Manual composite sampling in edge-offield surface runoff for assessing nonpoint source pollution from agricultural lands and residential areas

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Abstract: While there are several surface water quality sampling techniques such as flowinterval, time-interval, and composite sampling, it is still a challenging task to select the appropriate sampling technique for edge-of-field surface runoff water quality monitoring. We hypothesized that manual composite sampling gives comparable results with discrete flowpaced sampling for edge-of-field surface runoff water quality. We collected discrete flowpaced and manual composite surface runoff water samples from sugarcane (Saccharum officinarum L.) fields, pasture lands, and residential areas from October 2002 to October 2003 and analyzed for total suspended solids (TSS), total combustible solids (TCS), five-day Biological Oxygen Demand, nitrate/nitrite-nitrogen (NO₃/NO₃-N), soluble reactive phosphate (SRP), total phosphorus (TP), total nitrogen (TN), and pH in the Vermilion-Teche River Basin in Southwestern Louisiana. Overall, compared to the flow-paced sampling, average five-day Biological Oxygen Demand, TSS, TCS, SRP, TP, NO₃/NO₂-N, and TN concentrations using composite sampling were lower by 4.3%, 8.1%, 8.2%, 9.5%, 4.1%, 36.8%, and 8.2%, respectively. As expected, the constituent concentrations with the flow-paced sampling and the composite sampling were significantly ($\alpha = 0.05$) positively correlated. Although TSS, TCS, and SRP concentrations slightly declined with flow levels and TP, NO₂/NO₂-N, and TN concentrations showed a general trend of slight increase from 15,142 L (4,000 gal) to 227,125 L (60,000 gal), correlation analysis of the pooled dataset showed no significant correlation $(\alpha = 0.05)$ between flow level and water quality constituents in this study. Similarly, no significant differences were found on event loads of TSS, TCS, SRP, TP, NO₃/NO₂-N, and TN calculated from flow-paced sampling and manual composite sampling strategies. Therefore, manual composite sampling is suggested over flow-paced sampling for edge-of-field water quality monitoring in agricultural lands and residential areas because, while producing comparable results, it reduces the cost of laboratory determination.

Key words: edge-of-field sampling—flow-paced sampling—manual composite sampling—pasture lands—residential sites—sugarcane fields—surface runoff—water quality

Nonpoint source pollution of surface water bodies is a major environmental concern worldwide. Various sources of nonpoint source pollution include surface runoff from agricultural lands, residential areas, urban areas, forest land, roads and parking lots, and abandoned mining sites. In recent years, edge-of-field surface runoff water quality monitoring has become a common approach for assessing nonpoint source pollution from these landuse types. Water quality indicators commonly used in the edge-of-field assessment of the nonpoint source pol-

lution include biological oxygen demand, total suspended solids, total dissolved solids, nutrients, pH, and fecal coliform. The use of appropriate surface runoff sampling techniques for edge-of-field surface runoff water quality monitoring is important for an accurate characterization of surface runoff water quality from these nonpoint sources and also for developing effective management strategies for nonpoint source pollution control.

Several techniques, such as grab method, composite sampling, flow-interval sampling, and time-interval sampling, are commonly

used sampling strategies for water quality monitoring and research (APHA 1998; Harmel and King 2005; Stone et al. 2000). While the selection of appropriate sampling strategy is very important for an accurate estimate of loads (King and Harmel 2003), guidance on the selection of appropriate sampling strategies is limited, especially for edge-of-field water quality monitoring (King et al. 2005). As many water quality monitoring and research programs are constrained by time, personnel, and laboratory resources, it is important to ascertain which sampling strategy is most accurate and most cost-effective.

Available literature suggests the appropriateness of flow-paced sampling (Stone et al. 2000); composite sampling (Harmel and King 2005); the combination of discrete, manual, and full cross-sectional flow sampling (Sansalone and Kim 2008); as well as single-stage, or random low-frequency sampling strategies (Toor et al. 2008) for water quality monitoring, depending on various factors such as the availability of laboratory resources, personnel, time, the size of the watershed, and the land use types. Stone et al. (2000) reported more accurate loads of nitrate-N (NO₂-N), ammonia-N, and total Kjeldahl nitrogen (TKN) from flow-proportional sampling compared to time-composited and grab sampling strategies in a watershed located in the Coastal Plain region of eastern North Carolina. On the other hand, time-interval sampling is considered better for point discharge sampling for which specific time of discharge is known.

With the availability of automated samplers and their capacities of holding 24 bottles, sampling techniques are often adopted to fit the instrumentation capacity. In automated samplers, discrete sample (i.e., one sample per bottle) or composite sample (i.e., more than one sample per bottle) can be collected. Also, composite samples can be formed manually in the laboratory by proportionally compositing samples.

As a part of a larger ongoing water quality monitoring project, this study was conducted to compare manual composite sampling with flow-paced sampling for five-day Biological

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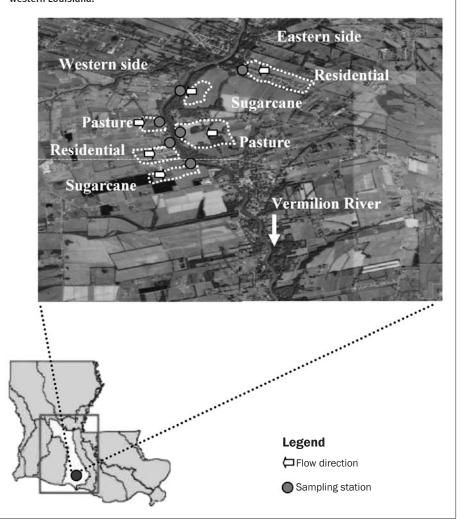
Oxygen Demand (BOD₅), total suspended solids (TSS), total combustible solids (TCS), soluble reactive phosphate (SRP), total phosphorus (TP), NO₃/NO₂-N, and total nitrogen (TN) concentrations and storm event loads in edge-of-field surface runoff and to understand the relationship between constituent's concentrations and flow levels in surface runoff from sugarcane fields, pasture lands, and residential areas.

Materials and Methods

Site Description. Six sites selected for edgeof-field surface runoff water quality monitoring in this study included two residential areas, side-by-side farmer-managed sugarcane fields, and two pasture lands on both sides of the Vermilion River in the lower region of the Vermilion-Teche Basin in southwestern Louisiana (figure 1). While Coteau Silt Loam (fine-silty, mixed, active, hyperthermic Glossaquic Hapludalfs) dominated the eastern side water quality monitoring sites, the dominant soil type for the western side water quality monitoring sites included Patoutville Silt Loam (fine-silty, mixed, superactive, thermic Aeric Epiaqualfs). Given the similar particle size distribution and the occurrence of these soils in similar slopes (<1.1%), the inherent effect of soil types on erosion and surface runoff is expected to be similar in this study. Drainage profile surveys were done for each site using a level laser and a level rod. Using aerial photographs and information gathered from the survey, a drainage boundary was established for each monitoring location. Then the total drainage area for each site was calculated using the polygon feature in ArcView GIS. The drainage areas for the two sugarcane fields were 0.97 ha (2.40 ac) and 1.77 ha (4.37 ac) and for the two pasture lands were 3.44 ha (8.50 ac) and 1.51 ha (3.73 ac). Similarly, the two residential sampling sites contained drainage areas of 2.79 ha (6.90 ac) and 2.28 ha (5.63 ac), with 22 houses and 24 houses, respectively.

The sugarcane field and the pasture land on the eastern side were under the best management practices (BMPs) plan with USDA Natural Resources Conservation Service. The BMPs implemented in the sugarcane field included the installation of drop structures, reduced tillage, nutrient management, and the application of herbicides to eliminate summer cultivation. Similarly, the pastureland under the BMP plan included drop pipes, fencing, water points, nutrient management,

Figure 1
Edge-of-field surface runoff water quality study site in Vermilion-Teche River Basin in southwestern Louisiana.



forage planting, and rotational grazing. The western side sugarcane field and the pasture land were managed following the standard conventional management practices.

The eastern side sugarcane field included a crop planted in the first week of August 2000, which was harvested in the fall of 2001, 2002, and 2003. The western side sugarcane field had the first sugarcane crop of this project planted in August 1999. The crop was harvested in the fall seasons of 2000, 2001, and 2002. The field was fallowed from October 2002 to August 2003. Then the second crop was planted in August 2003. In the eastern side pasture land, the warm season grasses bermudagrass (Cynodon dactylon L.) and bahiagrass (Paspalum notatum Flugge) formed the forage base, which was overseeded with annual ryegrass (Lolium multiflorum Lam.) for winter grazing. The cow-calf herd or replacement heifers (40 to 50 head) rotationally grazed the eastern side pasture land in short duration cycles at 20- to 30-day intervals, which allowed adequate forage regrowth. The western side pasture land had unimproved mixed warm season grasses. The producer normally allowed a portion of his 150-cow herd to irregularly graze this field during the warm season. When forage growth was sufficient, some 30 to 40 head of the crossbred cows and calves grazed, and occasionally the excess growth would be harvested once during the summer as hay.

Data Collection. All six water quality monitoring sites were fully instrumented with flowmeters (the 4250 Area Velocity Flowmeters and culverts in the two residential sites and the two sugarcane fields, and the 3230 model Bubbler Flowmeters and

H-Flumes in the two pasture sites) and the ISCO 6712 automated samplers. The autosamplers and the flowmeters were powered by 12-volt batteries and 20-volt solar panels (figure 2). The 4250 Area Velocity Flowmeters in the four sites were connected with the Area Velocity (AV) probes, while the two sites with 3230 model Bubbler Flowmeters had bubbler gauges installed on the 45.72 cm (18 in) H-Flumes (86.36 cm [34 in] wide, 172.72 cm [68 in] long, and 45.72 cm [18 in] high]). The 4250 Area Velocity Flowmeter utilizes the AV probe submerged in the flow stream for flow measurement. The 3230 Model Bubbler Flowmeter detects changes in the level of the flow stream by measuring the amount of air pressure required to force an air bubble from the end of a submerged tube. In order to protect the equipment from cows, fences were built for two pasture sites. Each site was equipped with a standard rain gauge. Surge protector lightening rods were installed at each site. Six wooden storage boxes were constructed to house each set of sampling equipment on site. Edge-offield surface runoff water quality sampling started on September 17, 2002, and ended on October 10, 2003. In order to keep up with the surface runoff sampling within the stipulated time, we monitored weather radar in the computer, kept updated with the local weather forecasts, kept the field instrumentation up to date, visited the monitoring sites regularly, and established local contacts so that people from the local communities would call us when there was a rain event at the site. Although we were hoping to sample all runoff events from these six sampling stations, our number of sampling events were affected due to several reasons including malfunctions of the field instruments due to lightening, power failures, backing up of runoff water from the ditch to the sampling station, clogging of the suction hose, and the costs of laboratory determinations. In order to keep the cost of the laboratory determination within the available budget, we skipped a few runoff events, especially those for extended rain events, as well as those following immediately after a runoff sampling event for a monitoring site. In addition, despite being relatively close in their locations, we observed variations in rainfall amounts and the occurrence of surface runoff across the six sites (table 1). On average, runoff volume from sugarcane fields, pasture lands, and the residential areas consisted of 14%, 22.4%, and

Schematic diagram for the field instrumentation of edge-of-field surface runoff water quality sampling in the Vermilion-Teche River Basin, southwestern Louisiana.

Electrical safety rod

Solar panel

Wooden box

Auto-sampler

Flow direction

H-Flume

Battery

Area velocity probe

Suction tubes

22.1% of the amount of rainfall, respectively. Since our site-specific rainfall data collection was limited to those rain events for which we collected runoff samples and were recorded at the time of sample collection, we obtained rainfall data from the nearby weather station located at the University of Louisiana at

Lafayette Research Farm at Cade, Louisiana, for monthly rainfall analysis. The results are presented in figure 3.

Initially, we had decided to sample at every 3,785 L (1,000 gal), 7,570 L (2,000 gal), 15,142 L (4,000 gal), 30,283 L (8,000 gal), 45,425 L (12,000 gal) and so on edge-of-

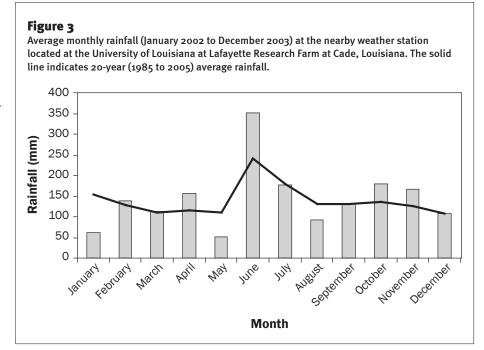


Table 1Total rainfall and the discharge amount for sampling events in the sugarcane fields, pasture lands, and the residential areas in Vermilion-Teche River Basin, Louisiana.

	Date	Precipitation (mm)	Discharge (mm)	Number of flow- paced sample	Site
Sugarcane	10/26/2002	123.4	9.36	7	Eastern side
fields	02/25/2003	53.4	3.13	2	Eastern side
	10/10/2003	87.6	14.01	9	Eastern side
	10/10/2002	10.2	1.71	3	Western side
	10/26/2002	125	17.11	21	Western side
	11/05/2002	52.6	20.51	13	Western side
	12/04/2002	32.2	6.84	8	Western side
	02/21/2003	23.2	4.28	5	Western side
	06/03/2003	54	1.71	2	Western side
Pasture	12/04/2002	18.4	2.65	6	Eastern side
lands	02/21/2003	21.4	1.77	4	Eastern side
	06/11/2003	41.4	6.61	15	Eastern side
	01/30/2003	19.4	19.0	19	Western side
	02/07/2003	11.8	2.1	2	Western side
	02/21/2003	26.4	7.02	7	Western side
	06/03/2003	27	2.01	2	Western side
	06/11/2003	40	5.01	5	Western side
Residential	10/10/2002	4.4	3.25	4	Eastern side
areas	11/05/2002	57	1.63	3	Eastern side
	12/04/2002	30.6	7.6	14	Eastern side
	12/13/2002	7	4.34	3	Eastern side
	02/07/2003	11	3.8	7	Eastern side
	02/10/2003	5.8	1.63	3	Eastern side
	10/26/2002	116	22.58	33*	Western side
	11/05/2002	56	6.64	10	Western side
	12/04/2002	16.8	3.98	6	Western side
	01/30/2003	17.2	6.64	10	Western side
	02/21/2003	22.8	15.27	23	Western side
	06/03/2003	50.8	9.96	15	Western side

^{*} Sampling was done twice for this extended rain storm (Hurricane Lily).

field surface runoff from the monitoring sites. However, after considering the large number of samples generated and the large runoff volume occurring at the monitoring sites, we decided to follow an equal flow-paced sampling protocol and collected surface runoff water samples at every 15,142 L interval so that flow-paced sampling occurred at 15,142 L, 30,283 L, 45,425 L, 60,567 L (16,000 gal) and so on, and the automated ISCO samplers were set to begin accordingly. The 1 L (0.264 gal) flow-paced water sample bottles (two or several from each sampling station) from the automated ISCO samplers were put in an ice chest with ice packs and were transported to the laboratory, and then the manual composite sampling was done by taking 400 mL (13.53 fl oz) sub-samples from each bottle considering the proportionality of the flows and mixing thoroughly in a bucket and collecting one composite sample of 600 mL (20.29 fl oz) per storm event. The 600 mL of water sample from each bottle was allocated for flow-paced water constituent's

determination. Thus each rain event sampled consisted of several flow-paced samples and one composite sample (table 1), resulting in a total of 261 flow-paced samples and 29 composite samples for laboratory determination. For all of these samples, TSS, TCS, TN, TP, BOD₅, NO₃/NO₂-N, SRP, and pH were determined using standard methods (APHA 1998). Flow data were recorded directly from the flow meter for each runoff event.

Data Analysis. For flow-paced discrete sampling, the flow-weighted average of each water quality constituent was calculated by multiplying constituent concentration at each flow interval with the corresponding flow volume (L), summing them up, and then dividing by the total flow volume (L) of the runoff event. Event loads of water quality constituents for each runoff event were calculated by multiplying total flow volume with flow-weighted averages as well as composite sampling concentrations. To understand how the constituent's concentrations change with respect to flow levels, average values for

each constituent were calculated for flow levels ranging between 15,142 L (4,000 gal) to 227,125 L (60,000 gal) by landuse types. The reason for selecting this range of flow level was the presence of flow-paced samples beyond 227,125 L discharge only in a limited monitoring site and having only one or two data points at each flow category. There were only five sampling events, two of them for the western side sugarcane field (302,832 L [80,000 gal] total discharge on October 26, 2002, and 363,400 L [96,000 gal] total discharge on November 5, 2002), two for western side residential areas (514,816 L [136,000 gal] total discharge on October 26, 2002, and 348,258 L [92,000 gal] total discharge on February 21, 2003), and one for western side pasture land (287,691 L [76,000 gall total discharge on January 30, 2003) having flow-paced samples beyond 227,125 L flow level. Otherwise, all the flow-paced samples were included in the analysis.

For comparison of the two techniques, water quality constituent's concentrations and event loads using flow-pace sampling and composite sampling were analyzed and compared by three landuse types as well as by pooling together, for overall comparison, the dataset representing the three landuse types. Average constituent concentrations as well as event loads from these two techniques were compared using student t-test in Statistical Analysis Systems (SAS 2003). Linear regression between flow-weighted averages and composite sampling concentrations were done. Descriptive statistics such as mean, range, and standard error were calculated for each of the water quality constituents by landuse types as well as for the overall dataset for flow-paced sampling and the composite sampling.

Results and Discussion

Runoff Volume Constituent Concentrations. Except for BOD, in the residential area and the TSS and TCS in pasture land (figure 4), there was no noticeable decline in the average concentrations of the constituents and pH with the amount of flow in sugarcane fields, pasture lands, and the residential areas (figures 4, 5, and 6). Since we were able to collect runoff samples for only two runoff events, one on October 26, 2002, and another on November 5, 2002, in the western side sugarcane field generating runoff beyond 151,416 L (40,000 gal) flow, the constituent's result in figures 4, 5, and 6 for

Table 2Average (composite sample) and weighted average (flow-paced sample) five-day biological oxygen demand (BOD₅), total suspended solids (TSS), total combustible solids (TCS), soluble reactive phosphate (SRP), total phosphorus (TP), nitrate/nitrite-nitrogen (NO₃/NO₂-N), total nitrogen (TN), and pH in edge-field surface runoff from sugarcane fields, pasture lands, and residential areas in Vermilion-Teche River Basin, Louisiana.

		Sugarcane field runoff		Pasture land run	Pasture land runoff		Residential area runoff	
		Composite sample	Flow-paced sample	Composite sample	Flow-paced sample	Composite sample	Flow-paced sample	
$BOD_5 \; (mg\;L^{\mathtt{-1}})$	n	9	9	8	8	12	12	
	Average	6.57 (± 2.24)	6.88 (±2.05)	10.62 (±2.29)	10.77 (±2.19)	4.08 (±0.62)	4.45 (±0.57)	
	Range	1.35 to 23.82	2.25 to 22.67	1.20 to 20.82	1.70 to 19.05	0.10 to 7.95	0.90 to 7.25	
TSS (mg L-1)	n	9	9	8	8	12	12	
, ,	Average	651.01 (±208.54)	680.44 (±205.81)	33.07 (±14.49)	54.04 (±24.95)	22.21 (±5.51)	33.30 (±12.04)	
	Range	36.00 to 1,691.53	45.70 to 1,865.83	0.19 to 126.58	4.95 to 216.11	3.91 to 66.76	6.64 to 133.47	
TCS (mg L-1)	n	9	9	8	8	12	12	
, , ,	Average	571.37 (±189.79)	598.42 (±189.08)	19.55 (±9.45)	33.53 (±14.32)	12.06 (±4.71)	22.93 (±10.47)	
	Range	15.70 to 1,543.70	25.10 to 1,713.40	0.10 to 77.90	1.90 to 117.20	0.10 to 51.20	0.40 to 113.20	
SRP (mg L ⁻¹)	n	9	9	8	8	11	11	
, ,	Average	0.14 (±0.03)	0.16 (±0.03)	0.65 (±0.16)	0.77 (±0.20)	0.37 (±0.05)	0.37 (±0.05)	
	Range	0.05 to 0.33	0.06 to 0.33	0.26 to 1.65	0.27 to 2.05	0.18 to 0.73	0.14 to 0.71	
TP (mg L ⁻¹)	n	4	4	7	7	6	6	
, ,	Average	0.32 (±0.04)	0.48 (±0.11)	1.00 (±0.28)	1.04 (±0.28)	0.57 (±0.09)	0.50 (±0.11)	
	Range	0.21 to 0.42	0.22 to 0.68	0.45 to 2.56	0.54 to 2.63	0.34 to 0.89	0.19 to 0.93	
$\mathrm{NO_{3}/NO_{2}\text{-}N}~(\mathrm{mg}~\mathrm{L}^{\mathrm{-1}})$	n	9	9	8	8	11	11	
	Average	0.27 (±0.10)	0.44 (±0.19)	0.78 (±0.30)	1.26 (±0.41)	0.32 (±0.08)	0.44 (±0.13)	
	Range	0.02 to 1.00	0.01 to 1.50	0.03 to 2.66	0.04 to 3.33	0.01 to 0.86	0.15 to 1.53	
TN (mg L ⁻¹)	n	4	4	7	7	6	6	
	Average	1.53 (±0.25)	2.00 (±0.38)	3.94 (±0.81)	4.32 (±0.56)	1.66 (±0.13)	1.55 (±0.25)	
	Range	1.03 to 2.20	0.94 to 2.73	1.22 to 6.61	2.27 to 6.69	1.24 to 2.13	0.51 to 2.27	
На	n	2	2	3	3	1	1	
•	Average	5.89 (±0.12)	5.81 (±0.26)	6.35 (±0.10)	6.23 (±0.14)	6.81	6.6	
	Range	5.77 to 6.00	5.56 to 6.07	6.18 to 6.55	5.97 to 6.42			

Note: Numbers in parentheses are ± standard error of mean.

the sugarcane fields beyond 151,416 L flow represents the western side sugarcane field and the two above mentioned rain events. The NO₂/NO₂-N concentrations in these two runoff events in the western side sugarcane field ranged between 0.01 mg L⁻¹ to 0.07 mg L⁻¹ on October 26, 2002, and 0.01 $mg L^{-1}$ to 0.02 $mg L^{-1}$ on November 5, 2002. The NO₂/NO₂-N concentration for the preceding runoff event on October 10, 2002, in the western side sugarcane field ranged between 0.40 to 0.55 mg L⁻¹. The decline in NO₃/NO₂-N in surface runoff at a later date in this field might have been associated with plant uptake, leaching losses (Poudel et al. 2001), or losses with runoff water. Water quality samples for the determination of TP and TN for the two runoff events were discarded due to their failure to meet laboratory QA/QC (quality assurance/quality control) protocols. Hurricane Lily on October 26, 2002, brought as high as 125 mm (4.92 in) of precipitation at the time of sampling and was the major rainstorm event during this study. However, we were able to collect runoff samples from only three sites, two sug-

arcane sites and the western side residential site for this rain storm event. Reasons for the failure to collect samples from the remaining sites included the damage of samplers due to lightening and tree falls, disruption of the runoff flow, and back up of water from the ditch, especially in the eastern side residential area.

For the flow-paced samples beyond 227, 125 L (60,000 gal) discharge, the BOD₅, TSS, SRP, and NO₂/NO₂-N showed average concentrations (n = 3) of 2.9 mg L⁻¹, 249.6 mg L⁻¹, 0.29 mg L⁻¹, and 0.13 mg L⁻¹, respectively, at 348,258 L (92,000 gal) flow (data not shown), further suggesting that except for BOD5, there was no indication of substantial reduction in the concentrations of these water quality constituents, even at a considerably higher edge-of-field flow volume. Similarly, average TP and TN concentrations (n = 2) at 287,691 L (76,000 gal) flow volume were 0.67 mg L⁻¹ and 4.4 mg L⁻¹, respectively. Furthermore, for a single runoff event that was sampled on October 26, 2002, in the western side residential area, the BOD₅, SRP, and NO₃/NO₂-N ranged

between 4.44 mg L^{-1} to 4.74 mg L^{-1} , 0.41 mg L^{-1} to 0.49 mg L^{-1} , and 0.11 mg L^{-1} to 0.23 mg L^{-1} , respectively, for flow volumes that ranged between 393,683 L (104,000 gal) and 514,816 L (136,000 gal).

Overall for the three landuse types, water quality constituent concentrations did not appreciably change with the runoff volume (figure 7). While average concentrations of BODs, TSS, TP, and TN for 15,142 L (4,000 gal) flow were 8.53 mg L⁻¹, 344.9 mg L-1, 0.59 mg L-1, and 2.53 mg L-1, respectively, average BOD, TSS, TP, and TN for 227,125 L (60,000 gal) flow were 7.32 mg L⁻¹, 133.3 mg L⁻¹, 0.78 mg L⁻¹, and 3.8 mg L⁻¹, respectively, suggesting comparable levels of concentrations between the 15,142 L and 227,125 L edge-of-field flow volume. Also, we found no significant correlation (\alpha = 0.05) between flow level and BOD, TSS, TCS, SRP, TP, NO₃/NO₃-N, TN, and pH for the pooled dataset. These results clearly indicate that the concentrations of water quality constituents in this study were substantially high, even after a large volume of surface runoff from sugarcane fields, pasture lands, and residential areas.

Average concentration of five-day biological oxygen demand (BOD_c), total suspended solids (TSS), and total combustible solids (TCS) in edge-offield surface runoff from (a and d) sugarcane fields (b and e), pasture lands, and (c and f) the residential areas in Vermilion-Teche River Basin in southwestern Louisiana using flow-paced sampling. Sugarcane field (d) Sugarcane field (a) ■ TSS 1,800 30 ■ BOD_e □ TCS Concentration (mg L⁻¹) 1,600 Concentration (mg L⁻¹) 25 1,400 20 1.200 1,000 15 800 10 600 5 400 200 0 45,425 121,133 136,275 151,416 166,558 211,983 30,283 60,567 75,708 90,850 105,991 181,700 196,841 0 75,708 105,991 30,283 45,425 136,275 151,416 166,558 211,983 15,142 90,850 121,133 181,700 60,567 196,841 Flow-paced sample (L) Flow-paced sample (L) (b) **Pasture land** (e) **Pasture land** □ BOD, 14 Concentration (mg L⁻¹) 160 **■ TSS** Concentration (mg L⁻¹) 12 140 □ TCS 10 120 8 100 80 6 60 4 40 2 20 75,708 45,425 30,283 136,275 151,416 166,558 136,275 151,416 166,558 30,283 75,708 90,850 121,133 181,700 196,841 211,983 45,425 60,567 90,850 121,133 181,700 211,983 227,125 60,567 105,991 196,841 15,142 105,991 Flow-paced sample (L) Flow-paced sample (L) (c) Residential area (f) Residential area □ BOD_E Concentration (mg L $^{-1}$) Concentration (mg L⁻¹) 80 ■ TSS 7 70 6 5 4 ☐ TCS 60 50 40 3 30 2 20 15,142 45,425 60,567 75,708 90,850 136,275 151,416 166,558 181,700 196,841 211,983 227,125 15,142 75,708 30,283 105,991 121,133 151,416 166,558 45,425 105,991 121,133 136,275 181,700 211,983 30,283 90,850 196,841 60,567 Flow-paced sample (L) Flow-paced sample (L)

Figure 4

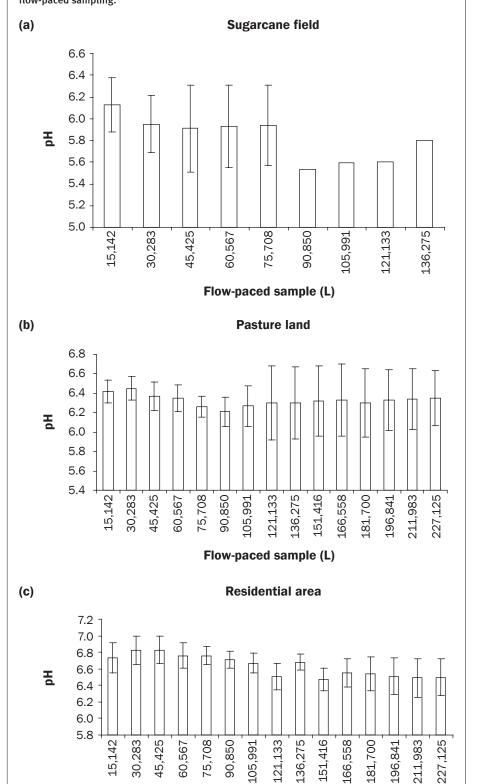
Figure 5 Average concentration of total nitrogen (TN), nitrate/nitrite-nitrogen (NO₃/NO₂-N), total phosphorus (TP), and soluble reactive phosphate (SRP) in edge-of-field surface runoff from (a and d) sugarcane fields (b and e) pasture lands, and (c and f) the residential areas in Vermilion-Teche River Basin in southwestern Louisiana using flow-paced sampling. Sugarcane field (d) Sugarcane field (a) ■ TN □ TP 3 0.7 Concentration (mg L-1) Concentration (mg L⁻¹) $\square NO_3/NO_2-N$ □SRP 0.6 2.5 0.5 2 0.4 1.5 0.3 1 0.2 0.5 0.1 166,558 45,425 75,708 151,416 196,841 15,142 30,283 60,567 90,850 -05,991121,133 136,275 181,700 211,983 227,125 0 15,142 30,283 75,708 136,275 45,425 90,850 121,133 151,416 166,558 181,700 196,841 211,983 227,125 60,567 105,991 Flow-paced sample (L) Flow-paced sample (L) (b) **Pasture land** (e) **Pasture land** ■ TN □ TP $\square NO_3/NO_2-N$ □ SRP 10 Concentration (mg L⁻¹) 9 Concentration (mg L⁻¹) 1.8 1.6 8 7 1.4 6 1.2 5 1 4 0.8 3 0.6 0.4 0.2 0 196,841 227,125 15,142 30,283 45,425 60,567 75,708 90,850 105,991 121,133 136,275 151,416 166,558 181,700 211,983 30,283 45,425 75,708 121,133 136,275 151,416 166,558 211,983 227,125 15,142 60,567 90,850 105,991 181,700 196,841 Flow-paced sample (L) Flow-paced sample (L) **Residential area** (f) (c) Residential area □ TP ■ TN Concentration (mg L⁻¹) $\square NO_3/NO_2-N$ □ SRP 3 Concentration (mg L⁻¹) 2.5 1 2 0.8 1.5 0.6 1 0.4 0.5 0.2 45,425 75.708 121,133 136,275 151,416 166,558 181,700 196,841 211,983 15,142 30,283 50,567 90,850 227,125 30,283 60,567 75,708 90,850 .05,991 45,425 105,991 121,133 136,275 151,416 166,558 181,700 211,983 227,125 15,142 196,841

Flow-paced sample (L)

Flow-paced sample (L)

Figure 6

Average pH in edge-of-field surface runoff from (a) sugarcane fields (b) pasture lands, and (c) the residential areas in Vermilion-Teche River Basin in southwestern Louisiana using flow-paced sampling.



Flow-paced sample (L)

Constituent Concentrations Using Flowpaced Sampling and Composite Sampling. There was a significant ($\alpha = 0.05$) positive correlation between flow-weighted averages and manual composite concentrations for BOD_r (r = 0.98), TSS (r = 0.98), TCS (r = 0.98)0.98), SRP (r = 0.96), TP (r = 0.94), NO₂/ NO_2 -N (r = 0.73), and TN (r = 0.89) (figure 8). Except for NO₂/NO₂-N, which had a relatively weaker correlation coefficient compared to other constituents, these results clearly indicate that manual composite sampling and the flow-paced discrete sampling result in comparable water quality constituent concentration in edge-of-field surface runoff water quality monitoring.

No statistically significant differences on the constituent's concentrations using the flow-paced sampling and the composite sampling were observed for each landuse type (table 2). However, composite sampling resulted in consistently less average concentration compared to the flow-paced sampling. Contrasting differences were found with respect to NO₂/NO₂-N concentration. The NO₂/NO₂-N concentrations using composite sampling in the sugarcane field, pasture land, and the residential areas were less by 38.6%, 38.1%, and 27.2%, respectively. This relatively large difference of the means of NO₂/NO₂-N from the two sampling techniques deserves some attention. The reason for this difference between flow-weighted average NO₂/NO₂-N and the composite sampling NO₂/NO₂-N concentration is unclear, but we suspect the following two factors: (1) NO₂/NO₂-N transformation due to the aeration of composite samples while manual compositing in the laboratory as subsamples from each flow-paced samples were poured into a bucket and were thoroughly mixed prior to collecting a composite sample, and (2) the adsorption of particulate organic matter and clay particles on the container's surface while compositing the subsamples.

While statistically not significantly different ($\alpha = 0.05$) by student t-test, average manual composite concentration for BOD₅, TSS, TCS, SRP, TP, and TN for the pooled data were less by 4.3%, 8.1%, 8.2%, 9.5%, 4.2%, and 8.2%, respectively, compared to the corresponding flow-weighted average (table 3). The NO₃/NO₂-N composite concentration was 36.8% less compared to the flow-weighted average NO₃/NO₂-N concentration. These results indicate that with appropriate sample collection, handling and

Figure 7

For pooled data, average concentration of (a) five-day biological oxygen demand (BOD₅), (b) total suspended solids (TSS) and total combustible solids (TCS), (c) total nitrogen (TN) and nitrate/nitrite-nitrogen (NO₃/NO₂-N), (d) total phosphorus (TP) and soluble reactive phosphate (SRP), and (e) pH in edge-of-field surface runoff from sugarcane fields, pasture lands, and the residential areas in Vermilion-Teche River Basin in southwestern Louisiana using flow-paced sampling.

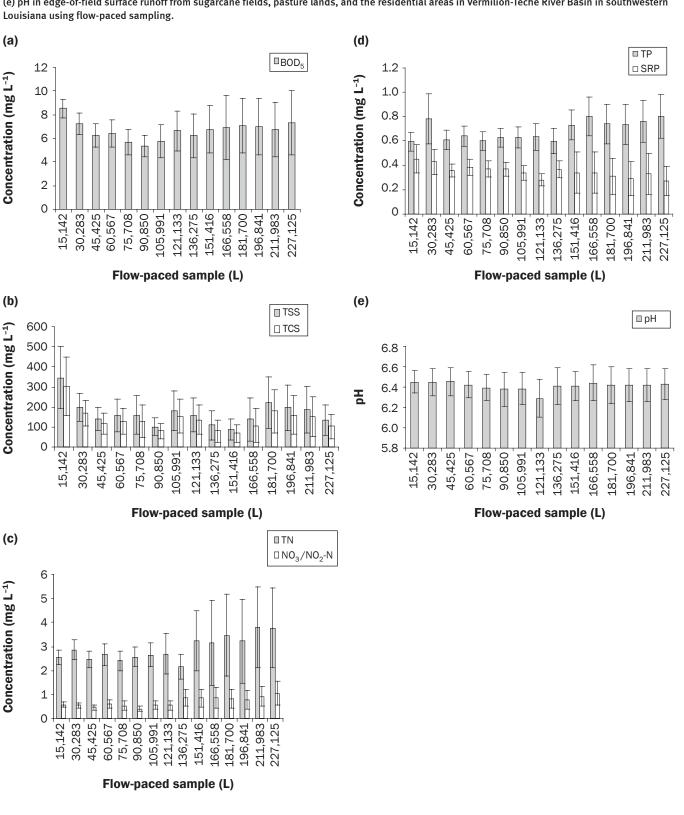


Figure 8 Correlations between average (a) five-day biological oxygen demand (BOD.), (b) total suspended solids (TSS), (c) total combustible solids (TCS), (d) soluble reactive phosphate (SRP), (e) total phosphorus (TP), (f) nitrate/nitrite-nitrogen (NO₂/NO₂-N), and (g) total nitrogen (TN) concentrations from flow-paced sampling and the manual composite sampling in edge-of-field surface runoff from sugarcane fields, pasture land, and residential areas in Vermilion-Teche River Basin in southwestern Louisiana. (a) (e) weighted flow average weighted flow average 25 3.0 $= 0.942x + 0.741, r^2 = 0.97$ $y = 0.957x + 0.064, r^2 = 0.89$ 2.5 20 2.0 15 1.5 10 1.0 0.5 5 0 0 10 15 20 25 30 1.5 2.0 2.5 3.0 0 1.0 0 5 0.5 TP (mg L-1) composite sampling BOD₅ (mg L⁻¹) composite sampling (f) (b) weighted flow average weighted flow average 2,000 1,800 3.5 $y = 1.125x + 22.117, r^2 = 0.97$ $y = 1.033x + 0.383, r^2 = 0.53$ NO₃/NO₂-N (mg L⁻¹) 3.0 1,600 2.5 1,400 1,200 2.0 1,000 1.5 600 1.0 400 0.5 200 0 800 1,000 1,200 1,400 1,600 1,800 0.5 1.0 1.5 2.0 2.5 3.0 TSS (mg L-1) composite sampling NO₃/NO₂-N (mg L⁻¹) composite sampling (c) (g) 1,800 weighted flow average weighted flow average $y = 1.128x + 20.176, r^2 = 0.97$ $y = 0.832x + 0.685, r^2 = 0.80$ 1,600 1,400 6 TN (mg L⁻¹) 1,200 5 4 1,000 800 3 2 1 600 400 200 0 800 1,000 1,200 1,400 1,600 1,800 TN (mg L-1) composite sampling TCS (mg L-1) composite sampling (d) 2.5 weighted flow-average $= 1.192x - 0.038, r^2 = 0.93$ 2.0 1.5

1.5

SRP (mg L-1) composite sampling

1.0 0.5

Table 3

Average concentration of five-day biological oxygen demand (BOD $_5$), total suspended solids (TSS), total combustible solids (TCS), soluble reactive phosphate (SRP), total phosphorus (TP), nitrate/nitrite-nitrogen (NO $_3$ /NO $_2$ -N), total nitrogen (TN), and pH for the pooled data in edge-of-field surface runoff water quality using manual composite and flow-paced sampling from sugarcane fields, pasture lands, and residential areas, Louisiana.

		Composite sample	Flow-paced sample
BOD ₅ (mg L ⁻¹)	n	29	29
-	Average	6.65 (±1.05)	6.95 (±1.00)
	Range	0.10 to 23.82	0.88 to 22.67
TSS (mg L ⁻¹)	n	29	29
	Average	220.35 (±82.81)	239.85 (±83.33)
	Range	0.19 to 1,691.53	4.95 to 1,865.83
TCS (mg L ⁻¹)	n	29	29
	Average	187.70 (±74.63)	204.45 (±75.48)
	Range	0.10 to 1,543.70	0.40 to 1,713.40
SRP (mg L ⁻¹)	n	28	28
	Average	0.38 (±0.06)	0.42 (±0.08)
	Range	0.05 to 1.65	0.06 to 2.05
TP (mg L^{-1})	n	17	17
	Average	0.69 (±0.13)	0.72 (±0.14)
	Range	0.21 to 2.56	0.19 to 2.63
$NO_3/NO_2-N \text{ (mg L}^{-1})$	n	28	28
	Average	0.43 (±0.10)	0.68 (±0.15)
	Range	0.01 to 2.66	0.02 to 3.33
TN (mg L ⁻¹)	n	17	17
	Average	2.57(±0.43)	2.80 (±0.41)
	Range	1.03 to 6.61	0.51 to 6.69
pH	n	6	6
	Average	6.27 (±0.15)	6.15 (±0.15)*
	Range	5.77 to 6.81	5.56 to 6.60

Note: Numbers in parentheses are ± standard error of mean.

processing protocols, especially for NO₃/NO₂-N concentrations, the constituent's concentrations resulting from using composite sampling are quite comparable to the flow-paced sampling.

Event Loads. Except for NO₂/NO₂-N event loads across the three landuse types, the two sampling techniques resulted generally in comparable event loads, with some level of differences in TSS and TCS event loads in pasture lands and the residential areas for the water quality constituents being studied (table 4). Corresponding to average NO₃/ NO2-N concentrations in surface runoff from the three landuse types being studied using the two sampling techniques (table 2), the NO₃/NO₂-N event loads using composite sampling in sugarcane fields, pasture lands, and the residential areas were lower by 24.7%, 32.7%, and 32.1%, respectively, compared to the flow-paced sampling.

No statistical differences were observed ($\alpha = 0.05$) between the storm event loads calculated from the two sampling strategies (table 5) for the pooled data. Overall average

event loads for the constituents calculated from manual composite sampling were lower by 7.7% for SRP, 3.3% for TP, 8.1% for TN, and 31.2% for NO $_3$ /NO $_2$ -N compared to event loads calculated from flow-paced sampling. Overall TSS and TCS event loads from composite sampling were lower by 0.9% and 1.2%, respectively, compared to the flow-paced sampling. Based on these results, we can safely state that the two techniques result in comparable event loads for nutrients and suspended solids from sugarcane fields, pasture lands, and residential areas.

Summary and Conclusions

Manual composite sampling of edge-of-field surface runoff resulted in comparable concentrations of BOD₅, TSS, TCS, TN, TP, SR P, and pH with flow-paced sampling in surface runoff water quality monitoring from sugarcane fields, pasture lands, and residential areas. Similarly, average event loads for TSS, TCS, TN, TP, and SRP between the manual composite sampling and the flow-paced sampling were comparable in these landuse types.

However, average NO₂/NO₂-N concentration using manual composite sampling in sugarcane fields, pasture lands, and residential areas were lower by 38.6%, 38.1%, and 27.2%, respectively, compared to the flow-paced sampling. Corresponding similar differences were observed between these two techniques with regard to NO₃/NO₂-N event loads for these landuse types. This relatively lower level of NO₃/NO₂-N concentrations and event loads in manual composite sampling is believed to be associated with NO₃/NO₂-N transformation due to the aeration of composite samples and the adsorption of particulate organic matter and clay particles on the container surfaces while manual compositing. It is believed that this difference could be corrected by programming the autosampler for collecting a composite sample in the field as well as by using glass containers for sample processing. The total number of samples in manual composite sampling for laboratory determination was 89% less compared to the total number of samples using flowpaced sampling. Considering the remarkable reduction in the number of samples for laboratory determination and having the comparable results from these two sampling techniques, manual composite sampling is suggested, especially for long-term monitoring of edge-field surface runoff water quality for nonpoint source pollution control in agricultural lands and residential areas in the coastal humid tropics.

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^{*}Average of the flow-interval pH, not a weighted average.

Table 4Average storm event load of total suspended solids (TSS), total combustible solids (TCS), soluble reactive phosphate (SRP), total phosphorus (TP), nitrate/nitrite-nitrogen (NO₃/NO₂-N), and total nitrogen (TN) in edge-of-field surface runoff from sugarcane fields, pasture lands, and residential areas in Vermilion-Teche River Basin, Louisiana, using composite sample and flow-paced sample.

		Sugarcane field runoff		Pasture land runo	Pasture land runoff		runoff
		Composite sample	Flow-paced sample	Composite sample	Flow-paced sample	Composite sample	Flow-paced sample
TSS (g ha ⁻¹)	n	9	9	8	8	12	12
	Average	60,104.3 (±23,788.3)	57,149.17 (±20,417.26)	1,953.16 (±1,129.56)	3,361.11 (±1,897.28)	1,400.43 (±521.26)	2,243.37 (±1,038.17)
	Range	615.90 to 190,711.10	781.90 to 159,854.70	5.00 to 9,611.90	130.70 to 16,087.80	214.90 to 6,650.40	198.50 to 13,295.80
TCS (g ha-1)	n	9	9	8	8	12	12
,	Average	52,163.16 (±20,454.40)	49,378.31 (±17,445.95)	1,271.57 (±833.18)	2,448.20 (±1552.32)	729.87 (±422.68)	1,542.01 (±899.68)
	Range	268.61 to 160,369.64	429.44 to 138,917	1.76 to 6,956.03	48.95 to 13,052.80	3.26 to 5,100.34	12.21 to 11,275.54
SRP (g ha ⁻¹)	n	9	9	8	8	11	11
	Average	9.97 (±2.75)	12.24 (±3.75)	31.57 (±11.94)	34.24 (±9.18)	27.74 (±8.21)	28.82 (±8.99)
	Range	2.57 to 23.88	3.75 to 30.91	5.21 to 112.41	5.41 to 91.45	3.91 to 85.80	3.91 to 97.09
TP (g ha ⁻¹)	n	4	4	7	7	6	6
,	Average	20.99 (±12.71)	23.95 (±10.53)	51.75 (±20.10)	55.68 (±21.34)	39.81 (±12.23)	37.17 (±13.55)
	Range	5.65 to 59.01	9.41 to 54.79	11.83 to 167.66	10.83 to 179.09	6.51 to 88.66	5.37 to 92.64
NO_3/NO_2 -N (g ha $^{-1}$)	n	9	9	8	8	11	11
	Average	21.90 (±14.85)	29.07 (±19.31)	78.34 (±61.35)	116.39 (±75.70)	21.86 (±6.53)	32.20 (±12.90)
	Range	2.91 to 140.49	4.11 to 182.64	0.79 to 506.79	1.06 to 634.44	0.43 to 57.78	3.09 to 152.41
TN (g ha ⁻¹)	n	4	4	7	7	6	6
	Average	105.52 (±67.97)	120.85 (±68.37)	271.37 (±158.53)	301.01 (±163.40)	111.32 (±30.14)	110.45 (±36.23)
	Range	26.18 to 309.08	34.39 to 323.13	61.17 to 1,213.64	84.43 to 1,274.61	27.52 to 210.79	22.14 to 226.13

Note: Numbers in parentheses are ± standard error of mean.

Table 5

Average storm event load for total suspended solids (TSS), total combustible solids (TCS), soluble reactive phosphate (SRP), total phosphorus (TP), nitrate/nitrite-nitrogen (NO_3/NO_2-N), and total nitrogen (TN) for the pooled data in edge-of-field surface runoff from sugarcane fields, pasture lands, and residential areas, Louisiana, using composite sample and flow-paced sample.

		Composite sample (g ha ⁻¹)	Flow-paced sample (g ha ⁻¹)
TSS	n	29	29
	Average	19,771 (±8,743)	19,591 (±7,750)
	Range	5.00 to 190,711	130.70 to 159,855
TCS	n	29	29
	Average	16,841 (±7,564)	16,637 (±6,372)
	Range	1.76 to 160,370	12.21 to 138,917
SRP	n	28	28
	Average	23.12 (±4.92)	25.04 (±4.73)
	Range	2.57 to 112.41	3.75 to 97.09
TP	n	17	17
	Average	40.29 (±9.74)	41.68 (±10.28)
	Range	5.65 to 167.66	5.37 to 179.09
NO ₃ /NO ₂ -N	n	28	28
	Average	38.01 (±18.17)	55.25 (±23.23)
	Range	0.43 to 506.79	1.06 to 634.44
TN	n	17	17
	Average	175.9 (±67.71)	191.36 (±70.72)
	Range	26.18 to 1,213.64	22.14 to 1,274.61

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