

**Puerto Rico Water Resources Research Institute
Annual Technical Report
FY 2006**

Introduction

The Puerto Rico Water Resources and Environmental Research Institute (PRWRERI) is one of 54 water research centers established throughout the United States and its territories by Act of Congress in 1964 and presently operating under Section 104 of the Water Research and Development Act of 1984 (P.L.98-242).

The general objectives of the Puerto Rico Water Resources and Environmental Research Institute are (1) to conduct research aimed at resolving local and national water resources problems, (2) to train scientists and engineers through hands-on participation in research, and (3) to facilitate the incorporation of research results in the knowledge base of water resources professionals in Puerto Rico and the U.S. as a whole.

To accomplish these objectives, the Institute identifies Puerto Rico's most important water resources research needs, funds the most relevant and meritorious research projects proposed by faculty from island universities, encourages and supports the participation of students in funded projects, and disseminates research results to scientists, engineers, and the general public.

Since its creation, the Puerto Rico Water Resources and Environmental Research Institute has sponsored a substantial number of research projects, supported jointly by federal, state, private, and University of Puerto Rico's funds. Through its website, the Institute's work is more widely known to the Puerto Rican community and, at the same time, provides means of information transfer with regard to the reports produced through the institute's research activities.

The PRWRERI is a component of the Research and Development Center of the University of Puerto Rico at Mayaguez. As such, it acts as official liaison of the University of Puerto Rico with industry and government for all water resources research activities. The Institute also functions as a highly recognized advisor to these two sectors on water resources issues. This role translates into multidisciplinary functions and activities that add relevance and impact to the research program the Institute supports.

By virtue of the local relevance of its research and the prestige and leadership of the investigators it has supported, the Institute has become the focal point for water-related research in Puerto Rico. Meetings, seminars, technical reports, and a quarterly newsletter are used by the Institute to keep the water resources community and general public informed about advances in research. Approximately once every two years, the Institute organizes major conferences on water-related research in Puerto Rico and the Caribbean, in collaboration with other technical organizations in the region. All these activities facilitate the translation of the research sponsored by the Institute into practical applications of direct benefit to industry, government, and the general public.

Research Program

In FY 2006 the PRWRRRI submitted 10 research and technical project proposals to federal and state government agencies, municipalities, and private sector. Five were approved for total funds of \$300,619. Four were rejected and one is still pending. The proposals are as follows.

1. Professional Development for PREPA's Engineers, PR Electric Power Authority, \$10,166, (Rejected)
2. Safe Yield Study for the Southwestern Reservoir System - PR Electric Power Authority, \$97,536, (Approved)
3. Innovative Onsite Wastewater Disposal System Outreach and Demonstration Project, PR Department of Natural and Environmental Resources, \$35,000 (Approved)
4. Yaguez River Profile and Cross Sections Survey, Mayaguez Municipality, \$2,583, (Approved)
5. Cumulative Impacts of Multiple Stressors (MultiStress), NOAA/NOS/NCCOS/CSCOR, \$1,000,000, (Rejected)
6. Mayaguez Bay Watershed: A Prevention and Conservation Project, USEPA \$899,983, (Pending)
7. Removal of Heavy Metals from the Thickener Tank Effluent at the Miradero Filter Plant at Mayaguez, CDM Caribbean Engineers, \$25,423, (Approved)
8. Not-Accounted-for Water Study for the West Region of Puerto Rico, PR Aqueducts and Sewer Authority, \$59,700, (Rejected)
9. Evaporation Alternatives for the Parguera's Wastewater Treatment Plant Effluent, PR Aqueducts and Sewer Authority, \$12,209, (Rejected)
10. Use of Recycled Waste Tire Crumbs for Removal of Metals, Organic Compounds, and Anti-Microbial Agents from Polluted Water Streams, Solid Waste Management Authority, \$140,077, (Approved)

During FY 2006 the PRWRRRI administered three projects funded under Section 104B (two new projects and one extended from FY2005), in addition to other projects funded by other agencies, as per approved proposals. Previous fiscal year continuing projects include

1. Regional Water Quality Coordination project in USEPA Region II, in collaboration with Rutgers University and Cornell University.
2. Comprehensive Integrated Management Plan for the Mayaguez Bay Watershed.
3. Establishment of the Center of Excellence for Water Quality.
4. Operational Hydraulic Model for the Distribution System of Western Puerto Rico.
5. Nutrient Criteria Development for Rivers and Lake in Puerto Rico.

A Call for Proposals to the research community of Puerto Rico was issued in October, 2006. Only one submission was received.

Dr. Jorge Rivera-Santos continued to monitor the progress of the research projects and continued to be a liaison between the University of Puerto Rico and other agencies including the Caribbean Office of the US Geological Survey. The director targeted other local government agencies to become directly involved with through the arrangement of Memorandums of Understanding (MOUs). An agreement has been signed with the PR Electric Power Authority. This new agreement has already produced a new project.

Monitoring Nutrients Content in the San Juan Bay Estuary using Hyperspectral Remote Sensing

Basic Information

Title:	Monitoring Nutrients Content in the San Juan Bay Estuary using Hyperspectral Remote Sensing
Project Number:	2005PR20B
Start Date:	3/1/2004
End Date:	12/31/2006
Funding Source:	104B
Congressional District:	
Research Category:	Water Quality
Focus Category:	Nutrients, Nitrate Contamination, Non Point Pollution
Descriptors:	
Principal Investigators:	Fernando Gilbes

Publication

RESEARCH PROPOSAL

1. Title

Monitoring Nutrients Content in the San Juan Bay Estuary using Hyperspectral Remote Sensing.

2. Focus Categories:

NU, NC, NPP, WQL

3. Keywords:

Remote Sensing, Estuaries, Estuarine Modeling, Nutrients, Pollutants

4. Duration:

March 1, 2005 to February 28, 2006

5. Federal Funds Requested:

\$20,000

6. Non-Federal Funds Pledged:

22,402

7. Principal Investigator:

Dr. Fernando Gilbes, Department of Geology, University of Puerto Rico, Mayagüez, Puerto Rico.

8. Congressional District: N/A

9. Statement of the critical water problems:

The San Juan Bay National Estuary System (SJBNES) is located in the northern coast of Puerto Rico contained within a drainage basin of 240 square kilometres. The estuary consists of the San Juan bay connected by a series of natural and dredged channels to four lagoons: Laguna del Condado, Laguna San José, Laguna La Torrecilla, and Laguna de Piñones. Point and non-point source water pollution is a potential threat to preserving the current environmental balance at the site and to the Atlantic Ocean, where the estuary discharges. Most of these pollution problems are associated with excessive nutrients loadings (i.e., nitrogen, ammonia, phosphorus) reaching the bay, particularly to the Laguna San José. Eutrophication conditions prevail at this site due to such excessive nutrients loadings.

The use of satellite sensors, through remote sensing imaging techniques, is a state-of-the art procedure currently used to assess environmental pollution

problems around the world. Hyperion is a hyperspectral imaging sensor that could provide the necessary spatial and spectral resolution to monitor nutrients contamination at a complex land ecosystem such as the SJBNES. The objective of this project is to design and validate a mathematical algorithm, based on the reflectance characteristics of bacteria present in the nitrification process, to be used as a *proxy* for nutrients contamination monitoring through the use of the Hyperion satellite sensor at the SJBNES. This research project will serve as the Doctor in Philosophy (Ph.D.) degree dissertation in Civil Engineering for Luis F. Campos.

10. Statement of the Results or Benefits

The project is expected to be completed within one year. A hyperspectral reflectance algorithm will be developed to determine nutrients concentration (nitrates as leading indicator) using a satellite image. The project will provide multiple benefits to the environmental engineering field. The use of hyperspectral imaging in nutrients pollution control in estuaries will greatly improve non-point source pollution management practices currently employed at the local, regional and national levels. Accurate description of concentration, source contribution, seasonal variability and contaminants extent will not only provide detailed information related to the effect on the estuaries but also on the oceans to which it discharges, with potential deleterious effects on national and international waters. It will also be very useful on the development of a regional database for further investigation of other rivers or estuaries in Puerto Rico with the use of satellite image interpretation techniques.

11. Nature, scope, and objectives of the research

The San Juan Bay National Estuary System (SJBNES) is located in the northern coast of Puerto Rico contained within a drainage basin of 240 square kilometres (See attached figure). The estuary consists of the San Juan bay connected by a series of natural and dredged channels to four lagoons: Laguna del Condado, Laguna San José, Laguna La Torrecilla, and Laguna de Piñones. Point and non-point source water pollution is a potential threat to preserving the current environmental balance at the site and to the Atlantic Ocean, where the estuary discharges. Most of these pollution problems are associated with excessive nutrients loadings (i.e, nitrogen, ammonia, phosphorus) reaching the bay, particularly to the Laguna San José. Eutrophication conditions prevail at this site due to such excessive nutrients loadings. The presence of bacteria, such as *Nitrosomonas* and *Nitrobacter* in nitrification processes may serve as indicators of nutrients pollution in the SJBNES. It is of utmost importance to identify and use other monitoring alternatives to adequately measure seasonal nutrients contamination and its extent inside the SJBNES. The use of hyperspectral remote sensing is a state-of-the art procedure currently used to assess environmental pollution problems around the world. Hyperion is a hyperspectral imaging sensor that provides high spatial and spectral resolution and it has a tremendous potential to monitor nutrients contamination at a complex land ecosystem such as the SJBNES. The objective of this project is to design and validate a mathematical algorithm, based on the reflectance

characteristics of bacteria present in the nitrification process, to estimate nutrients contamination as monitored by Hyperion at the SJBNES.

12. Methods, Procedures and Facilities

(a) General

The SJBNES is located inside the San Juan metro area in the north coast of Puerto Rico. Several point and non-point sources pollution have been identified and represent a potential threat to the site in maintaining its environmental balance and protection of the local surviving species. During 1994 and 1995, the United States Geological Survey (USGS), in cooperation with the United States Environmental Protection Agency (EPA), and the Puerto Rico Environmental Quality Board (EQB), conducted water and sediments sampling survey on the SJBNES. While on certain section of the SJBNES the conditions have improved, there are still degraded conditions at the Caño Martin Peña and Laguna San José, the results of the survey reflected presence of toxic sediments deposited in the above surface water systems. Furthermore, anoxic and abiotic conditions persisted at both systems caused by stagnant water conditions with virtually no mixing during daily ocean tides events.

Monitoring of water pollution with satellite imaging will provide needed information related to the nutrients loadings along the SJBNES. Remote sensing techniques are appropriate due to the spatial and temporal complexity of the reserve's ecosystem. Another purpose of this study is to develop a new tool to monitor nutrients pollution that could be used in other estuaries.

(b) Satellite Sensor

Hyperion Hyperspectral Instrument (HIS) was developed by the National Aeronautics and Space Administration (NASA) and installed at NASA's EO-1 satellite. It provides a spatial resolution of 30 meters with a high spectral resolution (220 bands), ranging from the ultra-violet to the infra-red spectral bands (0.4 to 2.5 μm). Such variety in spectral bands is necessary to identify different vegetation species present inside a small area such as the SJBNES, particularly swamp lands (NASA, 2002), distinguish between the bay's bottom bed and brushes, and identify planted areas. Other sensor alternatives, such as Thematic Mapper (installed in the Landsat 7 satellite), have been considered. However, most of the available sensors have much lower spatial and spectral resolutions not useful for the SJBNES study due to the site's small area.

(c) Image Processing

ENVI software, developed by Research Systems, will be used to process and analyse the SJBNES images to be used for our study. ENVI provides needed geometric correction, terrain analysis, radar analysis, raster and vector Geographic Information System (GIS) capabilities. This software will be used to evaluate the hyperspectral images. Such software will be installed at the Geology Department Laboratory facilities where a significant amount of the study activities will be completed. The images required will be purchased from NASA, with minimum amount of clouds.

(d) Field Data

All terrain and water resources data will be obtained from available sources, such as the United States Environmental Protection Agency (USEPA), the United States Geological Survey (USGS), the United States Department of Agriculture's Natural Resource Conservation Service (NRCS), the National Oceanic and Atmospheric Administration (NOAA), the Puerto Rico Department of Environmental and Natural Resources (PRDENR), the Puerto Rico Environmental Quality Board (PREQB), and others. All satellite imaging related data will be obtained from NASA and NOAA, and others.

These data will be converted to ENVI format for processing. Any maps will be digitized into a GIS using digitizing tables available at the UPRM. The tables will be converted to dBase format and incorporated as GIS files using optical character recognition software (OCR), also available at UPRM. Digital data will be directly included as a separate file for processing by ENVI.

Field measurements of radiance and irradiance will be obtained with a spectroradiometer in order to calculate the remote sensing reflectance. These data will be used to validate and calibrate the spectral data of the image. It will be used to validate some of the estimated parameter as:

- Vegetation indices
- Surface albedo
- Sea surface temperature
- Chlorophyll-a

(e) Algorithm Development

The Hyperion images will be concurrently undertaken with *in-situ* sampling of the bay's waters for ammonia, organic nitrogen, nitrites and nitrates, and for determination of *Nitrobacter* and/or *Nitrosomonas* bacteria counts with locations identified by a field grid. It is anticipated that such locations will be at the SJBNES and at least two of the tributary lagoons. The field sampling will be

accomplished to test and validate the developed algorithm. Microorganism identification data will be statistically correlated with surface nutrients concentrations and with the spectral data obtained after image processing. Based on the above, a preliminary Hyperion algorithm for nutrients concentration will be defined using nitrates as a leading indicator.

(f) Time Table:

Task	Time Table (month)											
	1	2	3	4	5	6	7	8	9	10	11	12
Review and Evaluation of Existing Data	X											
Literature Search	X											
Visits and Contacts with Government Agencies	X											
Field Sampling		X		X		X		X				
Field Data Interpretation and Conversion			X		X		X		X			
Image Data Interpretation and Conversion				X	X	X	X	X	X			
Preliminary Development of Algorithm									X	X		
Test and Validation of Algorithm											X	X

13. Related Research

Barry, P; *“EO-1/Hyperion science data user’s guide, Level 1_B”*; TRW Space, Defense and Information Systems, Redondo Beach, CA, Rep HYP.TO.077; 2001.

Brando, V and Dekker, A.; *Satellite Hyperspectral Remote Sensing for Estimating Estuarine and Coastal Water Quality*; IEEE Transactions on Geoscience and Remote Sensing, Vol. 41, No. 6; June, 2003.

Catanzaro, D, Causey, B, Delaney, J.; *Status of Coral Reefs in the U.S. Caribbean and Gulf of Mexico: Florida, Texas, U.S. Virgin Islands, Navassa*; 2002, pg. 257.

De Haan, J.F and Kokke, J.M.; *“Remote sensing algorithm development toolkit 1: Operationalization of atmospheric correction methods for tidal and inland waters”*; Beleidscommissie Remote Sensing, The Netherlands, Rep 96-16; 1996

National Aeronautics and Space Administration; *NASA’s Earth Observing Satellite Proves a Success*; Public Release; 2002; www.eurekalert.org/pub_releases/2002-06/nsfc-neo062402.php.

Research Systems; *ENVI: From Images to Information*; 2003, www.rsinc.com/envi/index.asp.

San Juan Bay Estuary Program; *Comprehensive Plan for the Conservation and Management for the San Juan Bay Estuary*; San Juan, Puerto Rico; 2002.

Wharton, R.A. 1994; *McMurdro Dry Valleys LTER: An overview of 1993-1994 research activities*; Antarctic Journal of the United States- Review 1994, pp. 224-226.

14. Training Potential

FIELD OF STUDY	UNDERGRADUATE	MASTER'S DEGREE	PH.D. DEGREE	POST PH.D	TOTAL
Chemistry					
Engineering: Agricultural					
Civil	2		1		3
Environmental					
Chemical					
System (industrial)					
Other*	1				1
Geology					
Hydrology					
Agronomy					
Biology					
Ecology					
Social Science					
Computer Science					
Geography					
Law					
Resources Planning					
Other (Specify)					

TOTAL: 4

15. Investigator's Qualifications

PROFESSIONAL PREPARATION

1988-University of Puerto Rico at Mayagüez, Biology, B.S.

1992-University of Puerto Rico at Mayagüez, Marine Sciences, M.S.

1996-University of South Florida, Oceanography, Ph.D.

1997-University of Puerto Rico at Mayagüez, Remote Sensing, Post-Doc

APPOINTMENTS

01/02-Present	Assistant Professor, Department of Geology University of Puerto Rico at Mayagüez
08/03-Present	Director, Center for Hemispherical Cooperation in Research and Education in Engineering and Applied Science (CoHemis) University of Puerto Rico at Mayagüez
08/02-07/03	Co-Director, Center for Hemispherical Cooperation in Research and Education in Engineering and Applied Science (CoHemis) University of Puerto Rico at Mayagüez

08/92-12/96	Research Assistant in Remote Sensing Department of Marine Science, University of South Florida
04/90-07/92	Biological Assistant U.S. Fish and Wildlife Service, Caribbean Field Office
January 1991	Consultant to U.S. Geological Survey - Caribbean Office

SELECTED PUBLICATIONS

- Schellekens, J.H., **F. Gilbes**, G.D. Rivera, Y.C. Ysa, S. Chardon, Y. Fong. (2004) Reflectance spectra of tropical vegetation as a response to metal enrichment in the substrate of West-central Puerto Rico: Submitted to Caribbean Journal of Earth Sciences.
- Ramirez-Beltran, N.D., **F. Gilbes**, J.M. Castro. (2004) A stochastic-Dynamic Model to Predict Fecal Coliforms at the Mouth of the Añasco River, Coastal Environment V, Incorporating Oil Spill Studies. C.A. Brebbia J.M. Saval Perez, and L. Garcia Audion (Editors), WIT Press.
- Singh, H., R. Armstrong, **F. Gilbes**, R. Eustice, C. Roman, O. Pizarro, J. Torres (2004) Imaging Coral I: Imaging Coral Habitats With The SeaBED AUV, Subsurface Sensing Technology and Applications, 5(1):25-42.
- Gilbes, F.** and R. A. Armstrong (2004) Phytoplankton Dynamics In The Eastern Caribbean Sea As Detected With Space Remote Sensing. International Journal of Remote Sensing, 25(7-8): 1449-1452.
- Armstrong, R.A., **F. Gilbes**, R. Guerrero, C. Lasta, and H. Miazán. (2004) Validation Of SeaWiFS-Derived Chlorophyll For The Rio De La Plata Estuary And Adjacent Waters. International Journal of Remote Sensing, 25(7-8):1501-1505.

C. Identify the Information Transfer Plan

1. Define the subject matter and the problems to be addressed

Please refer to Section B-11.

2. Identify the target audience

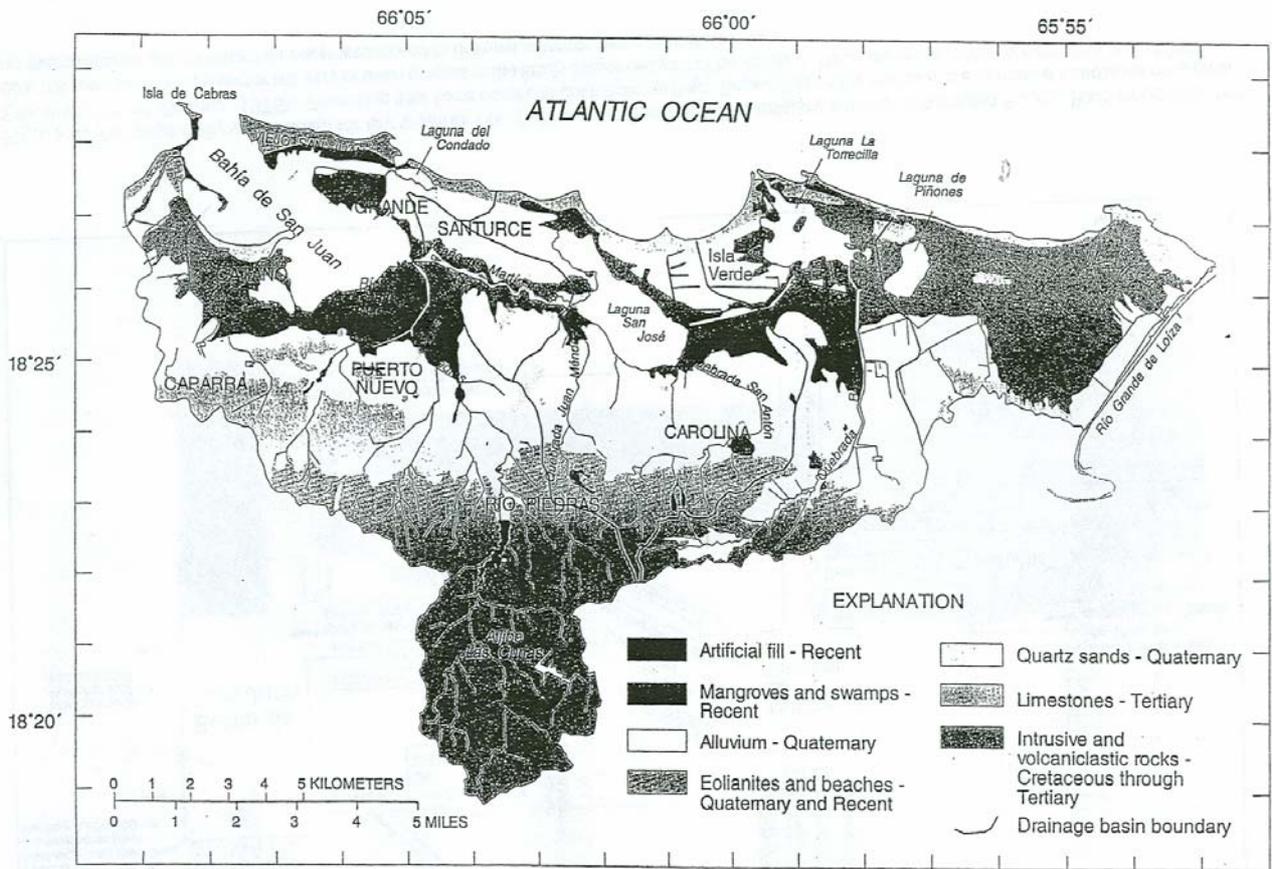
General public, academia, civic and community groups, local, national and international scientific population.

3. Indicate the strategies to be employed

Environmental workshops, seminars, peer reviews, scientific publications.

4. Identify the cooperators

University of Puerto Rico at Mayagüez (Department of Geology, Department of Civil and Environmental Engineering), United States Environmental Protection Agency, United States Geological Survey, Puerto Rico Department of Natural Resources, Puerto Rico Environmental Quality Board, San Juan Bay Estuary Program.



Use of Waste Tire Crumb Rubber to Remove Inorganic (Arsenic, Mercury) and Polycyclic Aromatic Hydrocarbons (PAHs) Species from Aqueous Solutions

Basic Information

Title:	Use of Waste Tire Crumb Rubber to Remove Inorganic (Arsenic, Mercury) and Polycyclic Aromatic Hydrocarbons (PAHs) Species from Aqueous Solutions
Project Number:	2006PR28B
Start Date:	3/1/2006
End Date:	2/28/2007
Funding Source:	104B
Congressional District:	
Research Category:	Water Quality
Focus Category:	Treatment, Toxic Substances, Water Quality
Descriptors:	
Principal Investigators:	Oscar J Perales-Perez, Felix Roman

Publication

1. Alamo, Luis, 2006, Sorption of ETX from aqueous solutions, MS Thesis, Dept. of Chemistry, UPR-Mayaguez, Mayaguez, Puerto Rico, 100 pages Nieto, Sorelis, 2006, Removal of antimicrobials from aqueous solutions, MS Thesis, Dept. of Chemistry, UPR-Mayaguez, Mayaguez, Puerto Rico, 140 pages
2. Alamo Luis; Perales, Oscar; Roman, Felix, 2007, Sorption of ethylbenzene, toluene and xylene onto crumb rubber from aqueous solutions Sorption of ethylbenzene and xylene in CLEANTECH, NSTI, Santa Clara, CA, p. 22-36.
3. Perales, Oscar; Roman, Felix; Alamo, Luis; Sanchez, Diana; Cruz, Jose, 2007, Evaluacion de nuevas opciones para reciclaje de goma, GACETA OF THE U OF PUERTO RICO AT MAYAGUEZ (V9, Y1, January '07) (in Spanish)
4. Perales, Oscar; Roman, Felix; Alamo, Luis; Sanchez, Diana; Cruz, Jose; 2007, Evaluacion de nuevas opciones para reciclaje de goma, DIALOGO (MAGAZINE OF THE UNIVERSITY OF PUERTO RICO). February '07.
5. Sanchez, Diana; Roman, Felix; Perales, Oscar 2007, Removal of Copper Ions from Aqueous solutions using waste tire crumb rubber as sorbent PRISM 2007, Cayey, PR (poster presentation)
6. Alamo, Luis; Roman, Felix; Sanchez, Diana; Perales, Oscar, Jose, 2007, Use of recycled crumb rubber to remove organic pollutants from aqueous solutions, PRISM 2007, Cayey, PR (poster presentation)
7. Torres, Heidy; Roman, Felix; Alamo, Luis; Perales, Oscar, 2007 Comparison between GC-MS Ion Trap, GC-MS Quadrupole and GC-FID techniques used in sorption studies of xylene onto crumb rubber, PRISM 2007, Cayey, PR (oral presentation)
8. Lopez, Jose; Nieto, Sorelis; Perales, Oscar; Roman, Felix; 2007, Sorption of Tetracycline onto waste tire crumb rubber, PRISM 2007, Cayey, PR (poster presentation)
9. Alamo, Luis; Sanchez Diana; Perales, Oscar; Roman, Felix, 2007, Use of recycled crumb rubber to remove inorganic and organic contaminants from aqueous solutions, EXPOCHEM 2007, Mayaguez,, PR (poster presentation)
10. Lopez, Jose; Nieto, Sorelis; Perales, Oscar; Roman, Felix, 2007, Sorption of Tetracycline onto waste tire crumb rubber, EXPOCHEM 2007, Mayaguez, PR (poster presentation)
11. Alamo, Luis; Sanchez, Diana; Roman, Felix; Perales, Oscar, 2007, Sorption of ethylbenzene, toluene and xylene onto crumb rubber from aqueous solutions, ACS 233rd National Meeting & Exposition, Chicago, March 25-29, 2007
12. Lopez, Jose; Sanchez, Diana; Alamao, Luis; Perales, Oscar; Roman, Felix, 2007, Removal of tetracycline, organic solvents and metal ions from from Aqueous solutions using waste tire crumb rubber as sorbent, USDA, Mayo 2007, Washington DC, (poster presentation)
13. Alamo, Luis; Perales, Oscar; Roman, Felix 2007, Sorption of ethylbenzene, toluene and xylene onto crumb rubber from aqueous solutions, CLEANTECH, Santa Clara, CA, May 24-25, 2007 (poster presentation)

Problem and Research Objectives:

Protecting water bodies from contamination is essential for health and safety. Typical inorganic pollutants are heavy metals that form highly soluble solid products (e.g., Hg), or no solid at all (As-oxyanions like arsenite and arsenate), after conventional alkaline precipitation. The limitations of conventional approaches become more evident at very dilute concentrations of contaminants as those observed in effluents from water treatment plants using conventional alkaline treatment, or ground waters polluted by hazardous species mobilized by leaching and/or percolation throughout soil substrates. Optional solvent extraction and ionic exchange systems are very expensive and they are tailored for high ion selectivity, which limits the removal of all contaminants in a single-step operation. In Puerto Rico, main problems of heavy metal pollution (e. g., Pb and Cd) have been reported in different types of effluents. The mercury pollution problem in Juncos and the presence of lead in some wells in Gurabo are also examples of the aquifers contamination issue.

Polycyclic Aromatic Hydrocarbons (PAHs) are a group of more than a hundred organic compounds composed of two or more carbon rings derived from benzene. These compounds have received a significant attention due to their suspected mutagenic and carcinogenic nature. PAHs arise mostly from incomplete combustion processes and are ubiquitous in the environment. The main outdoor sources of PAHs include combustion from gasoline and diesel engines, combustion of coal and oil for power generation, wood burning and incineration, among others. In turn, major indoors sources of PAHs include cooking, smoking, and burning of natural gas and incense. Indoor PAH concentrations in air as high as 1000 ng/m³ and 110 ng/m³ for 2 member rings-PAH have been reported in Japan and USA. It has been confirmed that PAHs can enter water directly from the air with dust and precipitation, or on particles washed from the soil by runoff. PAHs dissolved in water can be "taken up" by plants, and are released into soil and water when the plants die, decompose or are burned. PAHs can also be mobilized into the aquatic environment through discharges from industrial and domestic sewage effluents, leaks of PAHs-containing materials (e.g. oils), runoff from paved roads, parking lots, and the grounds of wood preservation plants, among other sources. Accordingly, the development of a low-cost, environmental friendly and efficient removal process for PAHs compounds from effluents (gas and water) becomes indispensable.

In the United States, approximately 240 million tires were discarded in 1990 on the basis of the tire industry's estimation (U.S. EPA, 1991) and it has been suggested that discarded tires reaches 10 billion every year, worldwide. In 2001, the United States generated approximately 273-million scrap tires. Although, markets now exist for 76% of these scrap tires –up from 17% in 1990- the remaining are still stockpiled, or land filled. On a local basis, over 4-million tires are discarded annually in Puerto Rico. It represents near to 15,000 tires per day, which makes the problem of solid waste management even more difficult to handle. Approximately 800,000 tires are reused each year, the remainder is land filled or illegally dumped. Stockpiled scrap tires pose potentially serious health and safety problems. Whole tires served as breeding grounds for diseases carrying mosquitoes and rodents. Also, tire piles are fire hazards and, once ignited, they can burn out of control for months, producing acrid black smoke and a hazardous oily residue. Widespread illegal dumping poses the same problem associated with stockpiling. Thousands of abandoned scrap tires are found in streams, rivers and roadsides throughout the Island. The mismanagement of millions of scrap tires every year represents a significant waste of resources. A very recent example is the case of the 8,000 tons of chopped-up tires in the barge docked in Guayama since July 23rd, 2002, a problem without a definitive solution, at least in the short term.

Based on the above premises, the search of alternatives to expand the re-use possibilities for waste tires sounds justified. The present proposal addressed the systematic evaluation of crumb rubber as a suitable material to remove extremely toxic PAHs compounds from aqueous solutions through a low-cost and easy-to-scale technology based on the sorption properties of this waste

material. The present remediation option is based on the presence of carbon black, zinc oxide, and sulfur in crumb rubber, with potential capability to absorb/adsorb hazardous species from water or gaseous streams. This fact has been verified in preliminary results reported in our previous works where the very efficient removal of inorganic Cu(II), Cd(II) and Pb(II) as well as organic BTEX (ethylbenzene, xylene, toluene) species have been demonstrated. Sorbent waste tire crumb rubber will be kindly provided by Rubber Recycling and Manufacturing Corp., REMA, a Puerto Rican company that produces crumb rubber at different particle sizes from scrap tires.

Accordingly, the present proposal dealt with the detailed study of the sorption capability of waste tire crumb rubber for PAHs compounds, e. g. naphthalene, among others, of environmental concern. We proposed to investigate the conditions leading to maximization of uptake capacity and sorption rate, a factor of critical importance to determine the potential use of the proposed sorbent on a large scale remediation application.

Methodology:

Methods and Procedures

Granular crumb rubber, screened at different mesh sizes, was provided by REMA Corp. a tire rubber recycling company located in Caguas, Puerto Rico.

1 Chemical stability of granular crumb rubber

The behavior of crumb rubber in aqueous solutions at different pH values and particle sizes has been evaluated already. It has been verified that crumb rubber do not release any toxic inorganic species into the aqueous phase.

2 Sorption tests in aqueous phase

The basic set-up for the sorption tests includes temperature-controlled water shaker baths, stirrers, pH-meters and filtration systems, drying ovens and GC/MS and LC/MS systems, currently available in Roman's laboratory. The term sorption here is used to include both adsorption, which refers to the retention of solutes by the surfaces of a solid material, and absorption, which refers to the retention of the solutes within the polymeric matrix. Sorption processes result from physical, chemical and electrostatic interactions between the solid surfaces and the sorbate.

In PAHs sorption tests screw cap vials with Teflon-lined septa were used instead of common glass beakers and agitated on a hematological mixer until equilibrium will be reached. In order to minimize vapor loss and allow a suitable mixing, the head space in the vial after addition of the sorbent and sorbate, was kept at approximately 1 ml. HgCl₂ was employed as a biocide to avoid degradation of the organic compounds by bacteria or fungi. Vials will be samples periodically and analyzed for PAHs. Solid Phase Microextraction (SPME), GC/MS and LC/MS were used to determine the concentration of the PAH in the initial solution and at the end of the sorption stage. During the first step of the experimental work, the sorbent was contacted with solutions containing single species. The results of the experimental work permitted to determine the equilibrium uptake, sorption rates, and removal efficiency.

Principal Findings and Significance:

Once the optimum conditions for the quantitative determination of PAHs by the GC-MS techniques were determined, our experimental work was focused on the evaluation of the sorption behavior of the following PAHs: phenanthrene (PN), acenaphthylene (ACN) and acenaphthene(ACNP) from aqueous solutions under room-temperature conditions. In order to minimize any loose of the PAHs by volatilization, all experiments were carried out at a fixed concentration of PAHs (500 ppb for PN and 900 ppb for CAN and ACNP).

The solution pH was kept constant at 6.0. The concentration of crumb rubber (mesh 14-20) was varied between 0.03 g/L and 10 g/L in all tests. The terminal concentration values (i.e., the concentration at the equilibrium) were used to determine the removal efficiency of the crumb rubber. Experimental values were fitted to Langmuir and Freundlich isotherms. In general, the sorption behavior of all systems was well described by Freundlich's equation.

The higher concentrations of crumb rubber (10 g/L and 5 g/L) allowed both, the highest removal efficiencies and extremely short contact times. For instance, 99.2% and 98.8% of PN was removed at the end of 30 minutes of contact for 10 g/L and 5 g/L of crumb rubber, respectively. The corresponding terminal concentrations were 4.2 ppb and 5.8 ppb. The equilibrium conditions were achieved only after 28 hours when the concentration of crumb rubber was 0.01 g/L. The removal efficiency was 77% (114 ppb of PN in the final solution). The experimental data were well fitted by Freundlich equation ($r=0.988$).

In the case of CAN, two hours were required to achieve a 95% removal when the crumb rubber concentration was 10g/L. The removal dropped to 55% (20 hours of contact) when 0.03 g/L of crumb rubber was used instead. Again, the terminal concentration were well fitted by both Langmuir ($r=0.9994$) and Freundlich ($r=0.9969$) isotherms.

Crumb rubber was also an excellent sorbent to remove ACNP from aqueous solutions. The terminal concentration of ACNP was as low as 18 ppb (from starting 900 ppb ACNP solutions) after 2 hours of contact and 10g/L of crumb rubber. The corresponding removal efficiency was 98%. Only 76% of starting ACNP was removed after 20 hours when 0.03 g/L of crumb rubber was employed. Langmuir ($r=0.9769$) and Freundlich ($r=0.9854$) equations fitted experimental data very well.

Based on the above comments, the capability and efficiency of waste tire crumb rubber (mesh 14-20) to remove the selected PAHs compounds have been experimentally verified. Obtained results suggest that crumb rubber can be considered an excellent sorbent to clean-up aqueous effluents polluted by PAHs compounds. Ongoing work will address the evaluation of the sorption behavior under competitive conditions (co-existence of two and three PAHs compounds in the same solution) in batch and continuous (column) tests.

DISSOLVED OXYGEN DYNAMICS IN TWO RESERVOIRS OF CONTRASTING TROPHIC STATUS IN PUERTO RICO

Basic Information

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Publication

1. Fernando Pantoja, 2007, Dinámica fisicoquímica y fitoplanctónica del embalse Guajataca, MS Thesis, Department of Biology, UPR Mayaguez, 190 pages.
2. Sotomayor-Ramírez, D. G.A. Martínez, L. Pérez-Alegría 2006. Nutrient management for improved agricultural production and environmental quality. Invited presentation at EXPOCHEM, November 2006. Mayagüez, PR.
3. Sotomayor-Ramírez, D. G.A. Martínez, L. Pérez-Alegría, C. Santos. 2007. Seasonal pattern of dissolved oxygen and stratification in two tropical reservoirs. 30th Congress of the International Association of Theoretical and Applied Limnology. Montreal Canada, August 12 to 18, 2007. <http://www.SIL2007.org/> (projected)
4. Pantoja F., C. Santos, D. Sotomayor-Ramírez, and G.A. Martínez. Physicochemical and planktonic dynamics in a tropical reservoir. 30th Congress of the International Association of Theoretical and Applied Limnology. Montreal Canada, August 12 to 18, 2007. <http://www.SIL2007.org/>

Problem and Research Objectives:

Low dissolved oxygen (DO) has been identified as the cause of impairment in the principal reservoirs of Puerto Rico (PREQB, 2002). A proper understanding of the DO dynamics in reservoirs cannot be drawn from historical water quality data gathered in reservoirs by public agencies in Puerto Rico because measurements have been rather sporadic in a temporal and spatial scale (3 months apart in the best cases), in very rare occasions have these measurements consisted of depth profiles which could provide some insight as to the factors controlling DO dynamics, and concentrations have not been related to other water quality parameters. The eutrophic conditions due to inputs of sediments and nutrients were identified as the primary reason for the lakes not meeting the water quality standard for DO, yet the waters did not exceed the numeric standards for nutrients (PREQB, 2003). Numerical nutrient reference values for reservoirs of Puerto Rico suggests that the majority exhibit some impact from anthropogenic activities, with six classified in the mesotrophic category, twelve in the eutrophic category and one in the hypereutrophic category (Martínez et al. 2005).

The variations in trophic status across lakes can vary due to non-point source inputs, in-lake geomorphologic characteristics, and circulation patterns due to variations in thermal stability, that will affect DO content and dynamics. Most reservoirs consistently exhibit anoxia at some depth, which causes a significant drop in water column average values. It is unclear whether this is a natural phenomena characteristic of tropical systems or whether is a result of water impairment and thus require remediate actions to be implemented. There is substantial evidence that suggests that tropical reservoirs, even oligotrophic reservoirs, commonly experience temporal hypolimnion anoxia (Townsend, 1996). If this is the case in Puerto Rico, the USEPA criteria of 5 mg DO/L would have to be modified to be more sensitive to natural conditions. There appear to be substantial differences in DO dynamics between tropical reservoirs and temperate systems (Townsend, 1998; Townsend, 1999; Lewis, 2000) which demands a thorough characterization of tropical lake behavior prior to adopting management guidelines developed in temperate areas. The effect of stratification, short-term variations in DO concentrations, as well as the elucidation of natural conditions leading from hypoxic to anoxic conditions must be considered.

This on-going study is characterizing the DO dynamics in two reservoirs as a first step towards the future establishment of DO criteria for Puerto Rico and for providing baseline data for modeling DO dynamics in Puerto Rico. The overall objectives are to assess the limnological conditions of selected reservoirs as a means to provide a benchmark to gauge future change and by which to anticipate water quality management. The specific objectives are to:

- 1) Characterize the circulation and stratification status of two reservoirs, for determination of the degree of hypolimnetic anoxia.
- 2) Establish cause-effect relationships between causative (temperature, light, nutrients) and DO concentrations in the reservoirs.
- 3) Relate DO concentrations to variables relating lake productivity, nutrient dynamics, reservoir stratification, and morphometric criteria.

Methodology:

Study sites: Two stations have been established at damsite within Lago Guajataca and Lago Cerrillos (Table 1). Two additional stations were later added which consisted of the transitional zone in Lago Cerrillos and the entrance of Lago Dos Bocas. We have opted to modify the original sampling strategy which was to sample Lago Dos Bocas. We hypothesized that the large sediment loads entering that lake during runoff/storm events would confound interpretation of the data and evaluation of dissolved oxygen dynamics within the water column. Sediment blocks sunlight from reaching deeper depths of the water column thus primary production limitation is due to sediments and not algal biomass within the lake. In addition, the high sediment oxygen demand rates that may be exhibited in that lake may difficult the elucidation of natural mechanisms governing dissolved oxygen dynamics in tropical reservoirs. A preliminary survey of Lago dos bocas will be performed on 26 June 2007.

To date, eleven samplings have been performed in Guajataca and nine samplings have been performed in Cerrillos (Table 2). We expect to study Lago Cerrillos and Guajataca through July 2007, and will be making and will be making sporadic visits to Lago Dos Bocas.

Instrumentation and water quality data collection: Climatic variables for each lake are being gathered from corresponding climatologic stations administered by USGS, which include: mean daily temperature, daily precipitation, wind velocity, reservoir height. Water samples were collected with a 1-L Van Dorn sampler at (i) surface (i.e. approx. 20 cm from the surface), (ii) 1 m depth and (iii) at the extinction coefficient depth ($1.7 \times SD$) (Wetzel, 2001), and decanted to acid-washed polyethylene bottles. On 15 and 16 November 2006, sampling was performed within selected depths of Lago Cerrillos and Lago Guajataca, respectively. Samples were transported in ice coolers ($<6^{\circ}C$) to the Soil and Water Chemistry Laboratory at the University of Puerto Rico – Mayagüez Campus. A 250 mL portion of the sample was acidified with H_2SO_4 to $pH < 2$ and stored frozen; a second 250 mL portion was filtered through glass-fiber filter for Chlorophyll-a analysis using Turner TD-700 Model fluorometer; and a third 250 mL portion was used for metal analysis or stored frozen in reserve.

Turbidity was quantified in the laboratory with a LaMotte portable turbidity meter. The parameters quantified were: total Kjeldahl nitrogen (TKN) (EPA method 351.2), dissolved nitrate (NO_3) (EPA method 353.1), total phosphorous (TP) (EPA method 365.4), dissolved phosphorus (DP) (365.2) and chlorophyll “a”(EPA method 445.0). Nutrients quantified in dissolved form were filtered through a $0.45 \mu m$ membrane. All nutrients were quantified using a BRAN+LUEBBE Ion Auto-Analyzer. Metals were quantified in water samples on selected dates (November profiles) and depths by Univ. of Georgia Soil, Plant and Water Testing Laboratory (<http://aesi.ces.uga.edu/>).

In situ measurements were pH, electrical conductivity, dissolved oxygen, water temperature, photosynthetically active radiation, and oxidation-reduction potential with a CTD-12 multiparameter probe (Applied Microsystems Inc.; Sidney, BC, Canada). The deployment depth was calculated after correcting the actual pressure for atmospheric pressure using the equation by Wetzel (2001, p. 152). The measured redox potentials were converted to potential in the system relative to standard H_2 electrode ($E_{h,actual}$) and corrected for pH and temperature. Electrical conductivity were expressed as that at $25^{\circ}C$

(Radtke et al. 1998). Parameters were gathered in 1m intervals to the bottom in descending and ascending manner. All sensors were checked for proper functioning in the laboratory, prior to field sampling and calibrated as needed. Water transparency (Secchi depth) were determined with a 20-cm disk with alternating black and white quadrants in the shaded side of the boat.. Lake depth at the sampling point was determined with a marked tag-line.

The thermocline was determined from the maximum rate of change of temperature with depth and the top and bottom of the metalimnion was determined from the second derivative of the rate of change in temperature at two consecutive depths. The hypolimnetic volume was determined from the bottom of the metalimnion to estimated in-lake median depth. Hypolimnetic volume-weighted dissolved oxygen (VWDO) concentration were calculated from dissolved oxygen concentration and corresponding depth related water volume. The DO per unit area were computed from VWDO, hypolimnion depth and estimated hypolimnion area (Burns, 1995; Pelletier, 1998).

Principal Findings and Significance

Lake characteristics: Lago Guajataca has a greater drainage and lake area, but lower mean depth than Cerrillos; hence the latter has a greater volumetric capacity (Table 1). We hypothesize that Cerrillos has a greater proportion of anoxic sediment overlain by lake water hypolimnetic volume (hypolimnetic volume / mean anoxic sediment area) than Guajataca. Also, sediment load to Guajataca has historically been greater than in Cerillos. These two indicators suggest that the bottom sediments in Guajataca play a much more important role in recycling nutrients to the water column which could be used by phytoplankton during lake turnover (meromixis or holomixis).

Epilimnetic water quality characteristics: Sechi disk depths ranged from 1.5 to 4.0 m and from 1.8 to 3.0 m in Lago Guajataca and Cerrillos, respectively. Chlorophyll-a values (0 to 1 m) ranged from 2.5 to 5.8 $\mu\text{g/L}$ from August 2006 to February 2007 in Guajataca, after which a large flush in chlorophyll-a values were observed on March 2007 (Figure 1). Values tended to be higher in the entrance than in the damsite of Guajataca. A similar pattern was observed in Cerrillos, but the peak in chlorophyll-a concentration in March 2007 was not as large. The peaks in chlorophyll-a values were coincident with those observed for turbidity (Figure 2), yet in general there was a poor association between chlorophyll-a and turbidity.

Similar nutrient (N and P) concentrations as those quantified by Martínez et al. (2005) were observed during the sampling period for both lakes.

Lake profile water quality characteristics: A depth profile taken on 14 November 2006, in Lago Cerrillos, showed that Chlorophyll-a increased from the surface to 6 m depth and thereafter did not change with depth increase. Profiles taken on February and March 2007, during the expected period of overturn, showed that maximum chlorophyll-a concentrations occurred from the surface to about 8 m, with higher values on the March 2007 sampling. On 16 November 2006, in Lago Guajataca, chlorophyll-a concentrations increased with depth from the surface and peaked at 8 m, thereafter decreasing with depth. On the February sampling in Guajataca, maximum chlorophyll-a

concentration was at 1 m. Profile concentrations increased for the March sampling, with maximum values of between 21 and 34 $\mu\text{g/L}$ at between 1 and 4 m depth. A preliminary *in-situ* chlorophyll-a profile taken on 13 December 2006 in Lago Guajataca (E. Otero) revealed that the maximum depth of chlorophyll-a had moved deeper to between 10 and 12 m. In both lakes, turbidity increased with depth with maximum values at about 12 m being 2x surface values (2 NTUs). 10% of the maximum photosynthetically active radiation did not exceed seven meters in both lakes.

In general, water pH increased from the surface to near the metalimnion and then decreased with depth, with values being slightly greater in Guajataca (Figure 3 and Figure 4). This trend is consistent with water quality profile data gathered during November 2006 which showed that Lago Guajataca had greater water hardness (mean of 36.1 vs. 124.1 meq/L for Lago Cerrillos and Guajataca, respectively), Ca, Mg, K, Na, and Si concentrations than Lago Guajataca. Only total Fe and Mn appeared to consistently increase with depth in Lago Guajataca, and did not occur in Lago Cerrillos. Electrical conductivity values generally increased slightly with depth and were generally higher in Lago Guajataca (Figures 3 and 4).

Lago Guajataca was strongly stratified between 6 and 7 months of the year, from April to November. There was a weak stratification for the months of December, February and March (Figure 5). The bottom of the metalimnion ranged from 4.8 to 7.1 from August to December, which in the latter time period evidences the initiation of mixing within the water column (Table 4). Evidence for the formation of the thermocline was again observed on 30 April 2007. The stratification in Lago Cerrillos was not as strong as that in Lago Guajataca, with delta temperature values less than 1°C (Figure 6). Stratification was stronger for the months of April to September (approximately 5 months) and weak during October and November. We estimate that there was no stratification from December to March, and were taken as the months of holomixis or meromixis.

The rate of mixing in Lago Guajataca was apparently much slower because by December complete mixing had occurred in Lago Cerrillos, yet in Lago Guajataca it was still on-going (probably due to the fact that Guajataca experienced much higher epilimnion temp and that temperature gradients (epilimnion vs. hypolimnion) were much higher at Guajataca than at Cerrillos).

Dissolved oxygen concentrations generally decreased with depth, at both sites but were always at or above saturation values throughout the epilimnion and the top part of the metalimnion. DO concentrations sharply decreased to less than 10% saturation values in the hypolimnion and in most instances thereafter were effectively zero (< 1 mg/L) (Figures 7 and 8). A similar pattern was observed in Lago Cerrillos except once complete overturn occurred (15 December 2006), concentrations ranged from 87 to 45% throughout the water column to 22 m depth. The oxidation-reduction potential patterned DO patterns during the epilimnion and metalimnion with the redox-cline occurring well below DO minimum (Figures 7 and 8). This is reflective of the presence of alternate redox couples in the absence of oxygen, and further exhaustion of these with increasing depth (Figure 3b and 3d). Volume weighted DO concentrations in Lago Guajataca ranged from 1.3 to 3.8 mg/L, which indicates that the lake does not meet PREQB water quality standards of 5 mg/L. Volume weighted DO concentrations in Cerrillos ranged from 2.6 to 5.9, and was in violation of PREQB standards on selected dates.

Hypolimnetic oxygen content and dynamics: Burns (1995) has shown that estimated hypolimnetic oxygen consumption rates are unrealistically low when DO concentrations fall below 2 mg/L because the DO depletion rates are first order with respect to oxygen concentrations. In Guajataca, 90% of all of the volume-weighted hypolimnetic concentrations measured were below 2 mg/L, so that the computed data may not adequately serve to compare to other lakes, nor to quantitatively show the relationship between oxygen depletion and trophic state of the two lakes evaluated. The hypolimnetic DO concentrations in Guajataca were always less than 1 mg/L. The profile taken on January revealed that DO concentrations persisted to between 1 and 4 mg/L well below the expected thermocline, but concentrations were exhausted by the next sampling date increased in the hypolimnion.

In Cerrillos, a strong oxycline occurred for the months of September to November and in May. At all other times, there were variable hypolimnetic DO concentrations. Hypolimnetic concentrations generally were less than 2 mg/L until November. An increase in hypolimnetic DO concentrations was observed on December and persisted until February after which concentrations were exhausted by the May sampling. Further refinements in DO volumetric contents will be made by obtaining detailed bathymetry data, such that the water volumes corresponding to each of the hypolimnetic depths can be estimated more accurately. Work is also underway to estimate the degree of stratification by quantification of lake water column stability.

Information Transfer Program

The PRWRERIs Information Transfer Plan included the publication and dissemination of final reports of sponsored projects, announcements and distribution of these reports, and quarterly newsletter containing information of interest to the islands community of water resources professionals. The Institute maintains a catalog listing the titles of every research report it has published. This catalog can be accessed at our WebSite. Copies of the old original research reports are also available for a nominal charge covering the cost of reproducing and shipping. Other reports are being made available to the public, free of charge, through our web page.

The Institute has updated the hardware for its server and has engaged in a digitalization project, where older research report, and other published material, has been made available to the general public through the Internet. It has become standard procedure to publish every research project in our Web Page. A web-master maintains and expands the web site of the PRWRERI as necessary. The internet address is <http://www.ece.uprm.edu/prwrri>.

The Institute has developed an agreement with a professional organization (PR section of AWWA). The Memorandum of Understanding (MOU) has been signed. This MOU allows the Institute to share technical information with a bigger audience and to have a real presence among this group of professionals. Annual meetings are held where the Institute is invited as exhibitor and to present their research findings.

Training and education is gaining more importance in Puerto Rico, the Caribbean, and Latin America. The Institute updated, and expanded the short course offering of its professional development program. A new course was added and offered in January, 2007. The course titled Sampling and Testing for Indicator Organisms (Total Coliform/E.coli/Enterococci) in Fresh and Sea Waters was created with EPA sponsorship.

Student Support

Student Support					
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	3	0	0	0	3
Masters	10	0	0	0	10
Ph.D.	1	0	0	0	1
Post-Doc.	0	0	0	0	0
Total	14	0	0	0	14

Notable Awards and Achievements

Publications from Prior Projects