Municipality	Population	Live births		Deat	Deaths	
		Number	Rate	Number	Rate	
Guánica	17,810	461	25.9	117	6.6	
Yauco	39,000	944	24.2	245	6.3	
Guayanilla	20,370	521	26.1	122	6.0	
Peñuelas	19,010	468	24.6	123	6.5	
Ponce	183,380	4,946	27.0	1,273	6.9	
Juana Díaz	42,810	1,089	25.4	236	5.5	
Santa Isabel	18,540	515	27.8	131	7.1	
Salinas	26,040	678	26.0	192	7.3	
Guayama	45,270	1,080	23.9	324	7.2	
		<i>,</i>				

Source: Puerto Rico Department of Health

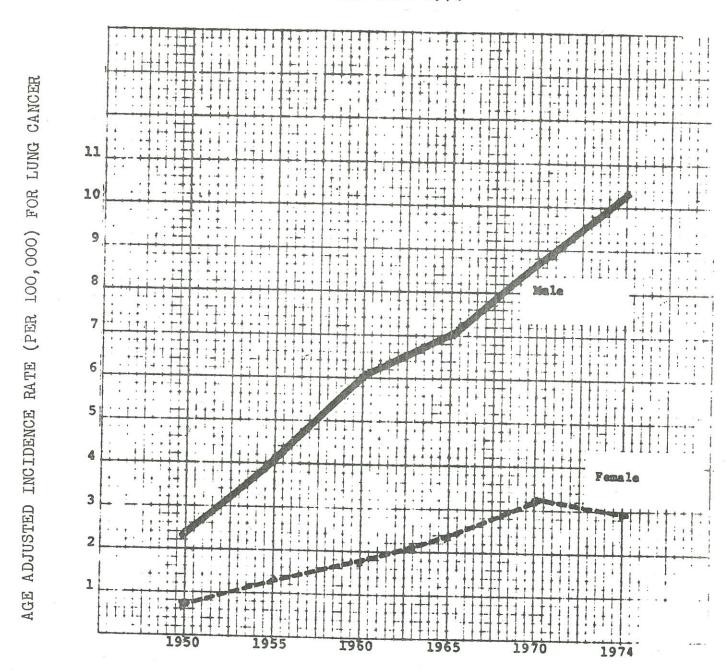
Figure 4



Source: Puerto Rico Department of Health

Figure 5

## TREND OF INCIDENCE OF LUNG CANCER PUERTO RICO 1974



Source: Puerto Rico Department of Health

TABLE V1

1978 PROJECTED AIR QUALITY LEVELS

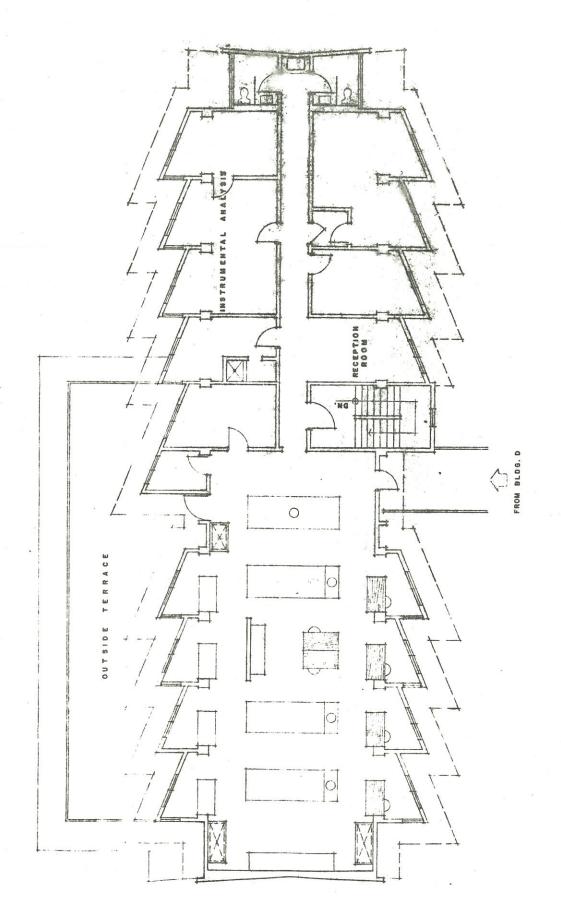
ANNUAL ARITHMETIC MEAN

(µg/m³)'

AQMA	v. 0	Point and Area Particulate	Sources
San Juan		115	86
Ponce		78	28
Mayaguez		100	20
Caguas		37	13
Guanica		71	42
Dorado		94	70
Guayanilla		98	85
Lares-Utuado-Adjuntas		36	20
Aguadilla		65	14
Arecibo	*	44	44
Guayama		45	64
Yabucoa		40	73

Source: Environmental Quality Board (EQB)

APPENDIX II



SECOND FLOOR BLDG. "E" SCALE 1/8" : 1.

# UNIVERSIDAD CATOLICA DE PUERTO RICO



Ponce, Puerto Rico - 00731

May 11, 1978

Eng. Pedro Gelabert Executive Director Environmental Quality Board San Juan, PR 00902

Dear Engineer Gelabert:

We are convinced that there exists a causal relationship between pollution levels and certain damages suffered by our society. Thus, it is necessary now, as it was in 1970, to set new goals in light of new knowledge. Since the goals of a clean environment cannot be achieved in isolation, we, at Catholic University of Puerto Rico, have decided to contribute by developing the concept of an Institute for Energy and Biomedical Sciences. The Institute will study the environmental impacts of energy producing the consuming operations following a systems approach.

Interdisciplinary and multidisciplinary research efforts employing the resources of Catholic University will help our government, as well as other sectors, in harmonizing environmental considerations with the requirements of an energy policy. Our biomedical approach will help in establishing the quantitative expression of the relationships between exposure to specific pollutants, and the type and extent of the associated damage to a target population. For example, by identifying locations of susceptible populations exposed to relatively hazardous levels of pollutants, the effects of allocating specific pollution control resources can be assessed. In this regard, the data required to develop physical or biological damage functions will be obtained through epidemiological, field, clinical, toxicological, or laboratory investigations. To help achieve these objectives, we have decided to construct special laboratory facilities. Microbiology, biochemistry, organic chemistry, physiology, tissue culture, infectious diseases, and analytical chemistry laboratories will be finished in the next few weeks.

The administration in collaboration with our faculty is already preparing research proposals oriented to:

better understand how physical, chemical and biological agents interact

better understand the transport and transformation of synthetic chemicals

better understand human risk factors

better trained research scientists and science undergraduates APPENDIX III

Eng. Pedro Gelabert Page 2 May 11, 1978

With this concept in mind, we wish to invite you to give us a presentation covering your areas of interest and those problems in which our Institute can contribute more effectively to the solution of regional needs. I will be looking forward to your reaction on these and other matters.

Cordially yours,

Francisco J. Carrera

President

1es

Received

JUN 28 1978

C. U. P. H. SCHOOL OF MENIUME

15 de junio de 1978

Dr. Francisco J. Carreras Presidente Universidad Católica de Puerto Rico Ponce, Puerto Rico 00731

Estimado Dr. Carreras:

Junta de Calidad

mbiental

En respuesta a su comunicación del día ll de mayo, deseo indicarle que en la Junta de Calidad Ambiental estamos comprometidos en la búsqueda de soluciones a los problemas ambientales presentes y futuros. Por tal motivo, coincido con usted en que es necesario que continuamente evaluemos los logros alcanzados y nos fijemos nuevas metas a la luz de los nuevos conocimientos científicos. Creemos además que es imprescindible la integración de los esfuerzos institucionales públicos y privados para poder lograr la meta de la conservación y protección de nuestro ambiente.

La iniciativa de ustedes al crear el Instituto de Energía y Ciencias Biomédicas es digna de encomio y por los objetivos que se han fijado estoy seguro que harán una contribución importante a la solución de la problemática ambiental de Puerto Rico. Les felicito por tan brillante idea.

Tan pronto tenga oportunidad me gustaría programar para compartir con ustedes aquellos problemas y áreas de interés particular en las cuales yo considero que el Instituto podría contribuir efectivamente a la solución de necesidades y problemas regionales.

Mi ayudante ejecutivo el Sr. Wilfrido Soto de Arce se comunicará con su oficina para fijar la fecha y hora más conveniente para ambas partes.

(1: Or alfred M. Bongiovanni

Pedro A. Gelabert /

Cordialmente

Director Ejecutivo

JUN2 0 1978

que usted desea, en el ambiente que le rodea.

APPENDIX IV

## CURRICULUM VITAL

NAME:

Juan Jose Rigau Sepulveda

PERSONAL DATA:

Date of Birth

November 24, 1939

Place

Sabana Grande, Puerto Rico

Status

Married, four children

POSITIONS:

Consultant on Energy and Environment 1977-

Director - Office of Petroleum Fuels
Affairs, 1973-1976 - Office
of the Governor, Commonwealth
of Puerto Rico

Consultant - Economic Development Administration, 1969-1973

EDUCATION:

1956 - University of Puerto Rico High School, Rio Piedras, Puerto Rico

1960 - Bachelor of Science University of Puerto Rico

1965 - Master of Science University of Puerto Rico

1969 - Doctor of Philosophy Wayne State University Detroit, Michigan

DISSERTATIONS:

"La Esteroquímica de B-Hidroxisulfoxidos", M.S. thesis, University of Puerto Rico, 1965

"Sterochemical Studies in Organo-Sulfur Chemistry", Ph.D. thesis, Wayne State University, 1969. <u>Dissertation Abstr</u>. Intern'1, 32 (5), 2612-B (1971)

#### RESEARCH EMPERIENCE:

<u>kesearch Assistant</u> - Puerto kico Nuclear Center 1960-1962, in charge of the Radiochemistry Laboratory of the Radioisotope Division, Instructor for the Radioisotope division, Radioisotope Techniques Course.

Research Assistant - Puerto Rico Nuclear Center 1962-1965 in the Organic Sulfur Chemistry Program under the supervision of Dr. H. Harry Szmant.

Research Fellow - Wayne State University 1965-1969, Exploratory Research in Sulfur Chemistry under the direction of Dr. Carl R. Johnson.

<u>Senior Scientist</u> (Ad Honorem) - Puerto Rico Nuclear Center

Lecturer (Ad Honorem) - Department of Chemistry, University of Puerto Rico, Mayaguez Campus

Member - University of Puerto Rico (Rio Piedras Campus) Graduate Examination Committee.

1972 - Dr. Ju-Chao Liu, Ph.D., Organic Chemistry.

1973 - Dr. James Sanabia, Ph.D., Organic Chemistry.

1974 - Carmen López, MSc., Bio-Organic Chemistry.

Member - University of Puerto Rico (Medical Sciences Campus) Graduate Examination Committee.

1974 - Francisco Fuentes, MSc. Candidate, Microbiology.

1977 - Jesús González, MSc. Candidate, Environmental Health.

1977 - Leocadio Melendez, MSc. Candidate, Environmental Health.

# RESEARCH ADVISOR GRADUATE PROGRAM:

Mr. Jorge Pichardo, "Thermodynamics of Anions in Solution" 1973, University of Puerto Rico, Chemistry Department, Rio Piedras Campus in collaboration with Dr. Gerald Stevenson.

Miss Carmen López, "Toxicity Effects of Selected Organo Sulfur Compounds on Microbial Organisms" 1972, (School of Medicine, University of Puerto Rico in collaboration with Dr. Fermín Sagardía).

Mr. Francisco A. Fuentes, "Repression by Glucose of the Degradation of Benzothio-phene by <u>Pseudomonas Aeruginosas</u> PRG-1, and Reversal by Adenosine-3', 5' Monosphosphate", 1974, (School of Medicine, University of Puerto Rico in collaboration with Dr. Fermin Sagardía).

Mr. Jesús González, "Isolation and Identification of Microbial Products from Benzothiophene" 1977, (Department of Environmental Health, Graduate School of Public Health, in collaboration with Dr. Heriberto Torres).

HONORARY SOCIETIES:

Phi Lambda Upsilon Sigma Xi Who's Who in Government

PROFESSIONAL SOCIETIES:

American Chemical Society Division of Organic Chemistry and Petroleum Chemistry, Inc.

British Chemical Society

College of Chemists of Puerto Rico Member of the Board, College of Chemists, 1972

PUBLICATIONS:

"Intramolecular Hydrogen Bonding in cis-2-Phenylmercaptoindanol", H.H.Szmant and J.J. Rigau, <u>J.Org.Chem</u>., <u>31</u>, 2288 (1966).

PUBLICATIONS CONT.

"Substituent Effects in the Co-Oxidation Reaction of Indene and Aromatic Thiols, Evidence for Classical-Bridged Radical Equilibrium", H.H. Szmant and J.J. Rigau, Tetrahedron Letters, 3337 (1967).

"Non Sterospecific Oxidative Addition of Benzene Thiol to Indene", H.H. Szmant and J.J. Rigau, presented in part at the 147th Meeting of the American Chemical Society, Philadelphia, April, 1964, Published in J. Org. Chem., 37, 447 (1972).

"The Trans-Cis Ratio of Products Formed in the Oxidative Addition of Aromatic Thiols to Indene", H.H. Szmant, A.J. Mata, J.J. Rigau and J.P.A. Castrillón, presented in part at the 154th Meeting of the American Chemical Society, Chicago, September, 1967.

"N' Alkylation of Sulfilimines", C.R. Johnson, J.J. Rigau, M. Haake, D. Mc-Cants Jr., J.E. Keiser, and A. Gerstsema, <u>Tetrahedron Letters</u>, 3719 (1968)

"Sulfimines and Sulfoximines Derived from 4-t Butyl-thiane", C.R. Johnson and J.J. Rigau, <u>J. Org. Chem.</u>, <u>33</u>, 4340 (1968).

"Oxidation of Sulfides with t-Butyl Hypoclorite Evidence for a Tetracovalent Sulfur Intermediate", C.R. Johnson and J.J. Rigau, J.Amer. Chem., 91, 5398 (1969).

"Sterochemical and Mechanistic Studies in the Oxidation of Sulfides by t-Butyl Hypoclorite", C.R. Johnson and J.J. Rigau, presented in part at the Metrochem 71 Meeting of the American Chemical Society, San Juan, May, 1971, Paper submitted for publication, J.Amer. Chem. Soc.

"Infrared Studies of Alkoxysulfonium Salts", J.J. Rigau and C.R. Johnson, presented at the 7th Caribbean Chemical Conference, Mayaguez, Puerto Rico.

PUELICATIONS CONT.

"The Sterochemistry of Oxidation at Sulfur. Oxidation of 2-Methylthiolane", J.J. Rigau, C.C. Bacon and C.R. Johnson, J. Organ. Chem., 35, 3655 (1970).

"Reduction of Sulfoxides with Sodium Hydrogen Sulfite", C.R. Johnson, C.C. Bacon and J.J. Rigau, J. Org. Chem., 37, 919 (1972).

"Structure of Trans-4t-Butyl-l-N-Ethyl N-p-Toluenesulfonylamino-l Thioniacyclohexane Fluoroborate, Evidence for p (N)-d(S)- Bonding", R.E. Cook, M.D. Glick, J.J. Rigau and C.R. Johnson, J. Amer. Chem. Soc., 93, 924 (1971).

"Substituent Effects of the trans-cis Ratios of the Products Formed in the Cooxidation of Aromatic Thiols and Indene", H.H. Szmant, A.J. Mata, J.J. Rigau, and J.P.A. Castrillón, J. Org. Chem., 37, 0000 (1972).

"New Organo Sulfur Scrubbing Agents:
A Novel SO\_-Sulfoximide Adduct", J.J.
Rigau, L.R. Lizardi, S.C. Tsai, G.
Barrio and L. Boada, presented in part
at the 7th Caribbean Chemical Conference,
Mayaguez, Puerto Rico.

"Degradation of Benzothiophene and Related Compounds by an Oil Pseudomonas in an Oil Aqueous Environment", F. Sagardía, J.J. Rigau, A.Martínez-Lahoz, F.Fuentes, C.López and W.Flores, Appl. Microbiol. 29, 772 (1975).

"The Effect of Glucose on Benzothiophene Degradation by P. aeruginosa PRG-1", J.J. Rigau, J.I. Colón, F.A. Fuentes, C.J. Lopez de Fuentes, J.C. Liu, F. Sagardía (dec.) Paper presented by F.A. Fuentes at IX Caribbean Chemical Conference, Dec.10,1977.

"Effect of Glucose on the Degradation of Benzothiophene by <u>Pseudomonas Aeruginosa</u> PRG-1", Fuentes, F.A., Sagardia, F., Colon, J.I., Liu, J.C., Lopez de Fuentes, C.J. and Rigau, J.J., Submitted for publication.

PUBLICATIONS CONT.

SPECIAL REPORTS:

"Effect of c-AMP and Phosphodiesterase Inhibitors on the Metabolism of Benzothiophene by <u>Pseudomonas aeruginosa</u>, PRG-l", Fuentes, F.A., Sagardia, F., Colón, J.I., Liu, J.C., Lopez de Fuentes, C.J. and Rigau, J.J. Submitted for publication.

"Recent Aspects of Sulfur Chemistry in Petroleum", November 1969, prepared for the Department of Research and Development, Commonwealth of Puerto Rico.

"An Institute for Petroleum Research and Sulfur Studies: A Program for the Application of the Scientific Resources of Puerto Rico in the Environmental Control Field", April 1970, research proposal prepared for the Department of Research and Development, Commonwealth of Puerto Rico.

"Control Techniques for Sulfur Air Pollutants: Preliminary Evaluation of Schemes for the Removal of Sulfur Dioxide from Smelter Gases", May 1970, research proposal prepared for the Department of Research and Development, Commonwealth of Puerto Rico.

During his tenure as Director of the Office of Petroleum Fuels Affairs of the Commonwealth of Puerto Rico, prepared and/ or coordinated the preparation of the following proposals:

- "Toxicity Studies of Sulfur-containing Petroleum Fractions"
- "Development of a Simulation Model of Puerto Rican Refineries for the Assessment of Fuel Availability as a Function of Refinery Configuration and Raw Material Inputs"
- "The Isolation, Identification and Quantitation of Reactive Hydrocarbons in Selected Environments and their Photochemical Reactions in the Atmosphere of Puerto Rico"

SPECIAL REPORTS CONT.

ADDITIONAL ORAL PRESENTATIONS:

- "The Office of Petroleum Puels Affairs Petroleum Energy Resources Education Program"
- "Desulfurization of Organo-Sulfur Compounds and Petroleum Fractions by Microorganisms"
- "The Puerto Rico Energy Model: An Aid for the Decision-Making Process"

"The Application of Science and Technology to the Pollution Control field in the Petroleum Industry", 30th Annual Convention, College of Chemists of Puerto Rico, Hotel San Jerónimo, 1971.

"New Approaches of the Economic Development Administration Directed to a Greater Development of the Petroleum Industry in Puerto Rico", Seminar on the Petroleum Industry sponsored by the Institute of Chemical Engineers, Ponce, 1971.

"Gas Chromatographic Techniques in Compositional Studies of Sulfur Compounds in Petroleum", Seminar on Gas Chromatography sponsored by Perkin-Elmer and Durpec Sales, Hotel San Jerónimo, 1972.

"Research Work at the Department of Research and Development of Fomento and its Relation to EDA'S Programs", Monacillos Rotary Club, 1972.

"Industrial Aspects of Sulfur Chemistry", 1972 Seminar Program, R&D Department, Economic Development Administration.

"Modern Techniques for the Control of Pollutants in Petroleum Refineries", Deep Water Ports Seminar sponsored by the Institute of Chemical Engineers, July 7, 1973.

Multiple presentations covering matters related to the petroleum-petrochemical industry and the Puerto Rico energy future of which the following are typical: "La Oficina sobre Asuntos de Combustibles Derivados del Petróleo: Análisis de Nuestra Actualidad Energética", Colegio Universitario de Cayey, 18 de julio de 1975.

"La Estructura de la Industria Refinadora y el Mercado de Combustibles en Puerto Rico". Presented as the closing speech for the "III Convención Centroamericana y del Caribe de Expendedores de Petroleo", San Salvador, 24-26 abril, 1975.

"Nociones sobre el Impacto de los Proyectados Aumentos del Petróleo", Taller sobre Costo de la Vida, 19 de agosto de 1975.

"La Explotación de Potenciales Yacimientos Petrolíferos en Puerto Rico", Asociación Americana de Profesores de Física, Sección de Puerto Rico, Colegio Universitario de Cayey, 3 de septiembre, 1975.

"La Problemática de la Energía y Estrategias de Conservación Ante un Petróleo que se Agota", Convención Anual Asociación de Detallistas de Gasolina de Puerto Rico, 5 de octubre, 1975.

"Marco para la Formulación de Políticas de Conservación de Energía en Puerto Rico", Taller de Costo de la Vida, 30 de octubre, 1975.

"Aspectos de la Problemática Energética Puertorriqueña", Colegio Sagrado Corazón, 12 de febrero, 1976.

"La Lengua y las Ciencias Técnicas", Comentarios del doctor Rigau en representacion del Colegio de Químicos, Instituto Augusto Malaret, 17 de febrero, 1976.

"Producción de Energía, su Tecnología y el Ambiente", Departamento de Física, Universidad de Puerto Rico, Recinto de Rio Piedras, 8 de abril, 1976.

ADDITIONAL ORAL PRESENTATIONS CONT.

"Petroleo: Su Futuro e Impacto Ambiental" Simposio Sobre Crisis Energética, ¿Problema Sin Solucion?, sponsored by the Faculty and Bachelor of General Studies of the University of Puerto Rico and the Center for Energy and Environment Research, November 30, 1977.

"Energy Status in Puerto Rico", Sociedad de Economistas del Gobierno, 23 de abril, 1976.

"El Status de la Situación Energética en Puerto Rico", Colegio Regional de Carolina, Il de mayo, 1976.

"La Contribución de un Modo de Transportación por Bicicletas a los Problemas Locales de Energía", Seminario-Taller sobre Transportación por Bicicletas en P.R., Hotel Racquet Club, 13-14 de mayo, 1976.

"El Petróleo y su Potencial en las Costas de P.R.", Colegio Universitario de Huma-cao, 11 de junio, 1976.

"Energy Status in Puerto Rico: An Assessment of the Petroleum Situation", presentado en el Third Annual UMR-MEC Conference on Energy, Universidad de Missouri-Rolla, 12-14 de octubre, 1976.

"Nuestro Dilema Energético: Ciencia, Tecnología y Algo Más", comentarios presentados por el Dr. Juan J. Rigau, en el Colegio de Ingenieros, Arquitectos y Agrimensores ante foro auspiciado por la Administración de Pequeños Negocios, 27 de octubre, 1976.

Member, Environmental Advisory Committee to the President, University of Puerto Rico, 1972.

Program Chairman - "Analytical Techniques for the Control of Atmospheric Pollution", seminar held in Ponce, August 23-25, 1972.

SPECIAL ACTIVITIES:

SPECIAL ACTIVITIES CONT.

Special Advisor to the Chairman, Gasoline Price Commission, 1973.

Chairman-Seminar on "The Petroleum-Petrochemical Industry - An Analysis of Some Key Factors, Hotel Flamboyán, September 19-21, 1973.

Member-Organizing Committee, Annual Seminar on "Environmental Pollution Abatement", 1972.

Chairman-"First Conference on Energy-Environment-Public Health", Medical Sciences Campus, University of P.R., June 15-17, 1977.

Advisor in several capacities to the President of the University of Puerto Rico, 1974-1977.

Advisor to the President, Catholic University of Puerto Rico, 1977-

Advisor to the President, University of the Sacred Heart, 1974-

Member-Puerto Rico Task Force for the reorganization of the Puerto Rico Nuclear Center, 1976.

Director, Project 60, Center for Energy and Environment Research, University of Puerto Rico, 1977-

Member-Senior Advisory Committee, Center for Energy and Environment Research, University of Puerto Rico/ERDA, 1977.

Consultant, to the Faculty of Natural Sciences, Catholic University of Puerto Rico, 1977

Consultant, Catholic University Medical School, 1977-

Consultant to the Department of Environmental Health, Graduate School of Public Health, Medical Sciences Campus, University of Puerto Rico, 1977

#### RESEARCH INTERESTS:

Chemistry of sulfur compounds in petroleum and petroleum products, petroleum composition, and desulfurization studies. Energy planning and economics.

REFERENCES:

Dr. H. Harry Szmant, Chairman, Department of Chemistry, University of Detroit, Michigan

Dr. Carl R. Johnson, Professor, Department of Chemistry, Wayne State University, Detroit, Michigan

Dr. Ismael Almodovar, President University of Puerto Rico Rio Piedras, Puerto Rico (Give the following information for all professional personnel listed on page 3, beginning with the Principal Investigator.

Use continuation pages and follow the same general format for each person.)

NAME	TITLE	BIRTHDATE (Ma., Day, Yr.)
Richard R. Eckert	Associate Professor of Physics	July 15, 1942
PLACE OF BIRTH (City, State, Country)	PRESENT NATIONALITY (If non-U.S. citizen, indicato kind of visa and expiration date)	SEX
Youngstown, Ohio, U. S.A.	U. S. A.	Male Female

EDUCATION (Begin with baccalaureste training and include postdoctoral)  INSTITUTION AND LOCATION  DEGREE  CONFERRED  FIELD					
University of Kansas, Lawrence, Kansas	Ph.D.	1971	High Energy Physics (Experimental		
Iniversity of Kansas, Lawrence, Kansas	M.S.	1966	Solid State Physics (Experimental		
Case Institute of Tech., Cleveland, Ohio	B.S,	1964	Physics		

HONORS

Academic Achievement Scholarships, Case Institute of Technology (1962-64) Teaching Assistantship, Kansas University (1964-66, 1968-69) Research Assistantship, Kansas University (1970-71)

MAJOR RESEARCH INTEREST	ROLE IN PROPOSED PROJECT
Environmental Monitoring	Principal Investigator

RESEARCH SUPPORT (See instructions)

None

RESEARCH AND/OR PROFESSIONAL EXPERIENCE (Starting with present position, fist training and experience relevant to area of project. List all or most representative publications. Do not exceed 3 pages for each individual.)

## Positions Held

- 1. Physics Professor, Catholic University of Puerto Rico, Ponce, P.R. (Assistant Professor 1971-73; Associate Professor 1973-77; Tenure granted 1976).
- 2. Graduate Research Assistant, Physics Department, University of Kansas 1969-71.
- 3. Visiting Professor of Physics, Faculty Exchange Program sponsored by the Ford Foundation Universidad de Oriente, Cumana, Venezuela, 1966-68.
- 4. Graduate Teaching Assistant, University of Kansas Physics Department 1964-66.
- 5. Research Technician, Youngstown Sheet & Tube Research Lab. Summers 1963-65.

#### National

- 1. Two talks given at the National Meeting of the American Physical Society and the American Association of Physics Teachers in New York, Winter, 1971.
- 2. Invited talk on the Undergraduate Research program to monitor particulate contamination in Ponce, P.R., given at the National Summer Meeting of the American Association of Physics Teachers, June, 1977.
- 3. Invited Participant in Faculty Summer Institute on "Energy Production and the Environmen sponsored by Oak Ridge Associated Universities, Oak Ridge, Tennessee, July, 1977.

#### At the Catholic University

- 1. System Manager for the Digital Equipment Company Computer (11/03and 11/34) in the Physic Department, 1976-77.
- 2. Computer programming consultant for various professors at the Catholic University.

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- Coordinator of the "First Educational Congress on Energy", Ponce, Puerto Rico
- 4. Research Director of a Student Project to Monitor Particulate Air Contamination in Ponce, Puerto Rico 1976-77

## Publications

- R.R. Eckert N Kwak, M. Nicholas, and R. Stump, "Final State with Visible K°-meson in K<sup>-</sup>D Interactions at 3.4 GeV/c,"II Nuovo Cimento 7A, 605 (1972).
- 2. R. R.Eckert, N. Kwak, M. Micholas, R. Stump, "Final States with a visible ^-hyperon in K<sup>-</sup>D Interactions at 3.4 GeV/c," NuovoCimento 8A, 173 (1973)
- M. L. Nicholas, N. Kwak, R.R. Eckert, R. Stump, "The K-and Final States in K-D. Interactions at 3.4 GeV/e,"
   Il Nuovo Cimento 14A, 363 (1973).
- R. R. Eckert, "El Desarrollo de una Colonia de Organismos en un Modelo para Computadora Electronica" Science-Ciencia, Vol 2. Num. 3 (1975)
- 5. Maritza de Jesus, Wanda I. Melendez, Jose H. Perez, Richard R. Eckert, A Measurements of Particulate Air Contamination in Ponce, Puerto Rico A Student Involvement Project", AAPT Announcer Vol. 7, No. 2, P.71 (May 1977) (full article to be published).

SECTION II - PRIVILEGED COMMUNICATION

## BIOGRAPHICAL SKETCH

(Give the following information for all professional personnel listed on page 3, beginning with the Principal Investigator.

Use continuation pages and follow the same general format for each person.)

NAME ,	TITLE	BIRTHDATE (Ma, Day, Yr.)
Carrasquillo, Arnaldo	Associate Professor	7/12/37
PLACE OF BIRTH (City, State, Country)	PRESENT NATIONALITY (If non-U.S. citizen, Indicate kind of visa and expiration date)	SEX
Santa Isabel, Puerto Rico	บร	Male Female

INSTITUTION AND LOCATION	DEGREE	YEAR CONFERRED	SCIENTIFIC FIELD	
University of Puerto Rico, Rio Piedras, P. Univeristy of Puerto Rico, Rio Piedras, P. Ohio State University, Columbus, Ohio		1959 1966 1971	Chemistry Organic Chemistry Organic Chemistry	

HONORS

MAJOR RESEARCH INTEREST	ROLE IN PROPOSED PROJECT
Organic Chemistry	Senior Research Participant
RESEARCH SUPPORT /See instructional	

None

RESEARCH AND OR PROFESSIONAL EXPERIENCE (Starting with present position, list training and experience relevant to area of project. List all or must representative publications. Do not exceed 3 pages for each individual.)

1974 - Director of the Catholic University of Fuerto Rico Biomedical Research Program

1973 - Abbutance Professor of Chemistry, Catholic University of Fuerto Rico

1972 - Mil nesearch faculty participant.

1971 - Assistant Professor of Chemistry, Catholic University of Puerto Rico, Ponce, P.R.

1966 - Research Assistant of Organic Chemistry, Ohio State University, Columbus, Ohio

1962 - Research Assistant, Puerto Rico Nuclear Center, University of Puerto Rico, Rio Piedras, P.R.

1959 - Chemistry Instructor, University of Fuerto Rico, Rio Piedras, P.R.

#### Fublications:

Chemistry of Organoboro compounds - 1966, M.S. Thesis

Cyclopropylnitrenium Ions - J. Chem. Soc. Chemical Communications, 495 (1969)

Ring Expasions and Ring Contractions via Nitrenium Ions, Tetrahedron Letters, No. 2,109 (1971)

Reactions of Strained Rings with Electron Deficient Acetylenes, Ph. D. Thesis, 122p (1971)

3974 - Studies on Ovicide Activity - Arnaldo Carrasquillo, Ernesto Pereira - second M.B.S. symposium New Orleans.

MIH 398 (FORKERLY PHS 398) Rev. 1/73.

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#### Publications

- 1974 Ernesto Pereira and Arnaldo Carrasquillo Lavicidal effect of tropical plants extract on Aedes Aegypti second M.B.S. symposium, New Orleans, La.
- 1975 Arnaldo Carrasquillo, Ernesto Pereira and John del Valle <u>Isolation</u> of the active principle of a lavicidal plant extract third annual Xavier M.B.S. Biomedical symposium April 29-30, 1975 New Orleans, Loisiana.
- 1976 Ernesto Pereira, Arnaldo Carrasquillo and James Mayol Larvicidal activity of extractions from Piper Marginatym leaves on Aedes Aegypti fourth M.B.S. symposium New Orleans, Louisiana.
- 1977 Arnaldo Carrasquillo, Ernesto Pereira, Javier Rivera The nature of the major components of the Larvicidal extracts from Piper Marginatum Leaves. American Chemical Society Junior Technical Meeting, San Juan, P.R. September, 1977.
- 1977 Aranldo Carrasquillo, Ernesto Pereira, María del Carmen Pagán Larvicidal activity of the essential oils of Piper Marginatum Fife MBS Symposium New Orleans, La.

## BIOGRAPHICAL SKETCH

(Give the following information for all professional Personnel listed on page 3, beginning with the Principal Investigator.

Use continuation pages and follow the same general format for each person.)

NAME	TITLE	BIRTHDATE (Ma., Day, Yr.)		
Infante, Gabriel A.	Assistant Professor of Chemistry	Nov. 3, 1945		
PLACE OF BIRTH (City, State, Country)	PRESENT NATIONALITY (If non-U.S. citizen, indicate kind of vise and expiration date)	SEX		
Havana, Cuba	American	Mase Female		

EDUCATION (Begin with bacca)	laureate training and	include postdoctorel	)
INSTITUTION AND LOCATION	DEGREE	YEAR CONFERRED	SCIENTIFIC FIELD
Catholic University of P.R., Ponce, P.R. University of Puerto Rico, Mayaguez, P.R. Texas A & M University, College Sta. Texas Carnegie Mellon Institute, Pittsburg, Pa.	B.S. M.S. Ph. D.	1967 1969 1973 1973	Chemistry, Biology Chemistry Chemistry Chemistry

HONORS Dean honor list 4 times during B.S. studies. Medals in Organic, Analytical, Physical and Industrial Chemistry courses. Outstanding Graduate Student Award, Texas A & M Univ. 1973. Outstanding Educator of America, 1975 and Who's Who in South and Southeast,

MAJOR RESEARCH INTEREST	R	OLE IN PROPOSED P	ROJECT		
Radiation Chemistry and Biology, Water Pollution and Instrumental Analysis		Partici	pant		
RESEARCH SUPPORT (See Instructions)					
Research Corporation	frep.	1974-1975	943	\$ 7,800.00	
Research Corporation		1975-1976	400	\$10,000.00	
Catholic University of P.R.	-	1974-1976		\$ 5,400.00	

RESEARCH AND/OR PROFESSIONAL EXPERIENCE (Starting with present position, <u>list training</u> and experience relevant to area of project. List all or most representative publications. Do not exceed 3 pages for each individual.)

Assistant Professor of Chemistry, Chem. Dept. Catholic University of P.R. 1973 to date. Visiting Fellow, Radiation Research Lab., Carnegie-Mellon University, Pittsburg, summer, 1974. Graduate student and instructor Analytical Labs., Texas A & M University, Texas, 1971-73. R.A. Welch Foundation Fellowship 1972-73. A.E.C. Research Assistantship 1971-72. Instructor, Chemistry Dept., Catholic University of Puerto Rico 1969-71. Auxiliar Instructor, Chem. Dept., University of P.R., Mayaguez 1968-69. M.S. and Ph.D. Radiation Chem. Biological Systems Radiation Research Laboratory, Carnegie Mellon University, Summer 1973-74. Radiobiology Techniques - Puerto Rico Nuclear Center, Mayaguez, 1967-69. Nuclear Sciences Division, Puerto Rico Nuclear Center, Mayaguez 1967-69.

#### Publications:

- .1. O. H. Wheeler, D. Julian and G. A. Infante, "Radiolysis of Peptides", Nuclear Science Abstract, 23, 8, 13745, 1969.
- 2. G. A. Infante, "Radiolisis of Peptides", Master Thesis, Edited by the Puerto Rico Nuclear Center, 1969.
- 3. O. H. Wheeler, A. Julian and G. A. Infante, "Radiolysis of Glycine Andydride" Revista Lationoamericana de Química, 2, 1/12, 1971.



# Publications:

- 1966 A human pathogenic fungus recovered from soil for the first time in Puerto Rico. Torres-Blasini, G. and Carrasco-Canales, J.A. Mycopath. et Micolog. Appl. 28:330-332.
  - Soil studies in Puerto Rico. Torres-Blasini, G. and Carrasco-Canales, J.A. Mycopath et Mycolog. Appl. 29: 177-181.
- 1972 Bacterial ultrastructure. Carrasco-Canales, J.A. (\*) Paper presented at the Second International forum on Treatment of Infectious Disease sponsored by the Veterans Administration and the University of P.R. School of Medicine, San Juan, P.R.
- 1975 Structure and function of bacteria. El Koury, A., Carrasco-Canales, J.A. and Borrero, G. Paper presented at the Round Table on Core Concepts in Teaching Microbiology to Pharmacy Students. Annual Meeting of the American Society for Microbiology
- 1976 Study on the adaptation of nuclei acid hybridization techniques to the classification of fungi using the Microsporum gypseum complex. Carrasco-Canales, J.A. (\*), Colon, J.I. Annual Meeting of the Association of Clinical Scientists. Annals of Clinical and Laboratory Science.

Genetic vontrol of interferon synthesis in chick fibroblasts monolayers. Colón, J.I., Ríos Olivares, E., Rodríguez Nieves M., and Carrasco-Canales, J.A. Annual Meeting of the Association of Clinical and Laboratory Science, Annals of Clinical and Laboratory Science.

(\*) Author presenting paper.