Modeled Inflow Validation & Nutrient Loading Estimation in Two Subwatersheds of the Lower Laguna Madre

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Executive Summary

South Texas is growing fast and depends upon a drainage system to move urban and agricultural runoff to the coast and control flooding during severe rainfall events. With population growth and climate change, it is likely that inflows to the coast will increase so quantification of Lower Laguna Madre (LLM) inflow quantity and quality is important to understand and manage inflow.

In 2012, Texas Senate Bill 3 (SB3) Environmental Flows Program completed a critical assessment of freshwater inflow impacts on the Lower Laguna Madre. Seagrass decreases were attributed to periodic, large pulses of ungaged inflow from coastal subwatersheds, associated especially with the Arroyo Colorado-North Floodway and Brownsville Resaca system. As part of developing an adaptive management plan, SB3 recommended that an analysis be performed to determine the linkage between ungaged inflow regimes from major LLM subwatersheds and nutrient loading which accompanies inflow pulses. The Arroyo Colorado (#22903) and Brownsville (#22902) subwatersheds were identified as particularly important ungaged watersheds for south Texas. Both watersheds drain large areas of land (103,246 hectares in Arroyo Colorado subwatershed and 58,677 hectares in Brownsville subwatershed), thus contributing significant inflows to the LLM during rainfall events.

This study was designed to:

-Estimate nutrient loading contributions from four ungaged subwatersheds in south Texas;

-Determine if nutrient loading of the selected subwatersheds were related to differences in land use/land cover;

-Verify the Texas Rainfall Runoff model (TxRR) for four ungaged subwatersheds of South Texas and - Assess whether calibrating the TxRR model with observed land use-land cover data in the select watersheds improved simulated runoff estimates.

In four subwatersheds, automated storm water samplers and Acoustic Doppler Current Profilers (ADCP) were installed in each drain to collect water samples and collect flow data during baseline periods (no rain) and runoff events. Collection of water samples was triggered either by increasing water depth in channel and low conductivity water or triggered remotely by personnel who monitored weather conditions.

The water sampling period ran from June 2014 to November 2015. Water samples were analyzed for dissolved reactive phosphate, ammonia nitrogen, nitrate-nitrite nitrogen, total dissolved nitrogen (subset of samples) and 15N isotope (subset of samples). Total ungaged nutrient loading was calculated for the Brownsville and Arroyo Colorado drains after nutrient-flow relationships were developed for each drain. Nutrient loading for the drainages was calculated by multiplying nutrient concentration $(g/m³)$ by the average instantaneous discharge (m^3/hr) for each hour of sampling. Total area of each land use type in the subwatershed were calculated from LU/LC GIS maps. Nutrient loading for those land use types was estimated based on baseline and runoff event data.

The Texas Water Development Board uses the Texas Rainfall Runoff model (TxRR) to estimate daily stream flows in ungaged watersheds following precipitation events. The model was verified using two methods- apply TxRR to a gaged watershed with records of stream flow and then compare model estimates against the gaged flow record and/or record and use stream flows in ungaged subwatersheds and compare these measurements against model estimates of stream flow. The assessment of whether runoff estimates are improved when TxRR is calibrated for current land use-land cover was done by

adjusting the maximum soil moisture (SMMAX) parameter to reflect existing land use-land cover in each subwatershed. The land use-calibrated TxRR estimates were compared with the uncalibrated estimates and with observed streamflow from sondes and ADCPs deployed as part of this study to ascertain whether land use-calibration improves TxRR runoff estimates.

Eleven sampling events were captured from June 2014 to November 2015- five in Brownsville subwatershed (2 baseline events, 3 rainfall events) from June 2014 to January 2015 and six in Arroyo Colorado subwatershed (2 baseline events, 4 rainfall events) between May 2015 to November 2015.

The four drainage areas sampled differed in area and dominant land use types: POB north- 63,353 ac with grassland and salty grassland, POB south- 29,322 ac with urban and grassland, Drain A- 4908 ac with grassland and row crops, and Drain C- 16,155 ac with row crops, urban and grassland.

Nitrate was usually but not always the dominant nitrogen form. Nitrate was noticeably high at POB north (Brownsville drain) while ammonia was highest at Drain C (Arroyo Colorado drain). Organic nitrogen was the dominant nitrogen form for select dates at all sites except Drain C. Nitrogen isotope data suggested that wastewater treatment plant discharge may have caused elevated nitrogen (organic nitrogen, nitrate and ammonia) and dissolved organic carbon levels at POB north and Drain C sites. Total nutrient load estimates likely underestimated load due to partial sampling of rainfall events or use of discharge data from upstream gage site. There are potential impacts of nitrogen input to the Lower Laguna Madre, especially for seagrass.

Texas Rainfall Runoff model (TxRR) runoff estimates for watershed #22909 (Brownsville) appear to have deficiencies in the representation of baseflow/low flow conditions. This is an indication that the model input parameters for that watershed probably need to be re-calibrated.

Calibrating TxRR for current land cover, particularly in the Brownsville-north subwatershed, results in improved estimates of runoff during large runoff events. Calibrating TxRR with the SMMAX parameter representing grassland significantly improves runoff estimates in both the west Arroyo Colorado and the Brownsville-north subwatersheds during major runoff events. Further research is needed to ascertain whether the same result is valid for the east Arroyo Colorado and the Brownsville-south subwatersheds.

Introduction

In 2012, Texas Senate Bill 3 (SB3) Environmental Flows Program completed a critical assessment of freshwater inflow impacts on the Lower Laguna Madre (LLM). Seagrass decreases (24% in last 10 years) were attributed to periodic, large pulses of ungaged inflow from coastal subwatersheds, associated especially with the Arroyo Colorado-North Floodway and Brownsville Resaca system. As part of developing an adaptive management plan, SB3 recommended that an analysis be performed to determine the linkage between ungaged inflow regimes from major LLM subwatersheds and nutrient loading which accompanies inflow pulses (DeYoe et al. 2012). The Arroyo Colorado (#22903) and Brownsville (#22902) subwatersheds were identified as particularly important ungaged watersheds for south Texas. Both watersheds drain large areas of land (103,246 hectares in Arroyo Colorado subwatershed and 58,677 hectares in Brownsville subwatershed), thus contributing significant inflows to the LLM during rainfall events. The LLM TxBlend model showed low salinity plumes emanating from these areas during large inflow pulses (DeYoe et al. 2012). The Brownsville subwatershed encompasses much of the City of Brownsville and surrounding agricultural lands. The Arroyo Colorado subwatershed is characterized by large areas of crop land which result in numerous ungaged sources adding an unknown quantity of agricultural runoff to the Arroyo Colorado.

Figure 1. An overview of the project study area.

This information will be used to evaluate current model (TxRR) performance in estimating ungaged inflows and to establish a relationship between ungaged inflows and nutrient loading regimes to the LLM. Data gathered through this research will provide state resource agencies including the Texas Water Development Board (TWDB) and the Texas Parks and Wildlife Department (TPWD) important information to manage estuarine and coastal wetland habitats in Texas bay systems and freshwater inflow conditions.

The TxRR model has not been calibrated for land use-land cover in these two watersheds. Land use-land cover datasets compiled during the course of this study will also be used to calibrate the TxRR model to represent current land use-land cover conditions. An assessment will be made on whether calibrating the model for land use in a watershed improves runoff estimates.

Nutrients causing coastal eutrophication come from terrestrial sources including industry, sewage treatment plants, and urban and agricultural runoff. The contribution of the last two sources is dependent on rainfall although agricultural irrigation runoff may be significant even during dry periods. Runoff waters reach the coast by rivers, streams and drainage canals. In south Texas, few of these waterways are monitored for water flow or quality.

South Texas is a semi-arid subtropical region. Annual precipitation is so variable that mean annual rainfall does not have much meaning. The topography of the region is generally flat with few natural, major drainages (Fig. 1). The Lower Rio Grande Valley is overlaid with an irrigation system and drainage system. Most of the surface water in the Brownsville subwatershed is carried to the coast by the Resaca/drainage canal system while in the Arroyo Colorado subwatershed most of the water is carried by the drainage system which includes the Arroyo Colorado to the coast. Very little of the region's drainage enters the Rio Grande. Due to flooding events, the region's drainage system is being modified to improve drainage of some areas and increase the amount of water the system can accommodate and travel time to the coast.

Study Goals and Objectives

One goal of the project is to characterize nutrient loading rates into the Lower Laguna Madre (LLM) from subwatersheds of the Arroyo Colorado (#22903) and Brownsville (#22902, #22908) by monitoring stream flow and water quality (particularly nitrogen and phosphorus). The second goal is to validate the Texas Rainfall Runoff (TxRR) model for portions of the Brownsville and Arroyo Colorado subwatersheds. The third goal is to calibrate the model for land use-land cover found within the subwatersheds.

Objectives of the project were to:

-Estimate nutrient loading contributions from four ungaged subwatersheds in south Texas;

-Determine if nutrient loading of the selected subwatersheds were related to differences in land use/land cover;

-Verify the TxRR model for four ungaged subwatersheds of South Texas and

- Assess whether calibrating the TxRR model with observed land use-land cover data in the select watersheds improved simulated runoff estimates.

Methods

Subwatershed Delineation

A GIS (Geographic Information System) environment was used as the integrating system for spatial data analysis. Figure 2 presents GIS map locations of the ungaged subwatersheds sampled for this study.

Figure 2. Brownsville and Arroyo Colorado subwatersheds and sample sites overlaid onto digital 2012 USDA-NAIP infrared photoimagery. Sampling site locations are indicated as: POB-N and POB-S for the Brownsville subwatersheds; Drain A, Drain C, & AC-POH for Arroyo Colorado subwatersheds. Blue areas are the Arroyo subwatersheds, and purple areas are the Port of Brownsville subwatersheds.

There are numerous ungaged drains in the Brownsville and Arroyo Colorado subwatersheds. Land Use/Land Cover (LU/LC) GIS map of these ungaged subwatersheds was developed from 2012 USDA-National Agricultural Inventory Program (NAIP) digital photoimagery to locate drains and verify land use. NAIP digital imagery was obtained from TNRIS archives (Texas Natural Resources Information System, Austin, Texas). Two ungaged sources in the Brownsville subwatershed (Port of Brownsville north and Port of Brownsville south) and two ungaged sources in the Arroyo Colorado subwatershed (Drain A and Drain C) plus the Arroyo Colorado itself (AC-POH, at the Port Of Harlingen) were identified (Fig. 2 and Table 1). The Brownsville drains were selected because they captured a large portion of drainage from Brownsville. The sampling sites were positioned as far downstream as possible to capture all ungaged sources. These sites were unavoidably near the seawater interface so were affected by minimal tidal action.

The Arroyo Colorado sites were selected because one drain covered largely agricultural land and the other was largely urban land. Both emptied into the tidal segment of the Arroyo Colorado and were not tidally influenced.

Table 1. Sampling site locations and general characteristics.

Brownsville subwatershed

Port of Brownsville north (POB north)- 25.99708, 97.36167, main drain for Brownsville with two branches- one mostly urban, other mostly agriculture. Slight tidal influence- 6.2 km from site to San Martin Lake

Port of Brownsville south (POB south)- 25.95693, 97.37464, drain for south Brownsville, Significant tidal influence- 350 m from Brownsville ship channel

Arroyo Colorado subwatershed

Arroyo Colorado- 26.19747, 97.59955, Arroyo Colorado upstream of Port of Harlingen turning basin, Slight tidal influence- 50 km from Lower Laguna Madre.

Drain A- 26.27401, 97.5558, small drain, largely agricultural land, no tidal influence, 913 m upstream of Arroyo Colorado confluence

Drain C- 26.25853, 97.59234, medium drain, 1.4 km upstream of Arroyo Colorado confluence

The total areas drained by each site and land use/land cover of each drainage area (ignoring Arroyo Colorado site) differed over a four-fold range (Table 2 and Figures 3, 4, 5, 6). The largest drainage area was for the POB north drain (63,353 ac) which was at least twice as big as the next other drainage sites. However, the west Arroyo Colorado site (drain C) had 70.6 % combined acreage of agriculture (row crops/orchards) and urban land use in a total area of 16,155 acres, the most of these LU types of the subwatersheds (ca 48.3 % for POB-S and only 14.5% for POB-N, 37.4 % for east Arroyo site), and indicative of a potentially highly disturbed area. Further description and analysis of the differences in LU/LC types between the subwatersheds is given under the nutrient loading and TxRR modeling section of the report.

Figure 3: Land cover types in the west Arroyo Colorado watershed

Figure 4: Land cover types in the east Arroyo Colorado watershed.

Figure 5: Land cover types in the Brownsville-north watershed.

Figure 6: Land cover types in the Brownsville-south watershed.

Table 2. Modeled LandCover/LandUse acreage and descriptions for Port of Brownsville and Arroyo Colorado subwatersheds (Classified data from TPWD Ecosystems Mapping).

Table 2 shows the total area of each land use type in the subwatershed as calculated from LU/LC GIS maps. The LU/LC data was derived from Ecosystems Mapping Survey data compiled by Texas Parks and Wildlife Dept. from their statewide project (TPWD 2014 Reference), and verified by overlay comparison with the 2012 NAIP photoimagery. The modeled LU/LC category data was used later in the TxRR ungaged runoff modeling work, and for correlation analysis with the subwatershed nutrient loading results.

Nutrient Source Monitoring and Nutrient Loading Calculations

In each subwatershed, automated storm water samplers and Acoustic Doppler Current Profilers (ADCP) were installed in each drain to collect water samples and collect flow data during baseline periods (no rain) and runoff events. Rainfall event were generally sampled if there had been no significant rainfall in the previous seven days. For each rainfall event, composite water samples (two 400 ml samples every 2 hours) or hourly samples (800 ml samples every hour) were collected for 24-48 hours using automated samplers equipped with temperature, conductivity and water level sensors. Collection of water samples was triggered either by increasing water depth in channel and low conductivity water (to avoid seawater sampling) or triggered remotely by the PI who monitored weather conditions.

The water sampling period ran from June 2014 to November 2015. Within 12 hrs of collection, water samples were filtered through Whatman GF/C filters and frozen for later analysis. Water samples were analyzed for dissolved reactive phosphate, ammonia nitrogen, nitrate-nitrite nitrogen, total dissolved nitrogen (subset of samples) and ¹⁵N isotope (subset of samples). Three analyses were performed inhouse on water samples- nitrate-nitrogen, ammonium-nitrogen, and soluble reactive phosphorus. All analytical methods were EPA Methods (nitrate- EPA Method 0353.2, ammonium- EPA Method 0350.2, soluble reactive phosphorus- EPA Method 0365.2). Total dissolved nitrogen analysis of water samples was performed by TAMU-CC using the uses combustion oxidation and chemiluminescence detection method (ASTM). To characterize the nitrogen source of drains, a subset of water samples were analyzed by University of Texas Marine Science Institute for ¹⁵N/¹⁴N isotopes of particulate matter.

Using the total area of land use-land cover in the subwatersheds calculated in Table 2, nutrient loading for those land use types was analyzed and interpreted based on baseline and runoff event data.

To estimate the total ungaged nutrient loading from the Brownsville subwatershed drains and the Arroyo Colorado subwatershed drains, nutrient-flow relationships were developed from hydrologic and water quality data collected at the drain sampling sites. Nutrient loading for the drainages was calculated by multiplying the measured nutrient concentration ($g/m³$) by the average instantaneous discharge (m³/hr) for each hour recorded by ADCP sampling. Nutrient loading rates for the Arroyo Colorado were derived from the in-channel Arroyo Colorado site (just above the tidal segment). Total nutrient load for each event and each site was calculated by summing the hourly loading rates over the course of the sampling period.

TxRR Model Verification

TWDB staff relies on the Texas Rainfall Runoff model (TxRR) to estimate daily stream flows in ungaged watersheds following precipitation events. The original model was calibrated for representative watersheds using gaged stream flow records and precipitation records and by adjusting parameters for soil type and land use. TWDB staff will verify the performance of the TxRR model for ungaged subwatersheds draining into the LLM, focusing on watersheds #22902, #22903, and #22908.

Model verification will be done using two methods. The first will be to apply TxRR to a gaged watershed with known records of stream flow (e.g., watershed #22909 measured by International Boundary and Water Commission gage #8470400) and then compare model estimates against the gaged flow record. The second method will be to record stream flows in an ungaged subwatershed and compare the measurements against model estimates of stream flow.

The assessment of whether runoff estimates are improved when TxRR is calibrated for current land useland cover will be undertaken by adjusting the maximum soil moisture (SMMAX) parameter (Matsumoto, 1992) to reflect existing land use-land cover in each sub-watershed.

We use the relationship between runoff curve number and maximum soil moisture, which was established by the latest recalibration of the TxRR model undertaken for twenty (20) ungaged coastal watersheds by the Texas Water Development Board in 2011 (TWDB, 2011) to derive new values of SMMAX.

SMMAX is derived using the following equation:

$SMMAX = -0.1x + 21.2$

Where, $x = Curve$ number

Curve numbers are obtained by consulting the U.S. Department of Agriculture – Natural Resources Conservation Service report TR-55 titled 'Urban Hydrology for Small Watersheds' (Cronshey, 1986). The selection of curve number requires a determination of Hydrological Soil Groups (HSGs) within a watershed. We use the county-level soil data for Cameron County, obtained from the Soil Survey Geographic (SSURGO) database [\(http://websoilsurvey.sc.egov.usda.gov/App/WebSoilSurvey.aspx\)](http://websoilsurvey.sc.egov.usda.gov/App/WebSoilSurvey.aspx), to obtain HSG maps for the sub-watersheds. The HSGs within dominant land cover types found in the subwatersheds are used to obtain the runoff curve number associated with each HSG. Dominant land cover types are defined as cover type (or 2-3 cover types) with an area (or cumulative area) accounting for seventy percent (65–70%) or more of a sub-watershed's total land area.

The land use-calibrated TxRR estimates are compared with the uncalibrated estimates and with observed streamflow from sondes and ADCPs deployed as part of this study to ascertain whether land usecalibration improves TxRR runoff estimates.

Results

Nutrient Loading Estimation

Eleven sampling events were captured from June 2014 to November 2015- five in Brownsville subwatershed (2 baseline events, 3 rainfall events) from June 2014 to January 2015 and six in Arroyo Colorado subwatershed (2 baseline events, 4 rainfall events) between May 2015 to November 2015. Rainfall data for the Brownsville subwatershed sites was obtained from the National Weather Service office at the Brownsville, TX airport (10.6 km SSW from POB south and 7 km SSW from POB north). For the Arroyo subwatershed sites, rainfall data was obtained from the Harlingen airport (6.8 km WSW from Drain C and 10.6 km WSW from Drain A). Due to technical problems, no events at Brownsville or Arroyo Colorado subwatersheds had both water quality and discharge data at all sites on the same date. There were a number of rainfall events in which discharge data or nutrient data are missing which prevented calculation of nutrient loading rates. Tidal influence did affect two sites, the POB north and especially POB south sites. POB north discharge varies with tidal stage (Fig. 7) and POB south with salinity increase nutrient levels drop (Fig. 8).

Table 3. Sample events for the Brownsville and Arroyo Colorado subwatersheds for 2014-5.

POB north site

June baseline event- Sampling for this event captured a period with no rainfall and outgoing tide conditions. Discharge ranged from 0 to 7458 m^3 /hr (Figure 8 and 9). Nutrient concentrations were highest for nitrate-nitrogen (average 3.31 $g/m³$, maximum 5.27 $g/m³$) which declined during sampling period (Table 4 and Figure 10). Ammonia and phosphate values were low (average 0.067 g/m³ and 0.19) $g/m³$, respectively). Loading rate was highest for nitrate with an average value of 7.94 kg/hr (Table 4 and Figure 11). Average loading rates for ammonia and phosphate were both less than 0.5 kg/hr. Total nutrient load for the sampling period was highest for nitrate at 159 kg (Table 5).

November rainfall event (2.86 inches)- Discharge increased through sampling period and was still increasing at end of sampling period so the completion of the event was not captured (Fig. 12). Highest discharge at end sampling period was 40,000 m³/hr while average discharge was 12,108 m³/hr. Nutrient concentration for nitrate declined during the event with little change in ammonia and phosphate levels (Fig. 13). Average nitrate, ammonia, and phosphate concentrations were 2.26, 0.057, 0.12 $g/m³$, respectively (Table 4). Loading rate was highest for nitrate with two peaks (Fig. 14) and an average of 27.4 kg/hr. Loading rates for ammonia and phosphate were less than 1.5 kg/hr. Total nutrient load for the portion of the event captured was highest for nitrate at 468 kg and was at least 16 times greater than loads for ammonia and phosphate (Table 5).

POB south site

August rainfall event (1.7 inches)- A modest rainfall event was captured with peak discharge of 4,228 m^3/hr and average discharge of 2217 m^3/hr (Fig. 15). Average nutrient concentration was highest for nitrate at 0.26 g/m³ and less than 0.1 g/m³ for ammonia and phosphate (Fig. 16). Mean nutrient loading rate was highest for nitrate 0.57 kg/hr with a peak 2.4 kg/hr while mean loading rates for ammonia and phosphate were less than 0.2 kg/hr (Figure 17). Total nutrient loads for this event were approximately 10, 0.8 and 4 kg for nitrate, ammonia and phosphate, respectively (Table 5).

Table 5. Total nutrient loadings for select events by site.

Arroyo Colorado

Due to malfunction of ADCP, discharge data for this site were derived from an IBWC gaging site in Harlingen (14.6 km upstream of water sampler). Discharge values were likely higher at water sampling site due to addition of ungaged drainages between the gaging station and the water sampler sites. As a

result, nutrient loading rate calculations will be lower than true values at water sampling site.

August rainfall event (2.21 inches)

Estimated discharge rate was increasing when water sampling stopped so the first half of rainfall event was captured (Figure 18). Peak flow was estimated to be at least 6349 m³/hr. Nutrient concentration for all nutrients did not change dramatically during event (Figure 19). Average nitrate concentration was 0.33 g/m³, ammonia average was 0.10 g/m³ and phosphate average was 0.24 g/m³ (Table 4). Nutrient loading rates for all nutrients paralleled the increase in discharge (Fig. 20).

September rainfall event (3.65 inches)

The first half of the rainfall event was captured so discharge rate was increasing during water sampling period (Fig. 21). Nitrate concentrations were higher than ammonia and phosphate (Fig. 22) and averaged 0.27, 0.15 and 0.13 g/m3, respectively (Table 4). Nutrient loading rate was highest for nitrate and had plateaued by the time sampling stopped (Fig. 23). Total nutrient load was about twice as high for nitrate (65 kg) compared to ammonia (33 kg) and phosphate (29 kg) (Table 5).

Drain A

September rainfall event (3.65 inches)

Discharge was modest (Fig. 24) indicating that rainfall in the drainage area was significantly less than rainfall recorded at the Harlingen airport. Mean nutrient concentration was highest for ammonia (0.053 $g/m³$) followed by nitrate (0.043 $g/m³$) and phosphate (0.022 $g/m³$)(Table 4 and Fig. 25). Nutrient loading rates were slightly higher for ammonia than nitrate (Fig. 26). Total nutrient load was at least twice as high for ammonia (1.49 kg) as nitrate (0.66 kg) and phosphate (0.21 kg)(Table 5).

Drain C

October rainfall event (2.47 inches)

Due to problems with the ADCP discharge data for this site was estimated by the TxRR model (Fig. 27). Use of rainfall data from the Harlingen airport was appropriate since the airport was in the drainage area for this site. Estimated discharge was peaking at the end of the sampling period so total nutrient load for this event was likely underestimated. Nutrient concentration was highest for ammonia but with a nitrate peak at the end of the sampling period (Fig. 28). Mean nutrient concentration was highest for ammonia (0.22 g/m^3) followed by phosphate (0.12 g.m^3) then nitrate (0.076 g/m^3)(Table 4). Nutrient loading rates during the first half of sampling was similar among the nutrients but as discharge increased so did nutrient loading rates (Fig. 29). Total nutrient load was highest for ammonia (18.5 kg) followed by nitrate (11.82 kg) and phosphate $(11.42 \text{ kg})(\text{Table 5}).$

Overview

Dissolved organic carbon (DOC) for events with a sample time series values start high and decline (Table 6a and b). The highest DOC value (22,599 μ M) was in Drain C. Average DOC was highest for the Arroyo Colorado sites (2,936 μ M, SD 4807) compared to the Brownsville sites (1055 μ M, SD 925)(Table 6a and 6b). Mean % organic nitrogen for Brownsville sites was 58.4 (25.5 SD) and 42.6 (31.1 SD) for the Arroyo Colorado sites. Of the Brownsville sites, POB south had the higher mean % organic nitrogen (67%)(Table 6a) while mean values in the Arroyo Colorado area were higher for Drain A (55%) than Drain C (42%) which was typically dominated by ammonia nitrogen (69%)(Table 6b).

Average nitrate concentrations were higher for POB north, POB south and Arroyo Colorado than ammonia and phosphate (Table 4). Ammonia levels were higher than nitrate and phosphate at Drains A and C. POB north had the highest mean nitrate concentration among all the sites. The Arroyo Colorado sites had higher mean ammonia levels compared to the Brownsville sites. Phosphate concentrations were highest at the Arroyo Colorado site.

Nitrate load for POB north events exceeded all other sites (Table 5). Loads for dissolved phosphate were lower than nitrate. Ammonia load was slightly higher than nitrate load for the two Drain A and C events.

Particulate $\delta^{15}N$ values were higher at POB north than POB south (Table 7). $\delta^{15}N$ values at Drain C were in the same range as the POB north site values and twice as high as Drain A values (12.3 vs. 5.4) with Arroyo Colorado site values being intermediate. High $\delta^{15}N$ values at POB north and Drain C suggest sewage loading (ref).

Comparison of TxRR modeling results with discharge data

The comparison of TxRR simulated runoff in watersheds #22909 and #22911 with gaged streamflow data at the the IBWC gages # 470400 and #470200 reveal that:

- TxRR estimates over watershed #22909 capture most of the major rain events but has an underestimation of baseflow/low flow events. The magnitude of some of the larger rain events is overestimated [Fig. 31(a)].
- TxRR estimates over watershed #2211 capture most of the major rain events and their magnitudes quite satisfactorily. Base flow/low flow estimates are also very close to observed values. However, there is a rapid decrease in the hydrograph of rain events compared to observations. The magnitudes of some of the larger rain events are over-estimated [Fig. 31(b)].

When TxRR is calibrated for current land cover types found in the west Arroyo Colorado and the Port of Brownsville-North watersheds, the runs with SMMAX representing grassland result in runoff estimates that closely match (in terms of timing and magnitude) observed rainfall events in both watersheds (Figs. 32 and 33).

Using the average SMMAX derived from all dominant land cover types, and the SMMAX for the land cover type with the most extensive (i.e. row crops for the west Arroyo Colorado watershed) or second most extensive land cover type (i.e. marshland for the Port of Brownsville-North water), improve on the uncalibrated TxRR runoff estimates for the Port of Brownsville-North watershed. In the west Arroyo Colorado watershed, these runs yielded large over-estimates of runoff during the large runoff events. In both sub-watersheds, TxRR runoff estimates calibrated for grassland matched best with observed streamflow.

Discussion/Conclusions

Several potential deficiencies can be noted for the nutrient loading datasets:

1. No winter baseline data was obtained for any site. It is possible that seasonal variations in nutrient runoff occur, especially if related to agricultural activity.

2. Other potentially important ungaged drains in the LRGV have not yet been sampled.

3. No data was obtained on nitrogen component transformations during conveyance of nitrogen to the mainstem of the Arroyo Colorado or the Lower Laguna Madre.

4. Total nutrient loadings likely underestimated total load due to partial sampling of rainfall events or use of discharge data from upstream gage site (Arroyo Colorado site).

Despite these limitations, several observations and inferences can be drawn from the data:

1. Nitrate was usually but not always the dominant nitrogen form. Nitrate was noticeably high at POB north (Brownsville area) while ammonia was highest at Drain C (Arroyo Colorado area). Organic nitrogen was the dominant nitrogen form for select dates at all sites except Drain C. Due to analytical cost, not all water samples could be analyzed for total dissolved nitrogen limiting the calculation of organic nitrogen.

2. There appears to be a reasonable correlation between forms of nitrogen (NO3 vs NH3 vs org N) with specific LU/LC types in the watershed, although more examples should be studied.

3. Location of wastewater treatment plants may have increased nutrient levels at POB north and Drain C. This is based on the interpretation of 15N isotope signatures for particulate nitrogen in these drains. The del ¹⁵N values for POB north and POB south ranged from $7 - 13.5$, consistent with mixed amounts of agricultural and urban nitrogen runoff. Conversely, the del¹⁵N source for Drain A (5.5) is consistent with agriculture as a N source, which the LU/LC data confirms. Likewise the del¹⁵N source for Drain C (11 - 13) is consistent with urban wastewater as a N source, which the LU/LC data confirms. Wastewater treatment plant discharge may have caused elevated nitrogen (organic nitrogen, nitrate and ammonia) and dissolved organic carbon levels at POB north and Drain C sites.

4. TxRR runoff estimates for watershed #22909 appear to have deficiencies in the representation of baseflow/low flow conditions. This is an indication that the model input parameters for that watershed probably need to be re-calibrated.

5. Calibrating TxRR for current land cover, particularly in the Brownsville-North watershed, results in improved estimates of runoff during large runoff events. Calibrating TxRR with the SMMAX parameter representing grassland significantly improves runoff estimates in both the west Arroyo Colorado and the Brownsville-North watersheds during major runoff events. Further research needs to be undertaken to ascertain whether the same result is valid for the east Arroyo Colorado and the Brownsville-South watersheds.

In conclusion, this study has demonstrated that:

a) nutrient loadings can be successfully measured in ungaged watersheds from discrete runoff events; b) ungaged runoff can be accurately measured in such watersheds using TxRR modeling, with the recognition that LU/LC data should be updated periodically as LU/LC changes in the watershed; and c) integration of ungaged runoff modeling with water quality monitoring provides an accurate method for determining nutrient loadings to and managing the potential environmental impact from such ungaged watersheds.

Table 6a. Dissolved organic carbon, total dissolved nitrogen, nitrate nitrogen, ammonia nitrogen and calculated organic nitrogen for select dates in Brownsville subwatershed.

Table 6b. Dissolved organic carbon, total dissolved nitrogen, nitrate nitrogen, ammonia nitrogen and calculated organic nitrogen for select dates in Arroyo Colorado subwatershed.

Date	Hr Brownsville sites	Land use type	$\delta^{15}N$
9/1/2014	POB North drain	72% coastal prairie	10.4
9/14/2014	POB North drain	72% coastal prairie	6.9
11/8/2014	POB North drain	72% coastal prairie	8.0
1/7/2015	POB North drain	72% coastal prairie	13.5
1/7/2015	POB Northwest arm	grassland	9.0
9/1/2014	12 POB South drain	44% urban, 34% grassland	7.9
9/1/2014	24 POB South drain	44% urban, 34% grassland	9.2
9/1/2014	46 POB South drain	44% urban, 34% grassland	8.8
11/8/2014	POB South drain	44% urban, 34% grassland	7.1
1/7/2015	POB South drain	44% urban, 34% grassland	9.3
Date	Arroyo Colorado sites	Land use type	
5/13/2015	Drain A	61% grassland, 35% row crop	5.7
9/13/2015	Drain A	61% grassland, 35% row crop	5.1
4/15/2016	Drain C	45% row crop, 26% urban	11.3
9/13/2015	Drain C	45% row crop, 26% urban	13.3
8/21/2015	Arroyo Colorado	mixed	8.1
9/13/2015	Arroyo Colorado	mixed	9.9

Table 7. Particulate ¹⁵N isotope values for select sites and dates.

Table 8. Dominant land cover type with associated Hydrological Soil Group and Maximum Soil Moisture (SMMAX) values for the four sub-watersheds.

Figure 7. POB south site salinity and nutrient levels for September 2014.

POB north, June 18-22 hydrograph

Figure 8. Hydrograph for POB north site 18-22 June 2014 baseline period. Arrows indicate start and end of water sampling.

Figure 9. Hydrograph for POB north site June 2014 baseline sampling period.

Figure 10. POB north site nutrient concentrations during June 2014 sampling period.

Figure 11. POB north site nutrient loading rates for June 2014 sampling period.

Figure 12. Hydrograph for POB north site during November 2014 rainfall event.

Figure 13. POB north site nutrient concentrations during November 2014 rainfall event. POB North, November 2014 Nutrient loading rate

Figure 14. POB north site nutrient loading rates during November 2014 rainfall event.

Figure 15. POB south site hydrograph for August 2014 rainfall event.

POB south August 2014 Nutrient concentration

Figure 16. POB south site nutrient concentrations for August 2014 rainfall event.

Figure 17. POB south site nutrient loading rates for August 2014 rainfall event.

Figure 18. Arroyo Colorado hydrograph for August 2015 rainfall event.

Arroyo Colorado, Nutrient concentration, August 2015

Figure 19. Arroyo Colorado nutrient concentrations for August 2015 rainfall event.

Figure 20. Arroyo Colorado nutrient loading rates for August 2015 rainfall event.

Figure 21. Arroyo Colorado hydrograph for September 2015 rainfall event. Arrows indicate initiation and termination of water sampling.

Figure 22. Arroyo Colorado nutrient concentrations for September 2015 rainfall event.

Figure 23. Arroyo Colorado nutrient loading rates for September 2015 rainfall event.

Figure 24. Drain A hydrograph for September 2015 rainfall event.

Figure 25. Drain A nutrient concentrations for September 2015 rainfall event.

Figure 26. Drain A nutrient loading rates for September 2015 rainfall event.

Figure 27. Drain C modeled hydrograph for October 2015 rainfall event.

Figure. 28. Drain C nutrient concentrations for October 2015 rainfall event.

Figure 29. Drain C nutrient loading rates for October 2015 rainfall event.

Figure 30. Location of the four sub-watersheds within TxRR watersheds and the location of the IBWC gages used to compare TxRR estimates with gaged estimates.

Figure 31. (a) Comparison of TxRR runoff estimate with streamflow at IBWC gages for the watershed #22909, and (b) same as (a) but for watershed and #22911.

Figure 32. Comparison of uncalibrated TxRR runoff estimate from watershed #22093 with land cover-calibrated TxRR runoff estimate and observed streamflow in the west Arroyo Colorado watershed; where (a) depicts calibrated runoff estimates with the average SMMAX for the dominant land cover types, (b) depicts calibrated runoff estimates with the SMMAX value for the land cover type covering the greatest total area (i.e. row crops) of the watershed , and (c) depicts calibrated runoff estimate with the SMMAX value for grassland.

Figure 33. Comparison of uncalibrated TxRR runoff estimate (red) from watershed #22902 with land cover-calibrated TxRR runoff estimate (green) and observed streamflow (blue) in the Port of Brownsville-North watershed where (a) depicts calibrated runoff estimates with the average SMMAX for the dominant land cover types, (b) depicts calibrated runoff estimates with the SMMAX value for the second-most extensive land cover (i.e. Marshland) in the watershed, and (c) depicts calibrated runoff estimate with the SMMAX value for grassland.

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