CEER-PE-033

RESEARCH PRE-PROPOSAL ?

_ ENVIRONMENTAL PROTECTION AGENCY ?

y Minot Inetitions Research Support Progam ¢

?THE CHARACTERIZATION OF AIRBORNE PARTICULATES,

AND THEIR TOXIC PROPERTIES IN ?

?A PETROLEUM-PETROCHEMICAL INDUSTRIAL ENVIRONMENT i

?Submitted by:

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

Catholic Univesity of Puerto Rico

In collaboration with

| GENTER FOR ENERGY AND ENVIRONMENT RESEARCH ae

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* Proyeet Director: 4

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CEER - PE 3

RESEARCH PRE-PROPOSAL

to the

ENVIRONMENTAL PROTECTION AGENCY

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Bron rs msason ocean

(Center for Enerzy and Envionment Research (CEER)

University of Puerto Rico

Project Director:

?President, UPR

A.

fector, CEER

---Page Break---

Table of contents

Abstract

Biographical sketch of Key Personnel

Resumes of Key Personnel

Organizational chart

objective of this Project

a. Principal Objective

b, Subordinate Objective

cs Statement of Problem

Results and/or Benefits Expected

Work Plan

a. Research Approach

1. Background

2. Description of specific Research Plan

3. Rationale for selected Approach

4, Unusual Features

b, Methods of Procedure, Analysis and Evaluation

ce. Schedule of Accomplishments

4, Personnel Responsibility for Bach Part of the

Work Plan

e. Facilities and Equipment Presently Available

Budget Schedule

References

Appendix

Aad

*

wnee

4

16

16

16

25

59

6

63

64

67

nm

7

78

85

---Page Break---

?THE CHARACTERIZATION OF AIRBORNE

PARTICULATES AND THEIR TOXIC PROPERTIES IN

A PETROLEUM-PETROCHEMICAL INDUSTRIAL ENVIRONMENT

abstract,

Selected hydrocarbons, and other air contaminants in particu
late 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 establioh the size distribution of airborne particu-
lates and to identify the nitrogen and sulfur containing polycyclic
aronatic heteroconpounds, volatile hydrocarbons and potentially
toxic trace elements. Associated mtagenic and teratogenic effects
of selected fractions will be studied in an effort to define
some toxic properties of help in predicting potential hazards con-
cerning hunan health, Knowledge of composition and size distribu-

tion of particulate material, chenical transformation of pollutants and its asséciated toxicological effects will support bionedical studies in Puerto Rico dealing with a very wide spectrum of personal

Aisconfort and illness. "of particular significance to the study is

the fact that (1) major industrial plants in the south coast petro Leum-petrochemical complex have reduced operations or closed dow temporarily. This could help establish the impact of their respec-

?tive operations in the overall quality of the region airborne pai

?ticulates; and (2) current efforts to obtain a dispensation fron

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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.

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Biographical sketch of Key Personn:

guan J. Rigau, Ph.D., Project Director

center? for Energy and Environment Research, University of

Puerto Rico

Institute for Energy, Environment and Biomedical scien

catholic University of Puerto Rico

Richard R. Bckert, Ph.D., Principal Investigator

Institute for mergy, Bivironment and Biomedical scienc

catholic University of Puerto Rico

Arnaldo Carrasquillo, Ph.D., Principal Investigator

Institute for ergy, Mvironment and Biomedical sciences,

catholic University of Puerto Rico

Gabriel A. Infante, Ph.D., Principal Investigator

Institute for Energy, Bnvironment and Biomedical sciences,

Catholic University of Puerto Rico

Hilda pez Ubpez, Ph.D., Principal Investigator

Center for mergy?and Evironment Research and

Medical Sciences campus, University of Puerto Rico

gos6 A. Carrasco, Ph.D., Principal Investigator

Center for Energy and mhvironment Research and

Medical Sciences Campus, University of Puerto Rico

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guan J. Rigau, B.Sc. MeSce,

Previous position:

RESUME

University of Puerto Rico; Ph.D.,
wayne State University; Head Possil
Fuels Research, Director, Project 60,
Biodegradation of Organic sulfur Com
pounds in High Sulfur Crude Oils, and
Project 48, Biodegradation of Hydro~
carbons in? Venezuelan Extra-Heavy Crude
Gils. Research interests in sulfur
chemistry in petroleum, petroleum and
coal biodegradation, fossil fuels con
position, and environmental impacts of
fossil fuels utilization. Secondary
interests on energy and environment
policy formulation, high volume appli-
cations of sulfur and solar energy.

Director, Office of Petroleun Fuels
Affairs, ?Office of the Governor, 1973?
1976; ergy and Environment consultant,
to the Economie Development Administra-
tion, 1969-1973; Research Fellow, Sulfur
chemistry exploratory research, Wayne
State University, 1965-1969; Research

Assistant, Puerto Rico Nuclear Center

1960-1965.

consultant to several institutions of higher education; former menber "Senior Energy Advisory Committee", CHER, former president College of Chemists of Puerto Rico; Member Signa XI, Phi Lambda Upsi~ Jon, Wno's Who in Government, ACS, Col- Lege of chemists. Has published over ten papers in referee journals and made extensive oral presentations in his re- search fields of interest.

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ROE CORRECULIM VITAB

Richard R, Rokert

age: 36 years

Marital Status: Married, 1 daughter

Pab.» University of Kansas, Kansas, Physics, 1971

M.S.) University of Kansas, Kansas, Physics, 1965

B.S.» Case Institute of Technology, Cleveland, Physics, 1964 Glonors)

Position: Professor of Physics, Catholic University of Puerto Rico

1978 + eo gate

?Tenure granted in 1976

Associate Professor ~ 1973-1978, CUPR

Assistant Professor ~ 1971-1973, UcPR

Publications - about 15 papers in the areas of Physies, air pollution

and computer models

Richard Eckert, 1979, *Particulate Contanination in Puerto Rico

?te Physice Zescher $1, 32-32,

Bresentations; about 20 oral presentations in the sane ftelde.

Services: President, Puerto Rico Chapter of American Association

of Physics Teachers, 1978-1979.

Principal Investigator for NIU-MES Grant No. 34606-RR-08067-0851,

Atmospheric Particulate ae a Public Health Hazard

Catholte University representative on the Puerto Rico Counc?

fof Higher Education, Accreditation Connittee for Flectronie

Data Provesaing Colleges,

---Page Break---

Amaldo Carrasqutllo

Birth Dates December 7, 1937

U.S. citizen vee

? sueation

. Ph.D. Organic Chemistry, Ohio State university, Columbus, 1971

i M.S." Organic Chenlstry, University of Puerto Rico, nfo Piedras, 1966

BIS. Organic Chemistry, University of Puerto Rico, Rfo Piedras, 1959

Positions:

Professor of Chenistry, Catholic University of PR, 1979 - to date

?Tenure granted in 1976

Bionedieal Research Progran Director, 1976-1978, CURR.

Associate Professor, CUPR, 1973-1978

Assistant Professor, CURR, 1971~1973

President, Puerto Rico Section, American Chenteal society

Research Areas

Organic Chemistry, Natural Products Chenistey, Photochentstry,

Environmental Chemistry

Rotearch Grants

Bionadical Research Grant from MAS Progran, U.S, National Institute

of Health,

Publications:

?About ten (10) publications in organte chentetry

About thixty (20) oral presentations in the. same areas,

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BRIEF CURRICULOM VITAE

Gebrier A. tnfante

Birth Date: Novenber 3, 1945 Address; Department of chentstry

Place: Havana, Cube Catholic University of PR

Citizenship: United States Ponce, PR 00731

me.

Education:

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

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

PRD. ?Chenistry, 1973, Texas AGM University, Texas

Post-Doctoraly Radsation Chemistry, 1974, Carnegie Mallon University, Pittsburg

Undergraduate: Medals analytical, Organic Physical and Industrial chemistry

Graduate: Graduate Outstanding hard, Texas AGM University, 1973

Professional: Outstanding Educator of America, 1975

Wio's Who of South and South West, 1976

Chairman Anerican Chemical Society, Puerto Rico, 1977

Genera Chairman, IX Caribbean Chemical Conference, Decesber 1977

Chaiznen Advisory Comittee on Chemistry 1977-1978

Positions: Associate Professor with Tenure, Departnent of Chemistry

Catholic University Of Puerto Rico, 1976 ~ to date

Directér Bionedical Research Progrem

Catholic University of Puerto Rico, 1978 ~ to date

Associate Scientist, Center for Eneray and Environnent Research.

Research Areas

Radiation cheaistry, Cancer Research, Micellar Chentetry,

Environnont Chanistty and Pollstion.

ch Grants

?Biomedical Research Support Grant from WS Program and

National Cancer Institute, U.S. Hational Institute of Health

U.S. ?Beery Office throught the Puerto Rico Center for Eneray

and Environment Research,

Publications

About forty (40) publications in scientific Journals mainly in the

areas of Radiation Ghenistry, Micellar Chenistyy and Pollstion

Aout sixty (60) oral presentations in scientifte meetings and

conferences in the sane areas described above,

vit

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Wide Tépen-Lopez, B.Sc., M.Sc+,'PH.D. - University of Puerto kico;

100 165% Assistant Professor, Department of
Anatomy, School of Medicine, Uni-
versity of Puerte Rico, Primary
area of interest on Eubryology,

: suet of tovarens oo Daron

Medicine, Catholic University of
P.Re, 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 Psk., 1965
1975; Research Assistant, University
Of P.R., 1964-1965,

collateral, interest: Director of the Bnbryology and the

: Musculo-skeletal courses of Human
Biology I for Medical students; Di-
rector 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 Medi-
cine, University of P.Rez Member of
the Munan Biology I Committee; Menber
of the Cardiorespiratory, and the
Renal and Urogenital sub-committees
of Hunan Biology I; Member of Beta,
Beta, Beta Honorary Society. Has
worked in three investigations (in
preparation for publication) and made
Several oral presentations in her re~
search findings on cytological change:
: in the pars distales of the hypophysis
: ©f anoline lizards under various con-
. aitions.

vidi

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kes

gosh A. Carrasco-canales, B.Sc, M.T., MoS, Ph.D., Assistant Professor, De

Previous Position:

collateral Interest:

partment of Microbiology and Medical Zoolecy, School of Medi~ cine, University of Puerto Rico. Primary area Of interest, Mycolo- gy, Molecular genetics and Muta~ genicity of carcinogens on Bac- feria. Secondary interest on Microbiel Physiology and Inmunol~ egy.

Instructor in Microbiology, Dept. of Microbiology, School of Medi- cine of the University of Puerto Rico 1963-1974; Assistant in My- cology, Dept. of Microbiology,

School of Medicine of the Univer sity of Puerto Rico 1962-1963.

Directot of the Infectious Di-

seases Block for 2nd year Medical Students, Monber of the Hunan Bi-Ology II Comittee. Menber of the Promotions Committee for 2nd year Medical students, Menber of the Avard's Comittee of the Univer sity of Puerto Rico School of Medi-cine. Has worked on investiga~ tong in Mycology and Molecular genetics leading to four publica-?ions and one more in progress.

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1. Qbiective of this project

?his proposal attenpts to develop an interdisciplinary coopera-

tive program involving the recently created institute for Energy,

Bavironment, 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:

. Principal objectives ?

Le

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3.

Initiate a systematic effort to characterize potentially

toxle trace elements and organic constituents (especially sulfur and nitrogen derivatives) downwind and upwind the neighborhood of a petroleun-petrochemical complex. correlate the structure of the molecules detected with ?their possible mutagenic and teratogenic effects. Ex tracté from particulate matter of various sizes will be obtained and evaluated for biological activity.

Improve our knowledge of sources of toxié substances by studying airborne particulate composition with an orien-

tation to establish (a) if the particulate matter in the

south coast industrial complex is responsible for inpact-ing the atmosphere from neighboring cities downwind from the complex and (b) if the particules bearing these con-?taminants are small enough to be deposited efficiently in

human lungs.

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Subordinate objectiv

qe

study the transfornation of individual reactive cheai-
cals and that of their prinary conversion products by
?exposing them to filtered air from the region of in-

terest and/ot to specific major contaminant:

Brploy air pollution computer similation methods to
correlate the'chenical nature of the contaminants with?
?the prevailing meterology of the region.

conduct research in areas renote from inmediate sources
of pollution to provide background values in areas ai ~
rectly unaffected by point source emissions.

?rain research scientists and students in environmental

health research by developing an interdisciplinary re-

?search program to increase our knowledge of toxic sub-

stances in the environnent.

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c. Statement of Probles

Im the last three decades, Puerto Rico has experienced a ni

highly significant economic development, based on the industrial

sector (Appendix 1,Table I). A considerable number of industries

stablished annually. They exploit petroleum derivative:

both as raw material and as energy sources directly and indirect-

ly (Appendix I,Table X12) and generate environmental impacts of :ééa-
cern to the general population. Appendix I, Figure la shows
some chemical considerations relevant to the sulfur and nitrogenes
derivatives present in crude of1, Knowledge of crude ofl compo:
sition is necessary to better understand the complexity of the
stéck emissions in a refining-petrochenical complex. val
Both with respect to point and area sources, the industrial ..
areas comprising the Cataflo and Guayanilla-Pefuelas municipalities
(ippendix I, Figure 2) bears the brunt of the pollucants enitted in
Puerto Rico,? therefore, because of its vicinity to catholic uni-

versity of Puerto Rico research facilities, and the fact that the

petroleun-petrochemical complex has been the subject of numerous
citizens complaints because of its emitted pollutants, we have
selected the Guayanilla-Pefuelas area as the subject of thie pro-
posal with a long range objective of studying other sites and the
effects of air pollutants on hunan health in Puerto Rico. Figure 2
shows some major afr pollution related issues.

South coast residents living close to or downwind from the

Guayanilla-Pefiuelas industrial site are potentially exposed to

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cs Statenent of Problen

In the last three decades, Puerto Rico has experienced a sai

highly significant economic development, based on the industrial,

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ly (appendix 1,table 112) and generate environmental impacts of scn~

?ce to the general population. Appendix I, Figure la shows

sone chemical considerations relevant to the sulfur and nitrogenes

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stick emissions in a refining-petrochenical complex. nal
Both with respect to point and area sources, the industriale-
areas conprising the Catafio and Guayanilla-Peftuelas municipalities
(Appendix I,Pigure 2) bears the brunt of the pollucants emitted in
Puerto Rico.? therefore, because of its vicinity to catholic Uni-
versity of Puerto Rico research facilities, and the fact that the
petroleun-petrochemical complex has been the subject of nunerous
citizens complaints because of its emitted pollutents, we have
selected the Guayanilla-Pefuelas area as the subject of this pro-
posal with a long range objective of studying other sites and the
effects of air pollutants on human health in Puerto Rico. Figure 1
shows sone major air pollution related issues.

south coast residents living close to or downwind from the

Guayanilla-Pefiuelas industrial site are potentially exposed to

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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 chenical and refining complexes of CORCO, Union Carbide, and the PPG Industries chloro-alkali plant (Appendix T ?Table Iv). A thermoelectric (1,396,000 Kw) and combined cycle units can be found in the Aguirre (Salinas) area (Tabl2 I). Total population at the representative south coast municipalities of Guénica, Yauco, Guayanilla, Pefluelas, Ponce, guana pfaz, Santa Isabel, Salin-?a8, and Guayama in 1976 was 412,230 with a population density of

769 (per square mile).

In general, the major pollutants of concern in the Guayan{lla-Peftuelas area, are those associated with fossil fuel combustion (Appendix I, Teble Iz) and those related to petroleun-petrochenical operations (Appendix I, Pugure 3), Production and subsequent reactivity or degradation of the constituents of these emissions in combination with particular meterological conditions hae led to photochemical oxidants, chenical carcinogens, and particulate materials. These

particles are heterogeneous in size, shape, chemical contents, etc.,

@ending on the type of process and other parameters. All the poly-

nuclear aronatic 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 98,123 tons in 1970 which were gen

erated in the Guayanilla-petuelas area.

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?The damages associated with air pollution include the costs

sociated with damage to human health, the costs of pollution

related cleaning and maintenance activities, the costs of inhibi-

end the re-

tea growth and destruction of plant and animal 1:f¢

auction in property values.?~4

For instance, 80,,an acidic, cor-
rosive, poisonous gas produced almost entirely by the burning of
fuel containing sulfur as an impurity can cause tenporary or per-
manent injury to the respiratory system. When particulate matter
ie inhaled with adsorbed sulfur dioxide, health damage may in-
crease significantly, Sulfur dioxide can irritate the upper res-
piratory tract. Carried into the lungs on particles, it can in
jure delicate tisaue.® rt has been known that some of the mech~
anions 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 surfac

of solid particles. rt is entirely
possible that more than one of these mechanisms may contribute concurrently to the conversion of sulfur dioxide to sulfate in the atmosphere.©

on the other hand, hydrocarbons represent unburned and wasted fuel. Nornally, 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~

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carbons, sulfurated, nitrogenated, and ox/genated substances which have been shown to exhibit carcinogenic and co-carcinogenic propertics?® in experimental animals and have been associated with

the incidence of various types of cancer in man. Although great efforts are underway to study thé isolation, identification, and reactivity of these compounds in other parts of the world, very Little or no information is available for Puerte Rico.

cuayanilla's air, containing one of the highest pollution levels in Puerto Rico, ie the source of numerous resident complaints of pollution related health problems, and two medical studies have found evidence to back their allegations.°"'+ 1 cuayanitia, residential neighborhoods Lie several miles downwind from a highly integrated petroleum-petrochemical complex with the combined snoke-

etacks of PPG, the Conmonwealth O11 Refining Co., Union carbid

Water Resources Authority of Puerto Rico power plants, and other factories. Residents of different neighborhoods, including villa el Rio, the Guayanilla beach, and Magas, have bended together in

the past three years to form anti-pollution comnittees.

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

Malic re has been found that it ie from small particles which

contaminants are most effectively extracted into the human blood-

strean,"* hus particl

less than about lum in equivalent aero

aynamic diameter deposit predominantly in the alveolar regions of

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the? lung where the absorption efficiency for most trace elenents

is 60 to 80 percent. targer particles, on the other hand, deposit

in the nasal, pharyngeal, and bronchial regions of the respiratory

system and are renoved by cilial action to the stomach vhere ab-

sorption efficiency is comonly only 5 to 15 percent for most trace

elements. the lung constitutes then the major gateway to the blood~

stream for toxic elements that are present in airborne particl
More recent results illustrate that over 90% of polycyclic aromatic hydrocarbons is found on the particles smaller than jm! ana that about 75% of the benzo (4) pyrene and 85% of the coronene are associated with particles of aerodynamic diameter less than 0,26 am, 12¢ 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 Am), 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?° gound that more than 30 per~ centof all patients admitted into emergency rooms in catafio and Guayenilla during 1975 and 1976 suffered from pollution-related ailments (e.g., asthma, allergy, irritation and broncho-pulmonary diseases). In relatively pollution-free Luguillo and Naguabo, how-

ever, only ten percent of the cases were linked to pollution, Further-

more, the study alleged to have found a correlation between cancer

Geaths and polluted areas. southern coastal plain vital statistics are

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shown in Appendix I, Table 4.

?romés Morales Cardona, @ biophysicist and professor at the University of Puerto Rico Medical school, measured the lung capacity of 454 residents of catafio and found that more than five percent of them had an obstructive respiratory disease, such asthma, bronchitis or emphysena, and 50 percent suffered fron problems in their upper respiratory system such as allergi

jaz

nasal problens, and sore throats. 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 Guayanitla, told us he will finish analyzing his data in the

next few month:

The Environmental Quality Board (B98) is now asking the federal government to designate Guayanilla and catafio as ?central regions" under the Clear Air Act. This designation would prohibit

any more air polluting industri:

from coming in. The BOB 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 (298) prohibited the use and sale of fuel of] any-

where 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

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recently, on April 2, 1979 the Water Resources Authority (WR) 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 {f the closed PPG, oxochem and

sed

Puerto Rico Olefins plants become active again no incr health hazard will occur.

Jn Guayanilla, 208 has eight intermittent monitors, four to measure particulates and four for sulfur dioxide, which give a reading every six days. Tt also records data from eight water Resources Authority sulfur dioxide monitors which operate contin uously, The intermittent samples, which give only about 50 read ings in @ year, are ?statistically valid, but may miss many of the

highs in pollution levels, which vary widely betwen different days and different hours of the day. Today there exists a better understanding of the process of environmental assessment (Appendix %, Figure 1b) and the influence of heavy fuel of1 composition and boiler conditions on particulate emissions has beon reported.2?

Atmospheric contamination depends on a host of factors, the most pertinent being the type, quantity, and location of the emis sion source and the particular atmospheric patterns capable of dis- placing and Giluting the gaseous and particulate pollutants. the Ailuting effect is produced by weather conditions, temperature, wind direction, and velocity, humidity, and rainfall, etc. Pre~ cipitation helps in ridding the air of solid impurities depositing

them on pastures, rivers, lakes, etc. Some of the contaminants

oe

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

Finally, the predicted particulate and sulfur dioxide concentra~

?tion for 1978 and'1985 are shown herein (Appendix I, Tables VI-VIT, and Figure 6), The predicted particulate air quality levels for both 1978 and 1985 were found to exceed the primary particulate standards (75 mg/nm? annua? geometric mean) in the following Air Quality Maintenance

Areas (ROMA):

san guan = Cuayanilia

= Ponce (2985 only) = Mayaguez

= Dorado = Gabnica (1985 only)

?The sulfur dioxide standara (80 mg/m? annual arithnethic mean)

was also found to ve exceeded both in 1978 and 1995 in several AQMAS.

= san guan = Guayama (1985 only)

= Guayanitia = Yabucoa (1985 only)

= dorado (1985 only)

?these results show an indication of the seriousness of our en-

vironmental problem, however, any interpretation of anbient level

measurenents and air quality trends must consider the serious 1imi~ tations 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 photo

chemical oxidants,"5-2

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ee

?To help solve this crucial lack of environmentally significant information, work will be conducted by researchers of the Institute

for Rersy, Environment and Biomedic:

Sciences of catholic univer-

sity of Puerto Rico in collaboration with the Fossil uel 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-pefuelas area.

Clearly, this study is badly needed to support preveative medical

care programs in Puerto Rico. (Appendix I, Figure 4 and 5)

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2. Results and/or Benefits Expected

?This proposal attempts to: wee

1, Improve our knowledge of the chemical composition of the

volatile hydrocarbons and the acidic, basic, nuetral, and

polar fractions isclated from airborne particulates in the

neighborhood of a petroleun-petrochemical environment. This

is nécessary to obtain a better understending of the poten-

tial health hazards associated with transport and penetr:

tion of particulates into the respiratory system.

+ Measure both the size distributions and chenical composition of particles in anbient air, in order to understand the sources, and the behavior of airborne particulates in the atmosphere.

Observations on size distributions of trace elenents 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.

Correlate toxic properties such as mutagenic and teratogenic effects with the chanical composition ef selected test frac tions.

The proposed research will be of significance also to:

cancer epidemiology studies underway at the Center for

Energy and Environment Research of the University of

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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 Bergy, Environment and Biomedical sciences

Help initiate work toward establishing a danage function

for the Guayonilla-Pefuelas 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 pol-

lutants. -

Strengthen the infrastructure for compositional studies

related to the atmospheric emissions arising from coal

or coal-oil slurries combustion power plants. these fos.

sil fuels are aiternatives presently wider the active

consideration of our government energy policy maker:

Studies on the nature of air enissions will affect de-

cisions regarding control techniques before or after con-

bastion.

Provide public officials with an effective data base for

efficiently allocating Limited resources anong the many

conflicting demands for pollution control and other as

pects 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

ergy and Environment Research.

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Work Plan

Research Approach

2. Backurowna

Although the reactive hydrocarbons have been fully

Fecognized in the ast two decades as having an inportant

role in the photochemical reactions of air pollutants,

?the techniques for the isolation and quantitation of the

ambient hydrocarbons, because of their sub-ppm concentra~

?tion?and complex mixture, only recently have started to

be reported in detail. For example: the earliest des-

exiption of atmospheric hydrocarbons was made by Eggeraten and Nelsen in 1959.7? procedure for trapping large volmes of air and some data for atmospheric analyses were included, A monitor of the c, to ¢, aliphatic hydrocarbons in the Los Angeles atnosphere was then presented by Beligan.2? The individual analysis of cy ~Cyy hydrocarbons in paris was made by Raymond and Guiochon.?4 auto exhaust was demonstrated a8 a connon source for most of the individual aliphatic and aromatic hydrocarbon species in the atmosphere.?5 touw, Rich ards and Faure have described a versatile GC method for the @etermination of ¢, -c,, volatile organic compounds in city ?air and applied it to the identification of more than 200 volatile oryanics occuring in the air of three large south

African cities.2*

Identification of the volatile compounds

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in city atmosphere has been accomplished by others en-

Ploying the more powerful GC/MS technique, ?5P* 25¢

268 nave reviewed the hydro-

Altshuller and Bufalini

carbon photooxidation mechanisms covered in the literature through 1964, More recently, Altshuller has reviewed?? the formation and removal of so, and oxidants from the at~ mosphere. 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?? reported rates of reaction of aliphatic hydrocarbons in the ultra-violet irradiation of atmospheric samples. How-ever, Altshuller and co-workers? cited that the acetylene

reaction is undetectable and butan

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 at-mospheric hydrocarbon mixtures with the laboratory ixradia-

tions 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/HP,lie

However, no data ie

available on these potentially carcinogenic conpounds in thie

island.

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he composition of polynuclear aromatics extracted

from airborne particulates will obviously be dependent

on the extraction and purification procedure involved

and coulé also depend on the size distribution of air-

borne partic

Recent reports, have shown the pres~

fence (Table 11) of a number of sulfur containing hetero-

eyctics,*° aza-arenes, "2 and polycyclics with partially

saturated rings. °?

compositional studies on particulates are of great environnental concern because of a wide environmental @istribution of particulates obtained from various con-bustion processes, and the potent mutagenicity of a nunber, of compounds adsorbed on particulates such as certain polycyclic aromatic hydrocarbons (PAH). (Pigure 2)

Azanarenes formed as trace pollutants by the incom-plete combustion of N-containing organic matter have been found in the basic fraction of New York City's suspended particulate matter.?2

Azanarenes, with the exception of neutral indcle 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,?? bioassay data have shown the basic fraction to be carcinogenic to infant mice when administered

subcutaneously. *4

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?The benzene extractable compounds from airborne par
ticulate matter froma residential area were separated
into neutral, acidic and basic substrates. #* Im the
neutral fraction, saturated aliphatic hydrocarbons, poly-
nuclear aromatic hydrocarbons and polar oxygenated sub-
stances were identified. the acidic fraction consisted
mainly of a homologue series of fatty acids and aromatic |
carboxylic acids, sone of them with hydroxy substitution.
?the basic faction consisted of the nitrogen containing
anoloques of the important polyaromatic hydrocarbons:

present in the neutral fraction.

Pierce and Katz?® nave described a method for the analysis of polycyclic quinones derived from polynuclear aromatic hydrocartons. 9,10 -Anthra-quinone, benzo (4)

pyrene - 6,12 ~ quinone, benzo (@) pyrene - 1,6 - quinone,

benzo () pyrene - 3,6 - quinone and dibenzo (b,def)

of

ehrysene ~ 7,14 ~ quinone were identified in sampl suspended particulate matter collected in Toronto, ont. the carcinogenic activity of a particular compound i¢ very dependent on its structure. shape, size, electronic, and steric factors; all seom to be important. For example, the addition of alkyl, substituent groups in different positions on the ring of certain FAH, can either have an

activating or deactivating influence. similarly, the

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eee

substitution of a sulfur for an ethylene group in a ring,
may increase or decrease the carcinogenic activity of that
particular compound. 7°

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 vari-

ous points and mobil sources, for that reason, it is re

sonable to expect PAH to differ quantitatively and qualita

?tively 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,? indicates that information about poly-eyelic heterocompounds mst be included in studies concern-ing the environmental hazards of petroleum related industrial operations.

Finally, the composition and size distribution of particu-late 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 par-

ticles, adsorption of gases, chemical reactions within the

particl

y mainly in the presence of liquid water and dry

o21-

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te mes

and wet removal. A detailed explanation of some properties of aerosols is described by Juenicke.°*

Since several organosulfur compounds have seen detected in atmospheric particulate matter the problen arises whether,

besides oxidation to sulfate, $0, might also react with other

specie: However, the concentration of various sulfur-containing 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 fron vari-

ous sources. (Will be interesting to see if when the Puerto

Rico Olefins, Inc. plant start operations the concentrations

pondingly). It is also reported that by equilibrating par-

ticulate matter with $05, sulfonic acid derivatives are
formed, the formation of these compounds seens to be of minor

importance in the conversion phenomena of $0,.7°° However,

sits importance in enhancing the toxic effects of these par
ticles. cannot be discarded at this moment. since the concen-
tration of pollutant aerosols with respect to particle size
is important in the evaluation of their atmospheric trans
port and penetration into the respiratory system several
studies have been conducted utilizing high and low volune

cascade impactors. 29-795

22.

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ne Re

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. 2% They can also be used in high mass load atmospheric environments to collect short term samples. Various workers have reported?®9-8* noyever, that high volune 920 #9 mint, oF 90.6 n? min") impactors very often experience particle bounce effects which result ina Gioplacenent of the larger particles mss 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 con siderable evidence that this error can be minimized by the application of an adhesive humecant to the impac-

tion stages, 2%

In addition many impacters now in use

sample air at the rate of about 1-2 m°/nrs., 0 that in

8 24 hour sampling? period only about 10-50ug of any one element will be present, distributed over several collection surfaces. Consequently higher sensitive analytical techniques must be used.? in order to collect

enough particles for chemical analy:

8, especially if or

ganic compounds are of interest, sampling times of 4-9

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days may be necessary, according to degree of air pol-

lution and weather conditions.

92-395

Recent investigations? fon composition and size
Aiotribution of in-stack particulate material at coal-
fixed 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; sev-

eral of the more volatile, toxic trace elements do ex-

hibit increased enrichments on the smaller particl:

and two elements, Fe and Ce, had decreasing enrictnents
with decreasing particle size.

Potentially toxic metals and organic compounds wil
be analyzed and results compared with those found in other
areas, For instance, elenents for hich EFI1 are refer-
red to as "enriched" elenents, and to determine their
origins, we must find sources vhose particles have equal

or greater erts,?%

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Description of specific Research Plan
A detailed analysis of organic end 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, Sampling and size-dietribution measure

0 obtain meaningful representation data, sampling loca~

Xn order

tions are very important, the data obtained must be

statistically related to different variables such a:

source, meterological conditions, time-of-day, etc. The sampling locations will be categorized according to the predominant tiature of the area (e.g., power plants, industrial, freeways or residentiale). The sample will be collected based on the results obtained from simulation uns employing the Environmental Quality Board's computer model. Proper conmunication with the QB 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 particulste matter will be carried out utilizing high volune samplers with glass fiber filters?? the glass fiber filter will be used to analyze for total inorganic

pollutants, particularly lead, mercury, iron, vanadium

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and nickel. The metal analysis as a function of particulate size distribution will supplenent work cuxrently 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.4?-44

Volatile hyarocarbons will be trapped by using either cryogenic collectors,*° of gas samples, ad~sorption of the organic components in the air?! on a high surface adsorbent or by means of the method of Youw, 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 chroma?tograph or one with a specific flame photometric detec-

tor, The cryogenic collection requires small volunes

(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 cryo-genic and adsorption methods are 10°. gm/iiter and 1072°

gn/Liter, respectively.

3. Analysis

a. Extraction - mxtraction of organic compounds

such as polynuclear aromatic hydrocarbons will be ac-complished by solid-1iquid®® or iguid-liquia®® extrac~

tion, Initial Liguid/solid extraction with ether will

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be followed ty a variety of common solvents such as Benzene, cyclohexane, chloroform, benzene/methanol, eves?? gther may tum out to be a convenient solvent,

because the loss of sample material during the evap-
oration of the extracts is reduced as compared to other

higher boiling solvents.*?# 11 extractions will be

done in? semi-darkness and precautions??

will be taken
0 ensure the uniform treatment of each sample and ex-
tract. After extraction, the solvents will be care-
fully evaporated in the dark at xoom tenperature under
reduced pressure,

?Separation ~ Separation techniques for extrac
tea conpounds from particulate matter could include gel-

48-482 46-49-50

permeation, colum chromatography? ?thine

layer chromatography, #9"1-54-55 yacor phase preparative
chromatography, °° glass capillary gas chronatography°°*
and high pressure Liquid chronatograpay (HpEc).°? mm.
particular, a generalized approach (used intensely in

our own laboratories) for the Liquid chromatographic an-

alysis of very complex hydrocarbon mixtures will be tried in this work. As in crude of1 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-

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o Re

lection of given peaks or groupe of peaks followed by reinjection into a different and convenient HPLC colum or into a Gc or Gc/us system.°? the HPLC approach (Pigure 3) will be supplemented by a modification ?of the procedure of Haines and Thompson®>* (Figure 4). This will generate conveniently separated fractions for further detailed analysis.

Colum chromatography, and preparative gas chroma

tography 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 60/100 mesh chromosorb W or a.support-coated open

tubular column (Scor) silicone pc-550 colum,?®
perature programmed.
Since mass spectra of isomeric compounds show little

Gifterence, prior chromatographic resolution is necessary

Re

ov? I

?Aromatics

Separate using

ncheptane ,.Porasil|

Separate using

H,0:MBOH gradient

2. Bondapak C18

t

collected Particulates

individual Compound

Identification by GC/MS

Figure 3: High Performance Liquia chromate

Scheme,

Organic Extracts

t

[oun

Separate using

?beheptane

paBondapak-Nil,

Filter

Asphaltenes

polars

separate estng

oyna ine

pibedaper Peng

ea

Tndividaal

?components

Note: HPLC modified with

a four way valve for

coluna backflushing.

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?ography Suggested Separation

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Particalate

solvent.

Extract

Anion resin

(pual silica-alumina)

Danece amberlyst 4-29

Less Acide 1 acide

cation resin :

BaEeSe amberlyst A-15

Less Acide L Bases

and Bases

Extract

a Ce Neutral,

Lene Acids; Bases re v3 Nitrogen

?and Neutra compounds

Nitrogen Compounds

Adsorption

saturates |

Sees

Tewcevice] [ators] [Ral Sasoane

FIGURE 4: Outline

of Separation Schene

Particulates Extracts.

=30-

for Organics in Airborne

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no he

snigh-resolution

for their identification. Inert gla:
capillary colums in such analysis will be desirable.
59-60 since glass capillary and convential gas chroma
tographic 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 prop
erties pertinent to the chromatogram are shown in Table
nm.

cs Gharacterization - Gaseous and Light hydrocarbons
in the part per-billion range will be characterized by
?flame-ionization gas chromatography.°' specific sulfur
detectors will also be used in this work.°!* por. relia~

ble sulfur analysis using a flame photometric detector

?the column should posess high resolution properties, since

Jarge amounts of hydrocarbon are known to quench the emis-

?sion of small quantities of sulfur compounds when eluted

simltaneously, A micro-coulonetric detector will be em

ployed if necessary. current work in our labs is finding

very useful the use of a microcoulonetric detector for

the analysis of benzo and dibenzothiophene derivatives in

petroleum, A system involving pyrolysis-cc-Microcoulo-

meter? as reported by Drushel will be employed ©? to ex-

plore the presence of sulfur containing families of ben-

zothiophene, dibenzothiophenes, ete.

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(5060304539 seK ?yeey ?ck ?Ape Peo ?HTH BEET Hens

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columns with graphitized carbon black could be

?used for gas chromatographic separations of hy@rocar-

bons. °?

typical retention times for a variety of
hydrocarbons are included for reference purposes (Table
ITT). Porouselayer open tubular columns using graphi-
tized thermal carbon black show high selectivity for
geometrical isomers, and allow difficult separations

at temperatures lower than with dexsil columis. By
changing the nature or the concentration of the station

azy 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 procedure:

igh pressure Liquid chromatography (HPLC) has many

distinct advantages over other forms of chromatography.°?

Resolution of isomers is equivalent to gas chromatography

with a greater nunber of theoretical plates (ez. 5,000).

Unlike gas chromatography, there is no requirement for

volatility or thermal stability, rt is only necessary

that the compounds be soluble in some solvent-aqueous or

organic, the efficiency of this technique, with its sup-

erior utility for the study of labile reactive molecules,

has made the study of chemical carcinogenesis and the

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Py

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.

Mage spectrometry will be used to identify complex samples (e.g., sulfur-containing and nitrogen containing polycyclies and polycyclic aromatic hydrocarbons in particulates). This instrument will be directly interfaced with a gas chromatograph with computerized data acquisition and ?used in conjunction with HPLC and colum chromatography

(co)

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 sone basic ring systems and standard addition will be per~ formed to determine the concentration range by integrating ?the mass spectrometer output. Although, confirmation of

the Adentities of many of the PAH reported in the literature

was accomplished by comparison of GC retention tines with

those of acquired standards, the accumslations of many

more standard compounds will be necessary to provide the

positive identification of all compounds.

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Table Ir

REPT ION MES ON ON PUIBY RD CARBON ACK

Tika: ih si-30 on CB-2

Coton nlm trogen 91°C, Neate

etgheetopeatn

23 dma betane

inehgteytapentene

z ee ia

iS ?ounatyiss sane

$e Raeetetpionane

2 Snot -traus-3-besene

2b nent

Getenest

Oetenest

Some?

mesgitoe

Potone

oat eloene

?ue eer. Seale, 8, Brrr nd ana

?nat Chem, 36,

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Uitraviolet-visible absorption spectroscopy

could also be employed in the identification and determination of polynuclear hydrocarbons; this affords the advantage that the vave Length maximum of & compound is independent of the presence of ?other compounds (Lf sufficiently diluted).

Muclear magnetic resonance spectroscopy on occasions could be employed for the determination of specific methyl-aronatic hydrocarbon mixtures

of structurally similar compounas.?9/°°

?The iden-
tigication of these carcinogens could be made on the basis of relative chemical shifts, methyl chenical shift at infinite dilution and peak multiplicity information.

?Atomic absorption spectrometry will be used for quantitative metal analysis, Details of the proce~ dure are discussed in Walsh et al. °°f nriefly, a portion of each sample filter is low temperature lashed, the residue is @issolved in AP and HNO, and ?the solution is diluted for direct injection ele~ mental analysie using a Perkin Elmer Yodel 503A atonic absorption spectrophotometer with a Model 2100 heated

graphite analyzer. Preliminary analysis will be per-

formed by means of an optical emission spectrograph.

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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 glas:

fiber filter paper are activated as shown by the Anes mutagenic test when exposed to filtered air. The

authors isolated strongly mutagenic substances includ-

ing the nitro derivatives. This suggests a simple way

to study some transformations of reactive atmospheric

pollutants present in the industrial sector of Guayanilla-Penuelas, The adsorbed samples will be selected from the manufactured basic petrochemicals and other industrial products of the area. (e.g., Appendix I,Pig. 3 and Table rv).

General Procedure - Atmospheric reactions involving basic petrochemical intermediates will be studied sub-mitting then to the following procedur

2., Selected contaminants will be allowed:to interact with the atmosphere under existing conditions in ?the neighborhood of a petroleum petrochemical complex.

2, the isolated contaninant material will be tested for (a) mutagenic activity and (b) the presence of transformation products.

3. the results will be compared with control experi-

ments,

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

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

In these experiments, the atmospheric air composi-
tion my be altered by filtration, drying and/or aaai-
tion of other components to simulate a typical condition
such as when a large eniesion 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 component's by modern analytical techniques.

The above simple experiments will help in understand-
ing possible effects of variations inair flow patterns,
chemical and physical changes, in general, the interact-

ion of meterological and chemical and physical proces:

?under conditions of extreme complexity as those encoun
tered 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.

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Ad Pollution Node:

?the power plant model is one of two gaussian
?type models employed by the Environmental Quality
Board of Puerto Rico capable of a dispersion ana-
lysis, Tt computes maximum quantities of 90, for
Gigterent stacks based on fuel ulfur content. ?This
model considers not all enission sources-only point
sources are used as a model, input emis:

consider

area sources are ignored. The model dot

terrain features by adjusting the effective plime

height based on local topography. In general, the

power plant model and the Air Quality Display Model

(90m) will be helpful in estinating the impact on

the anbient air of sources enitting particulates and \

sulfur dioxide, specific sampling sites will be #e-

lected with the aid offered by these planning and

regulatory tools.

Metereological Consideration:

Puerto Rico, located between 18°00" and 16°30!

North latitude, has a maritime tropicel climate ox-
cept at sone of the higher interior locations. this
clinate te characterized by small diuraal and sea-
sonal temperature changes, high humidity, persis-
tence of the northeast trade snd, and convective

cloud types.

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The mean annual temperature at Ponce, for
example, is 71.2°F. The mean daily maximum ten
perature is 88.1°P, while the mean daily minimum
temperature is 69.4°r, a diumal variacion of
18.7°r.

Relative hunidities are generally high in thie
climatic zone, being over 60% half the time.

Although poorly understood, the importance of
the meteorological parameters discussed above in

air pollution control is net denied. Temperature

and huniaity (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 vhich 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 iastes 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;

~A0-

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bebe

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 ue to effects introduced by the terrain, and in particular, by the diurnal oscillations produced by the land and sea breeze (Figs. 57). ?These two factors are the most crucial considerations in de~ termining the behavior of air contaminants releas- ed to the atmosphere in a coastal area.

Tne stability of the atmosphere and the induced effects upon horizontal and vertical fluctuations of the wind determine the horizontal and vertical Gispersion of the airborne material. wind speed, of course, is important in this respect, not only be- cause 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 traneport and

aiftusion of

imborne material: wind speed, wind di-
rection, and vertical stability will be considered
in analyzing the results of this work. wind rose

and other metereological information for Guayanilla

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has been recently generated by the 590° ac a
result of a contract arrangement with the old

office of Petroleum Fuels Affairs now the Puerto

Rico nergy Office (Pigure 8). This work was
performed during the tenure of Juan J. Rigau as

executive director.

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Source: Eavironnéntal Quality Board (QB):

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mutagenicity and teratogenicity of Airborne Pollutant:

this proposal will also establish vhether or not
selected aiztorne particulate extracts (in total par
siculate and/or specific size ranges) and/or its cheni-
cal transformation products are identified as mtagenic
to certain strains of bacteria and teratogenic to marmal-

fan organisms, Annually, significant anounts of sev
eral thousands of toxic chenicals fron the petroleun-
petrochemical industrial complex and power plant opera-
tions, are throw into the environnent, none of which
have been tested for mutagenicity or teratogenicity.
Amets mutagenicity nest

2, Background

The anets mutagenicity test is the method of choice
anong the assays utilizing bacteria, 1 series of speci
?fie strains of galnonelia tyshimiriun vere developed by
Ames! which are noted for their sensitivity to mitagenic
agents in the area of the genone regulating histidine
synthesie, the Salmonella typhimuriim strains are auxo-
trophic for histidine production so that when inoculated
into mininal media Where this aminoacid is absent they
can not grow, If the bacteria are mixed with a mtagenic

back mutations

agent, a potential carcinogen, it may cau:

in that part of the genome and reinstate the ability to

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we

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

Some substances? do not present mutagenic activity directly, but may acquire this property vhen processed by the cellular enzyme systems which convert then to active agents. Therefore any compound showing no airect mutagenicity is re-tested using a Liver microsomal preparation (5-9 mixture) and the bacteria. this procedure allows for metabolic processing rendering than as active carcinogens. once any of the tests has given positive results a quantitative test will be performed again but using different anounts of the tested

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mutagen, to determine its potency as a mutagenic agent.

678.

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, ace~

tone, dioxane or DIO. (Diagram 1)

by Direct spot Tests screening

4. the 4 tester strains of Salmonella typhims-

mul (92-98, TA-100, TA-1535, 1A-1537) are grow

separately overnight in nutrient broth.

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41, A portion of 0.1 ml of bacterial growth
is mixed with 2 mls. of molten agar, overlaid
fon minimal media and allowed to solidify. this
is done in triplicate for each strain per sub-
stance to be assayed.

444, A sample of 101 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 optinal concentration for mutagenesis
to occur. controls will be both negative,
plates having no careinogen added, and positive,
plates to which mutagenic agents known to affect
each specific strain will be acdea.

iv. The plates are incubated for 72 hrs. at 27°c.

colonies that appear in test plates are counted
and compared to negative controls. An increase
in at least two fold the numer of revertands
is considered positive.

Quantitative: plate incorporation assay.

i, Without microsomes (5-9 mixture) :

1, Test will be carried out as above but

utilizing a series of concentrations of each

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a

substance giving a positive result (0.2,
1 20 and 5001 per plate) added to the

molten agar and mixed with the bacteria.
«There should be a dose-response curve
for the agent corroborating the original
results and determining the "potency" of
the agent.

With microsomia (5-9 mixture)

1. the test will be utilized for substance giving negative results on the screening test.

- The procedure is 1ike 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. in-?cubation

compared to negative control plates.

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solubilized Particulate Fraction

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spot test (screening)

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positive negative

results: resulte:

colonies no colonies

plate incorporation plate incorporation

?assay in different assay + 5-9 mixture

concentrations (microsomes)

| in different concentrations

colonies £ v

dose-response pos. negative

curve colonies giving no colloni

?a dose non mutagenic

response curve

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B. Teratogenicity Test

1, Background

Recently sulfur containing aromatic hydrocarbons:

have been detected in airborne particulates" and re~

finery wastewaters, making toxicity test of substances

present in emissions and discharges to the environment

necessary when the hunan exposure to those substance:

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 dow for toxicological evaluation of most medical substances, However, teratogenicity is only one example of enbryotoxic 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. Tt 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 enbryotoxic in man, namely, methyl

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mercury which causes both preratal and postnatal toxicity

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vor the detection of possible teratogens in samples

of fractions of different size of aizborne particulate matter in areas near energy producing plants the follow ing procedures will be followed. It is important to ob- jerve that these procedures are currently being used in our laboratory testing benzothiophene as a possible tera- togen. (Diagram 2)

2, Methodology

(Work scheme as practiced in our laboratory)

unmated female mice weighing 30 9 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 iso- lated and considered zero days pregnant (see step 1 of Diagram 2). Some strains will be used in others to com pare the susceptibility to the teratosen. ?they are main tained in individual cages, fed a diet of Purina chow and water ad Libitun,

Experimental groups of pregnant mice will be weighed

and treated with intraperitoneal injections of appropiate

doves of the testing samples of fractions of airborne par-

ticulate matter. the initial dose of the teratogenic sam-

ple will be the acute, single L050 for mature mice. Ten

pregnant mice of 9-12 days of gestation will receive this

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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 uring 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 anes thetized with ether and the abdomen is opened. the uteri of control and treated mice are carefully exam- ined, the total number of Living and doad fetuses and implantation sites is regarded as the total number of conceptuses. Viable enbryos will be weighed and exan- ined grossly. Abdomens will be opened and stored in 20 per cent neutral formalin or Bauin's solution to be studied later. some will be extscerated, stored in 95 percent ethanol, and later cleared and strained for study of the osseous skeleton.

I£ all of the fetuses have been resorbed leaving only residual implantation sites in surviving pregnant

animals, further studies are pursued (see step 3).

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Many chemicals at doses causing resorption at the tine of implantation {£ given on one of the following 3 te

4 days allow fetuses to survive showing developmental abnomalitios at sacrifice on the eighteenth day of gestation.? since implantation in the uterine muco: is at about the end of the fifth and beginning of the sixth aay, ?groups of ten pregnant mice will receive the initial dose of sample fractions of particulate matter which will be tested for teratogenicity from Gays 6-8, 8-10, 10-12, and 12-16 of gestation respec tively. 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 ges- tational 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 oF puso by the skin.

In the case that no effect of the &

ting 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.

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However, if birth malformations are present in

the offspring of one or more of these groups of ex-

perimental 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 groupe 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 air

borne particulate matter (step 6). Also, the litter

1050 and the teratogenic range below Litter 1050 will be calculated for each sample.

In order to study the malformations, the fetuses will be subjected to free-hand razor blade sectioning technique? *which pemnits a gross study of all the organs and systems of the fetuses. After doing this, a cito-Logical study of each one of the malformed organs or systems will be done using histochemical and electron microscopical observations (steps 7-8). Besides, for tthe confimation of the absorption of the testing tera-togen 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

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fetuses, and compare the with those organs of the

control pregnant mice (steps 7''-8').

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3. Rationale for selected Approach

?This proposal covers an extrenely important arca of

preventive environnental 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-sources, this is an important factor if the experience generated in this project is to be applied leter to other heavily polluted and densely populated areas 1ike cataflo

fon the north coast of the island. catholic University took

the initiative to investigate the Guayanilla-Pefuel

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 nowledge of the petroleun-petrochenical industry, petroleum composition, the availability of trained personnel and good lab facilities.

Second, a multi@isciplinary 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 in~ crease our opportunities to help not only in defining the

?existing conditions in the south coast industrial complex,

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but also in communicating our results effectively to the Conmonweaith of Puerto Rico regulatory agencies and the covernor's office.

?Third, we feel that it is important that the research-

ere associated with the project are professionally quali-

fied and recognized as objective, and non-partisan. This

is essential every time solutions to sensitive and impor-

tant problems are involved; and

Fourth, we selected this project because we are con~

vinced of the need to explore areas of biomedical interest

associated to the process of energy consumption and pro-

Guction, this will facilitate integration into the field

of various groups already interested, planning and/or con~

Gucting research work at the basic sciences departments of

our two major Schools of Medicine.

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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 ina long time to come to explore under a professional perspective the

problems

sociated with the emissions of particulate

matter in a heavily industrialized sector. In particu Jar, problems associated with the emissions to the atmosphere in a fully integrated petroleun-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 emis-
sions in the aggregate of contaminants available for
characterization, This ofcourse, is an important and
unique event that could bring knowledge of great im-
portance to the United States Environmental Protection
Agency in its efforts to harmonize economic development
and environmental degradation. rt 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.

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c+ As previously expressed this work constitutes a

multidisciplinary effort involving researchers from

various backgrounds that are in position to induce

thenselves a multiplier effect by promoting additional

research in their respective institutions.

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Methods of procedure, analysis and evaluation

Experimental procedures and analysis have been described in detail in the corresponding sections of the plan of work. Bvaluation process will try to tie closely the findings of the work with current regulatory issues of interest to government, industry and, the acadenic sectors. Project management should also try to establish the inplications 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 main
tained throughout project development in order to keep all
Principal investigators avare of the progress made by the aif-
ferent groups. Monthly meetings of all project personnel will
serve to exchange views, help solve problems and revise the

plan of action,

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4. Personnel Responsibility for each part of the Work Plan.

1, Project Director (Dr. Juan J. Rigau) (50x) - 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 par-ticularly 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 rnfante) (25%) - ?This investigator will be in charge of the metal analysis in particulates. His participation will also include col- Jaboration in the separation, characterization, and quanti-

tation associated with chemical transformations of reactive

pollutants in the presence of local air contaminants.

35 pr 1 Investigator (Dr. do 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 collabo- rate in the characterization of nitrogen containing polycyclic

aromatic hydrocarbons.

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carry out continuous extractions and other routine analysis

of samples obtained from the field.

8. Iwo 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. B.Sc. Undergraduate Student - 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 tépez) (40x) will be in charge of the teratogenic tests and supervision of graduate students of the Department of Anatomy, UPR Medical School (e.a-, Me. Calixto soto; MSc., a graduate student, will be doing

teratogenic t

8 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 prepara-

tion 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 super-

vision of graduate students from the Department of Microbiology,

UPR, Medical School.

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13. Medical Technologist (100%) - will conduct work on

?the Ames test under the supervision of a well trained tech-

nician currently doing the Ames assay in our lab,

14, Utility Man ~ will take care of animals, cleaning of

cages and lab ware in the mutagenicity and teratogenicity

laboratories.

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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, Bavironment 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 stuGents and professors of the college of Sciences and the Medical school. Bquipment available for this project includes chemical and biological hoods, two research gas chromato

graphs, colorimeters, high vacuum line facilities, thin-layer

chromatography apparatus, ultracentrifuges, soxhlet extraction apparatus, and six high volume samplers. Major labora-

tory equipment available to the Institute from other on Campus

cilities 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.

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Genter for Energy and Environment Research

Research facilities at the Center for mergy 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, squipment available for the separation and characterization of petroleum fractions includes two research gas chromatographs with flame photometric and flane ionization detectors with glass capillary column capabilities, a HPLC instrument with UV and differential refractometer detectors and a back flush four way valve at~

tachment, 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 chemicai/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 micro scopy facilities, compound microscopes, and some cages are available as part of the facilities for the teratogenic work.

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Budget schedule

?The project director and principal investigators are active

participants in the energy-environment prograns started at the Institute for nergy, 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 esearch involvenent in the proposed project. salary is estima-ted based on the percentage of time that will be dedicated to

Project development using their yearly salary as a base.

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APPENDIX I

Table I: Socio-Economic and Energy Indicators in selected Fiscal Years Terminating on june 10.

Table II: Fuel Used by the Puerto Rico Water Resources Authority for Power Generation.

Table III: Puerto Rico Petroleum Flow Pattern and Relation of Energy Used and Lost in the Process Calendar Year 1976 in thousand Barrels.

Figure la: Chemical configurations Related to sulfur and Ni-

trogen Derivatives in Fuel Oil.

Figure 1b: components of Environmental Assessment.

Figure 2: Municipalities, standard Metropolitan Statistical

Areas, and Selected Places.

Figure 3: Existing Refining and Petrochemical Industry - 1975.

Table IV: Petrochemical Production in U.S. and Puerto Rico.

Table

Southern Coastal Plain Vital statistics.

Figure 4: Incidence Rates for Ten Conmon Primary Sites Puerto

Rico 1975.

Figure 5: Trend of Incidence of iung Cancer Puerto Rico 1974.

Table VI: 1978 Projected Air Quality Levels Annual Arithmetic

Mean.

Table VII: 1985 Projected Air Quality Levels Annual arithmetic

Mean.

Figure 6: Predicted Particulate Air Quality Annual Average-

Area Sources Only 1975-75,

APPENDIX 15

Diagram of catholic University of Puerto Rico Institute for

Energy, Gvironnent and Biomedical sciences Facilities.

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APPENDIX TET

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Letter of tntive Director (now President) of the avironmental

RRality board of Puerto Rico and the corresponding answers

APPENDIX IV

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APPENDIX T

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TABLE

Municipality Population Live births

Number Rate

Gufnica 17,810 461 25.9

Yauco 39,000 944 28.2

Guayanitla 20,370 sa. 26.1

Pefuelas 19,010 468 26.6

Ponce 183,380 4,946 27.0

Juana Diaz 42,810 1,089 25.4

Santa Teabel 18,540 sis 27.8

Salinas 26,040 678 26.0

uayama 45,270 1,080 23.9

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Source: Puerto Rico Department of Health

SOUTHERN COASTAL PLAIN VITAL STATISTICS

Deaths

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123

1,273

236

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INCIDENCE RATES FOR TEN COMMON PRIMARY SITES

Puerto Rico 1974

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Figure 5

?TREND OF INCIDENCE OF LUNG CANCER

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Puerto Rico Department of Health

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TABLE Vi

1978 PROJECTED AIR QUALITY LEVELS

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UNIVERSIDAD CATOLICA DE PUERTO RICO

Ponce, Puerto Rico - 00781

May 11, 1978

Eng. Pedro Gelabert

Executive Director

Environmental Quality Board

San Juan, PR 00902

Dear Engineer Gelaber'

We are convinced that there exists a causal relationship between pollution levels and certain damages suffered by our society. Thus. Fede necessary now, as it was in 1970, to set new goals in light of ew knowledge. Since the goals of a clean environment cannot be Sehieved in igolation, 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 Cavironmental inpects of energy producing the consuming operations folloving @ systens approach.

InterdisefpLinary and multidisciplinary research efforts enploy-ing the Tesources of Catholic University will help our government, 35 deli es other sectors, in harmonizing euvironmental considerations ith the requirenents of an energy policy. Our blosedical approach UHI help is establishing the quantitative expression of the relation

?Ships between exposure to specific pollutants, and the type and extent Sf the associated danage to'a target populetion. For example, by Saentitying locations ef susceptible popalations exposed to relatively harardova Levels of pollutants, the effects of allocating specific pollution contrel resources can be assessed. In this regard, the data Foquired to develop physical or Mological damage functions will be Sbtained through epiventological, field, clinical, toxicological, or SSboratery foveseigetions. To help achieve these objectives, we have decided to construct special laboratory facilities. Microbiolony. Mochenistry, organic chonistry, physiology, tissue colture, infec Mee Gisendce, and analytical chenletry Laboratories will be finished {in the next fev weeks.

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

better understand how physical, chenical and biological agents interact

better understand the transport and transformation of

aynthetic chemicals

better understand husan risk factors

better trained research scientists and science under-

graduates

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APPENDIX. IZ

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Eng. Pedro Gelabert

Page 2

May 11, 1978

With this concept in mind, ve 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 forvard to your reaction on these and other matters.

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1S de junio de 1976 SCHOOL OF MFHiCayE

Dr. Francisco J. Carreras

Presidente

Universidad Cat6lica de Puerto Rico

Ponce, Puerto Rico 00731

Estimado Dr. Carreras:

En respuesta a su comunicacién del dfa 1) de mayo, deseo indicarle que en la Junta de Calidad Ambiental estamos compronetidos en 1a busqueda de soluciones a los problemas anbientales presentes y futuros. Por tal motivo, coincide con usted en que es necesario que continuamente evaluemos los logros alcanzados y nos fijemos nuevas metas a la luz de los nuevos conocimientos cientificos. Creemos ademas que es imprescindible la integracién de los esfuerzos institucionales piblicos y privados para poder lograr la meta de la conservacién y proteccién de nuestro ambiente.

La iniciativa de ustedes al crear el Instituto de Energia y Ciencias Bionédicas es digna de encomio y por los objetivos que se han fijado estoy seguro que harén una contribucién importante a la solucién de la problenatica ambiental de Puerto Rico. Les felicito por tan brillante ide.

Tan pronto tenga oportunidad me gustarfa prograna r
para compartir con ustedes aquellos problemas y areas de
interés particular en las cuales yo considere que el Insti-
tuto podrfa contribuir efectivanente a la solución de ne~
cesidades y problenas regionales-

comunicara con su oficina para fijar la fecha y hora més

Mi ayudante ejecutivo el Sr. Wilfrido Soto de Arce sey
Sohitnsthte gt aguie nates J

| Pedro A. Gelabert
Director Ejecutivo

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APPENDIX. IV

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PERSONAL DAT?

Place

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seat

PosITroNs:

seATICN:

DISSERTATIONS:

Juan Jose Rigay Sepulvese

November 24, 2939

Sabana Grande, Puerto Rico

Mersies, four

Consultant on Energy and Environment

1977-

Director - office of Petroleum Fuels

Affaire, 1973-1976 - Office

©f the Governor, Commonwealth

of Puerto Rico

tant - Economie Develosment Adm:

istration, 1969-1973

1956 ~ University of Puerto Rico Bish

School, Rio Piedres, Puerto Rico

1960 ~ Bachelor of Seience

University of Puerso Rico

1965 - Master of science

University of Puerto Rico

1969 - Doctor of Philosophy

Wayne State University

Detroit, Michigan

Le Bsteroqu{mica de B-Hidroxisul foxidos",

M.S, thesis, University of Puerto Rico,

1965,

?Sterochemical studies in organo-sulfur

Chemistry", Ph.D. thesis, Woyne State

University, 1969, Dissertation Abstr.

Intern'1, 32 (5), 2612-8 (1971)

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RESEAKCH EXP

charge Of the hadio-

OF the adicisczope

Division, Instructor for the Radioisotope

@ivision, Radioisotope Techniques cours

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

Research Fi

ow - Wayne State University
11965-1953, Exploratory Research in Sul
fur Chemistry under the direction of Dr.
carl R. Johnson.

Senior scientist (ad Honoren) ~ Puerto
Rico Nuclear center

Lecturer (Ad Honorem) - Department of Ghemistry, University of Puerto Rico, wayaguez Campus

Monber ~ University of Puerco Rico (Rio Piedras Campus) Graduate Sraminetion Com nittee.

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

1973 = Dr. games Sanabia, Ph.D., Organic chemistry.

1974 ~ carmen Ibpez, MSc., Bio-Organic ?chemistry.

Menber - University of Puerto Rico (ed-ical Sciences Campus) Graduate Examina? tion Comittee.

1974 ~ Francisco Fuentes, MSc. Candidate, Microbiology.

1977 - gests Gonzhlez, usc. candidate,

Environmental Health.

1977 Leocadio Melendez, 1Sc. Candidate,

Environmental Health,

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HONORARY SOCIETIES:

PROFESSIONAL SOCIETIES:

PUBLICATIONS:

RESEARCH A?

ISOK GRADUATE

Mr, Jorge Pichardo, "Thermodynamics of

Anions in Solution" 1973, University of

Puerto Rico, Chenistry Department, Rio Piedras Campus in collaboration with Dr. Gerald stevenson.

Miss carmen Lopez, "Toxicity Effects of Selected Orcano Sulfur Compounds on M-bial Organisms" 1972, (School of Nesi-cine, University of Puerto Kico in col-Jaboration with Dr. Fermin Sagaréfa).

Me. Francisco A. Fuentes, "Repression by Glucose of the Degradation of Benzothio? phone by Pseudomonas Aeruginosss PRC-1, and Reversal by Adenosine-3', 5* Monos-phosphate", 1974, (school of? Medicine, University of Puerto Rico in collabora. tion with Dr. Fermin Sagaréfa),

Mr, gests Gonzélez, "Isolation and iden-tification of Microbial Products from Benzothiophene" 1977, (Department of En-vironmental Health,Craduste School of

Public Health, in collaboration

Heriberto Torres).

Phi Lanbda Upsilon

Sigma xi

Who's Who in Government

American Chemical society

Division of Organic Chemistry and Petro

leun Chemistry, Inc.

British chemical society

College of chemists of Puerto Rico

Member of the Board, College of Chemists,

1972

1974 - President, college of chemists

1975 - Member Advisory Board, College of

Chenists of Puerto Rico

?Intramolecular Hydrogen Bonding in ci

?2-Phenylmercaptoindanol", H.H,Szmant and

5.3. Riga, J.0rg.chem.,"31, 2288 (1966).

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Jed. Kices,

(1987).

?Non Sterospecific Oxidative naition

of Benzene Taiol to Inéene", #.8, csmant

and J.g. Rigas, presented in part at the

147th Meeting Of the American Chemical

Society, Pailadelpnia, april, 1964, Pub-

lines in Je 487 (3972).

?the Trans-Cis Ratio of Frogucts Formed in the Oxidative Addition of Aromatic Thiols to Indene", H.H. Samant, A.J. mata, J.J. Rigau and J.P.A, castrilién, presented in part at the 154th Meeting of the American Chenical Society, Chicago, Septenber, 1957.

ont alkylation of sulfilimines", C.R. Johnson, J.J. Rigau, M. Haake, D, Me? cante Ur., J.E. Keiser, and A, Gerst.

Sema, Tetrahedron Letzers, 2719 (2968)

?isulfimines and sulfoxinines Derives from é-t Sutyl-thiane", CR. Jonneon and gd. Rigau, J. Ore! Chen., 33, 4240 (2368). =

oxidation of sulfides with t-butyl Hypoclorite Evidence for a Tetracovalent Sulfur Intermediate", c.R. gohneon and 5.3. Rigas, J.Aner. Chen., 91, 5398 (369).

?sterochemical and Mechanistic studies in the Oxidation of sulfides by t-putyl Hypoclorite", C.R, Johnson and J.J. Rigau, presented in part at the Netrochem 71 Meeting of the American Chenical society, San Juan, May, 1971, Paper submitted for publication, J.Amer. Chen.

S08.

infrared studies of Alkoxysulfonium
Salts", J.J. Rigau and C.R. Johnson,
presented at the 7th Caribbean Chemi-
cal Conference, Mayaguez, Puerto Rico.

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PUBLICATIONS CONT.

?the Sterochenistry of Omdation a:
sulfur, Oxidation of 2-metnylthiolane?,
9-9. Rigau, C.C, Bacon ané C.R, gonn-
?son, J. Organ. Chem., 25, 3655° (2970).

"Reduction of Sulfoxides with Sodium
Hydrogen Sulfite", C.R. Johnson, ¢.C.
Bacon and J.J. Rigau, J. Ore. Chem,
22, 919 (1972).

?structure of Trans-4t-Butyl-1-n-Ethyl.

Nep-Toluenesul fonylamino-1 Thicniacyclo-

hexane Fluoroborate, Evidence for p. (Ii)-

(5)- Bonding", R-E. Cook, M.D. Glick,

J.J. Rigau and C.R. Johnson, 3. Amer.
924 (2971).

"substituent Effects of the trans-cis
Ratios of the Products Formed in the
cooxidation of Aromatic Thiols and In-
ene", H.H. Szmant, A.J. Mata, J.J.
Rigau, and J.P.A. Cestrillén, J. Ora.
Chem., 37, 0000 (1972).

New Organo Sulfur Scrubbing Agents

A Novel S0,-Sulfoximide Adduct?, J.J Rigau, L.R? Lizardi, S.c. Teai, G. Barrio and L. Boada, presented in part at the 7th Caribbean Chemical conference, Mayaguez, Puerto Rico.

?Degradation of Benzothiophene and Ri lated Compounds by an Oil Pseudomonas in an Oi1 Aqueous Environment", F. Segardia, J.J. Rigau, A.Martinez-Lahoz, F,Fuentes, C.lépez and W.Flores, Appl. Microbiol. 23, 772 (1975).

?the Effect of Glucose on Benzothiophene Degradation by P. aeruginosa PRG-1", J.J Riga, J.I. colén, F.A. Fuentes, C.J. Lo pez de Fuentes, g-c. Liu, F. sagarafa (éec.) Paper presented by F.A. Fuentes at IX ca-ribbean Chemical Conference, Dec.10,1977.

"Effect of Glucose on the Degradation of Benzothiophene by Pscudononas Aeruainosa PRG-1", Fuentes, F.A., Sagardia, F., Colon, J.t., Liu, J.C., Lopez de Fuentes, C.J. and Rigau, J-J-, Submitted for publication.

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PUBLICATIONS CONT.

SPECIAL REPORTS:

Effect of c-AMP ané Phosphosiecterase Inhibitors on the Netabolism o: thiophene by Pseudomonas PRO-1", ?Sagarcia, F., colén, J.I-, Lit, J-C., Lopez de Fuentes, C.J, and Rigau, 3.3. Submitted

for publication.

"Recent Aspects of Sulfur Chonistry in Petroleun", Novenber 1969, prepared for the Department of Research and Development, Commonwealth of Puerto Rico.

?An Institute for Petroleum Research and sulfur Studies: A Procram for the Application of the Scientific Resources of Puerto Rico in the Environmental control Fiel@", april 1970, research proposal pre~ pared for the Department of Research and Development, Commonwealth of Puerto Rico.

?control Techniques for Sulfur Air Pollutante: Preliminary Evaluation of Schemes for the Renoval of sulfur Dioxide from Smelter Gases", May 1970, research propo sal prepared for the Department of Research

and Development, Commonwealth of Puerto Rico.

During his tenure as Director of the of fice of Petroleun Fuels Affairs of the Commonwealth of Puerto Rico, prepared ané/ or coordinated the preparation of the fol- lowing proposals:

- "toxicity studies of sul fur-containing Petroleum Fractions"

= "Development of a Simlation Model of Puerto Rican Refineries for the Assess- ment of Fuel Availability as a Function of Refinery Configuration and Raw Ma~ terial Inputs"

- "the Isolation, Identification and Quantitation of Reactive Hydrocarbons

in Selected Environnents and their

Photochenical Reactions in the Atmos-

phere of Puerto Rico"

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?ADDITIONAL ORAL

PRESENTATIONS:

= "tne Office of Ferrolux Fuels Af

inirs Petroleum Eneroy kusources

Education Program"

= ?pesulfurization of Organo-Sulfur

compounds and Petroleum Fractions

by Microorganisms"

= "the Puerto Rico Enercy Model: An

alg for the Decision-vaking Process"

?me Application of Science and Tech-

nology £0 the Pollution Control field

in the Petroleum Industry", 30th Annual Convention, College of chenists of Puerto Rico, Hotel San Jerénimo, 1971.

"New Approaches of the Economie 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 Compounés in Petroleun?, Seminar on Gas Chronato? graphy sponsored by Perkin-Elmer and

Burpee Seles, Hotel San Jerénimo, 1972.

?Research Work at the Department of Research and Development of Fomento and its Relation to EDA'S Procrams", Mona? cilles Rotary Club, 1972.

?industrial Aspects of sulfur chemistry", 1972 Seminar Program, RED Department, Economie Development Administration.

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

multiple presentations covering matters related to the petroleun-petrochemical industry and the Puerto Rico enersy future of which the following are typical:

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?Le Oficina sobre Asuntos de Conbustibies Derivados del Fetréleo: Andlisis de Nu- estra Actualidad Eneraética", Colesio Universitario de cayey, 18 de julio de 1975.

?La Estructura de la Industria Refine dora y ?l Mercado de Conbustibles en Puerto Rico". Presented as the closing speech for the "III Convencién Centro- americana y del Caribe de Expendedores

Ge Fetroleo", San Salvador, 24-26 abril, 1975.

"Wociones sobre el Impacto de los Proyectados Aunentos del Petréleo", Taller Sobre Costo de la Vida, 19 de agosto de 1975.

?La Explotacién de Potenciales Yacimientos Petrol{feros en Puerto Rico", Asociacién Americana de Profesores de Fisica, Seccibn de Puerto Rico, Colegio Universitario Ge cayey, 3 de septiembre, 1975.

?La Problenitica de la Enercfa y Estrategias de Conservacién Ante un Petréleo que se Agota", Convencién Anual Asocia? cign de Detallistas de Gasolina de Puerto Rico, 5 de octubre, 1975.

wyarco para la Formulacién ée Polfticas

Ge Conservacién de Energfa en Puerto Rico", Taller de Costo de 1a Vida, 30 de octubre, 1975.

spectos de la Problenitica Energética Puertorriquefia", Colegio Sacrado Corazén, 12 de febrero, 1976.

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

?produccién de Energfa, su Tecnologia y el Ambiente", Departamento de Fisica, Universidad de Puerto Rico, Recinto de Rio Piedras, 8 de abril, 1976.

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ADDITIONAL ORAL PRESENTATIONS COS

SPECIAL ACTIVITIES:

?petrolec: su Futuro e Impacto Ambiente" Simposio Sobre Crisis nergétice, gProbles Sin Solucion?, sponsored by the Facsity and Bachelor. Of General studies of the university of Puerto Rico and the center for Energy and Environment Research, Nov-ener 30, 1977,

"Enersy Status in Puerto Rico", Sociedad Ge Econonistas del Gobierno, 23 de abril, 1976.

WEL Status de 1a Situación mergética en Puerto Rico", Colegio Regional de Carolina, 11 de mayo, i976,

"ia Contribución de un Modo de ?Transpor-tación por Bicicletas a los Problenas Lo-

caies de mergia", Seminario-Taller sobre

?Transportacién por Bicicletas en P.R

Hotel Racquet Club, 13-14 de mayo, 1975,

?EL Petréleo y su Potencial en les costes

Ge P.R.", Colegio Universitario Ge Huna-

cao, 11 de junio, 1976.

"mnerey Status in Puerto Rico: An Assese-

ment of the Petroleum Situation", presen

tado en el Third Annual UMR-MEC Conference

on Rnergy, Universidad de itissouri-Rolla,

12-14 de octubre, 1976.

wMuestro Dilema Bnergético: Ciencia,

?Tecnologia y Algo M&S", comentarios pri

sentados por el Dr. Juan J. Rigau, en el

Colegio de Ingenieros, Arguitectos y

Agrimensores ante foro auspiciado por la

Adninistracién de Pequefios Negocios, 27
de octubre, 1976.

Monber, Favironmental Advisory Committee
to the President, University of Puerto
Rico, 1972.

Program Chairman - "Analytical Technique:
for the Contrel of Atmospheric Pollution",
seninar held in Ponce, August 23-25, 1972.

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SPECIAL ACTIVITE!

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

Chairman-Seninar on "The Petroleun-Petro-

chemical Industry - An Analysis of some

Key Factors, Hotel Flamboyén, Septesber

as-2i, 1973.

Menber-organizing Committee, Annual Semi-

par on "Environnental Pollution Abatement",

1972.

Chairman-"First Conference on Energy-Bo-

vironnent-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 uni-

versity of Puerto Rico, 1977-

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

Menber-Puerto Rico Task Force for the re-organization of the Puerto Rico Nuclear center, 1976,

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

Menber-Senior Advisory committee, Center for Energy and Environment Research, Uni: versity 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 Environ
mental Health, Graduate School of public
Health, Medical sciences campus, Univer
sity of Puerto Rico, 1977

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RESEARCH INTERESTS:

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Chemistry of sulfur compounés in
petroleun and petroleur prosuct:
petroleum composition, ané des:
furization studies. mergy plan-
ning and economics,

Dr. H. Harry Samant, Chaizman,
Department of Chenistry, University

of Detroit, michigan

Dr. Carl R. Johnson, Professor,

Department of Chemistry, Wayne state

University, Detroit, michicen

Dr. Ismael Almodovar, President

University of Puerto? Rico

Rio Piedras, Puerto Rico

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Daivorsity of taneap, Tavrence, Kansas | Ph.D. 1971 | RRB FREER ATE

Vaiversity of Kansas, Lavrence, Kansas Ms. see | fglld geste, ovsicn

cose Institute of Tech., Cleveland, ohio | 3.8, 1964 Physics

?Acadenic Achievement Scholarships, Case Institute of Technology (1962-64)

?Teaching Assistentahip, Kanses University (1964-66, 1968-69)

Research Assistantohip, Kansas University (1970-71)

Environmental Monitoring

Positions Held

T. Physics Professor, Catholic University of Puerto Rico, Ponce, P.R. (Aaslatant Professor 1971-73; Associate Professor 1973-77; Tenure granted 1976).

2, Graduate Research Assistent, Physics Departnent, University of Kansas 1969-71.

3. Wieieing Professor of Physica, Faculty Exchange Program sponsored by the Ford Foundation Universidad de Oriente, Comana, Venezvela, 1906-68.

|. Graduate Teaching Assistant, University of Kansas Physice Department 1964-66.

5; Research Technician, Youngetom Sheet G Tube Research Lab. Sumers 1963-65.

National

Two talks given at the National Mecting of the Anerican Physical Society and the ?Anerican Association of Physics Teachers in Nev York, Winter, 1971.

2, Tavited talk on the Undergradutte Research program £0 monitor particulate contanination in Ponce, P-R., given at the National Sumer Meeting of the Anerican Association of Physics Teachers, June, 1977.

3. Invited Participant in'Paculty Sumer Institute on "Energy Production and the Bavironsen ?oponsored by Oak Ridge Associated Universities, Oak Ridge, Tennessee, July, 1977.

?At the Catholic University? ~

1. System Manager for the Digitel Equipment Compeny Computer (11/03end 11/34) im the Physic Department, 1976-77.

2. Computer programing consultant for various professors at the Catholic University.

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% Soyglinator of the "rirat Béucatonal Congress on Bnergy", Ponce, Puerto Rico

1976,

?+ Research Director of Student Project to Monstor Particulate Air Contanination

in Ponce, Puerto Rico? 1976-77

Roker Kwak, M, Nicholas, and R. Stump,

meson So KD Interactions at 3.4 Gav/e,"I1? Now Ginente Thy 608 s1972),

7K Ribckert, M- Kwak, M- Micholas, R. Stump, "Final Seates with a vietble

?Actyperon in KD Interactions at'3.4 Gav/e,? Muovecisense Marita Tseae

Mb Meholas, N. Kwak, RR. Eckert, R. Stump, "The K-

and Final States in KD. Interactions at 3.4 Gav/e,"

11 Nuovo Cimento 144, 363 (1973).

«- Feeeaeeakert, BL Desarrollo de una Colonia de Orgenisnos en vn Yodelo para

Computadora Electronica? Seience-Ciencia, Vol 20 Nua, 3 (9)

5 Rardtse de Jesus, Wands I. Malendes, Joe H. Peres, Richard R. Eckert,

?enbemuTonente of Particulate Air Contamination ia?Ponces Pusite fie? = A

An tnveagvexweneat Project" AAPT Announcer Vol. 7, tlos'2, Pri (icy 1947)

?a davited paper given at the AAPT Sumer meeting 18 Sea Sone; PS ade dary

(full article to be published)?

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7 ~ BIOGRAI CAL SKETCH _

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carranyuttio, Arsaldo Avsochate Professor eps

?santa Toabel, Puerto Rio us ate Orana

University of Puerto Rico, Rio Pedrasy Phe 1939 Cheatstry

Univeristy of Puerto Rico, Ho Piedras, 2h, i 3986 Organic Ghesistzy

Ohio State Tatversity, Golusbus, Ohio wh Organic Cheststry

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ine Cutholte Univerndty wf Iuncts {es jinardienl hromeeh brogeas

Vor of Cheaintry, Catholic Univeresty ef Suerto Wea

Agfa = MEL search faculty jartietyant.

1971 = Aceistont Protecuor of Chenisizy, Catholle Usiversity of Puerto Ricoy Poncey Psy

1966 = Research Ascistast of Organic Cheaistry, Ohio Stute University, Corusbus, Ohie

1962 ~ Researcn Assistant, Puerto Rico Nuclear Center, Universiy. of Puerto Rico, mio

Piedras, PR.

1959 ~ Chesistry ictructor, University of Fuerte Rico, Rio Pledeaay P.Re

Bubaeetions:

Chesistry of Organcbore cospounds = 1966, x5. Thesis

cyclepropylattreniss Tose = J, Chet. Soe. Chesieal cossunications, 495 (1969)

ing Zegastons cat Hing Contractions via titrestis Jone, Tetrahedron Letters tor 2,109

1977)

Heactions of Strained Kings with Flectron Deficient Acetylenes, Ph. Ds Thesis, 122p (1571)

3974 ~ Studies on Ovictée Activity - Arnaldo Carraaquilo, Ernesto Pereira ~ eecond ¥.B.S+

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Publications

1974 ~ Ernesto Pereira und Arnaldo Carrasquilio - Lavictésl effect of

tropical plante extract o> Ae: ?Geeond KEeS, eyaposiun,

ew Orbeate, Tar

1975 ~ Arnaldo Carrasquitio, Ernesto Pereira and Jeha del Ville-~ Toolation

of the active principle of a lavieidal plant extract - third aatual

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New Orleans, Loteiasa.

1976 ~ Eeneato Pereira, Arzaléo Carraaquillo and Janeo Yayo]

activity of extractions frox Pizer Mar,

Lervicttad

1977 ~ Arnaldo Carrasguitio, Ernesto Peretra, Javier Rivera ~ The ature

of she eajer conponenta of the Larvieldal extracts frac Piper

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Hpr Sas Toasy Poke Soptesbery 1977.

1977 ~ Arentde Carrenquitio, Eraesto Pereira, Marta dal Carson Pughs =

Larvictdal activity of the eocontial ofle of Fiper Marginatus ~ Fife

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Infante, Gabriel Ae seiotant Professor of Cheniatry| flows 35 1945

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Havana, Cuba . tes iat

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Gatholic Daiversity of P.R., Pouce, PR | Boe 1967 | Ghuslatey, Biology

ws. 1969 | Cuentstry

PDs 1973 | Cuentetry

1973 | Chentatey

?Doan honor ist 4 tines Guring B.S, otadied. Wadale in Organic, Amalytical, Fay=
sical and Industrial Cheatatry courses. Outotanding Graduate Student Award, Texas A & M
aiy. 1973. Outotanding Educator of Anerica, 1975 and Waote Who in South and Soutbeusty

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