Quality Assurance Project Plan

for

Assessment of Water Quality and Efficacy of Water Treatment Infrastructure in Southwestern Puerto Rico

Prepared by:

University of Puerto Rico, Agricultural Experiment Station

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Prepared for:

The US Environmental Protection Agency

Gulf Ecology Division

Gulf Breeze, Fl

A. Project Management

A1. Title and Approval Sheet

Assessment of Water Quality and Efficacy of Water Treatment Infrastructure in Southwestern Puerto Rico

Title	Name	Signature	Date
QAPP Manager, Project Manager	David Sotomayor-Ramírez		
Quality Assurance Officer	Gustavo Martínez		
Quality Assurance Coordinator	Luis R. Pérez-Alegría		
USEPA Program Manager			
USEPA Quality Assurance Officer			

A2. Table of Contents

List of Appendices

A3. Distribution List

The following individuals and organizations will receive a copy of the Assessment of Water Quality and Efficacy of Water Treatment Infrastructure in Southwestern Puerto Rico / Citizen Monitoring Program, approved Quality Assurance Project Plan (QAPP) and any subsequent revisions.

David Sotomayor-Ramírez	Professor, University of Puerto Rico, Mayagüez
Gustavo A. Martínez	Research Professor, University of Puerto Rico, Agricultural Experiment Station, Río Piedras
Luis Pérez-Alegría	Professor, University of Puerto Rico, Mayagüez
José Amador	Professor, University of Rhode Island
Judith Conde	Extension Professor, University of of Puerto Rico, Mayagüez
Dave Bachoon	Professor, Georgia College and State University, Milledgeville, GA
Carlos Ortiz	Associate Dean of Research, University of Puerto Rico, Agricultural Experiment Station

A4. Project / Task Organization

Title	Name	Institution	Responsibility
Professor UPRM / Project Manager and PI	David Sotomayor-Ramírez	University of Puerto Rico, College of Agric. Sci., Crops and Agro-environmental Sciences Department PO Box 9000 Mayagüez, PR 00681-9000 david.sotomayor@upr.edu 787-832-4040 x5819	Direct and coordinate project activities: field sampling, scheduling, laboratory analysis, data management, statistical analysis, report/ publication preparation, administrative management.
Research-Professor, UPRM / QA Officer	Gustavo Martínez	University of Puerto Rico, College of Agric. Sci., Crops and Agro-environmental Sciences Department 787-767-9705 x2243 tavomarti2011@gmail.com	Lead the laboratory analysis for nutrients, project QAPP, study design, training of volunteers and mentors, report/ publication preparation.
Professor, UPRM / QA Coordinator	Luis R. Pérez-Alegría	University of Puerto Rico, College of Agric. Sci., Agricultural and Biosystems Engineering Department luisr.perez1@upr.edu 787-832-4040 x 3337	Lead in selection of sampling sites, spatial analysis and GIS, process spatial data, study design, training of volunteers and mentors, report/ publication preparation.
Professor URI / Collaborator	José Amador	University of Rhode Island Laboratory of Soil Ecology and Microbiology 024 Coastal Institute – Kingston Kingston, RI 02881 USA 401 874 2902 jamador@uri.edu	Study design, report/ publication preparation.
Professor GSU / Collaborator	Dave Bachoon	Department of Biological and Environmental Sciences, Georgia College and State University, Campus Box 81, Milledgeville, GA 31061-0490, USA	Lead analysis of microbial markers
Extension Professor, UPRM / 4-H Volunteer Coordinator	Judith Conde	University of Puerto Rico, College of Agric. Sci., Agrucultural Extension Service. 787-617-2081 judith.conde@upr.edu.	Will lead and coordinate the participation of volunteers in sampling activities
UPRM / Field Sampling Leader		University of Puerto Rico, College of Agric. Sci., Crops and Agro-environmental Sciences Department	Under the direction of the QAPP Manager, lead all field sampling, field data gathering, equipment maintenance, laboratory support for microbial sample preparation.
UPRM /	Hector Torres	University of Puerto Rico, College	Carry out field sampling,

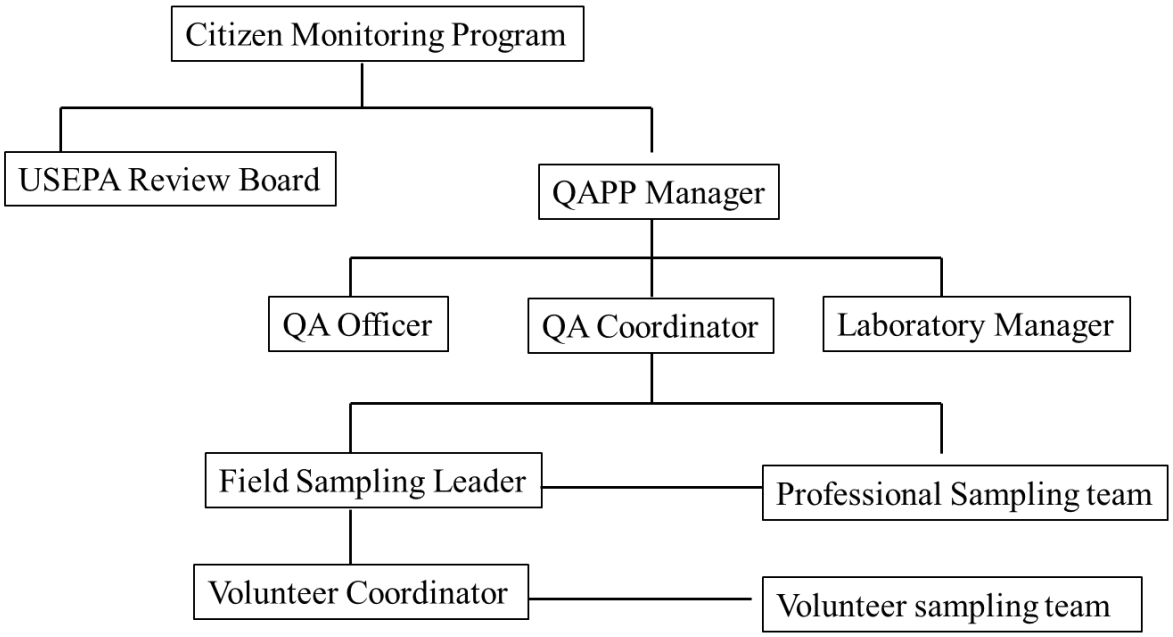
Title	Name	Institution	Responsibility
Research Assistant		of Agric. Sci., Crops and Agro-environmental Sciences Department	field data gathering, equipment maintenance, laboratory support for microbial sample preparation, data entry.
UPRM Research Assistant	Rosario Gaud	University of Puerto Rico, College of Agric. Sci., Crops and Agro-environmental Sciences Department	Carry out microbial analysis of water samples, data entry.

The QAPP Manager will be responsible for the overall implementation of the QAPP, allocate necessary resources to meet the project objectives, distribute sampling results, and ensure that technical and schedule objectives are met (Figure 1). The QAPP Manager is responsible for correspondence with USEPA and external groups, including agencies responsible for approving the QAPP and the users of the collected data.The QAPP Manager will resolve any procedural deficiencies identified during the data audits. The QA Officer, and QA Coordinator, and Field Sampling Leader will report to the QAPP Manager.

The QA Officer is responsible for reviewing the data relative to the Data Quality Objectives presented in Section 7. The QA Officer will revise the QAPP, document and report any data quality problems related to the Data Quality Objectives to the QA Coordinator and QAPP Manager. Also, the QA Officer will conduct evaluation of field activities and prepare audit reports, assess whether the laboratory and field sampling protocols are followed as mandated by the QAPP, and monitor laboratory compliance with this QAPP while overseeing verification activities. The QA Officer will also perform in house audit of field operations. The QA Coordinator is responsible for providing leadership and support in managing volunteers, equipment, and laboratory needs related to the water quality monitoring program. The QAPP Coordinator will ensure the QAPP implementation.

The Field Sampling Leader reports to the QAPP Manager and manages sampling trip-specific needs including volunteers' availability, training, equipment care, calibrations, and equipment preparation. The primary user of the data collected will be the University of Puerto Rico, Agricultural Experiment Station, as one of the Environmental Indicators Program components. Other users include, but are not limited to, the PR Environmental Quality Board, PR Department of Agriculture, PR Department of Natural Resources and Environment, PR Aqueduct and Sewer Authority, US Environmental Protection Agency, and stakeholders.

Figure 1. Citizen monitoring project organizational chart.



A5. Project Definition / Background

High concentrations of nutrients, fecal microorganisms, and sediments in surface waters can be a public-health threat and can negatively impact inland and coastal waters for designated uses. High levels of nutrients in a water body promote excessive algae growth which may eventually lead to eutrophication. Eutrophic conditions have adverse health effects on humans and animals; interfere with recreation, affect the population and diversity of insects and fish, and promote the growth of unsightly macrophytes, phytoplankton and periphyton. Major anthropogenic sources of nutrients are agricultural runoff, urban runoff, leaking septic systems, sewage discharges, and eroded streambanks (USEPA, 2009). A water quality assessment of wadeable perennial streams reported that nutrients followed by sediments were the primary contaminants of rivers and streams in the USA (USEPA, 2013).

In contrast, the 2008 water quality inventory of Puerto Rico reported that pathogens, arsenic, turbidity and dissolved oxygen were the primary causes of surface water quality impairment (PREQB, 2008). In general, the anthropogenic sources of pathogens are sewage treatment plant effluents, waterfowl, water runoff from fields with animal husbandry activities, and leaking septic systems. Reduction of pathogen presence in surface waters is important to prevent human disease and ecosystem degradation. Yet, there are numerous examples in which concentrations of enterococci as fecal indicators of contamination (FICs) have been determined in lakes, streams and drainage channels of both urban and rural areas in Puerto Rico (Sotomayor-Ramírez et al. 2006; Amador et al. 2008; Toledo-Hernández et al. 2013).

The Lajas and Guánica areas of southwestern Puerto Rico are important areas of study as more than 60,000 acres of land-area are hydrologically connected to an inland bay (Guánica Bay) and to fringing coral reefs. The area has a mix of urban, suburban and rural uses of which only selected urban communities are primarily connected to a sewage treatment infrastructure. The remaining areas use on-site disposal (septic systems) that may or may not be faulty or illegally discharge onto drainage channels or small streams. Insufficient or ineffective wastewater treatment is a threat to both public health (human pathogens) and aquatic resources (nutrients).

The coastal areas of Guánica Bay have been recently characterized in terms of fish communities, heavy-metal concentrations, nutrients, FICs, and pesticides (Whitall et al. 2013). The major findings by Whitall et al. suggest that a myriad of anthropogenic, industrial and agricultural factors may be contributing biological and chemical contaminants[1] in coastal waters. Management activities in upland watersheds of Guánica Bay may in the long-term improve coastal water quality and these can serve as examples for future management actions that can be implemented in other areas of Puerto Rico and the Caribbean.

The US Environmental Protection Agency (US EPA) through the Clean Water Act is entrusted to ensure that surface waters and aquatic ecosystems protect human health, support economic and recreational activities, and provide habitat for fish, plants, and wildlife. A high priority for USEPA's Office of Research and Development (ORD) is healthy, sustainable communities. Thus, USEPA through its Sustainable and Healthy Communities Research

[1] Contaminant refers to a substance that is at a concentration higher than would normally occur, but does not necessarily mean that it is causing any harm. Pollutant refers to a substance at a concentration that is higher than would normally occur, but it is causing harm of some type (Pierzinsky et al. 2005).

Program (SHC) is supporting research efforts that will characterize the efficacy of public sanitation infrastructure and that will provide tools and information that will lead to improve the quality of life (wellbeing). The University of Puerto Rico, College of Agricultural Sciences is collaborating with EPA, through this research, in accord with its mission to "Contribute through education, research and outreach to the sustainable and competitive development of agro-industrial activities and the natural resource conservation"[2].

There is a need to identify the extent of contamination with nutrients and fecal indicators of contamination (FICs), and to create awareness among local communities of their water quality status. These are first steps towards eventually developing mechanisms for surface and coastal water quality improvement. Preliminary work by our group in the Lajas Valley has shown that of 29 samples collected in three time intervals, all had enterococci concentrations exceeding 35 colonies/100mL (P.R. legal standard). Surface water quality tended to improve with distance from the source of the drainage channel which was the irrigation channel (point farthest northwest). There was poor correlation with nutrients, suggesting possible die-off of bacterial enterococci or that nutrient concentrations were being influenced by sinks (P sediment sorption-precipitation, N loss by volatilization and denitrification, or microbial uptake of N and P) (Figure 2). The proposed project will further examine the presence of nutrients, fecal indicators, and heavy metals, and examine potential relationships with land use in the area. The overall objective of the proposal is to increase public awareness of sanitation issues in the watershed that, in the long term, will lead to improved water quality conditions in the Lajas Valley and Guánica/Río Loco watersheds.

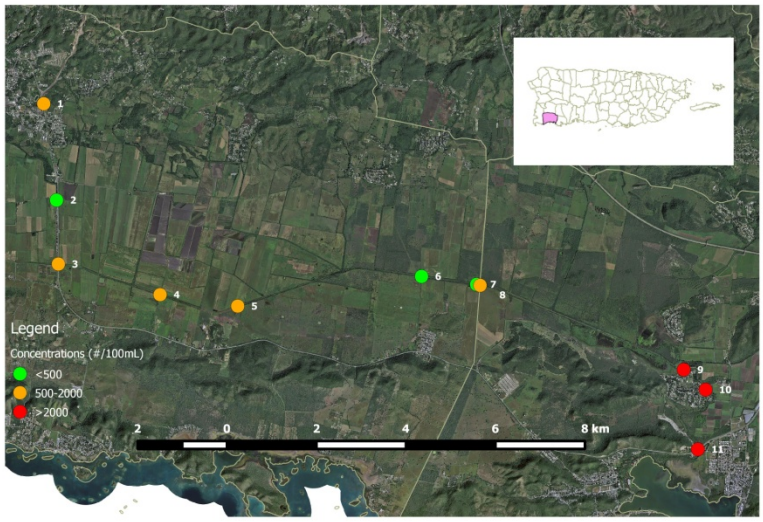


Figure 2. Means of enterococci in drainage waters of the Lajas Valley watershed and Río Loco in three sampling events from February to April 2012.

[2] http://agricultura.uprm.edu/documentos/estrategiascca.pdf.

Specific objectives:

1. Carry out contaminant (sediment, nutrient, metals and fecal indicators of contamination) monitoring.
2. Use GIS tools to identify point and non-point sources of contaminants
3. Use monitoring results in combination with GIS to link contaminants to specific sources
4. Improve public awareness of the threats of contamination and provide potential solutions to public health and environmental problems.

A6. Project Task Description and Schedule

In this project we will use a three-tiered targeted (Landuse, Area, and Sources) sampling approach in association with citizen volunteers to characterize the surface water-quality status within strategic points of interest of subbasins within the Lajas Valley, lower Guánica, and Río Loco watersheds (Table 1). We will target urban, suburban, and rural landuses (Landuse) within the subbasins. Within specific landuses we will target specific areas having sewage and non-sewage infrastructure (Areas) and agricultural and human sources (Sources). Potential sources to be characterized are point source inputs such as waste-water treatment plants and industrial facilities, and other non-point source inputs such as faulty septic tanks and animal feeding operations.

Samples will be analyzed for nutrients (total nitrogen and total phosphorus), suspended sediments, and *Enterococcus* spp. (as indicators of FICs). Specific water samples will be analyzed for heavy metal concentrations (as indicators of anthropogenic sources) and a specific microbial marker. We will quantify the presence of *Bacteroidales (H183)* marker, as a specific indicator of human fecal contamination (Hagland et al 2010). The concentrations of selected water quality indicators will be characterized during hydrologic low- and high-flows over a 16 month period.

Water chemistry and microbial analysis data in combination with a GIS will be used to identify contaminant contributing areas. A GIS geodatabase will be created that includes land-use, areas, and sources of contamination and hydrology covers that will aid in pinpointing the sources of contamination to surface waters. The information can be used by residents, land use planners and resource managers, to understand the effects of anthropogenic activities on environmental changes in surface and coastal waters. We expect to provide tools that will increase public and community awareness of sanitation issues in the area through public education, training, and participation of citizen volunteers in the assessments of water quality and wastewater management infrastructure.

Table 1. Potential scenarios that may be selected as sampling points, that can contribute fecal contamination to receiving waters.

Landuse	Area	Sources	
		Human	**Animal**
Urban	Sewage	WWTP, sewage transfer and pumping stations, WW sewage delivery infrastructure to WWTP, upstream from WWTP discharge points, downstream from WWTP discharge points	Urban animals (poultry, wildlife, dogs, cats)
	Non-sewage	Homes/buildings with septic tanks, sewage delivery infrastructure to WWTP	Urban animals (poultry, wildlife, dogs, cats)
Suburban	Sewage	WWTP, sewage transfer and pumping stations, sewage delivery infrastructure to WWTP, upstream from WWTP discharge points, downstream from WWTP discharge points	Suburban animals (poultry, wildlife, dogs, cats), small animal (hog, goat, and poultry) production facilities
	Non-sewage	Homes/buildings with septic tanks, sewage delivery infrastructure to WWTP	Suburban animals (poultry, wildlife, dogs, cats), small animal (hog, goat, and poultry) production facilities
Rural	Sewage	WWTP, sewage transfer and pumping stations, sewage delivery infrastructure to WWTP, upstream from WWTP discharge points, downstream from WWTP discharge points	Rural animals (poultry, wildlife, dogs, cats), dairy production facilities, small animal (hog, goat, and poultry) production facilities, large animal (horse) production facilities
	Non-sewage	Homes/buildings with septic tanks, sewage delivery infrastructure to WWTP	Rural animals (poultry, wildlife, dogs, cats), dairy production facilities, small animal (hog, goat, and poultry) production facilities, large animal (horse) production facilities

A6.1. Contaminant monitoring

Sites will be selected based on the combination of information gathered from a comprehensive GIS analysis corresponding to Landuse, Areas, and Sources (Table 1). Within specific landuses we will target specific areas having sewage and non-sewage infrastructure (Areas) and agricultural and human sources (Sources). Potential sources to be characterized are point source inputs such as waste-water treatment plants and industrial facilities, and other non-point source inputs such as faulty septic tanks and animal feeding operations. Subbasin outlets that integrate specific combinations of Landuse, Areas and Sources will be selected. Areas up- and down-stream (representing a range of land use qualities) of problem areas will be selected.

The precipitation pattern in the study area has a bi-modal distribution with rainfall predominating during the months of April to May and from late August to middle December

(here-after termed “wet” months. Samples will be collected during “wet” and “dry” months. In order to categorize samples as those collected during the wet season, the initial criteria will be months of the year and the second criteria will be antecedent precipitation of the sampling day (See section B1 for details).

The volunteer citizen monitoring will be carried out with participating 4-H students. There will be three or four sampling teams (groups) of 4 to 6 volunteers. There will be five samplings events (incursions) in pre-selected spatial locations throughout the study area. All samplings by the citizen monitoring will be done during the dry periods. Within each incursion, the citizen monitoring could potentially target 8 contaminant source scenarios (8 stations).

The professional monitoring will be carried out by UPRM personnel during dry and wet periods on selected stations. The professionally monitored stations will be different than those monitored by citizen groups. Samples collected during the dry period will be done manually and those collected during the wet period will be done using passive rising-flow stream collectors. Ten stations will be sampled by the professional group during the dry and wet periods, and four stations will be sampled by the professional group only during the dry period (thus the professional monitoring will target 14 stations).

Water samples collected for all stations and periods will be analyzed for nutrients and enterococcus (160 samples). Two events during wet and dry periods will be selected for analysis for Bacteroides human marker, heavy metals and OBs. Further exploratory analysis will be done for Bacteroides human marker on those samples with enterococci values > 138 CFU/100 mL. (See section B4). Water samples collected during storm events are expected to have at least three subsamples corresponding to varying hydrologic stages for each event ($Q1$, $Q2$, $Q3$). When an event that has been identified for analysis for Bacteroides human marker is identified, only samples corresponding to Q1, which is associated with the first portion or rising limb of the hydrograph, will be analyzed.

A6.2. Use a GIS for site selection and to identify point and non-point sources of contaminants

A GIS will be assembled with geodatabases obtained from the Census 2010 (housing units, population), hydrologic units (HU-12 numeration) from the Geological Survey (USGS), cover of stream gauge locations from USGS, Digital Elevation models (DEM) and soil from NRCS-Geodatabase data gateway, Sewer and potable infrastructure from Puerto Rico Planning Board (PRPB) and NPDES cover from USEPA, location of animal feeding operations from the Environmental Quality Board (PREQB) and landuse maps from PRPB.

A6.3. Use monitoring results in combination with GIS to link contaminants to specific sources

Some of the sites will include areas up-and down-stream (representing a range of land use qualities) of potential problem areas such as WWTP and animal feeding operations. Consideration will be given to whether a particular land use activity or potential source of pollution is having a potential impact. Special emphasis will be given to drainage systems and creeks in sub-basins with different sewage management systems (i.e. septic tanks versus WWTP). We will seek to identify sites having similar land use with similar geographic areas

with and without WWTP connection. Animal farm operations, and their corresponding manure deposition areas will be pointed out and water quality from these areas will be assessed.

Detailed GIS maps of the study area will be prepared to describe the spatial location and the magnitude of the results. Different map layouts will be prepared according to the areas and the parameters measured, and to guide the work of volunteers and reporting needs as deemed appropriate. These maps will be distributed among stakeholders to familiarize people with the physical and geographic relationships between each other and with the civil infrastructure (roads, wastewater treatment plants, filtration plants, industry, and commerce) and water quality in Guánica bay. Differences in concentration of fecal indicators from sites upstream and downstream of potential contributing sources can be used to infer microbial loading.

A6.4. Improve public awareness of the threats of contamination and potential solutions

Improve public awareness of the threats of contamination. The citizen monitoring groups will be assembled for training and for discussion of results. Initial training prior to sampling initiation will include the topics listed in Table 2, with 45 min duration each. We expect the training to be completed in two, half-day classroom-oriented workshops.

Table 2. Topics to be discussed during initial citizen monitoring training.

Topic	Description
Basic watershed concepts	Basic concepts concerning watersheds, river systems, the water cycle, stream habitat, and water quality
Reasons for monitoring	Describe why monitoring will be done and how will the data be used. Describe what water quality parameters will be measured.
Identifying point and non-point sources of pollution	Determine land use patterns; identify pollution sources; identify stream obstructions
Materials and methods for water quality sampling, and safety	Sample collection, sampling equipment, protocols to be followed, safety considerations.

A comprehensive survey of the geography, land and water uses, potential and actual contaminant sources, and history of the watershed will be assembled using published literature of the area, aerial maps and GIS-based spatial information. Initially, the GIS-based survey will be presented as a working tool in progress and will be used to create awareness among the citizen monitoring groups and to gather input for potential sources of pollution and support for the identification of sites for monitoring.

A visual stream-segment assessment of each of the designated sampling points by each group will be done. The field sampling activities will be supervised by the professional staff until it is assured that the protocols are being followed. The groups will be led by the professional leaders to each of the areas along a defined stretch of stream, observing water and land conditions, land and water uses, and potential changes over time. These observations will be georeferenced, recorded on maps and data sheets, by the volunteer leader, whom will pass the information to the 4-H leader.

Provide potential solutions to public health and environmental problems. At the middle and at the end of the study period, the groups will be assembled to discuss the data

results, and to establish potential links between the stream water quality results and land use. Potential solutions will be provided in the context of existing regulations and infrastructure.

A6.5. Expected Project Schedule

Task	Months										
	----------2014----------				----------2015----------						2016
	May-Jun	Jul-Aug	Sep-Oct	Nov-Dec	Jan-Feb	Mar-Apr	May-Jun	Jul-Aug	Sep-Oct	Nov-Dec	Jan-Feb
Volunteer training	x	xx									
SOPs refresh					xx						
Volunteer monitoring		xx			xx	xx	xx	X			
Data presentation to volunteers					xx					xx	
Dry period sampling		xx			xx	xx	xx	X			
Wet period sampling		x	xx	x				X	xx	X	
Water quality analysis		xx	xx	xx	xx	xx	xx	Xx	xx	xx	
Data processing and statistical analysis			xx	xx	xx	xx	xx	Xx	xx	xx	
QA/QC audits					xx			Xx			Xx
Report					xx						Xx

A7. Quality Objectives and Criteria

A7.1 Quality Objectives and Criteria for Measurement Data

The objective of the proposal is to increase public awareness of sanitation issues in the areas that will lead to improved water quality conditions. This will be accomplished via the combination of volunteer and professional monitoring of selected sites based on a three-tiered approach using GIS analysis. Water samples will be analyzed for nutrients, FICs, and heavy metals.

A7.2 Criteria for Measurement Data

This project will make use of two types of data sources: 1) data generated from existing databases, i.e. federal or state generated data such as data published by the USGS, the USDA-NRCS, the National Weather Bureau, the PR Environmental Quality Board (PREQB), PR Aqueduct and Sewer Authority; and 2) data generated by the research group from field sampling and instrumentation. The first set of data is made available as certified by the corresponding agency and is part of the public domain available to all and these include maps, DEMs, topographic maps, weather data, streamflow and water quality parameters. The second set of data includes that taken by this research group following protocols outlined in this QAPP and SOPs.

Geospatial data gathered in this project through GPS equipment will be consistent and compliant with the Federal Geographic Data Committee (FGDC) to ensure minimally acceptable data quality standards, transferability of data and the use of best available data. Geodetic data will be obtained using either a Trimble PROXR GPS or a GeoExplorer XH GPS, both instruments manufactured by Trimble Corporation.

Throughout the project, staff will ensure that samples and measured parameters are representative of the media conditions being measured. Measurement quality objectives for the various measurements made are expressed in terms of accuracy, precision, sensitivity, comparability, representativeness, and completeness (Table 3).

***Accuracy*.** The term "accuracy" is used synonymously with the term bias in this plan. It refers to the degree of agreement of a measurement (X) with an acceptable reference or true value (T). Usually, accuracy is expressed as the difference between the two values, X-T, or the difference as a percentage of the reference value, 100 (X/T)/T. Sometimes accuracy is expressed as a ratio, X/T or as a percentage of spike recovery,

$$\frac{(ALIQUOT + SPIKE) - ALIQUOT}{SPIKE} * 100$$

Laboratory accuracy for nutrients will be expressed in terms of percent recovery of a spiked sample, that is, a sample fortified with a Certified Reference Material (CRMs) of known concentration.

Accuracy of field measurements will be evaluated by the proper calibration of equipment, along with periodic calibration checks. On the day of each monitoring event before any field data is recorded, the YSI Professional Plus Meter will be calibrated for dissolved oxygen, specific conductance, and pH.

A true value or "standard" in terms of species occurrence and abundance for fecal enterococci does not exist in tropical environments.

Laboratory accuracy for metals is provided in Table 4.

Table 3. Performance objectives of nutrient parameters and field measurements of waters samples.

Parameter	Analysis type	Method	Units	Sensitivity[1]	Accuracy	Precision	Completeness	Holding time[2]
TKN	Laboratory	EPA 351.2	mg/L	0.12 mg/L	80–120%	RSD < 20%	90%	28 days@ 20ºC
Nitrate	Laboratory	EPA 353.1	mg/L	0.009 mg/L	80–120%	RSD < 20%	90%	28 days@ 20ºC
Total P	Laboratory	EPA 365.2	mg/L	0.006 mg/L	80–120%	RSD < 20%	90%	28 days@ 20ºC
Dissolved oxygen	Field	YSI Professional Plus	mg/L	<0.5 mg/L	±20%	RSD < 20%	90%	NA [3]
Temperature	Field	YSI Professional Plus	ºC	0.01 ºC	±0.15 ºC	±1.0 ºC	90%	NA
pH	Field	YSI Professional Plus	pH units	0.001 units	±0.002 units	±0.1 units	90%	NA
Specific conductance	Field	YSI Professional Plus	µmho/cm	0.01 µmho/cm	± 2 %	±10 µmho/cm	90%	NA
Enterococcus	Laboratory	Enterolert	CFU/100 mL	<1 CFU/100 mL	NA	RSD < 60%	90%	6 h

1- MDL studies for nutrients are included in corresponding SOPs

2- Holding times of preserved samples. Nutrient samples are preserved with H_2SO_4 (pH $\leq$2).

3- NA, information is not available.

Table 4. Performance objectives of metal analysis in surface water samples that will be quantified by the UGA laboratory. All samples analyzed as per method EPD 200.9 (See corresponding SOP).

Parameter	Reporting limits (mg/L)	Sensitivity (mg/L)	Accuracy (%)	Precision (%)	Completeness	Holding time[2]
Ca	0.01	0.001 – 0.1	110.7 – 115.2	1.51	90%	< 6 months
Mg	0.01	0.001 – 0.1	96.3 – 100.5	1.37	90%	< 6 months
K	0.01	0.001 – 0.5	80.4 – 94.2	5.17	90%	< 6 months
Na	0.01	0.001 – 0.1	93.9 – 102.3	3.36	90%	< 6 months
Fe	0.01	0.001 – 0.1	103 – 107.3	1.32	90%	< 6 months
Mn	0.0005	0.001 – 0.1	86 – 96	4.01	90%	< 6 months
Zn	0.001	0.001 – 0.1	96 – 108	3.60	90%	< 6 months
Cu	0.0025	0.001 – 0.1	65.2 – 102.8	14.6	90%	< 6 months
Al	0.01	0.005 – 0.1	78.3 – 106.4	11.2	90%	< 6 months
Cd	0.001	0.001 – 0.1	86 – 105	6.71	90%	< 6 months
Cr	0.001	0.001 – 0.1	70 - 118	17.7	90%	< 6 months
As	0.005	0.005 – 0.1	92.4 – 137.2	14.2	90%	< 6 months

1 – Samples acidified with concentrated nitric acid to pH <2, and stored <5^{o}C.

***Precision*.** Precision is a measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions. Precision is best expressed in terms of the relative standard deviation (RSD). For nutrients, metals, and fecal enterococci, for every 40 samples collected, triplicate analyses of an unknown sample will be performed to determine analytical precision. There are no accurate estimates of spatial variability of populations of fecal enterococci in tropical stream/rivers.

Precision of all laboratory data will be evaluated following SOPs. UPRM personnel and citizen volunteers will be trained in all field methods to achieve proficiency, minimize errors, and therefore minimize variability. Equipment will be calibrated prior to each sampling activity following the manufacturer specifications.

Laboratory precision for metals is provided in Table 4.

Sensitivity. Detection limits for all measured nutrient parameters have been defined in UPRM-AES SOPs. No limitations due to detection limits are expected. In cases where the analyte concentration is below the analytical detection limit, one-half of the detection limits will be used. Detection limits for fecal enterococci are 1 MPN/100 mL.

Laboratory sensitivity for metals is provided in Table 4.

***Representativeness*.** Representativeness will be achieved by ensuring compliance with the following areas: (1) the number of locations, matrices, and samples are sufficient to accurately depict site conditions; (2) the sampling procedures, preservatives used, and holding times have been designed so that individual samples accurately represent the chemistry or microbiology of the matrix from which they are collected; and (3) the appropriateness of the analytical method used to the type of sample obtained.

Water samples will be collected from 22 stations (professional sampling, 14; volunteer sampling, 8) encompassing different landuse, area and source combinations. Ten of the 14 stations (professional monitoring) will be sampled 5 times each during wet and dry periods, for a total of 100 samples. Four of the 14 staions will be sampled 5 times only during the dry period for a total of 20 samples. The 8 stations sampled by volunteers (citizen monitoring) will be sampled 5 times only during the dry period, for a total of 40 samples. A total of 160 samples are expected to be analyzed for nutrients and enterococci. Of the total samples collected (160 samples) 56 samples will be analyzed for Bacteroides human marker, heavy metals, and OBs, as two events from the five will be selected. We expect to have a completely balanced data-set of at least 56 samples, and an un-balanced data-set of 104 samples.

In order to identify sources, some of the samples will be collected in subbasin outlets and of known point sources close to possible contamination sources. At least one station will be located at the main sea water entrance from Guánica WWTP outfall.

***Completeness*.** Completeness is a measure of the amount of valid data obtained from any measurement system compared to the amount of data that was expected to obtain under correct and normal conditions by sampling all stations at the selected times. Completeness will be assured by collecting extra sample volumes so that if breakage occurs during shipment, sufficient sample will remain to complete analyses if still within the method-specified holding times. A completeness goal of 90% has been set for the various indicators being measured. A total of 160 samples are expected to be collected. Forty samples will be collected by the volunteer

group, and 120 samples will be collected by the professional group. The volunteer group will sample only during the dry period, while the professional group will sample during both dry and wet periods on selected stations.

Comparability. Comparability is the confidence with which one data-set can be compared to another. Comparability of reporting units and calculations, database management processes, and interpretative procedures will be assured through the use of published information in scientific journals and approved EPA methods (Tables 3 and 4), including adequate quality control, adherence to preservation and maximum holding times, the use of consistent units of reporting the data, and via an inter-laboratory comparison for nutrients.

The comparability of laboratory measurements for nutrients will be assessed through the use of field duplicate samples obtained from the dry sampling network. In this network, field duplicates for 10 sites, collected during a 2-week period will be obtained.

The subset of duplicate samples will be submitted to an EPA certified laboratory for an inter-laboratory comparison. The relative percent difference (RPD) between duplicate samples results from the two laboratories shall be less than 30 for each analyte of interest (TKN, NO_3, and TP) having a concentration greater than 3 times (3x) each of participating laboratory's method reporting limit (MRL). The RPD is calculated as follows:

$$RPD = \frac{C1 - C2}{\left((C1 + C2)/2\right)} x(100)$$

where, C1 is the larger of the results for a given analyte, and C2 is the smaller of the results for a given analyte. For samples 3x above MRL, if results for any analyte do not meet the RPD<30% limit criteria, calculations, methodology, and instrumentation will be checked. A repeat inter-laboratory comparison check will be required to confirm the results. Repeat failure to comply with the control limit will force the participant laboratories to identify and eliminate the source of the imprecision before proceeding. A successful inter-laboratory comparison will require a minimum of an 80% success rate (samples with less than 30%RPD) between laboratories for each analyte.

Data will be entered to a commercial spreadsheet package (MS EXCEL, Microsoft Corp.). Data will be summarized using descriptive statistics and frequency distributions. As needed, graphs will be prepared using Sigma Plot, (Jandell Scientific)] and statistical analysis will be done with SAS (SAS, SAS Institute, Cary, NC) or InfoStat (UNC, Córdova Argentina).

Statistical Analysis. Data will first be summarized via the preparation of contingency tables for all variables. Data will be checked for normality and graphical and numerical description of the data will be performed. Exploratory analysis of quantitative will be performed using frequency distributions, histograms, or box plots. Responses of these variables will be compared among classes of qualitative variables such as location and time. Descriptive statistics such as mean, median, mode, standard deviation, interquartile ranges will be computed as indicators of central tendency and variability. Regression (simple linear and multiple) techniques will be performed to examine relationships among quantitative variables with acceptance criteria at $P<0.05$ or $P<0.1$. Multivariate ordination methods to link selected land-use characteristics with the variables of interest will be done.

A8. Special Training/Certifications

Interested individuals that want to become part of the Volunteer Monitoring Program will participate in two half-day classroom-oriented workshops-training sessions led by the QAPP Manager, QA Coordinator, QA Officer, and Field Sampling Leader. The topics to be discussed are detailed in section A6.4. Also, safety precautions, emergency management, and general procedures will be discussed. One copy of the Standard Operating Procedures (SOPs) will be distributed among the attendees and to be use as a training textbook. The lecture training session will be interactive in order to give the participants opportunity to ask questions and to help them determine if the program fulfills their expectations and interests.

Training-evaluation forms will be distributed among the participants in order to measure the success of the training and - if applicable- to correct deficiencies and improve future training sessions.

A third training section will consist of a visual stream-segment assessment of each of the designated sampling points assigned to each group. The field sampling activities will be supervised by the professional staff until it is assured that the protocols are being followed. A Certificate of Qualification will be issued to those participants that satisfactory complete the classroom, and field training sections and participate in the programmed sampling events.

The QAPP Manager, QA Officer, QA Coordinator, Field Sampling Leader and/or Research Assistant will oversee all sampling by volunteers during each monitoring event.

A9. Documentation and Records

Any changes, corrections or modifications to the approved QAPP will be informed by the Project Manager to USEPA. All efforts will be made to keep the QA Project Plan current, and to account for any project developments or information that becomes known after the start of the project. Corrective action will be taken as each problem is identified. The UPR-Mayagüez Project leader and QAPP Manager, QA Coordinator, QA Officer, and Field Sampling Leader will coordinate the identification of problems, develop action plan, and implement corrective measures, until the problems are eliminated. If needed, a revised QA Project Plan will be submitted and shall be approved by USEPA Quality Assurance Officer. Annual Reports will be prepared and submitted to USEPA Project manager within ninety days after the yearly annual anniversary of the award.

Documentation will include originals and backup photocopies of all filled forms and laboratory notebooks. Records of hand-calculations, and computer outputs will be maintained by all personnel and photocopies will be kept on file by the Project Director.

All data will be stored as Microsoft Excel files (*.xlsx) or text files that can be read as ASCII ready files or through Excel Spreadsheets. All of the data will reside in computers within QAPP Manager, QA Coordinator, QA Officer in UPRM facilities. All data will be backed up periodically in external backup drives.

B. Measurement/Data acquisition

B1. Sampling Process Design

Definition of the study area. Three land areas will be assessed: Lajas Valley, lower Guánica and Río Loco watersheds. The Lajas Valley watershed is a large plain with slopes of 0 to 4% in the lower elevations that extends about 20 mi from Río Loco in the east to Bahía de Boquerón in the west. It includes parts of the municipalities of Yauco, Guánica, Sábana Grande, Cabo Rojo, and Lajas. The width of the valley ranges from 1 to 3 mi and is bounded to the north and south by a chain of hills of maximum altitude of 800 ft. The land area of the Eastern Lajas Valley watershed (*HU-12: 210100040104*), east of State Road 116 that drains towards Guánica Bay with a catchment area of 35,862 acres. Río Loco watershed will be split in three subbasins; Río Loco at Lajas Drainage channel outlet (*HU-12: 210100040106*) with 7,175 acres; the Río Loco at mouth (*HU-12: 210100040107*) with 3,255 acres and the coastal watershed east of Río Loco mouth (*HU-12: 210100040109*) with 5,892 acres (Figure 3). Further subdivisions of HU-12 will be done to segregate smaller subbasins and to select the sampling stations .

Other adjacent areas will be considered as alternative contributing area including Río Yauco at mouth (HU-12: 210100040202) with 18,365 acres; Coastal watershed south and north of Río Yauco (HU-12: 210100040207) with 2,978 acres (Figure 3).

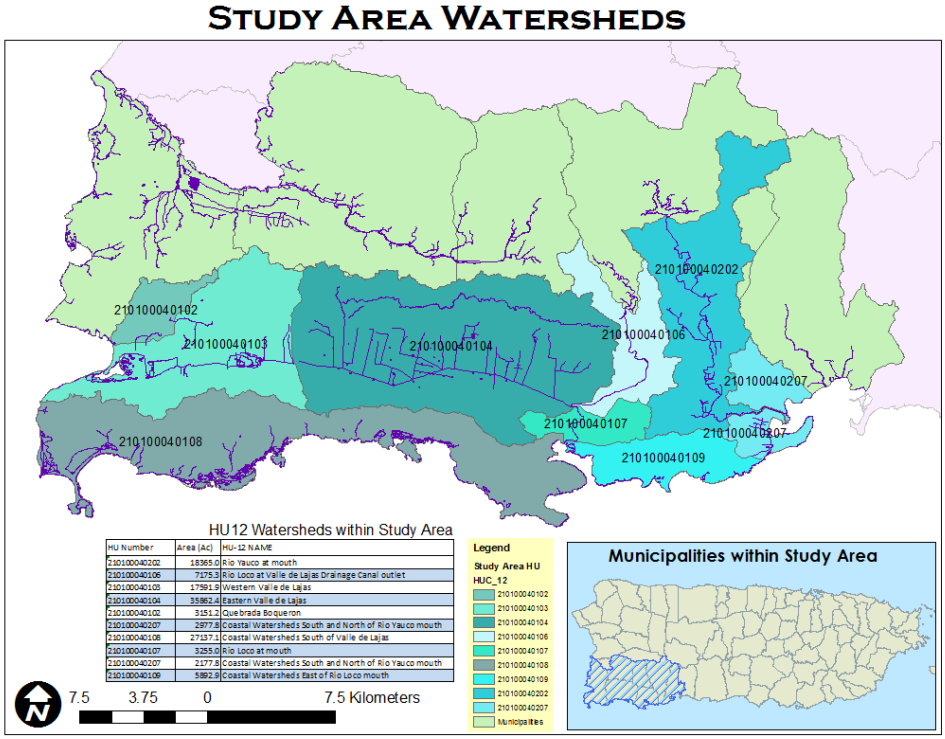


Figure 3. Watersheds (HU-12) and municipalities in the study area

Geographic information system. A GIS will be assembled for spatial analysis of available coverages (land cover, census data, hydrology, sewage utilities, agricultural animal feeding operations and NPDES sites). The spatial analysis will generate potential sampling sites for each combination of cluster variables (Landuse, Area, and Source). The following sources of

geospatial data will be used: GIS layer of Landuse: land use classification including specific uses relevant to the project as Urban, Suburban and Rural (Gould et al. 2004)

- GIS layer of Areas: sewage and potable water utilities infrastructure (PRASA obtained from PR Planning Board)
- GIS layer of Sources: Human and agricultural layers obtained from Census 2010 and the Animal husbandry office of the Puerto Rico Environmental Quality Board (PREQB, 2014).
- Hydrologic Unit cover. Spatial data with hydrologic sub-basin definition as defined by the USGS including 12-digit hydrologic unit definition (USGS).

The following data sources will be used.

- NPDES permit coverage (USEPA)
- Digital Elevation Models (NRCS, Geospatial Data Gateway)
- Soil geodatabase (NRCS, Geospatial Data Gateway)
- Climate data (NWS and public and private climate data collectors)
- Water quality data (USGS station network)

Site selection. Site selection will be based on the combination of information gathered from a comprehensive GIS analysis corresponding to Landuse, Areas, and Sources (Table 1). Within specific landuses we will target specific areas having sewage and non-sewage infrastructure (Areas) and agricultural and human sources (Sources). Potential sources to be characterized are point source inputs such as waste-water treatment plants and industrial facilities (NPDES), and other non-point source inputs such as faulty septic tanks and animal feeding operations (PREQB). Subbasin outlets that integrate specific combinations of Landuse, Areas and Sources will be selected. Access to the sampling points will be an important determinant in the selection process. Areas up- and down-stream (representing a range of land use qualities) of problem areas will be selected. Consideration will be given to whether a particular land use activity or potential source of pollution is having a potential impact. Up to 24 potential sampling site scenarios could be selected based on potential contaminating sources (Table 1), yet some scenarios are unlikely to be encountered.

Final coverage with potential sampling sites will be generated in the office. The sites will be loaded to a GPS (Trimble Geoexplorer Pro-XH) and use for navigation to the selected sampling site. Challenges in the field inspection may present, in which case, an alternative site will be selected and mapped for further analysis in the office and final decision on the selected alternate sampling site. All of the sites will be spatially geo-referenced with global positioning units.

Temporal criteria for sampling. The precipitation pattern in the study area has a bi-modal distribution with rainfall predominating during the months of April to May and from late August to middle December (here-after termed “wet” months). Annual precipitation ranges from 35 to 42 inches in the Lajas Valley to near 80 inches in the upper Río Loco watershed. Samples will be collected during “wet” and “dry” months. In order to categorize samples as those collected during the wet season, the initial criteria will be months of the year and the second criteria will be antecedent precipitation of the sampling day. Sampling for the dry period will be

done when the precipitation for the previous 7 days is at or below the 7-day,10-year flow ($7Q_{10}$) statistics, based on observed precipitation.

Ground truthing. After preliminary selection of the sampling points, ground truthing will be conducted to verify information obtained from GIS and satellite imagery of all sites. The team will navigate to the pre-selected sites at defined subbasin outlets using GPS (Geoexplorer proXH, by Trimble Corporation) and known road coverages within the areas. The field inspection will corroborate gathered information based on visual observation, accessibility to sites and other security issues that will aid in making the final selection of the sampling sites.

Volunteer citizen monitoring. The synoptic citizen monitoring will be carried out with participating 4-H students. Four sampling teams (groups) will be assembled. Each team will consist of 4 to 6 volunteers. Each team will have a leader that will respond to the 4-H leader. The plan will include five samplings events (events) in pre-selected spatial locations throughout the study area. All samplings by the citizen monitoring will be done during the dry periods. It is expected that up to two sites could be visited per day by each sampling team. Thus within each incursion, the citizen monitoring could potentially target 8 contaminant source scenarios. As stated each of the scenarios could be visited 5 times during the duration of the study, for a total of 40 sampling site*events (8 stations x 1 period x 5 events = 40 samples). Sampling will occur in the morning hours between 8:00 and 11:00 AM.

All of the sampling team activities related to sampling and sample management will be overseen by UPRM professional personnel. The citizen groups will be trained by UPRM-AES personnel on Standard Operation Procedure for Stream Water Sampling (See Appendices). Forms will be filled to document reliability and accuracy: (i) Field Data Record Form; (ii) Chain of Custody Form; and (iii) Equipment Calibration Form. All forms will be kept on file in UPRM office facilities. UPRM will provide the Citizen monitoring teams with all materials and equipment needed for field sampling and water quality data gathering.

Professional monitoring. Sampling during dry and wet periods will be conducted by UPRM-AES personnel according to SOP 019w. Forms will be filled to document reliability and accuracy: (i) Field Data Record Form; (ii) Chain of Custody Form; and (iii) Equipment Calibration Form. All forms will be kept on file in UPRM office facilities.

Ten stations will be sampled, during both wet and dry periods; each station will be sampled 5 times during both wet and dry periods (10 stations x 2 periods x 5 events = 100 samples); and four stations will be sampled during the dry period (four stations x 1 period x 5 events = 20 samples).

B2. Sampling Methods

Sample collection. Surface water samples during the dry period will be collected manually (grab) and during the wet period with stormwater samplers. Grab sampling during the dry period will be conducted according to Soil and Water Chemistry Laboratory, Agricultural Experiment Station, University of Puerto Rico (AES Lab) SOP 019w. Stream water samples for chemical analysis will be obtained 10 cm beneath the water surface with 1-L Nalgene bottles. Bottles will be preserved to pH<2 with H_2SO_4 in the field, transported in a cold ice-chest to the laboratory, and stored at 4°C until analysis. Samples for dissolved nitrate-N will be filtered to 25 mL scintillation vials, preserved to pH<2 with H_2SO_4 in the field, transported in a cold ice-chest

to the laboratory, and stored at 4°C until analysis. Manual stream-water samples for microbial analysis will be collected using a Whirl-Pak® sampling pole apparatus 10 cm beneath the surface and placed in sterile 500-mL Whirl-Pak® polyethylene bags (Sotomayor-Ramirez et al. 2006). Sample bags will be closed, sealed, and placed on ice in a closed cooler, and transported to the laboratory for processing within 6 hours of collection.

Water samples for the wet period will be collected using a passive rising-flow stream collectors (Gordon et al. 1992; Franklin et al. 2003). The sampler consists of a series of sterile 1-L Nalgene HDPE bottles (Nalgene Stormwater Samplers) placed within a protective mounting kit. After collecting a full liter of sample, the sampling mechanism closes to prevent cross-contamination with later water. Each bottle-kit combination will be placed perpendicular to the stream-flow at selected heights from the stream bottom. The heights correspond to those resulting from storm events; based on relationships between stream height and stream flow that will be developed for each site as described by Sotomayor-Ramírez and Pérez-Alegría (2012). The collectors have been used successfully in the area by Perez-Alegría (unpublished data). The morning following a rainfall event, the collectors will be inspected and samples collected. Samples will be split into sub-samples for chemical and microbial analysis and transported to an analytical laboratory for analysis of chemical and microbial parameters. Samples for chemical analysis will be transferred to 500 mL Nalgene bottles, preserved and transferred to the laboratory as described previously. Samples for microbial analysis will be transferred to 500-mL Whirl-Pak® polyethylene bags, and transferred to the laboratory as described previously.

It is expected that most if not all of the sampling stations will experience a storm event, simultaneously, and it will not be practical to sample all of the simultaneously the morning after a runoff event. Thus for each storm event, we will select 5 stations which will be sampled, on the day following the storm event. On the next successive storm an additional 5 stations will be sampled, and so on until all 14 stations have been sampled.

Field measurements. The field measurements will be taken immediately after water sampling during the dry period, and include: pH, temperature, and electrical conductivity. Stream-water temperature, pH, and electrical conductivity measurements will be taken *in situ* at mid-channel (at a depth of 15 cm from the water surface), with multi-probe systems (Yellow Springs Instruments). Prior to sampling, instrument settings will be corroborated using buffers and standard solutions and calibrated as needed. Water velocity will be measured with a Flow Probe Hand-held flowmeter (Forestry-Suppliers), at each of the selected stream cross-sections. Turbidity will be measured using a model 2020 turbidity meter (LaMotte).

B3. Sample Handling and Custody

The Field Sampling Leader will be responsible for recording all field observations in a field logbook. The field logbook will include: data and time of start of sampling, name of personnel, location of station (GPS coordinates), station description, field observations (weather, water conditions), stations depth, stream width, water velocity, number of grabs necessary and amount sampled, conductivity, temperature, and pH, area visual anomalies.

Labels will be fastened to outside each sample container. Labels will contain the following information: Project name, ID number, Station number, Station name, Replicate number, Date sampled, Sampling trip number.

A Chain-of-Records form will accompany every sample. Each person releasing a sample will sign and date the form and get the receiver's signature, with date and time, keeping one copy and giving one copy to the receiver. Chain-of-records documents will be maintained for each station. ID (a unique identification number for only that sample), station numbers and station names, leg number (sample collection trip batch number), and date collected will be included on each sheet.

B4. Analytical Methods

Water chemistry analysis. Samples will be analyzed for total Kjeldahl nitrogen (TKN) (EPA method 351.2; SOP 013w), nitrate-N (EPA method 353.1; SOP 021w), total phosphorous (EPA method 365.2; SOP 011w). Samples for dissolved nitrate will be passed through a 0.45-µm-pore size Gelman-Acrodisc filter before analysis. All nutrient analysis will be done by UPRM-AES personnel in the Soil and Water Chemistry Laboratory in Río Piedras. This laboratory has successfully undergone various inter-laboratory comparison exercises with the USEPA Region 2 Laboratory in Edison NJ (National Environmental Laboratory Accreditation Conference [NELAC] certified). Samples will be analyzed for heavy metals following USEPA protocols by University of Georgia Soil and Waters Chemistry Laboratory (http://aesl.ces.uga.edu/). Samples for heavy metals will be analyzed for one dry and one wet sampling event.

Fluorescence from optical brighteners (OB) – commonly found in laundry detergents – have been found to be a potentially useful indicator of contamination from septic systems and other household discharges in surface waters in Puerto Rico (Amador et al. 2008). Samples will be analyzed for OB using a Turner Designs Model 10-AU-005 field fluorometer (Turner Designs, Sunnyvale, CA) fitted with filters for excitation (360 nm) and emission (436 nm) (Hartel et al. 2007a; 2007b).

Water microbial analysis. Enterococci as indicator of FIC will be enumerated using the Enterolert™ system (IDEXX Laboratories) (Kuntz et al. 2003; Sotomayor-Ramírez et al. 2006). Water samples will be serially diluted with sterile distilled water to 10^{-1} and 10^{-2} in sterile manufacturer-supplied in sterile, 100-mL polystyrene bottles and mixed with manufacturer-supplied growth medium until dissolved. The contents of each bottle will be poured into a sterile Quanti-Tray® panel containing 97 wells and heat-sealed. Quanti-Tray® panels for fecal enterococci enumeration will be incubated at 41 ± 0.5ºC. The presence of fecal enterococci will be determined by detection of UV fluorescence at 365 nm. The number of positive wells will be converted to a most probable number (MPN) value based on the dilution factor and manufacturer supplied MPN tables. If samples are suspected to exceed maximum MPN values, samples will be diluted (10^{-2} and 10^{-3}) and the procedure will be repeated.

The presence of *Bacteroidales* human specific marker HF183 will be determined using quantitative polymerase chain reaction (PCR)-based analysis (Haugland et al. 2010), using modified methods (Hartel et al. 2007b). Duplicate water samples (100 mL) will be passed through sterile, 0.22-µm-pore nitrocellulose membrane filters, the filters stored in sterile Whirl-Pak bags at -20ºC, and shipped on dry ice by overnight courier to Kingston, RI. Filters will be processed with a MoBio Ultraclean™ Soil DNA Kit using a modification of the "Alternative Protocol" given by the manufacturer (Amador et al. 2008). Extracted DNA will be quantified using a Nanodrop ND-1000 spectrophotometer and visually inspected under UV light for

integrity on a 2% agarose gel stained with ethidium bromide. Microbial source tracking of fecal pollution for Human, will be performed by qPCR assays on a CFX 9600 (Bio RAD) for Bacteroides bacterial groups with specific host primers (HF183). All primers used in this study will be optimized to avoid non-specific cross-reaction and increased specificity. Standard curves, Negative and positive controls will be run with each assay.

All of the samples collected will be filtered for Bacteroides human marker quantitative PCR and stored. Two events from each of the stations will be selected for analysis. Further exploratory analysis will be done on samples having enterococci most probable number > 130 cfu/100 mL.

B5. Quality Control Requirements

All field samples collected will be identified with a specific site identifier label. Weather conditions and visual observations of each station will be recorded in the Field Data Sheet. A temperature control water sample will be checked to make sure the samples are maintained within the < 10^{o}C transport criteria. If the cooler temperature control is out of this temperature range, the results will be labeled "Results Questionable Temperature Control Exceeded 10^{o}C".

The Field Sampling Leader or QAPP Manager will be present during each monitoring event. They will check the field and laboratory QA/QC data for any deviation from the Data Quality presented of this QAPP. The Field Sampling Leader and/or QAPP Coordinator will ensure that all field equipment is appropriately maintained and/or calibrated, and inspect data for any measurements indicating equipment or method malfunction.

B6. Instrument/Equipment Testing Inspection and Maintenance

Not applicable

B7. Instrument/Equipment Calibration and Frequency

Field instrumentation will be checked through calibration prior to the sampling day under a controlled environment. On 25% of the sampling trips, the calibration will be performed at the end of the sampling day to ensure less than 20 % instrument drift in one sampling day. If the calibration check indicates that the instrument's calibration has drifted outside the calibration acceptance criteria, the data will be flagged and corrective action following instructions in the instrument manual will be taken. When not in use the YSI Professional Plus Meter will be stored in the laboratory. The instruments will be secured during transport. Records of precision measurements will be kept in the Chain of Custody Form. General field quality guidelines are included in the AES water sampling SOP #019w.

A maintenance schedule will be prepared and followed for all instrumentation and recorded. No entries will be erased from all data sheets. Instead the incorrect information will be crossed out with a single line and correct information will be entered and initiated. The YSI Professional Plus Meter will be sent to the manufacturer prior to the sampling initiation and thereafter annually for a certified manufacturer calibration and inspection. Sampling equipment will be checked daily for visual material and mechanical integrity.

B8. Inspection/Acceptance Requirements for Supplies and Consumables

No special requirements are needed. The Field Sampling Leader and/or QAPP Coordinator will be responsible for the appropriate inspection and maintenance of all field

equipment including the safety equipment. All equipment will be cleaned after sampling, and maintained as such in the the laboratory prior to subsequent sampling events.

B9. Non-direct measurements

- GIS layer of Landuse: land use classification including specific uses relevant to the project as Urban, Suburban and Rural (Gould et al. 2004)
- GIS layer of Areas: sewage and potable water utilities infrastructure (PRASA obtained from PR Planning Board)
- GIS layer of Sources: Human and agricultural layers obtained from Census 2010 and the Animal husbandry office of the Puerto Rico Environmental Quality Board (PREQB, 2014).
- Hydrologic Unit cover. Spatial data with hydrologic sub-basin definition as defined by the USGS including 12-digit hydrologic unit definition (USGS).
- NPDES permit coverage (USEPA)
- Digital Elevation Model for relevant areas (NRCS, Geospatial Data Gateway)
- Soil geodatabase (NRCS, Geospatial Data Gateway)
- Climate data (NWS-NOAA)
- USGS gage stations (USGS)

In order to ensure that the collected data is appropriate, records will be checked to assure conformance with established procedures from the agencies, and to assure that the data meet requirements described in Section A7. The data will be reviewed to be sure that their values fall within previously-observed and reasonable ranges, based summary statistics and graphical analysis. The summarized data will be compared to published literature, when available.

B10. Data Management

The name of all the volunteers who participate in each sampling event will be documented in the field data sheet. Volunteers will record the station name (station unique identification number), date, and time of sample collection. No entries will be erased if written mistakes are made; rather the incorrect information will be crossed out with a single line and the correct information will be entered and initiated.

The field data sheet will be reviewed by the QAPP Coordinator or Field Sampling Leader before leaving to each sampling site and then reviewed again at the end of the sampling event to ensure that the sheet is properly completed.

The data sheet will be returned to the QAPP Manager after the monitoring events. The QA Coordinator will enter the data into a Microsoft Excel spreadsheet following the monitoring event. This will help to evaluate and validate any unclear information and inconsistencies that may have occur during the process. The QA Officer will review the QA Coordinator's data entry into the spreadsheet in order to verify the data was transferred correctly and will implement necessary corrective actions.

All of the data will be entered and analyzed in computers within office facilities of the QAPP Manager, QA Officer and QA Coordinator in UPRM. The computers are in areas where entry is restricted to authorized personnel which may involve graduate students participating in

the project. All data will be backed up periodically in external backup drives. Documentation will be performed as described in Section A.9.

C. Assessment and Oversight

C1. Assessment and Response Actions

Volunteers will be under supervision by the QAPP Manager QA Officer, QA Coordinator and/or Field Sampling Leader. After the sampling activities, the Field Sampling Leader will meet with the participant volunteers to: (1) discuss problems encountered; (2) solutions proposed or implemented on site; and (3) to insure that the Program quality objectives are achieved. Any deficiencies and/or corrective actions taken will be documented by the Field Sampling Leader.

The reasons for any abnormal events experienced if the field will be identified and informed to the QA Coordinator and/or QAPP Manager along with any changes performed in the sampling procedures. The Field Sampling Leader should provide to the QAPP Manager a narrative supporting any decisions regarding this point.

Data quality audits will be conducted periodically by the QA Officer. Audits will consist of inspecting the Field Data Sheets, Laboratory QA/QC data, field duplicate RPD calculation, percent recovery of surrogate spikes, and data completeness. Similarly, field QA/QC audits will be performed periodically to evaluate the effectiveness of the sample collection techniques and that SOPs protocols has been followed. Any deficiencies will be reported to the QAPP Manager, who will oversee the resolution of deficiencies.

All of the project participants will review the final data to ensure that (i) all data sheets have been completed and checked for accuracy and legibility, (ii) all data meets the needs of the project, (iii) data quality meets the acceptance criteria, (iv) all documentation exists on all data sources, quality control, and procedures that were used to extract the data from its original source, (v) any normalizations that were necessary prior to the inclusion of the data was performed properly and (vi) any deviations are noted.

C2. Reports to Management

The QAPP manager and PI will keep in archive under his custody printed copies of all data collected or used by the group. The project team will meet on a monthly basis (or as needed) to discuss progress in all the schedule activities. An agenda and minutes of these meetings will be maintained to provide follow up of issues raised in the meeting.

Reports will be prepared and submitted to USEPA Project manager within 90 days of the end of said quarter. The report will be written by the project director. The report will be circulated to all participants for comments and containing all data collected and partial results of all activities targeted for the reporting period according to the schedule in Section A6.

D. Data Validation and Usability

D1. Data Review, Verification, and Validation

The Field Sampling Leader will provide the first data review for the volunteer monitoring. Also, the results will be reviewed by the QAPP Manager, QA Coordinator, or QA Officer at the time of sample collection. Careful attention will be given to any substantial variations in the field *in situ* measurements and that all notes are properly recorded and legible. Volunteers performing the scheduled calibrations of the YSI Professional Plus will be under the Field Sampling Leader and /or QAPP Manager's supervision. A volunteers monitoring training will be scheduled according to demand and if needed, reviews of the SOPs will be provided to citizen volunteers.

After the data is entered into Excel spreadsheets, it will be compared to the original records. If data entry errors are found to exceed 1%, all data will be validated under the direction of the QAPP Manager. Once data are checked for quality and accuracy, they will be made available to project participants. The QAPP manager will be the only person to alter data entries after the dataset has been validated and will record any such changes. Data will be summarized as descriptive statistics, in tabular and graphical form to allow for visual inspection and verification, and comparison to expected values.

D2. Verification and Validation Methods

Not Applicable

D3. Reconciliation with User Requirements

The data will be reviewed by the QAPP manager. Data will be verified if holding times have been met, calibration checks are adequate, qualitative and quantitative results are correct, documentation is complete, and QC results are complete and adequate. Data that do not comply with the project's requirements as outlined in this QAPP, will be flagged with an appropriate explanation noted in the data management Excel software spreadsheet. Uncertainties or questions due to illegible handwriting, unclear annotations or deviations from the SOPs will be discussed with the Field Sampling Leader and all other personnel that participated in data collection.

The summarized data will be evaluated in the context of published information that has been generated in scientific published documents. The results will be discussed on a regular basis with all project participants.

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