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Atrazine Transport Within a Coastal Zone in Southeastern Puerto Rico: a Sensitivity Analysis of an Agricultural Field Model and Riparian Zone Management Model

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Abstract Agrichemical runoff from farmland may adversely impact coastal water quality. Two models, the Agricultural Policy/Environmental eXtender (APEX) and the Riparian Ecosystem Management Model (REMM), were used to evaluate the movement of the herbicide atrazine to the Jobos Bay National Estuarine Research Reserve from adjacent fields. The reserve is located on Puerto Rico's southeast coast. Edge-of-field atrazine outputs simulated with the APEX were routed through a grass-forest buffer using the REMM. Atrazine DT_{50} (half-life) values measured in both field and buffer soils indicated that accelerated degradation conditions had developed in the field soil due to repeated atrazine application. APEX simulations examined both the measured field and buffer soil atrazine DT_{50} and the model's default value. The use of the measured field soil atrazine degradation rate in the APEX resulted in 33 % lower atrazine transport from the field. REMM simulations indicated that the buffer system had the potential to reduce dissolved atrazine transport in surface runoff by 77 % during non-tropical storm events by increasing infiltration, slowing transport, and increasing time for pesticide degradation. During a large runoff event due to a tropical storm that occurred close to the time of an atrazine application, the REMM simulated only a 37 % reduction in atrazine transport. The results indicate that large storm events soon after herbicide application likely dominate herbicide transport to coastal waters in the region. These results agree with water quality measurements in the reserve. This study demonstrated the sensitivity of these models to variations in DT_{50} values in evaluating atrazine fate and transport in the region and emphasizes that the use of measured DT_{50} values can improve model accuracy.

Keywords Water quality · Hydrology · Wetlands · Conservation Effects Assessment Project · Tropical estuary · Predictive models

1 Introduction

The recent work in Australia has shown that residues of atrazine (6-chloro-*N*2-ethyl-*N*4-isopropyl-1,3,5-triazine-2,4-diamine) and other herbicides in streams and rivers that drain agricultural uplands may threaten coastal ecosystems [1]. Numerous studies have also shown that herbicide transport to surface waters may be reduced through the use of conservation practices such as riparian buffers [2–5]. Riparian buffers have been adopted as a best management practice (BMP) in non-point source pollution control programs [6, 7] and are part of the United States Department of Agriculture (USDA)'s Conservation Reserve Program. Herbaceous vegetative strips can also be effective in reducing herbicide loads [3, 8–10] and can be incorporated into riparian forest buffer specifications. The original USDA riparian forest buffer specification included an herbaceous (usually grass) filter strip between the source area (field) and the forest buffer [11, 12].

To our knowledge, there have been few assessments on the efficacy of vegetated buffers in reducing agrichemical transport in coastal zones particularly in tropical regions. Because

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much of the agriculture in Puerto Rico is in coastal plain areas adjacent to ecologically sensitive coastal waters, movement of atrazine and other agrichemicals from farm fields into coastal waters is a concern [13, 14]. Jobos Bay National Estuarine Research Reserve (JBNERR) in south central Puerto Rico is typical of these areas. Because of the importance of understanding the non-point source pollution impacts of agriculture on coastal waters, the Jobos Bay Watershed was selected as a USDA-Natural Resources Conservation Service (NRCS) Conservation Effects Assessment Project (CEAP) Special Emphasis Watershed in 2008. CEAP is a nationwide project led by the USDA to quantify environmental effects of conservation practices on water quality and quantity at the national scale [15]. As a Special Emphasis Watershed, the Jobos Bay CEAP was designed to be a short-term (3-year) study to evaluate the environmental effects of conservation practices on coastal waters and associated habitats in a tropical ecosystem.

Process-based simulation models are useful tools in predicting transport mechanisms of agricultural chemicals on a landscape scale as well as in evaluating the effectiveness of conservation practices over time [16]. The USDA has recognized that process-based models are valuable tools for extrapolating regional findings to a national assessment. An important component of simulation model effectiveness is site-specific parameterization which reduces prediction uncertainty [17]. For pesticides, a key parameter is the degradation/dissipation rate. Sensitivity analyses have concluded that dissipation parameters may have the greatest impact on the ability of model simulations to reflect measured data [18–20]. Default values derived from published studies and/or documents used to support pesticide registrations are often used to describe dissipation kinetics. However, values may not reflect field conditions, especially in cases where accelerated dissipation may develop following a repeated application of a pesticide [21] causing soil to “adapt.” For example, Krutz et al. [22] observed a 10-fold decrease in atrazine DT_{50} (half-life) in soils from Colorado and Mississippi when they compared adapted and non-adapted soils. These rates were 18-fold lower than the values used by the US Environmental Protection Agency (USEPA) in atrazine risk assessments [22]. Potter et al. [14] reported that accelerated atrazine dissipation conditions had developed in the silage field at the study location.

Riparian buffers have been shown to be effective in mitigating the transport of agricultural pollutants to adjacent water bodies [10–12]. With limited information on the impact of three-zone riparian buffers on atrazine transport in tropical ecosystems where tropical storms play an important role, it was important to determine the effectiveness of a three-zone buffer system as a potential conservation program to mitigate atrazine transport. In this study, we evaluated the sensitivity of the Agricultural Policy/Environmental eXtender (APEX) to DT_{50} input values to output from the fields and the effectiveness of a three-zone buffer system on atrazine transport with the Riparian Ecosystem Management Model (REMM).

2 Materials and Methods

In this evaluation, the APEX [23] and the REMM [24, 25] were used in tandem to simulate waterborne atrazine transport (dissolved and sediment bound) from an upland field through a three-zone buffer with grass and forest vegetation. The APEX simulated upland transport to the buffer zone and REMM transport within and through the buffer zone. Both the APEX and REMM were calibrated and validated for the farm fields and buffer using soil and hydrologic data from the site [26]. Measured atrazine dissipation in the field and riparian soils of the site were also used [14].

2.1 Study Site

The study site is within the Central Aguirre Watershed, a subwatershed within the Jobos Bay Watershed in south central Puerto Rico (17° 56′ 36″ N and 66° 13′ 45″ W), about 5.6 km (3.5 miles) southeast of Salinas, Puerto Rico (Fig. 1). The climate is tropical with a mean annual precipitation of 991 mm (39 in.) (1971–2000) and a mean annual temperature of 26 °C, with a maximum of 28.6 °C in August and a minimum of 22.4 °C in January [27]. Seasons are defined as dry (November–May) and wet (June–October) with the wet season corresponding to the Atlantic hurricane season. The study focused on a 108-ha (267-ac) irrigated agricultural field and an adjacent vegetated buffer adjacent to JBNERR (Fig. 1). When the Jobos Bay Watershed was designated a CEAP Special Emphasis Watershed by the USDA-NRCS, farm operators agreed to provide management data and facilitate hydrologic and water quality monitoring by USDA, JBNERR, and cooperators.

Field soils are predominantly in the Cartagena and Ponceña Soil Series. Cartagena clay soils are very deep and somewhat poorly drained, and Ponceña clay soils are moderately well drained [28]. Both soils were formed in clayey sediments weathered from volcanic rocks and limestone. Cartagena soils are found in low-lying areas and are sodium enriched, while the Ponceña soils are in slightly higher topographic positions. Both the Ponceña and Cartagena soils are classified as hydrologic soil group D (poorly drained).

The farm was under center pivot irrigation for the first 2 years of study (2008–2009) and was divided into four quadrants of 27 ha (67 ac) each (Fig. 1). All were under reduced till. Multiple crops of corn (*Zea mays* L.), sorghum (*Sorghum bicolor* L.), and/or cow peas (*Vigna sinensis* L.) were grown in each subarea in 2008 and 2009. Because each quadrant was

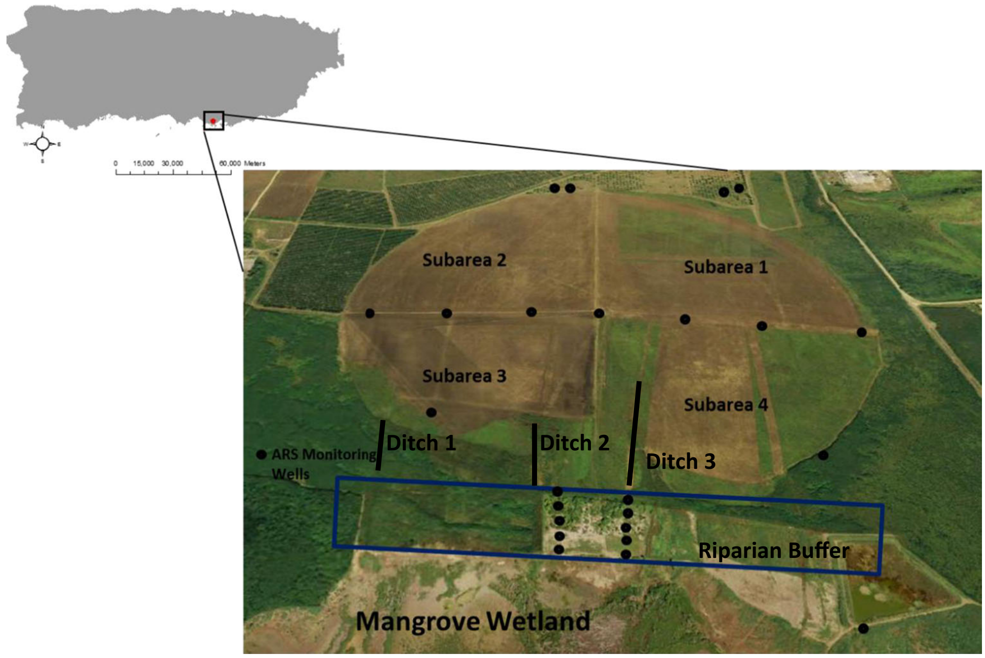

Fig. 1 Study site in southern Puerto Rico showing the location of the fields, the riparian buffer, and the mangrove wetland

managed differently, each was considered a subwatershed in the APEX and will be referred to as SA1 through SA4 (SA1, SA2, SA3, and SA4) (Fig. 1). Crops were not grown in 2010, and there were no agrichemicals applied because the irrigation system was not functioning.

Each subarea had multiple pesticide, fertilizer, and irrigation management operations for each planting. For the simulation period, subareas had an average of three plantings per year (Table 1). During the study period, individual pre-emergence atrazine applications ranged up to 962 g ha^{-1} (0.86 lb ac^{-1}) for each subarea with an annual average of 4760 g ha^{-1} (4.25 lb ac^{-1}) for all four subareas in 2008 and 2009 (Table 1). The total mass of atrazine active ingredient (AI) applied to the entire silage field during the study period was 514 kg (1133 lb). Commercial atrazine formulations were tank mixed with other herbicides and broadcast sprayed; there was no incorporation. Additional details of the farm management are given in [26].

Three drainage ditches cross the buffer area and create a hydrologic connection between the field and Mar Negro's tidal flats (Fig. 1). The drainage ditches were simulated in the APEX with an output from SA3. The flows that bypassed the riparian buffer were not simulated separately using the REMM because of model limitations, and all of the flow was simulated as if it went through the riparian buffer. The concentrated flow simulated from the upland field was distributed and simulated as overland and subsurface flows within the buffer.

The 16-ha (40-ac) buffer zone is situated in an area which lies between the farm field and the mangrove forest located on the landward edge of JBNERR (Fig. 1). The buffer soils are classified as tidal flats (TFs) which consist of low-lying areas, slightly above sea level, that are affected by seawater during storm tides. The TF soils averaged 43 % clay, 28 % sand, and 1.6 % organic carbon [26]. The buffer is 157 m (515 ft) wide from the upland field to the mangroves (perpendicular to the mangroves) and 1039 m (3409 ft) long (the dimension along the mangroves).

2.2 Use of APEX and REMM

Daily outputs from the APEX were used as daily inputs to the REMM. The APEX simulated the quadrants of the field as four separate fields (subareas). Upland fields SA1, SA2, and SA4 drained into SA3 which then became input for the REMM. The hydrologic component of the APEX [29] consists of all key processes that occur in the hydrologic cycle. Incoming precipitation may be intercepted by plant canopies, and when rainfall exceeds interception, the excess falls to the soil surface. Precipitation is then partitioned between surface runoff and infiltration. The surface runoff model in the APEX simulates runoff volumes and peak runoff rates, given daily rainfall amounts. There are two methods the user can choose from, the modified Soil Conservation Service (SCS) curve number technique [30] or the Green Ampt infiltration equation [31]. For this study, we chose the SCS curve number technique due to its reliability and relationship to soil type, land use, and management practices. The subsurface flow model includes vertical and horizontal components which are computed simultaneously using storage routing and pipe flow equations. The vertical or percolation component flows to groundwater storage and is subject to deep percolation and return flow. Return flow is added to channel flow from a subarea. Horizontal flow is partitioned into lateral and quick

Table 1 Planting, harvesting, and atrazine application schedule

Year	Subarea ID	Crop	Plant	Harvest	Atrazine applied (g ha^{-1})[a]	Atrazine application date
2008	SA1	Corn	5 February	26 April	962	28 February
2008	SA1	Corn	29 April	15 July	962	29 April
2008	SA1	Corn	30 October	19 January	1292	30 October, 13 and 28 November
2009	SA1	Cowpea	8 April	Tilled under	0	
2010	SA1	Fallow				
2008	SA2	Corn	18 January	20 March	962	19 March
2008	SA2	Sorghum	21 May	15 August	962	14 June
2008	SA2	Corn	16 December	2 February	1443	16 December
2009	SA2	Corn	1 June	31 August	1924	1 and 26 June
2009	SA2	Sorghum	14 September	7 December	721	17 September
2010	SA2	Fallow				
2008	SA3	Sorghum	19 March	23 July	962	19 March
2008	SA3	Sorghum	26 July	25 September	1924	31 July, 12 August
2008	SA3	Sorghum	27 September	7 December	0	
2009	SA3	Sorghum	4 February	24 March	962	5 February
2009	SA3	Sorghum	26 June	22 September	1443	26 June, 14 July
2009	SA3	Sorghum	26 October	7 December	962	9 November
2010	SA3	Fallow			0	
2008	SA4	Sorghum	18 January	26 April	0	26 April
2008	SA4	Sorghum	29 April	30 June	962	
2008	SA4	Sorghum	4 November	4 January	1924	4 and 25 November
2009	SA4	Sorghum	18 January	20 May	0	
2009	SA4	Sorghum	17 July	7 October	721	27 July
2009	SA4	Sorghum	12 October	7 December	0	
2010	SA4	Fallow				

[a] Grams per hectare of the active ingredient was applied to the field. Each field is 27 ha in size. Atrazine applied is the sum for multiple applications

return flow. Lateral subsurface flow enters the subarea immediately downstream and is added to that subareas' soil and water storage. Quick return flow is added to the channel flow from the subarea. The storage routing technique in the APEX allows flow from one soil layer to another when soil water content exceeds field capacity. Water drains from a layer as a function of layer storage and saturated conductivity until the storage returns to field capacity. Routing mechanisms also provide evaluation of interactions between subareas that involve surface and subsurface flows. Once overland processes have been simulated, the APEX routes water, sediment, nutrients, and pesticides across complex landscapes and channel systems to a watershed outlet. As a USDA CEAP Special Emphasis Watershed, this study was designed to be short term; therefore, a principal limitation was not having automated equipment to monitor surface flows. However, we did observe early that flows in the ditch were limited to storm events during the wet season (June–October) which corresponds to the Atlantic hurricane season.

The REMM simulated the buffer system in three distinct zones. The wide of zone 1 (nearest the estuary) was 77 m (253 ft), and the width of zone 2 was 40 m (131 ft). Vegetation in both zones was mostly leadtree (*Leucaena leucocephala* de Wit.), devil's horsewhip (*Achyranthes aspera* L.), and Egyptian river hemp (*Sesbania sesban* L. Merr.). Zone 3, which is furthest away from the mangroves, was 40 m (131 ft) wide and was covered with perennial grasses, primarily Guinea grass (*Megathyrsus* *maximus* Jacq.), signal grass (*Urochloa distachya* (L.) T.Q. Nguyen), and Johnson grass (*Sorghum halepense* L. Pers.). The slope length of the 108-ha (267-ac) contributing field was 1039 m (3409 ft), yielding a field-to-buffer area ratio of approximately 7:1. The ground surface slope from the upland field to the zone, where mangrove vegetation was predominant, was 1 %.

The REMM took upland outputs: surface runoff; subsurface flow; sediment yield; N, P, and C; pesticide in surface runoff, subsurface flow, and sediment generated by the APEX; and calculated loadings of water, nutrients, pesticides, sediment, and carbon based on the actual area of the zones in the buffer system. The APEX was executed three times with $DT_{50}=18$, 55, or 146 days. The DT_{50} values reflected measured values in field and buffer soils and the default value in APEX, respectively. The DT_{50} used in the REMM was the measured value in buffer soil. Other REMM inputs included daily weather (the same as those for the APEX), soil, plant, and litter properties by layer; vegetation type by zone and initial conditions for soil including physical and hydrologic properties; and initial carbon and nutrient pools. Other APEX model inputs included crops grown, planting and harvesting dates, tillage type and dates, and fertilizer and pesticide applications.

Weather measurements (minimum and maximum temperature, daily total solar radiation, precipitation, relative humidity, and wind speed) were obtained from a HOBO (Onset Computer Corp., Bourne, MA) weather station that was installed in 2008 (Fig. 1). Precipitation was measured using an Onset rain gauge smart sensor tipping bucket, wind speed was measured using an Onset wind speed and direction smart sensor, temperature and relative humidity were measured using an Onset temperature and relative humidity smart sensor, and solar radiation was measured using an Onset silicon pyranometer smart sensor, all of which were connected to an Onset Hobo Event logger. When data from the site were missing (January 2007 and December 2008), weather data were used from [32], a weather station which is 2 km (1.2 miles) away from the study location.

Soil layer depth, pH, percent organic carbon, bulk density, field capacity, wilting point, percentage sand and silt, saturated conductivity, cation exchange capacity, sum of bases, calcium carbonate content, and soil albedo were measured in the cultivated farm field by the USDA-NRCS [33] and in the riparian zone by the USDA-ARS, specifically for this study. Soils in the cultivated field were sampled by genetic horizons to a depth of 200 cm (79 in.) [33], and soils in the riparian zone were sampled in 10-cm (4-in.) increments to a depth of 140 cm (55 in.). The saturated hydraulic conductivity of the cultivated farm field and riparian buffer zone soil layers was estimated with the Rosetta model [34] using measurements of percentages of sand, silt, and clay; bulk density; and water retention at 33 and 1500 kPa.

2.3 Calibration and Validation of APEX and REMM

The hydrologic calibration and validation of both models are described in [26]. The APEX was calibrated for each subarea (Fig. 1) and the REMM for the buffer. The average simulated depths to water table for each subarea were within ±9 % of the corresponding observed values with the exception of SA2 for the validation period [26]. SA2 during the validation period was not cultivated and had substantial weed growth and volunteer sorghum regrowth. The APEX underpredicted the depth to the water table likely as a result of underestimated plant biomass and associated transpiration. REMM average simulated depths to the water table for the buffer area were within ±4 % of the corresponding observed values for both the calibration and validation periods [26].

APEX and REMM parameters used to evaluate the sensitivity of DT_{50} values for atrazine included solubility (33 parts per million), soil organic matter sorption coefficient (K_{oc}, 100), and atrazine DT_{50} in soil (days) (18, 55, and 146 days for the APEX and 55 days for the REMM). No further calibration beyond the hydrologic calibration described in [26] was conducted. Atrazine and atrazine degradation product concentrations were determined in monthly groundwater samples from wells in the silage field and were previously reported [14]. However, the APEX does not compute groundwater concentrations so calibration/validation with the groundwater concentration data was not possible. Limited surface runoff concentration data were available due to farming constraints [14].

Pesticides in the APEX and REMM can be intercepted by plant leaves, bound in soil, leached, transported in runoff water or on sediment in runoff [23]. The REMM is described in [35] and the REMM pesticide module in [36]. Pesticide transport in both the APEX and REMM is related to hydrology and sediment transport and is controlled by the amount of pesticide in soil and water pools. In turn, the amount of pesticide in the soil and water pools is controlled by soil sorption and desorption and dissipation. Dissipation in both models is described with a first-order kinetic equation with $DT_{50}=\ln(2)/k$ where k is the dissipation rate constant. Rate constants are adjusted for temperature and soil moisture. Because dissipation for pesticides may vary widely among soils and climate regimes [18–20], it is recommended that field-measured rates be used in model simulations [18–20]. This is especially true in tropical climates where dissipation may be more rapid [21, 37].

For this study, the measured atrazine DT_{50} averaged 18 and 55 days for the field soil and the buffer soil, respectively [14]. As noted, the difference between the field and buffer soil values was linked to accelerated atrazine degradation in the field soil after repeated atrazine applications [14].

2.4 Statistical Analysis

To compare atrazine loading between simulations, the data were tested for normal distribution using the Univariate Procedure in SAS [38]. The data were not normally distributed so non-parametric analyses were performed on atrazine loading data from the three APEX simulations and the three REMM simulations (based on the APEX loads into the REMM). The NPAR1WAY Procedure of SAS with the Kruskal-Wallis test [38] was used to test whether the loading scenarios had an effect on atrazine transport and to test whether the atrazine loading rates between the three positions in the REMM-simulated buffer (exiting zone 3, exiting zone 2, and exiting zone 1) were different from one another.

3 Results and Discussion

3.1 APEX Simulated Atrazine Transport

Total atrazine transport is reported for the entire simulation period (2008–2010) on a mass or mass per area basis. Simulated transport of atrazine in surface runoff (APEX) was significantly different ($p<0.001$) among the three simulations for the three atrazine DT_{50} values (Table 2). There was a significant difference ($p<0.001$) between the upland field as simulated using the APEX compared to each of the three riparian zone outlets as simulated by the REMM. Differences in outputs were up to 33 %. Daily atrazine mass transported in surface runoff was between 0 and 23 g ha^{-1} (0 and 0.02 lb ac^{-1}) for all scenarios (Fig. 2). Atrazine transport in surface runoff was significantly greater ($p<0.001$) when the default DT_{50}, 146 days, was used. When the measured DT_{50} was used, either 55 or 18 days, total loads were not significantly different ($p>0.05$). In all cases, the largest simulated atrazine losses in surface runoff occurred as a result of Tropical Storm Faye (August 15, 2008) when the area received 128 mm of rainfall in 24 h (Fig. 3).

Table 2 Mass of atrazine transported from the upland field (APEX), the buffer (REMM), and percent reduction in the simulated buffer for the study period (2008–2010)

APEX DT_{50} (days)	Upland field	Buffer	% reduction
Surface runoff (g ha^{-1})			
18	41^{a}	9.2^{a}	77
55	54^{b}	14^{a}	75
146	60^{b}	17^{a}	71
Subsurface flow (g ha^{-1})			
18	0.02^{a}	0.00^{a}	100
55	0.02^{a}	0.00^{a}	100
146	0.03^{a}	0.00^{a}	100
Sediment bound (g ha^{-1})			
18	0.17^{a}	0.08^{a}	50
55	0.26^{a}	0.13^{a}	50
146	0.46^{a}	0.27^{a}	42

Dissolved atrazine in surface runoff (APEX) among DT_{50} was significantly different ($p<0.001$) based on the Kruskal-Wallis test for 18-day DT_{50}

For the upland field and buffer, values with the same letter are not significantly different

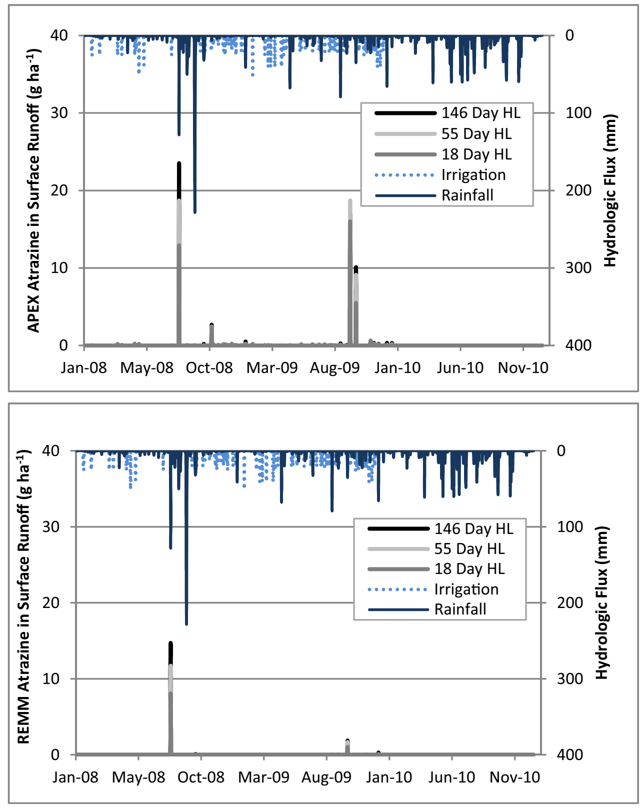

Fig. 2 Atrazine (18-, 55-, and 146-day DT_{50}) transport in surface runoff from the APEX and REMM

Intense rainfall during the wet season (June–October) is common in Puerto Rico [13, 39, 40] and is a major source of runoff which promotes water pollution from agricultural areas [13]. Two days prior to Tropical Storm Faye, 962 g ha^{-1} (0.86 lb ac^{-1}) of atrazine was applied to SA3. APEX simulations indicated that of the total amount of atrazine applied to SA3, 3 % (50 g atrazine ha^{-1}) was lost in surface runoff during the storm event when DT_{50} was 18 days, 4 % (80 g atrazine ha^{-1}) with the 55-day DT_{50} scenario, and 5 % (90 g atrazine ha^{-1}) for the 146-day DT_{50} scenario. The simulated proportion of atrazine applied that was in surface runoff was greater in some instances than measured losses from small plots under simulated tropical rain events in Brazil where 2 % of the applied mass was transported [41]. Subsequent runoff events approximately 30 days after Tropical Storm Faye cumulatively produced approximately 8 g atrazine ha^{-1} (0.02 % of atrazine applied) in surface runoff from the three simulation DT_{50} scenarios (Fig. 3c). Similar findings

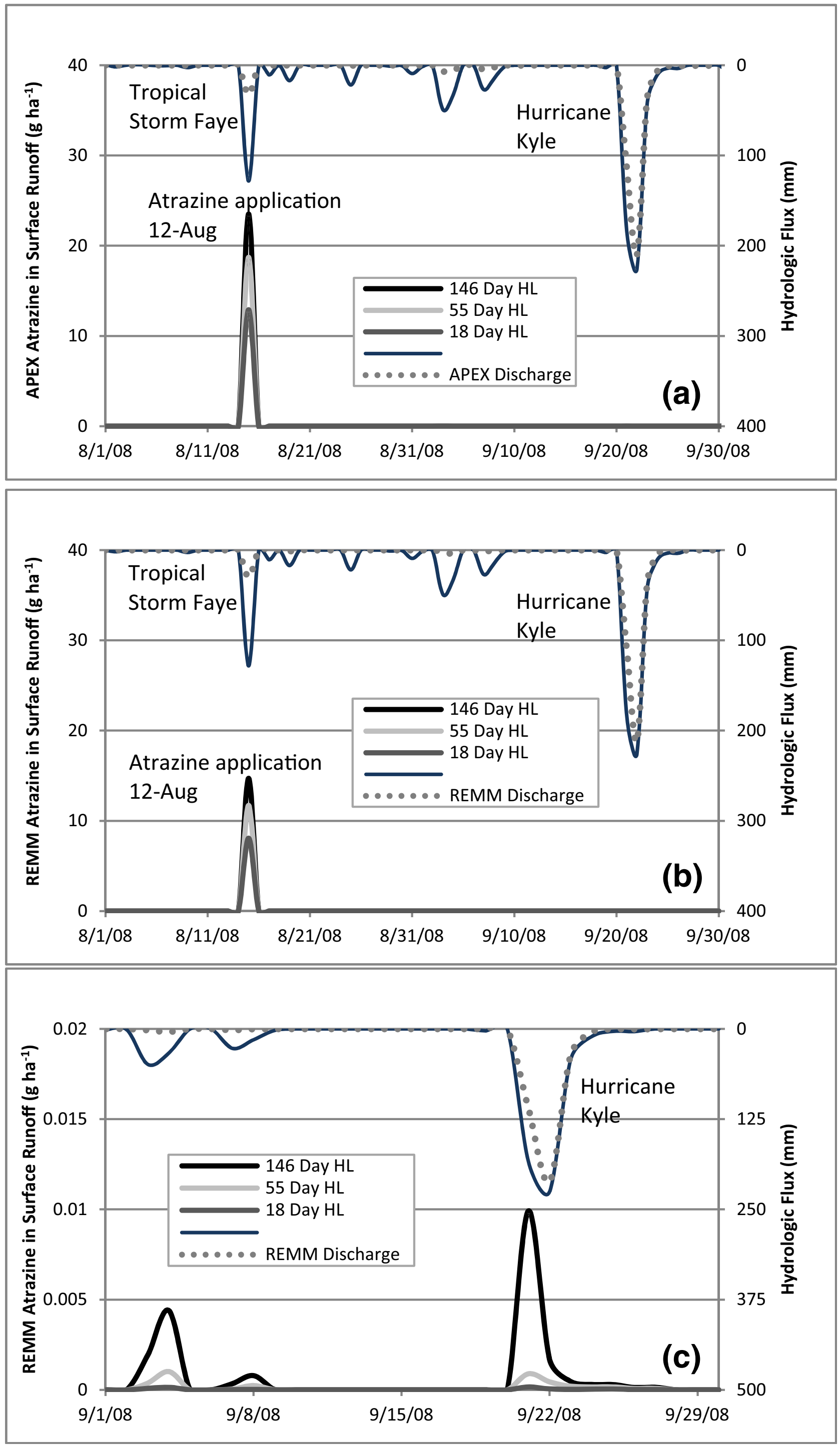

Fig. 3 Atrazine transport and discharge during Tropical Storm Faye (August 15, 2008) and Hurricane Kyle (September 21–25, 2008) for the APEX (**a**), REMM (**b**), and REMM highlighting Hurricane Kyle (**c**)

have been reported for runoff events after herbicide application in various field studies, i.e., a decrease in atrazine transport in surface runoff for a subsequent runoff event in both temperate [42–45] and tropical climates [41].

Simulated APEX sediment loads were also reflective of weather patterns. The annual APEX sediment transport in 2008 (28 Mg ha^{-1} [12.5 t ac^{-1}]) was greatest with 93 % of sediment transported due to Hurricane Kyle on September 21–25, 2008 (25.7 Mg ha^{-1} [11.5 t ac^{-1}]). The computed APEX sediment transport in 2009 and 2010 was 0.7 and 0.01 Mg ha^{-1}, respectively (0.3 and 0.005 t ac^{-1}, respectively) [26].

The APEX-simulated sediment-bound atrazine transport was much less than dissolved atrazine in surface runoff (Table 2). The mass of sediment-bound atrazine for each of the three DT_{50} dissipation scenarios was less than 0.02 % of atrazine applied. The APEX-simulated atrazine transport in subsurface flow was less than 0.05 g ha^{-1} (0.00004 lb ac^{-1}) for all scenarios (Table 2). There was no significance ($p > 0.05$) in the sediment-bound atrazine between the three DT_{50} scenarios; however, the mass of sediment-bound atrazine was greatest from the 146-day DT_{50} scenario. The low APEX-simulated subsurface transport was consistent with the relatively low groundwater concentrations reported elsewhere [14].

Overall, the total mass per area of atrazine transported using the 18-day DT_{50} in the APEX was 40.7 g ha^{-1}. This was 25 and 33 % less than that for the 55- and 146-day DT_{50} scenarios, respectively. All estimates were in the same range as those observed in other studies indicating a total loss of about 1 % of atrazine applied [43, 46, 47]. In addition, a large portion up to 93 % of the total was lost during a single storm event that occurred within 2 days of an atrazine application. The APEX simulations showed the importance of application timing in relation to storm events as well as the need to accurately simulate the dissipation of atrazine.

3.2 REMM Simulations

Generally, the greater the atrazine loading into the buffer, the greater the simulated output (Table 2). In total, the mass of atrazine transported from the REMM-simulated buffer was 23 % of the mass input from the upland. Nearly all simulated transports within the buffer were in the dissolved form in surface flow. The simulated mass transported in subsurface flow was less than 0.001 g ha^{-1} for the three loading scenarios. Sediment-bound atrazine transport was also low and primarily due to relatively low sediment loads [26] and atrazine's low soil organic matter water partition coefficient. A notable feature of simulations was buffer performance during the extreme event, Tropical Storm Faye (August 15, 2008). In this event, the REMM estimated 37 % retention of atrazine in the buffer, whereas for the entire study period, atrazine retention was 77 %. Arora et al. [44] reported a similar trend in atrazine retention in a vegetative buffer 2 days following an atrazine application and rainfall event in Iowa.

The extreme event coincided with detection of atrazine and its degradant, desethylatrazine (DEA), in near-shore estuary samples that were collected 4 days following Tropical Storm Faye. As previously mentioned, data suggests that application timing (Table 1) coupled with a significant rainfall event (128 mm [5 in.] in 24 h) was a likely cause for the detection [14]. REMM simulations indicated that 11.7 g ha^{-1} (40 μg L^{-1}) of atrazine was transported from the buffer to the estuary on the day of the rain event. The simulated volume-weighted concentration in runoff was 40 μg L^{-1}, nearly 100 times the highest measured value in estuary samples. The nearly 100-fold difference between the REMM predicted and the measured value was likely due to the fact that there were four full tidal cycles between the storm event and sample collection indicating substantial potential for dilution. REMM simulation of subsequent runoff events indicated little to no atrazine transport. This was likely due to rapid soil dissipation of atrazine; therefore, when runoff occurred, there was little or no atrazine in field soil available for runoff and any atrazine present was attenuated in the buffer.

One of the primary uses of the REMM is to evaluate buffer width and how the width of the overall buffer and the three zones are related to reductions in edge-of-field loadings. Field studies have shown a range of herbicide reduction (8 to 98 %) through vegetative buffer systems based on width [3–5, 45]. Wider vegetative strips generally reduce herbicide loads more as a result of longer contact with vegetation, increased infiltration, and increased deposition of suspended solids. However, it appears to be the relationship between the amounts attenuated and buffer width decreases exponentially [36]. For atrazine, studies have indicated that the dominant mechanism for reduction in buffers is via infiltration [48, 49]. As mentioned previously, in the case of this simulation, the dominant transport mechanism for atrazine was via surface runoff mostly associated with tropical storm events that came with heavy rains over a short period of time (Fig. 3).

The APEX-simulated total mass of atrazine transported under most likely atrazine loading rates, i.e., when measured field soil dissipation rates were used (18-day DT_{50}), and at the edge of each buffer zone is shown in Fig. 4. Total mass of atrazine transport from the field was 40.9 g ha^{-1} (0.04 lb ac^{-1}) with 18.1 g ha^{-1} (0.02 lb ac^{-1}) transported from zone 3, 12.5 g ha^{-1} (0.01 lb ac^{-1}) transported from zone 2, and 1 g ha^{-1} (0.0009 lb ac^{-1}) transported from zone 1. Over the entire study period, simulations indicated that there were significant differences ($p < 0.001$) in the atrazine transport between the upland fields and each of the buffer zones. There

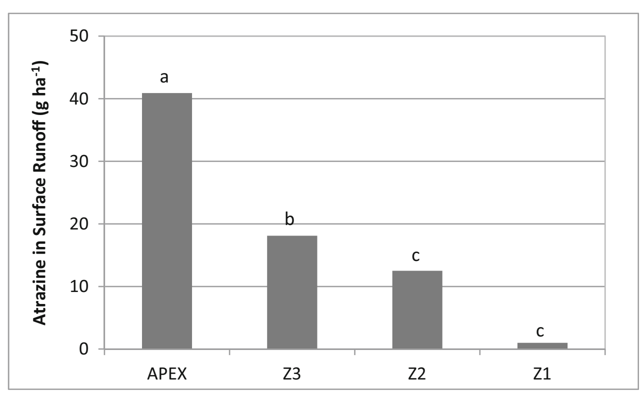

Fig. 4 Total atrazine output from the APEX (18-day DT_{50}) and REMM (55-day DT_{50}) by zone. Zone values are the total output per area from the zone. Values with *the same letter* are not significantly different based on the Kruskal-Wallis test

were also significant differences ($p < 0.001$) between atrazine from zone 3 (perennial grass) and zones 2 (mixed forest) and 1 (mixed forest). Simulated atrazine transported from the upland was reduced by 56 % at the edge of zone 3, by 70 % at the edge of zone 2, and by 77 % at the edge of zone 1. The greatest reduction ($p < 0.001$) of atrazine occurred in zone 3 which consisted of perennial grass and was consistent with field studies where grass buffers at the upslope edge of forest buffers reduced pesticide loadings [4, 5, 45].

Atrazine reduction between the edge of zone 3 (perennial grass) and zone 2 was 31 %, while it was 26 % between the edge of zone 2 (mixed forest) and zone 1 (mixed forest). There was a significant difference ($p < 0.001$) between the output from zone 3 and zone 2, but there was no significant difference ($p > 0.05$) between the outputs from zone 2 and zone 1 (Fig. 4). The combined width of zone 3 and zone 2 was 80 m (262 ft) compared to 157 m (515 ft) for the combined width of all three zones. Another aspect of buffer efficiency is buffer placement.

Williams et al. [26] calibrated and validated the hydrologic flux of the APEX and REMM using measured daily water table fluctuation. The overall reduction in water flow for the 3-year study period was 16 %. The REMM simulated an 8 % reduction of surface runoff for Tropical Storm Faye (August 15, 2008), but only a 1 % reduction in runoff from Hurricane Kyle (September 21–25, 2008) (Fig. 3). Due to the antecedent soil moisture conditions of the riparian buffer when Hurricane Kyle occurred and the intensity of the rainfall events, the reduction in surface runoff was small for Tropical Storm Faye and even smaller for Hurricane Kyle. Up until Tropical Storm Faye, the surface runoff reduction in the REMM was 100 % (Fig. 3b). A series of rain events occurring shortly after Tropical Storm Faye produced little to no surface runoff entering the buffer (Fig. 3b). However, saturated conditions in the buffer generated surface runoff from the buffer. Year 2009 was a dry year, and daily surface runoff reductions in the REMM ranged between 53 and 100 % with the exception of one rainfall event that occurred on December 25, 2009, that had 66 mm of rain with a 2 % reduction of surface runoff. Daily surface runoff reductions ranged between 18 and 100 % with an average of 82 % until October 6, 2010. Following this time, there was an increase in surface runoff by as much as 99 %. Similar trends were observed in [50], where they observed that the ratio of runoff versus precipitation, for consecutive storm events, was generally larger for a subsequent rainfall event than the previous day's event. The REMM-simulated surface runoff suggests that the riparian has the potential to significantly reduce surface runoff. However, intense rainfall events such as tropical storms and hurricanes have the potential to transport more runoff from the riparian zone to the bay (see Fig. 3b, c).

Finally, with regard to atrazine dissipation, the use of the measured field data appeared to provide a more realistic estimate of atrazine loss from the field. However, actual losses may have been less. The first-order kinetic model for dissipation that is used in both the APEX and REMM [23, 29, 35] provided a relatively poor fit to measured dissipation data (data not published). Data were more effectively described using a non-linear model. In this case, the measured DT_{50} in field soil samples was 2 days [14]. This suggests that atrazine transport to Jobos Bay may be lower than indicated with the linear first-order models used to describe atrazine dissipation kinetics in the APEX and REMM and that model accuracy could be improved by incorporating alternate kinetic models for pesticide dissipation in soil.

4 Summary and Conclusions

The sensitivity of APEX to variations in atrazine DT_{50} values and how loads may be attenuated by a buffer between the agricultural field and a mangrove wetland was evaluated using the REMM. The use of the two models in tandem provided an assessment of the capacity of a three-zone vegetated buffer to reduce atrazine transport from a farm field to Jobos Bay. There was as much as a 33 % difference in the atrazine output between the upland field simulations when the measured versus default atrazine DT_{50} values were used. REMM simulations indicated that the buffer system reduced atrazine transport by as much as 77 % (18-day DT_{50}) in surface runoff, 100 % in subsurface flow, and by as much as 50 % in sediment transport for the 3 years of the simulations. Percent reduction of atrazine in the buffer was less for large rainfall-runoff events. Atrazine application timing in relation to rainfall events was also shown to have a large impact on simulated field and buffer system losses. Accelerated dissipation as measured in the field [14] would be expected to lead to lower transport. The modeling results helped confirm this. The REMM-simulated buffer had the most atrazine reduction in zone 3 which consisted of perennial grasses. REMM simulations also indicated that a 157-m (515-ft) wide buffer (all three zones) was not significantly ($p > 0.05$) more effective than an 80-m (262-ft) wide buffer (zones 3 and 2 only). However, a shorter buffer width could also change the hydrology of the system by decreasing travel time leading to greater overland flow which may have unexpected adverse effects on atrazine transport to adjacent water bodies.

The incorporation of vegetated buffers in coastal tropical ecosystems has great implications with regard to conservation management. By design, these buffers regulate the flow of upland water entering adjacent water bodies but in tropical ecosystems where intense rainfall occurs over a period of days, buffers may do little in attenuating agricultural runoff during storm events [26, 51]. Buffers, like any conservation practice, are complementary to effective pesticide management. Further investigations should include simulations that would entail additional buffer width scenarios, especially in tropical climates that experience intensive runoff events at specific periods of the year. Lastly, investigations involving the use of predictive models to simulate pesticide transport should consider the sensitivity of these tools to variations in DT_{50} values as they would impact decisions regarding conservation management.

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