LAND USE AFFECTS THE TIMING AND MAGNITUDE OF MATERIAL DELIVERY TO HEADWATER STREAMS IN COASTAL NORTH CAROLINA

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A thesis submitted to the faculty of the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Master of Science in the Curriculum for the Environment and Ecology

CHAPEL HILL
2010

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ABSTRACT

REBECCA SCHWARTZ: Land Use Affects the Timing and Magnitude of Material Delivery to Headwater Streams in Coastal North Carolina
(Under the direction of Michael F. Piehler)

Headwater streams are both the transport vectors and receiving waters for landscape-derived materials. This high level of connectivity to their surrounding watershed imparts headwater streams with the ability to act as sentinels of impacts that may occur due to changing land uses. Determining the impacts of land use and precipitation patterns on material delivery by streams is requisite for quantifying and mitigating degradation resulting from watershed development. Headwater streams in the New River Estuary, NC, USA were monitored for one year, during which water samples were collected during base- and throughout storm-flow. Samples were analyzed for nutrient and total suspended solid (TSS) concentrations, and flow was measured continuously. This research determined that in developed watersheds, loading of some constituents (nitrate, ammonium, TSS) and stream discharge increased, as did the relative importance of storm flow delivery, when compared to reference watersheds. Flow measurement method and data analysis approach, both affected results.

ACKNOWLEDGMENTS

It is such a pleasure to thank all those who helped to make this thesis possible. First and foremost, my advisor, Dr. Michael F. Piehler, who always made ample time for my questions, and whose contagious enthusiasm encouraged my interests in aquatic and watershed ecology. I thank my two other committee members, Drs. Rachel Noble and Steve Whalen, for providing helpful guidance throughout my graduate studies in developing research ideas, and in preparation of this thesis.

I thank Suzanne Thompson for her rational, levelheaded constructive criticism in experimental design, data analysis, and in everything I’ve written. I have fond memories of discussing the topic of the day on NPR in the truck with you while dodging sweltering heat, chiggers and bombs at Camp Lejeune. I also thank the Pieher lab including Scott Ensign, Teri O’meara, Kaylyn Siporin, Ashley Smyth, and Ben Von Korff for field and laboratory assistance. Thanks Beth Van Dusen for moral support and morning coffee. Thanks to my parents; my dad, Stanley Schwartz, for instilling in me a love of science, and to my mom, Naomi Schwartz, for showing me the importance of balance.

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LIST OF ABBREVIATIONS

CJ-1	Camp Johnson Creek (least developed watershed)
Chl *a*	chlorophyll *a*
COG-5	Cogdels Creek (5^{th} most developed watershed)
FIB	fecal indicator bacteria
FRN-3	French Creek (2^{nd} most developed watershed)
GIL-3	Gillets Creek (3^{rd} most developed watershed)
HW	headwater
ISCO	ISCO automated sampler
LG	level gauge
N	nitrogen
NAPI	net anthropogenic phosphorous input
NH_4	ammonium
NO_X	nitrite + nitrate
NPS	nonpoint source
NRE	New River Estuary
P	phosphorus
PO_4	phosphate
TAR-6	Tarawa Creek (6^{th} most developed watershed)
TDN	total dissolved nitrogen
TRP-4	Trapps Creek (4^{th} most developed watershed)
TSS	total suspended solids

INTRODUCTION

Ecological and Hydrological Response to Coastal Watershed Development

Over half the population in the United States (US) lives within coastal watersheds, however, these ocean bound drainage basins make up only 17% of the nation's land (Beach 2002). Coastal regions continue to undergo rapid development, specifically; a 2002 estimate projected coastal populations to increase by 27 million people in 15 years (Beach 2002). Often associated with an influx of people is inefficient and sometimes improper land development. It is vital to understand how these regions of both increasing population density and increasing land alteration impact water quality due to its close proximity to downstream coastal aquatic habitats.

Watershed development degrades water quality, in part, by changing the composition and availability of materials (e.g. nutrients, sediment, fecal material) on land that can be transported to streams (Paul and Meyer 2001). Land uses associated with development increase sources of nitrogen (N) and phosphorus (P) from fertilizer application, septic systems, automobile exhaust, and pet waste. Land alteration such as deforestation and construction releases sediment, increasing the potential for relocation to streams during rain events. Abundance of fecal coliform bacteria has been shown to be positively associated with coastal development in tidal creeks (Holland et al. 2004).

Major sources of this pollutant are improperly treated human and animal waste (Mallin et al. 2000; Van Dolah et al. 2000). In addition to increasing pollutant sources, material fluxes through the watershed are altered spatially and temporally in anthropogenically impacted landscapes.

Transitioning from a pristine ecosystem to a developed landscape increases the amount of impervious cover (IC) associated with residential, commercial and industrial land uses. IC hinders percolation and diverts rainwater away from groundwater recharge directly to streams, creating periods of increased peak storm flows (Leopold 1968) of diminished duration (Seaburn 1969) with the potential for subsequent decreased base flows (Barringer et al. 1994). The net effect is an overall increase in annual runoff volume, particularly in the stormflow component. For example, an 18% increase in IC over an 18-year period led to an 80% increase in average annual runoff volume in a watershed near Indianapolis, Indiana. Additionally, this increase in runoff volume corresponded to a 50% rise in the annual average load of lead, copper and zinc (Bhaduri et al. 2000), suggesting that greater IC leads to increased nonpoint source (NPS) pollution load, or pollution stemming from diffuse sources, that enters riverine networks.

Coastal headwater (HW) streams are the primary receiving waters for landscape derived runoff and associated materials. It has been thoroughly documented that HW streams respond to development of their surrounding watersheds by an array of physical, chemical and biological indicators. Schueler (1994), Arnold and Gibbons (1996), Beach (2002), and Holland et al. (2004) have all linked increased urbanization and associated increases in population density and IC to decreased water quality of freshwater streams. Specifically, many studies have documented the sensitivity of HW streams to land use changes within their watershed in terms of changes in microbial water quality (DiDonato et al. 2009), the macrobenthic community (Lerberg et al. 2000) trace metals (Sanger et al. 1999a), and organic contaminants (Sanger et al. 1999b).

A high level of connectivity between HW streams and their surrounding watershed is demonstrated by the response of physical, chemical and biological characteristics of HW streams to watershed development. This imparts HW streams, perhaps even more so than receiving waters, with the ability to register hydrological alterations from the surrounding watershed, and suggests that HW streams have the ability to act as sentinels of negative impacts that may occur due to changing land uses. For example, because of close proximity to NPS pollution and minimal to no tidal flushing, microbial contaminants were found to be more highly associated with land use in HW streams than with streams of higher order and their adjacent open water counterparts (DiDonato et al. 2009). Additionally, HW streams have the capability to remove more than half the input of the dissolved inorganic nitrogen from their surrounding watershed (Peterson et al. 2001), which suggests that sampling must take place as far upstream as possible in order to monitor N that crosses the land-water interface.

The apparent sensitivity of HW streams to watershed impacts, along with easy access to sample locations via foot, as compared to open water environments that often require a boat to access, makes HW streams ideal locations to monitor impacts that changing land use has on proximate fluvial systems. Degraded water quality observed in HW streams is the first indication that anthropogenic alteration of a watershed is affecting ecosystem function. These systems are excellent indicators of when action must be taken to minimize risk of degradation to the entire riverine ecosystem.

Coastal HW streams are the confluence between the terrestrial biome and adjacent coastal ecosystems. Alexander et al. (2007) found that first order streams contributed 55% of the water volume and 40% of the N flux to 4^{th} order and higher streams, showing that HW streams impacted downstream water quantity and quality. Near shore estuaries and associated habitats (e.g. mangrove forests, salt marshes, and seagrass beds) are often referred to as nurseries because they provide shelter and food to support diverse assemblages of juvenile fish and invertebrates (Beck et al. 2001). They also serve as recreational areas for fishing, boating and swimming, and are assets to local economies. Degradation of coastal ecosystems can have widespread ecological and economic impacts.

The functional role that streams play as both processors and conduits of dissolved and particulate matter is vital for downstream waters, potentially buffering coastal habitats from upstream watershed development. Significant nutrient processing occurs in headwater streams because of shallow depths and the ratio of sediment to water interface. Large benthic surface areas relative to overlying water volume creates a location for increased contact, and therefore increased exchange of water and N with the hyporheic zone (Alexander et al. 2000, Peterson et al. 2001). Because headwater streams of less than 10m in width can make up a substantial portion (up to 85%) of the total riverine network length (Naiman 1983), they play a vital role in mitigating downstream material fluxes.

In-stream processing capabilities control material export to downstream reaches. Material storage or retention is achieved by biological assimilation of N and P into plant tissue, or by deposition onto riverbeds. Denitrification is an anaerobic, microbial mediated process that converts biologically available NO_3^- to inactive N_2 gas which is released to the atmosphere, essentially removing N from the system. Characteristics of coastal streams in developed watersheds may dictate rates of material processing.

Flat topography typical of coastal plain environments may promote increased material processing both on land and in water relative to regions of steeper gradients. Hydrologic processes affect instream N dynamics by altering flow paths and residence times (Alexander et al. 2007). Slower moving water caused by minimal gradients enables in-stream materials prolonged contact with organisms in the water column and the benthos, thereby increasing the potential for deposition, assimilation, and denitrification. Conversely, heightened water velocity associated with watershed development minimizes both terrestrial and aquatic processing capabilities. For example, hydraulic residence time largely influences nutrient recycling in lakes and streams (Essington and Carpenter 2000), so that decreased residence times may reduce the potential for assimilation, thereby increasing the distance downstream that nutrients can travel. This duality has implications on the fate and transformation of materials that enter riverine networks.

Nutrients and sediments pose a challenge for managers, as sufficient quantities of each are necessary for proper aquatic ecosystem functioning, but an overabundance can be detrimental. A minimal but proportional amount of N and P are necessary to support primary production to meet the consumptive needs of higher trophic levels. Additionally, sea level rise is counteracted by accretion in marshes absent of hard shoreline structures, necessitating delivery of ample amounts of sediment to coastal areas, in part, via riverine networks (Morris 2002). However, these materials in excess overwhelm ecosystem requirements and can degradation coastal habitats.

Turbid conditions due to inorganic suspended particulate material have been shown to reduce pelagic primary production, and also shift phytoplankton communities to those that are adapted to low light conditions by decreasing the depth of the photic zone (Allende et al. 2009). Cebrian (1999) has shown that the palatability and nutritional quality of primary producers impacts herbivory, so that alterations in phytoplankton abundance and community composition can impact energy flow within a system. In addition to an overabundance of sediment in the water column, excess nutrients can cause additional problems.

High rates of nutrient loading threaten valuable downstream ecosystems by stimulating eutrophication, or an increase in the rate of supply of organic matter (Nixon

1995, 2009). Eutrophication is the largest pollution problem facing coastal waters of the US (Howarth et al. 2000; NRC 2000), and the 3rd most detrimental force threatening the health of the nation's estuaries, after poor benthic conditions and wetland loss (EPA 2001). Additionally, eutrophication has been shown to cause hypoxic or anoxic conditions, depletion of seagrass beds, harmful algal blooms of longer duration and more frequent occurrence than in pristine conditions (Bricker et al. 2007), and decreases in biodiversity (NRC 2000).

Increases in both nutrient and sediment runoff to coastal zones has been shown to decrease the abundance of seagrass beds (Orth et al. 2006), which serve a number of important ecological functions such as affecting nutrient cycling, food web structure, and water flow (Hemminga and Duarte 2000), and also act as nurseries for economically important finfish and shellfish (Heck et al. 2003). Because seagrasses require high levels of light, they and are particularly susceptible to changes in water quality (Orth et al. 2006). Both increased sediment load, and increased nutrient supply that spurs macroalgal growth, can deleteriously shade seagrass beds (Hauxwell et al. 2003, Orth et al. 2006).

The historic paradigm that P is typically the limiting nutrient in fresh waters (Hecky and Kilham 1988), and N in estuarine (Howarth 1988), has been changing in watersheds that receive large amounts of anthropogenically derived nutrient input (Paerl 2009), and efforts to stem anthropogenically induced eutrophication need to reflect this shift. The authors of a 37-year nutrient addition experiment suggested that management efforts focus on decreasing inputs of P to freshwater, as well as to certain estuarine waters where conditions may favor N-fixing cyanobacteria (Schindler et al. 2008). This single nutrient management strategy would likely be sufficient for freshwater lakes and some upstream regions, but it ignores the connective nature of fluvial systems, and the potential for downstream eutrophication that may arise from not properly controlling N inputs. A dual nutrient management strategy must be employed to reduce eutrophication along the entire fresh- to saltwater ecosystem continuum (Conley et al. 2009, Paerl 2009).

Quantification of Watershed Development

A comprehensive understanding of how land use and precipitation influence material delivery to streams is instrumental in mitigating pressures on the environment that stem from an anthropogenically induced changing landscape. The ability to quantify impacts of development on fluvial systems is necessary to monitor the effects of altered landscapes and management efforts. The method chosen to quantify a stream's response to development will influence what can be inferred about the watershed. Three general methods have traditionally been utilized to connect water quality to magnitude and type of watershed development: concentration, modeled load, and measured load.

Concentration measurements of dissolved and particulate materials can be a misleading indicator of land use change, but have frequently been used as an indicator of watershed development in many systems including estuaries of South Carolina (Van Dolah et al. 2008), tidal creek ecosystems of the South East (Sanger et al. 2008), and mid-Atlantic coastal plain headwater streams (Megan et al. 2007). Concentration is a valuable metric that determines both instantaneous biological response (e.g. nutrient and phytoplankton concentrations) and risk to humans (e.g. FIB concentrations). The utility of concentration measurements lies in the idea that they describe what an organism ‘sees’ at the precise moment the sample is taken. In this way they can be beneficial in understanding food web interactions and the paths in which energy flows through a system. However, development simultaneously alters the amount of material available for transport and the hydrologic regime that transports these materials, altering both solute and solvent portions of the measurement ratio. Therefore, single measurements of concentration will not identify the total amount of material present, and if discharge is not measured, the mass of material crossing the land-water interface cannot be calculated.

Material load is a calculation of the mass of material that passes a stream reach over a span of time. Loads can be normalized to watershed area, enabling comparisons between streams of varying sizes, located in watersheds of varying sizes. Knowing material load that enters and exists a stream reach enables an understanding of not only material transport, but also material transformation. Transport and transformation are controlled by both stream morphology and the biogeochemical processes that occur within. The net function of a stream as a source or sink of a material is particularly important when considering the physical, chemical, and biological processes of sensitive downstream habitats.

A variety of modeling approaches have been employed to estimate material loading by streams over a range of systems with varying success (Alexander et al. 2002;

Seitzinger et al. 2005). The models reviewed by Alexander et al. (2002) predicted N export within 50% of measured export for large watersheds; this potential discrepancy may be too large if detailed measurements are needed. A specific limitation of some models is exemplified in LOAD ESTimator (LOADEST); a FORTRAN program used to estimate constituent load in streams (Runkel et al. 2004). It develops a regression model by combining known parameters with statistical methods, and requires that the user have an extensive background in statistics. Other models are hindered by physical characteristics of the watershed. For example, southeastern coastal plains are characterized by a shallow water table, which highly influences the hydrology of both surface and groundwater. Many models are limited in estimating loads from these areas because they don't simulate water table depth. Amatya et al. (2004) worked to overcome this limitation and modified DRAINMOD to estimate watershed scale N load from a flat, poorly drained, forested landscape in eastern North Carolina (NC). Measured N loads were compared to modeled N loads over a 5 year period and found to be close, with an R^2 of 0.77. Models such as the ones described here rely upon user specified data variables for robust load estimations. Field measurements that do not represent a wide range of conditions may erroneously skew the model. Additionally, accurate comparisons of modeled to actual loads depend on proper measurement techniques.

Russell et al. (2008) estimated net anthropogenic P inputs (NAPI) in the Chesapeake Bay region by summing all of the individual input and output sources of the watershed, and used this as an index of pollution potential. They calculated that 90% of P was retained in the landscape, based on their estimates of terrestrially derived P minus measured values of P in the Bay. The utility of NAPI was assessed by comparing watershed NAPI to measured P discharge from 9 major river basins monitored by the USGS, however, such a high P retention can be an additional source of P that was not accounted for in their estimates.

Benefits derived from NAPI and similar budget based models stem from the ability to calculate quick estimates based on readily available information. It is useful knowing potential sources of nutrient pollution, especially since NPS pollution is the leading cause of water quality degradation in the US (USEPA 2002), and leaches from ambiguous sources. However, nutrients are not the only material polluting streams; excessive total suspended solids (TSS), or the total amount of particulate matter, in the water column decrease the photic zone (Allende 2009), and are also a potential indicator of watershed development. TSS sources cannot be quantified, as they can be for, say, N, which is added to the landscape via fertilizer, etc. Instead, solids are dislodged both by natural weathering processes and by landscape uses that destabilize sediment and make it available for transport. Therefore, TSS load cannot be modeled using methods such as NAPI due to the ambiguity of its sources and sinks.

Methodological advancements have been made in modeling nutrient load, but precision is still lacking. Brock (2001) compared modeled N loading to the Nueces Estuary in Texas and found a maximum difference of 4284 x10^3 kg of N between their study and one performed by NOAA (1989). The N load of the 2001 study was less than the N load of the 1989 study, and since N use is on the rise, it is unlikely that such a large discrepancy was due to the time period over which the two studies were performed. When considering small watersheds with low levels of nutrient loading, it is requisite that uncertainty be minimized for load to be a valid indicator of watershed health.

The utility of directly measuring material load in streams is obvious, as is the need for standardized methods that enable cross-watershed comparisons. Recent studies have used direct measurements of material concentration and discharge to calculate load (Birgand et al. 2006, Sobota et al. 2009, Schaefer and Alber 2007). Often, sampling is infrequent due to cost and logistical challenges, and data may be extrapolated to a larger time frame without knowing the impact it can have on load values. Continuously and directly measuring water discharge along with multiple parameters of water quality is the most robust method, but it is time consuming and expensive. It is therefore imperative to understand the mechanisms that determine how the method of measuring discharge and the sampling regime influence load calculations.

This study was conducted in the New River watershed in Onslow County in the central coast of NC. Marine Corp Base Camp Lejeune (MCBCL) was the focus of the research, an ideal study location as it is a mosaic of land uses that mirrors civilian landscapes ranging from pristine ecosystems to industrial parks. Headwater streams of small subwatersheds (referred to as ‘watersheds’) draining into the New River Estuary (NRE) were routinely monitored for water quality parameters throughout base and storm flow conditions over the course of a single year.

Research Objectives

The goals of this study were twofold:

- To assess the impacts of land use on the magnitude and timing of material delivery to headwater streams in low gradient mixed-use watersheds.

- To assess the importance of several stream characterization methods to enable valid cross-watershed comparisons.

MATERIALS AND METHODS

Study Sites

The NRE, situated in NC's coastal plain (fig. 1), is composed of shallow (1-2m), broad lagoons, with water flow constrained at the mouth by barrier islands (Mallin et al. 2005). Median flushing time of this estuary has been estimated to be 64 days; a long time as compared to the Cape Fear Estuary, south of the NRE, with a median flushing time of just 7 days (Ensign et al. 2004). Despite improvements to sewage treatment plants in 1998, the NRE is still prone to phytoplankton blooms and periods of severe bottom water hypoxia that stem from nutrient sources from the upper reaches of the New River watershed (Mallin et al. 2005). Stormwater runoff from adjacent subwatersheds has not appeared to be a major source of nutrients to this estuary (Mallin et al. 2005). However, shallow, poorly flushed estuaries such as the NRE are particularly sensitive to nutrient inputs (Cloern 2001), as slow flushing times allows greater nutrient cycling within the estuary and may spur algal growth. This vulnerability makes it imperative that local nutrient sources remain minimal.

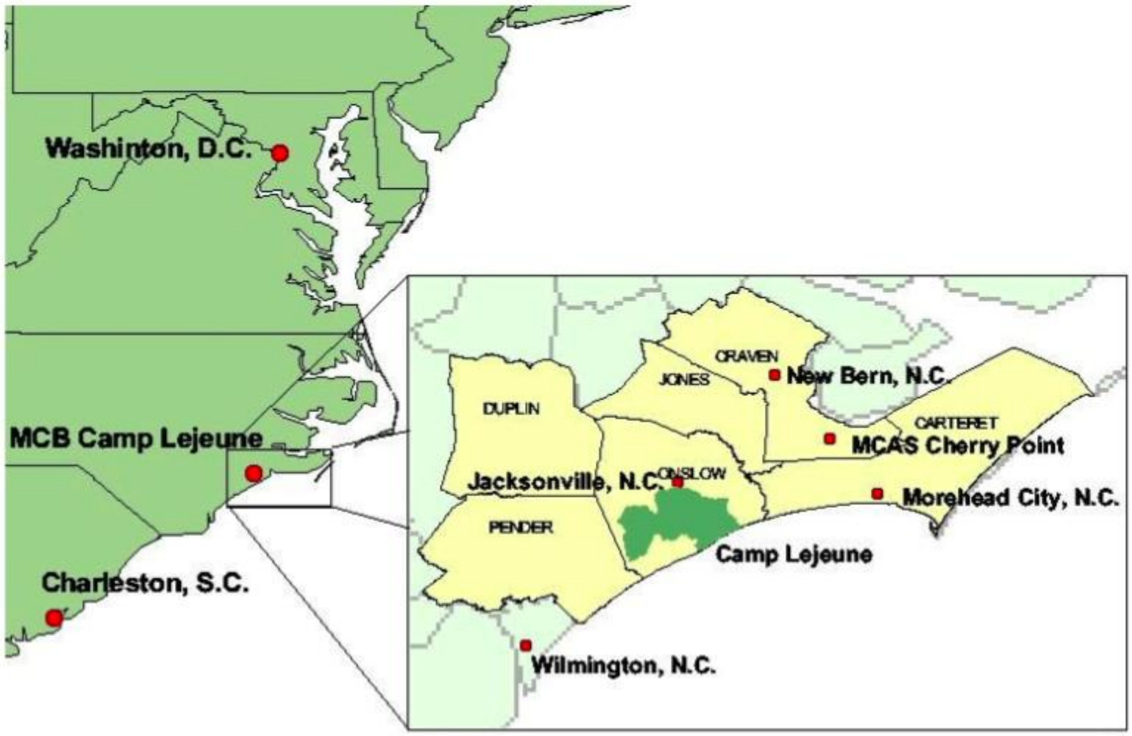


Figure 1. Location of study area in Eastern North Carolina. The green shaded area is Camp Lejeune.

Stream Name	Abbreviation	Order	% Developed	% Impervious Cover
Camp Johnson	CJ-1	1	1.61	0.27
French	FRN-2	2	5.69	1.06
Gillets	GIL-3	3	14.05	2.86
Trapps	TRP-4	4	29.45	4.13
Cogdels	COG-5	5	34.17	13.79
Tarawa	TAR-6	6	66.82	23.20

Table 1. Summary of creek name, abbreviation, and relative development as compared to the other creeks in the study.

Six mixed-cover subwatersheds of the NRE were investigated to assess impacts of various land uses on stream water quality and patterns of material delivery. The watersheds ranged in size from 22 to 836 hectare, and characteristics are summarized (table 1). Each of the 6 stream lengths investigated were characterized by varying extents of non-uniformity that could alter the flow path, including the straightness of the stream length, changes in elevation of the stream bed, and amount of both man-made and natural in-stream obstructions. The most drastically varied flow was in Camp Johnson, an ephemeral stream of riffles and pools. During baseflow conditions, the riffles were often dry and the pools stagnant. A dirt road also ran along the length of Camp Johnson just upstream of our sampling location, and affected the material composition found in-stream.

Each of the 6 watersheds drained into HW streams that were monitored for instream water quality and discharge from July 2008 through June 2009. The NRE lies within MCBCL, which is currently expanding to accommodate a large influx of Marines and their families. Land uses on MCBCL were typical of both military installations and some non-military uses and included residential neighborhoods, barracks, industrial parks, and impact zones. The characteristic low elevation and shallow slopes of the NC coastal plains have profound implications for mechanisms that deliver material to streams, altering loading patterns as compared to watersheds of a steeper gradient.

Coastal NC has a humid, subtropical climate, with average temperatures of 12.8-13.9°C and average precipitation of 142 cm per year. Rainfall is distributed almost evenly throughout the year, with a slight increase from June-September (FINRMP 2006), minimizing seasonal patterns of material delivery to streams. Precipitation for the study year was below average, with total precipitation between 89 and 102 cm (data from automatic rain gauges at Cogdels Creek, lat 34.657611 long 77.332861, and an additional site at lat: 34.60167, long: 77.266889).

Watersheds were delineated using 20-foot (6.1 m) elevation LIDAR (M. Brush) with ArcGIS (ESRI, Redland, CA). Resulting watersheds were converted to polygons and combined with the National Land Cover Dataset (NLCD) 2001 data to assign areas for each land use category (table 2), and %IC (fig. 3). The 'developed' category referred to in this paper refers to low, medium and high development. Development categories were classified using a Digital Elevation Model based on a 30m spatial resolution. Low Intensity was 20-49% IC, Medium was 50-79% IC, and High was 80-100% IC (fig. 2).

Land Use Classification for each Watershed

	CJ-1	FRN-2	GIL-3	TRP-4	COG-5	TAR-6
Water	0	0	0.1	0	0.9	0
Developed, Open	1.6	2.3	6.3	16.9	9.1	20.9
Developed, Low	0	3.3	7.8	12.5	8.2	31.2
Developed, Medium	0	0.1	0	0	11.1	9.3
Developed, High	0	0	0	0	5.5	5.5
Barren	0	10.2	4.8	2.7	3.1	0
Deciduous Forest	2.4	0.1	1.4	0	2.1	1.5
Evergreen Forest	53.6	9.1	13.9	11.3	26.1	15.6
Mixed Forest	17.7	0.7	0.4	0	5.1	0.5
Scrub/Shrub	8.5	7.2	12.4	12.9	4.7	2.9
Grassland/Herbaceous	1.2	38.9	18.2	14.3	8.4	3.3
Pasture/Hay	0	0	0	0	0	0
Cultivated Crops	3.2	0	0	0.0	3.0	8.8
Woody Wetland	11.7	21.5	34.1	29.5	11.6	0.3
Herbaceous Wetland	0	6.5	0.7	0	1.2	0.3
Total	100	100	100	100	100	100

Watershed Area (ha)	22	807	453	51	836	139

Table 2. Percent land cover and watershed area of study sites. 2001 National Land Cover Dataset. (M. Brush)

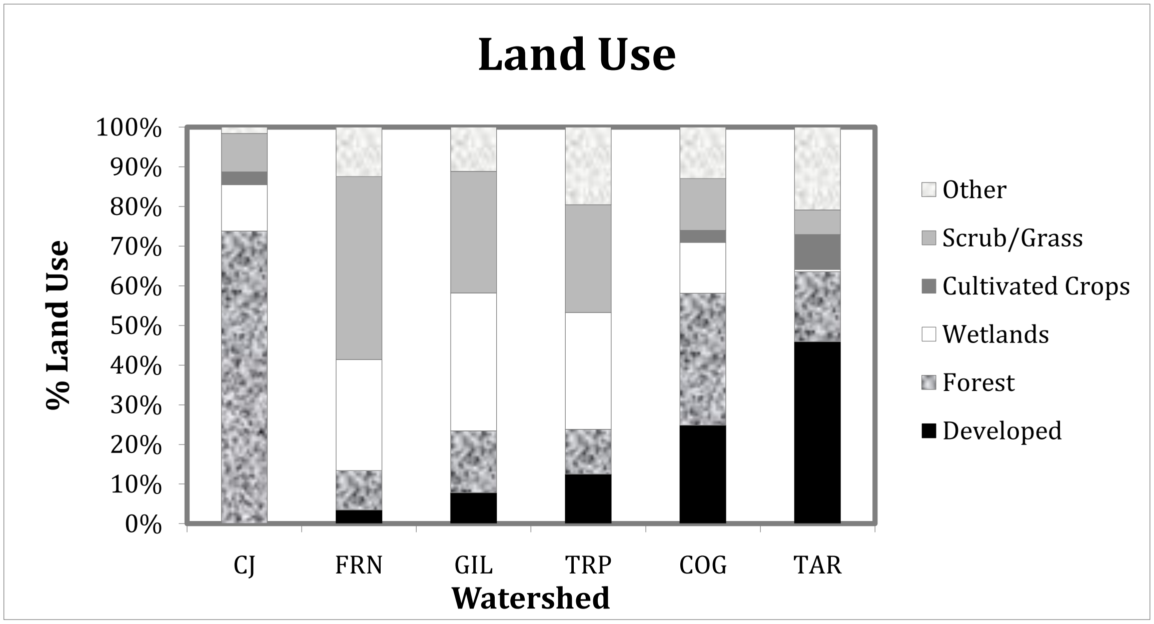


Figure 2. Summary of percent land use of watersheds in study: ‘Developed' includes low, medium and high development. 'Forest' includes deciduous, evergreen and mixed forests. 'Wetlands' includes woody and herbaceous. 'Scrub' includes shrub, grasslands, herbaceous, pasture and hay. 'Other' includes open development, water, and barren areas. (2001 NLCD).

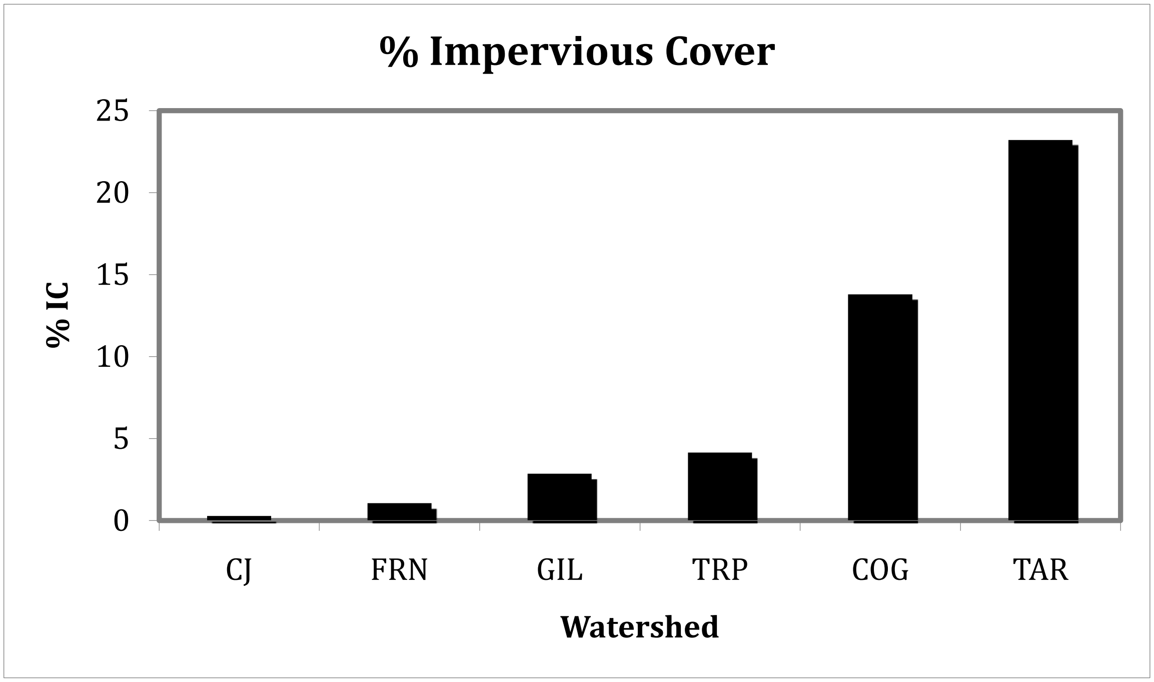


Figure 3. Percent impervious surface area for each subwatershed (M. Brush)

Watersheds were located in close proximity, which minimized spatial disparity and enabled comparisons across watersheds that were not complicated by deviations in temperature or precipitation patterns (fig 4).

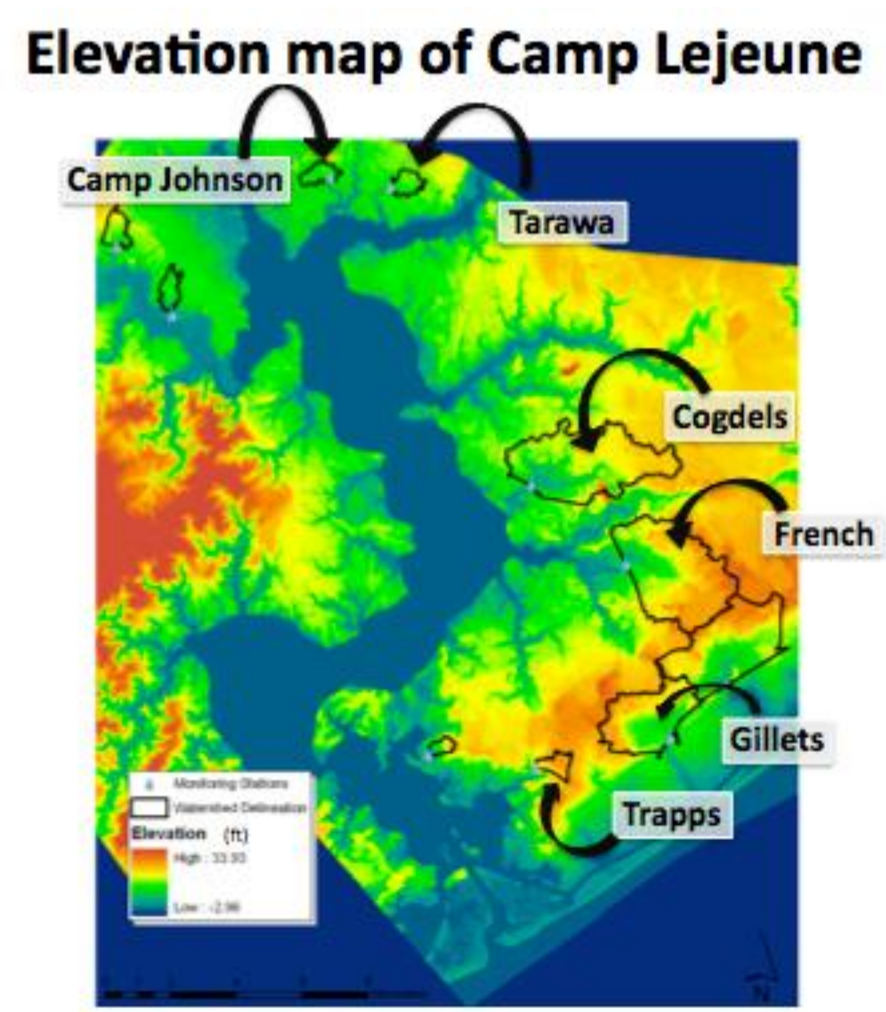


Figure 4. Elevation map of Camp Lejeune. The six labeled watersheds are used in this study. Courtesy of T. Minter.

Water Quality Analysis

Data collection throughout the study period consisted of manual sampling (water grab, water depth measurement, and water velocity using a Sontek Flowtracker Acoustic Doppler Velocimeter) that occurred every other week as well as after a rain event (defined as greater than 2.5 cm of rain). In addition, more frequent automated sampling was conducted to enhance resolution during storm events at three sites equipped with ISCO automated samplers (FRN-2, GIL-3, COG-5). Samplers were programmed to trigger above a threshold stream velocity set for storms and at flow-paced intervals once enabled. Automated grab samples were collected as soon as possible after a rain event and brought back to the lab for processing. Water samples were selected to encompass a period including before, rising, peak and falling limbs of hydrographs for each storm at each site. Samples were composited (by equal volume) when multiples were collected along those sections of the hydrograph.

All water samples collected were analyzed for nutrients ($NO_{2/3}^-$ -N (referred to as NO_X), NH_4^+ -N (NH_4), PO_4^{3+} -P (PO_4), and total dissolved nitrogen (TDN)), chlorophyll *a* (chl *a*), and total suspended solids (TSS). Water samples were filtered through Whatman GF/F glass fiber filters (25mm diameter, 0.7 µm nominal pore size) and the filtrate was analyzed with a Lachat Quick- Chem 8000 automated ion analyzer for $NO_{2/3}^-$ -N, NH_4^+ -N and PO_4^{3+} -P concentrations using standard protocols (Lachat Instruments, Milwaukee, WI, USA: NO_2^-/NO_3^- Method 31- 107-04-1-A, NH4 Method 31-107-06-1-A and PO_4^{3+} -P Method 31-115-01-3-G). The filters with residue were stored in aluminum foil and frozen for later chl *a* analysis. Chl *a* samples were extracted in 90% acetone at 0^{o}C for 18 hours, after being sonicated for 5 minutes. The extracted samples were analyzed by fluorometry (Welschmeyer 1994) using a Turner Designs Trilogy Laboratory Fluorometer, model #7200-000. Additional water was filtered through pre-cleaned and dried Whatman GF/F glass fiber prefilters (47mm diameter, 0.7 µm nominal pore size) and residue was dried and weighed for measurement of TSS using standard protocols ("Standard Methods for the Examination of Water and Wastewater" 20^{th} Edition, 1998 Method 2540 D, 2-57).

Nutrient concentrations that were below the detection limit but above zero were reported as the measured value. Detection limits were as follows in *u*M: NO_X 0.043, NH_4 0.182, PO_4 0.059, TDN 2.529. This was done instead of replacing values with the minimum detection value to avoid overestimating concentration and load calculations.

Flow Computation

Automated samplers (ISCO models 6700 or 6712) were placed near culvert pipes at French, Cogdels, and Gillets Creeks (referred to as 'ISCO sites'). Samplers were equipped with ISCO model 750 Area Velocity Modules with flow sensors placed in the culvert pipes that measured velocity (ultrasonic Doppler) and level (pressure transducer). Ultrasonic Doppler velocimeters emit sound waves into the water column, and the changes in frequency that occur when sound waves are intercepted by particulates or bubbles in the water column are used to measure water velocity. Velocity and level were measured continuously and recorded at 30-minute intervals throughout the study period, and volumetric flow rates were calculated using velocity and cross sectional area of water in the pipe. Rainfall data were recorded at Cogdels Creek at 30-minute intervals via a tipping gauge connected to the ISCO sampler.

Level gauges were placed in CJ-1, TRP-4, and TAR-6 (referred to as ‘LG Sites’). Water depth was recorded (pressure transducer) at 30-minute intervals throughout the study period. Discharge was calculated using the Manning Equation.

$$Q = V\,A$$

Or

$$Q = \left(\frac{1}{n}\right) A R^{2/3} S^{1/2} \times A$$

Where

A = area (m^2)

R = hydraulic radius (m)

S = channel slope (m/m)

n = Manning ‘n’ constant

V = velocity (m/s)

Q = discharge (m^3/s)

Field measurements were made of stream slope and other streambed characteristics to apply as parameters in the Manning Equation. Cross-sectional profiles were obtained by measuring channel width and height at three representative locations along the stream reach, and used to calculate (A) and (R). Water surface slope (S) was measured at three locations along the stream reach via the hydrostatic leveling technique described in Gordon et al. 2004. Slope was calculated as follows: CJ 0.0039, FRN 0.0018, GIL 0.001, TRP 0.0105, COG 0.0049, and TAR 0.0034. Adjustments were made to calibrate the Manning Equation calculated values to field measurements of water level and water velocity (Flowtracker) made during routine sampling.

Mechanical errors resulting in missing level or velocity data were estimated once discharge had been calculated. Baseflow was interpolated through periods of missing data. To estimate magnitude of missing storms, nearby storms from 2 to 3 months before and after the missing data time period were used as a model. In each storm, the difference in flow was calculated from base to peak, and from base to inflection point of the falling limb. A second order polynomial curve was fit to a scatter plot of storm precipitation total versus difference to peak discharge, or difference to inflection point. These equations were then used to calculate peak and inflection point discharges of missing storms based on the total precipitation during that missing storm. Placement of points on the time axis mirrored nearby creeks with similar precipitation patterns, and discharge was interpolated between points.

Load Calculations

A graphical separation technique (fig. 5) was utilized to delineate between the baseflow component and total stream flow during storm events (Ward and Robinson 2000). Groundwater contribution during storms was determined by extending antecedent conditions by interpolating from baseflow before the rain event to the point of greatest inflection on the falling limb of the hydrograph. A mass balance equation was used to determine the resultant storm flow contribution to nutrient, TSS, and chl *a* load.

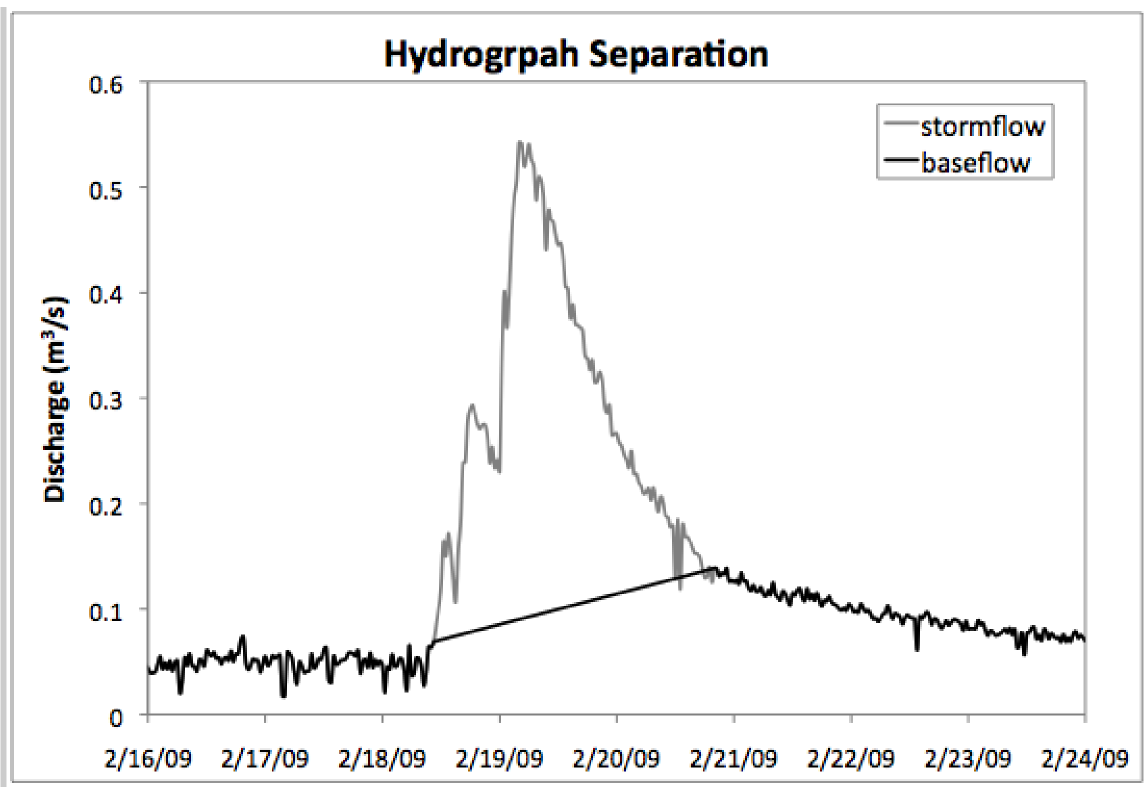


Figure 5. Hydrograph depicting the graphical separation technique used to isolate storm- and base-flow components of stream discharge.

Collection of water samples at ISCO sites (FRN-2, GIL-3, and COG-5) at a fine temporal resolution throughout storms enabled development of a continuous record of nutrient, TSS and chl *a* concentrations by interpolating between measured samples (referred to as 'interpolation technique'). In LG sites (CJ-1, TRP-4, and TAR-6), extrapolating measured data to half hour intervals was accomplished by applying seasonally averaged base and storm concentrations to each half hour interval. The averaged base and storm value was applied to each 30-minute time interval in the period that was used to calculate the average, regardless of whether or not there was an actual measured concentration point at that time (referred to as 'averaging technique').

Load Calculation Method Comparison

Annual loads for the 3 ISCO sites were calculated utilizing 4 different methods, and results were compared. Because level sensors in all three ISCO sites were placed within a culvert, the pipe dimensions were used in place of stream characteristic measurements. Load calculations were performed as follows:

Method #1: ISCO measured velocity and channel cross sectional area were used to calculate discharge. Measured concentrations were interpolated to each half hour interval using the 'interpolation technique' from above.

Purpose: Standard method used to calculate load for the three ISCO sites for the 6-creek cross-site comparison.

<u>Method #2</u>: ISCO measured velocity and channel cross sectional area were used to calculate discharge (same as Method #1). The 'averaging technique' was used to extrapolate measured concentration to each 30-minute interval. In this method, all sample bottles, including biweekly grab samples and automated storm samples, were used in the base and storm averages.

Purpose: Determine whether the method used to extrapolate measured concentrations to every 30-minute interval resulted in a difference in total load.

<u>Method #3</u>: ISCO measured velocity and channel cross sectional area were used to calculate discharge (same as Methods #1 and #2). The 'averaging technique' was used to extrapolate measured concentration to each 30-minute interval. However, in this method, only grab samples were averaged, leaving out samples collected by the automated sampler.

Purpose: Determine how the sampling frequency influences total loads. This method was meant to mimic the sampling frequency of the 3 LG sites, while using discharge calculations obtained from ISCO sites.

<u>Method #4:</u> The Manning Equation was used with ISCO measured level to calculate discharge. The 'averaging technique' was used to extrapolate measured concentration to each 30-minute interval. As in Method #3, only grab samples were averaged, leaving out samples collected by the automated sampler.

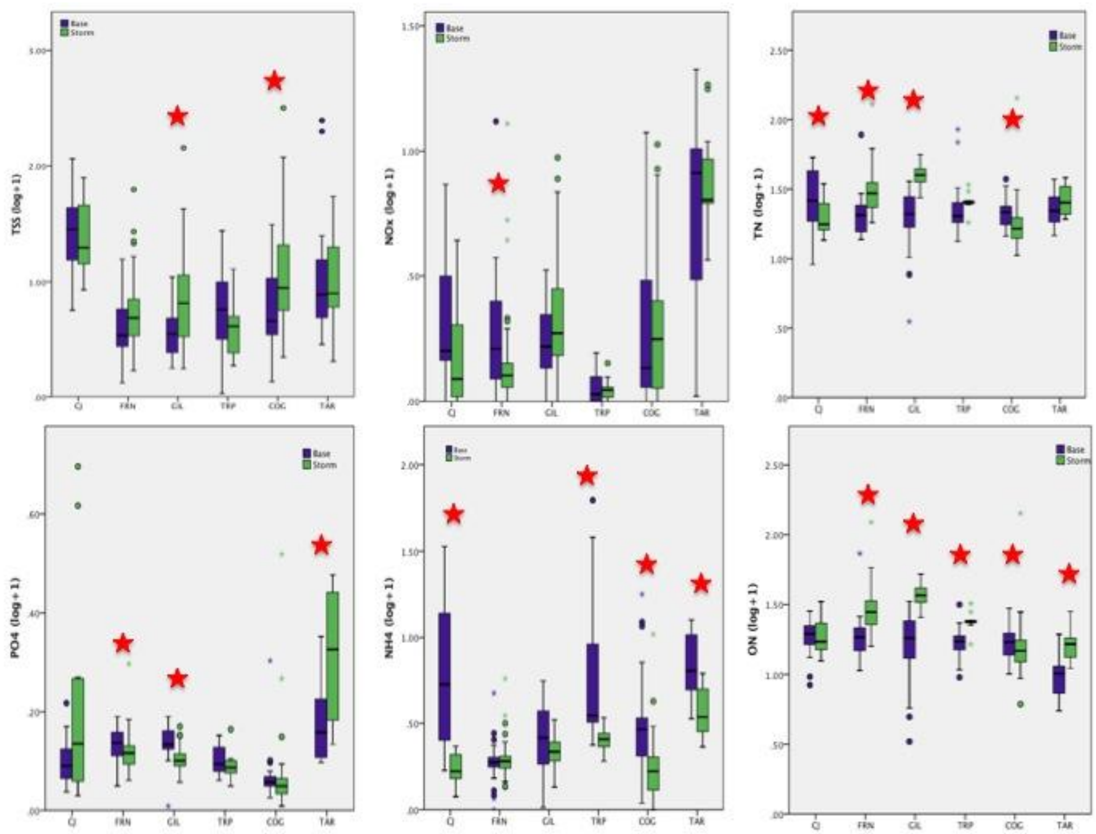
Purpose: Mimic the discharge calculation method, the sampling frequency and extrapolation technique used in Greenbox sites. Determine whether loads calculated using two different samplers (ISCO vs. LG) were comparable. Determine if a predictive pattern exists to compare one sampler to the other.

Statistical Analysis

Data was analyzed (SPSS; PASW 18.0) for differences between base and storm concentrations within each site, and for differences in concentrations among sites using Mann-Whitney U tests ($\alpha = 0.05$) or Kruskal Wallis tests ($\alpha = 0.05$), respectively. Raw data was used for both tests, but box and whisker plots display transformed data (Log_{10}+1) for ease of visualization. Linear regression analyses (PASW 18.0) ($\alpha = 0.05$) were performed to determine the relationship between % watershed development and material loads. CJ-1 was removed from this analysis because runoff from the dirt road running adjacent to the stream reach where our sampler was located overshadowed watershed wide conditions (based on visual observation in the field during rain events). This effect was exacerbated by the ephemeral nature of the stream, where the reach upstream of the sample location was dry during baseflow periods, disconnecting our sample location from the watershed as a whole. The purpose of the regression analysis was to correlate material load to development throughout the entire watershed, and in CJ-1, conditions at our sample location were not representative of the entire watershed.

RESULTS

Concentration



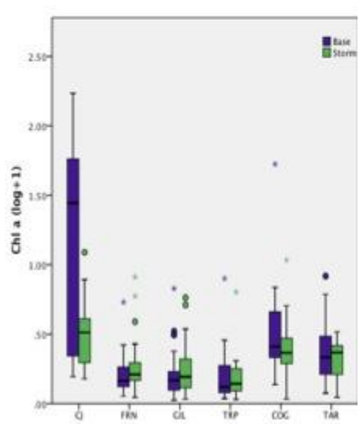


Figure 6. Log transformations of each material across 6 sites, showing base and storm concentrations. A red star signifies significant differences between base and storm concentrations within a creek ($p < 0.05$).

	Discharge (m^3/ha/yr)	TSS (mg/L)	NOx (µg N/L)	NH_4^+ (µg N/L)	PO_4^{3+} (µg P/L)	TN (µg N/L)	TDN (µg N/L)	Chl a (µg/L)	Site description
This study	1670 - 5332	0.14 - 7.24	1.90 - 101.3	13.71 - 96.29	5.17 - 23.57		266.2 - 454.8	0.83 - 26.70	6, 1st order mixed-use HW streams; Coastal plains NC
Houser et. al. 2006		4.0 - 10.1	17.0 - 29.2 (NO_3^-)	7.2 - 20.0	1.9 - 6.2				10, 2nd to 3rd order HW streams; west-central GA
Bhat 2006		4.15 - 10.30							7 streams; forest and military use; west-central GA
Sanger et al. 2008			~10 - 80	~ 50 - 250	~ 100 - 300		~ 900	~ 25 - 40	19 HW streams along SE coast
Megan et al. 2007	0.016 - 0.129 *		1440.0	60.0	17.0				82 HW streams; mid-atlantic coastal plains
Tufford et al. 2003			~ 40	~ 50			~ 450		HW streams, forest to mixed-use; coastal SC
Shelby 1999 - MS thesis		~ 36.0 - 65.0	~ 1700 - 12000	~ 500 - 5000					agr and silvi watersheds in coastal plains NC
Hoos & McMahon 2009						560			Upstream New River, NC
Hoos & McMahon 2009						300			Upstream Southwest Creek, NC
	* discharge in m^3/s								

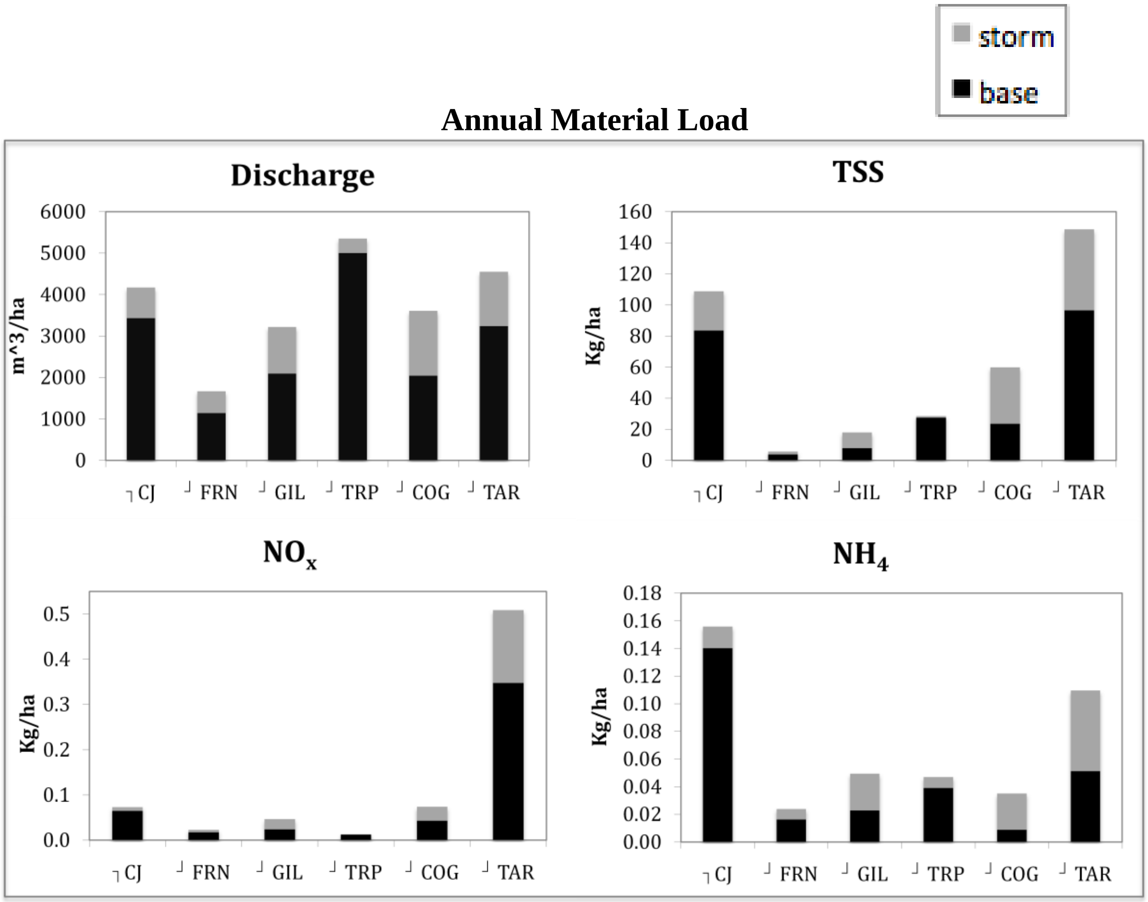
Tble 3. Concentrations from published studies along the east coast of the U.S.

Differences between baseflow and stormflow concentrations within each site were only associated with watershed development for NH_4 and PO_4 (fig. 6). NH_4 storm concentrations were significantly lower than base concentrations in the three watersheds with highest development. However, storm concentrations were also significantly lower than base concentrations in CJ-1, the watershed with lowest development. PO_4 concentration significantly increased from base to storm flow only in TAR-6, however, there were significant *decreases* from base to storm flow in FRN-2 and GIL-3, with TRP-4 and COG-5 decreasing (but not significantly) in mean concentration.

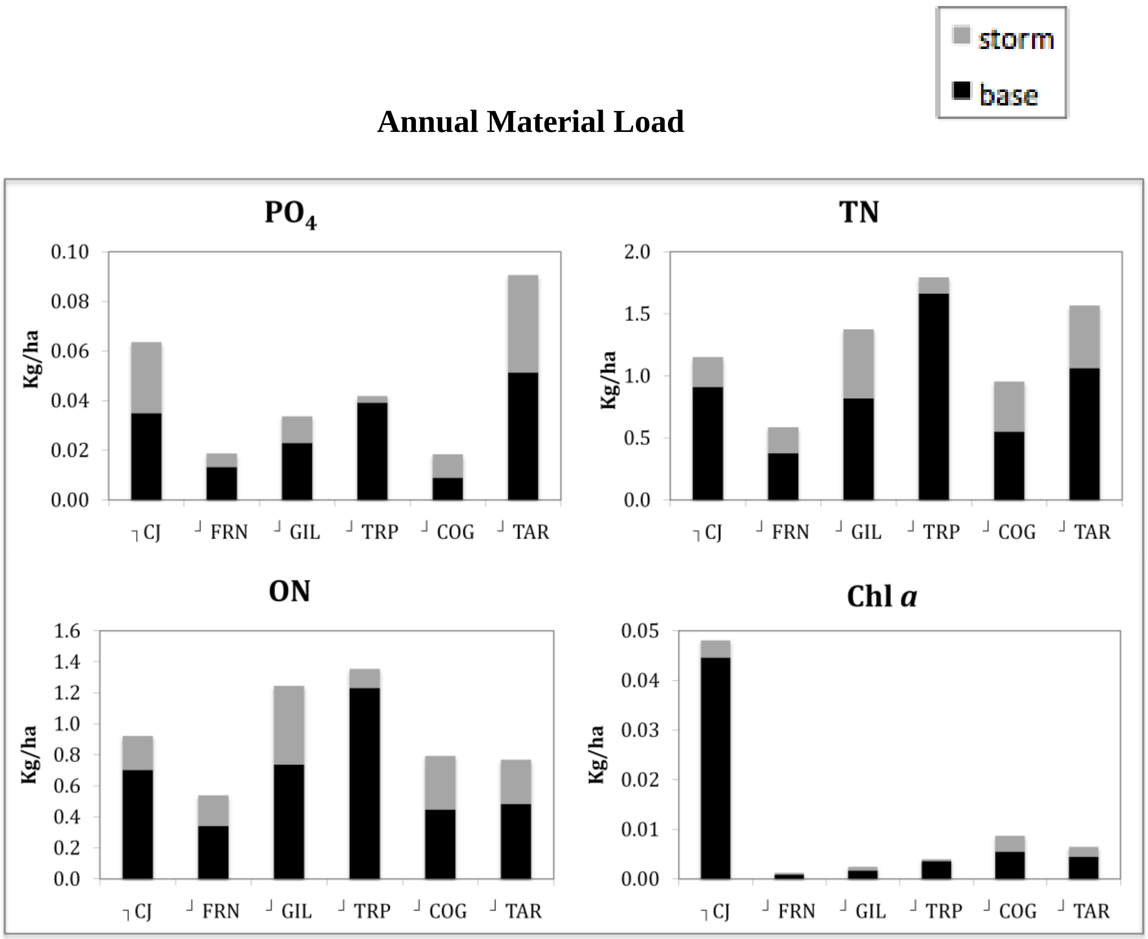
Mean baseflow TSS concentration increased from low to high development with two significant, but overlapping groups (creek #2,3,4,5) and (creek #4,5,6), however, TAR-6 also grouped withCJ-1. Mean NO_X concentration was significantly higher in TAR-6 than the other 5 creeks (and TRP-4 was significantly lower). NH_4 increased with increasing development during baseflow, grouped in two, overlapping groups (creek #2,3) and (creek #3,4,5,6, and 1). Mean baseflow concentration of ON was significantly lower at TAR-6.

Mean stormflow concentrations for all solutes/materials were much more variable than baseflow concentrations. NO_X was significantly higher in TAR-6, with no pattern related to level of development evident throughout the rest of the sites. PO_4 concentration was also significantly higher in TAR-6 (but not different than CJ-1), and the other 5 creeks *decrease* with increasing development. NH_4 concentrations generally increased from low to high development, but groups overlapped.

Annual Load



Figures 7-8. Bar graphs of annual, watershed normalized total load split into base and storm components for the 6 sites, in order of low watershed development to high watershed development.



Figures 7-8. Bar graphs of annual, watershed normalized total load split into base and storm components for the 6 sites, in order of low watershed development to high watershed development.

Study	Method	Type of Watershed	Location	TSS (kg/ha)	NOx (kg/ha)	NH4 (kg/ha)	TP (kg/ha)	TDP (kg/ha)	TN (kg/ha)	TDN (kg/ha)
This study	**Linear interp/ seasonal avg**	**Mixed-use**	**Coastal Plain NC**	**5.8 - 148.7**	**0.013 - 0.509**	**0.024 - 0.293**	**-----**	**0.018 - 0.091**	**----**	**0.59 - 1.79**
Correll et al. 1992	Composited samples each week	Cropland/ Pasture/ Forest, respectively	Rhode River Estuary, mid-Atlantic coastal plain		6.35/ 3.20/ 0.36	0.45/ 0.51/ 0.15	4.16/ 0.68/ 0.63		13.8/ 5.95/ 2.74	
Amatya 2004	Calculated- annual avg	Agr and silviculture	Coastal Plains NC						14.8 *	
Amatya 2004	DRAINMOD model	Agr and silviculture	Coastal Plains NC						13.7	
Shelby 1999 - MS thesis	Calculated - avg for each watershed over 4 years using linear interp	Agr and silviculture	Coastal Plains NC	26.0 - 252.0	3.7- 30.1 **	0.3 - 1.0				
Russell et al. 2008	NAPI model	mixed-use	Chesapeake Bay				1.65 - 19.62			
Hoos & McMahon 2009	SPARROW model	mixed-use	New River/ Southwest Cr., respectively (both headwaters; coastal plains NC)						8.0/ 4.1	

* nitrate + TKN using linear interp of concentrations

** only NO3

Table 4. Annual loads from published studies along the east coast of the U.S

There was a general increasing trend for watershed area normalized total annual loads (referred to as 'load') of most parameters (discharge, TSS, NO_X, NH_4, PO_4, and Chl *a*) with increasing level of development (figs. 7-8). CJ-1 stood out as the exception, with cumulative loads rivaling that of the more developed watersheds for many materials. TRP-4 creek had the highest discharge/ha, but material loads of all but ON were roughly as expected for intermediate level of development. No overall pattern stood out for ON/TDN, however the ON load decreased in watersheds with 'medium' and 'high' development (COG-5 and TAR-6). Chl *a* annual load in CJ-1 towered over all other creeks, but besides CJ-1, other creeks followed a general increasing load of chl *a* with increasing development. However, the pattern stopped after COG-5, as the annual load in TAR-6 was actually less than COG-5.

Storm Component

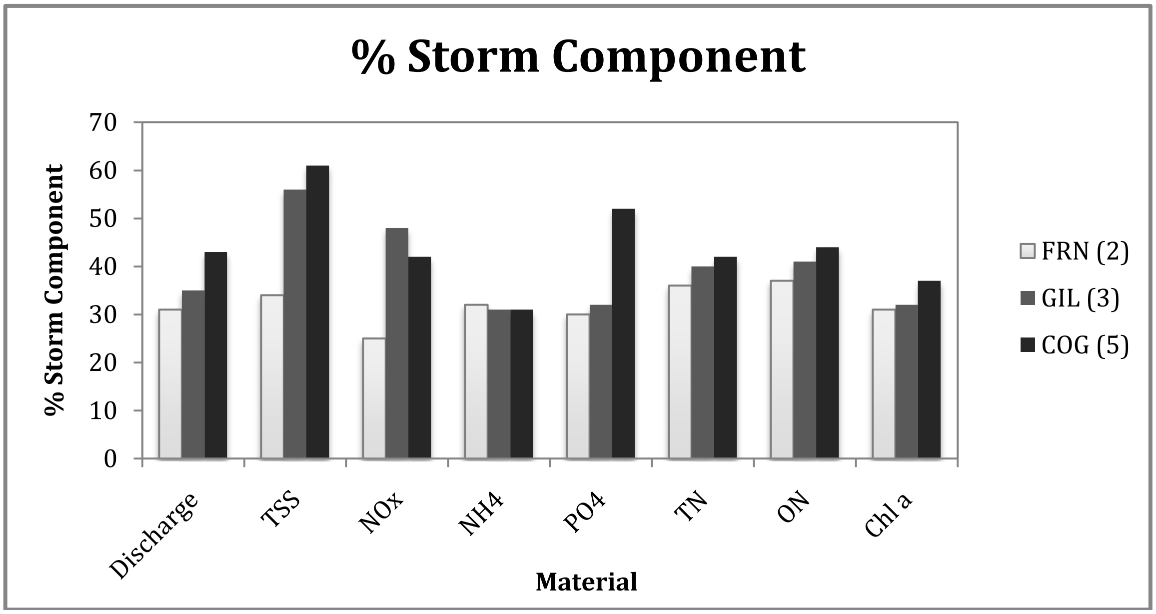


Figure 9. Percent stormflow component of each material delivered to the stream for the 3 ISCO sites, displayed in increasing order of watershed development.

Base and storm load analyses were limited to the three sites that housed ISCO automated samplers where complete storm records were available (fig. 9). For most parameters (discharge, TSS, PO_4, TN, ON, Chl *a*), the proportion of material delivered during stormflow increased with increasing development. NH_4 delivery during stormflow remained close to 30% of total load across development, and proportional stormflow delivery of NO_X appeared to increase with development, although there was little distinction between the more developed streams (GIL-3 and COG-5).

Correlation to Land Use

Regression analyses were conducted using raw load values and an α of 0.05. All load parameters were normally distributed except NO_X, but transformation methods attempted did not help. Total development (excluding open development) was positively correlated with IC (R^2 = 0.986, P = 0.000) and negatively correlated with total wetland area (R^2 = 0.940, P = 0.000). Because of this close association, total development was the only land use parameter chosen for the regression analyses. Total development was positively correlated with TSS load at baseflow (R^2 = 0.861, P = 0.015), stormflow (R^2 = 0.895, P = 0.015), and total flow (R^2 = 0.983, P = 0.001). Total development was also positively correlated with NO_X load at baseflow (R^2 = 0.830, P = 0.032), stormflow (R^2 = 0.852, P = 0.025), and total flow (R^2 = 0.839, P = 0.029). However, the regressions for NO_X were not significant if TAR-6 was removed from the analysis.

Load Calculation Method Comparison

Method #	**Sampling Frequency**	**Extrapolation Method**	**Flow Calculation**
1	Intensive – throughout storms	Interpolation between samples	ISCO flow
2	Intensive – throughout storms	Seasonal average for baseflow and stormflow	ISCO flow
3	Minimal – grab samples only	Seasonal average for baseflow and stormflow	ISCO flow
4	Minimal – grab samples only	Seasonal average for baseflow and stormflow	Manning Equation

Table 5. Summarized description of the 4 load calculation methods

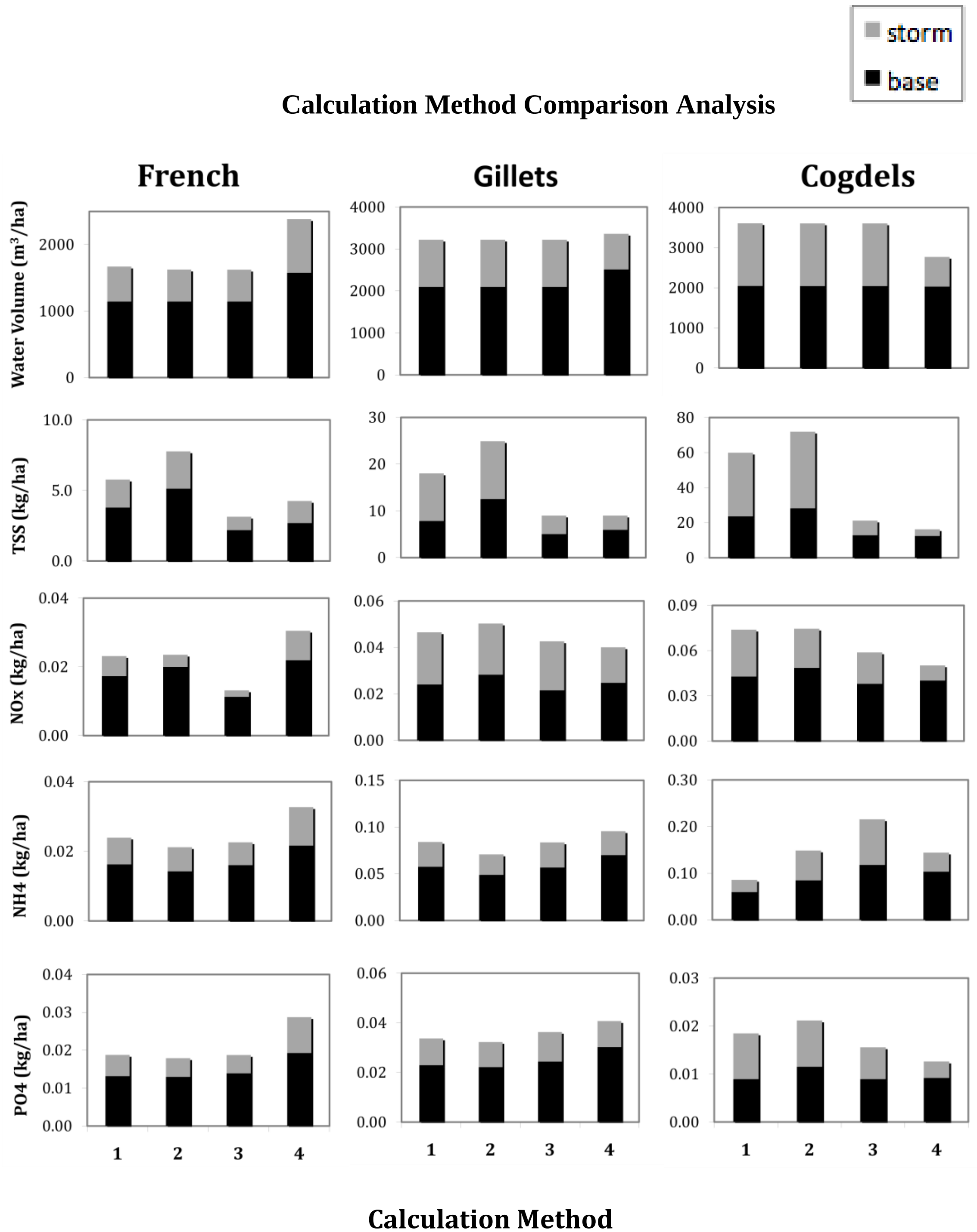


Figure 10. Displays annual load calculated via 4 different calculation methods. Graphs represent both base and storm components of total load.

In comparing Method #2 to Method #1, parameters increased in total load, with the most pronounced changes occurring in TSS (FRN-2 20%, GIL-3 38%, COG-5 20%) (fig. 10) (see appendix for raw values and for % increase/decrease for each method), and NH4 only in COG-5 (73% increase). All other parameters had a 16% change or less in total load. Although NO_X total load change was minimal (1-7% increase across the 3 sites), the variability of change in base and stormflow loads was much higher. NO_X baseflow load increased by 15% (FRN-2), 18% (GIL-3), and 13% (COG-5), while stormflow loads decreased by 39% (FRN-2), 2% (GIL-3), and 16% (COG-5). There were also large changes in TSS base and storm loads in all sites, ranging in magnitude from a 20% increase in COG-5 to a 60% increase in GIL-3.

Method #3 showed that both base and storm loads for TSS and NO_X underestimated load as compared to Method #2 by between -4% to -81%. The direction of change for PO_4 varied between creeks and between base and storm predictions, but the greatest decrease in both base and storm load was calculated for COG-5. NH_4 load was overestimated in all but one case (FRN-2 storm load decreased by 5%) for both base and storm load, with the most drastic increase in loads in COG-5.

Method #4 was compared to Method #3. Total load varied considerably between the 3 sites. A large increase in calculated total load occurred in FRN-2, a minimal change occurred in GIL-3, and a decrease in COG-5 for discharge, TSS, NO_X, NH_4, and PO_4. Miscalculations in base and storm load were even larger, up to 357% increase in NO_X stormflow load in FRN-2.

DISCUSSION

This study provides qualitative data showing that coastal HW streams are ideal locations to assess impacts of watershed development on stream water quality by quantifying material fluxes that cross the land-water interface. Water quality at the sampling stations was generally a good representation of watershed scale development, but there were examples when in-stream conditions were more strongly influenced by immediately proximate conditions. Altered water quality was evident in annual material load at very low levels of development, while concentration measurements served as an indicator of land use change only at the most developed sites. For the most accurate load calculation, water velocity should be measured directly, and frequent sampling of water quality during both base- and throughout stormflow is necessary to allow for interpolation between concentration measurements.

Anomalies in results

A major assumption in this study was that water quality parameters measured would be indicators of watershed scale conditions. Expected patterns based on this assumption are that, generally, material loads would increase with increasing watershed development. For example, the abundance of chl *a* was expected to increase with increased development in response to both increasing sources of nutrients, and increasing light availability due to the loss of riparian wetlands that is typically associated with development (Zedler and Kercher 2005). Anomalies in expected material load can be seen in the load figures and are described below, with attempted explanations of the sources of these derivations.

Housing developments located in TAR-6's watershed directly adjacent to the stream were demolished and rebuilt, beginning in November 2008 and continuing throughout the remainder of the study period. Every parameter for which load was calculated drastically increased in November or December of that year (figures not shown). After a jump in load in November, PO_4 monthly loads returned to about average for the rest of that year. This coincided with an increase in PO_4 in COG-5, implying that construction in TAR-6 did not impact PO_4 loads in that stream. However, every other parameter remained elevated after November or December, indicating that water quality in TAR-6 was extremely responsive to land use changes directly adjacent to the stream, regardless of the state of development in the remainder of the watershed. Land alteration from construction released materials that had been trapped in the sediment. Close proximity of the stream to this large construction site, combined with high levels of local IC associated with the original neighborhood restricted opportunities for material processing, and is likely responsible for the drastic spike in monthly material loads.

Material load in CJ-1 exceeded what would be expected from a relatively pristine watershed in all constituents, especially TSS, NH_4 and chl *a*, as compared to other watersheds in this study. NO_X load in CJ-1 was about double that of other creeks with minimally developed watersheds in this study, but there was no obvious source that could explain this. This suggests that errors in calculating load could be partially to blame for material overestimates in this creek, and therefore potentially in other LG sites as well. However, the extreme degree to which TSS and other particle bound materials were overestimated reflected the local conditions witnessed at this sampling location, namely, the close proximity to a dirt road that ran parallel to the creek for a small stretch. The dirt road was composed of loose, fine sediment, and during rain events this sediment was seen running down the banks and collecting in pools within the creek. This highlights a situation in which local conditions mask watershed scale conditions and diminish the ability to connect watershed scale changes to changes in material loading.

Water column phytoplankton biomass increased with watershed development along the entire development scale (besides CJ-1), but the load in TAR-6 was much smaller than what would be expected based the trends of the other watersheds in this study. Nutrient concentrations suggest that there was ample N and P available to drive primary production. It is possible that the extremely high amount of suspended particulate material in the water decreased the depth of the photic zone and inhibited water column primary production (Allende 2009). Furthermore, chl *a* production in small blackwater streams can be limited by the canopy effect from adjacent forests (Mallin et al. 2004), and in deeper blackwater rivers by low irradiance from light attenuation (Smock and Gilinsky 1992). It is therefore not chl *a* load itself, but its association with other parameters that could indicate extreme watershed impairment. Chl *a* is used for total maximum daily loads (TMDLs) in many circumstances, including in the Tar-

Pamlico basin of NC (http://www.epa.gov/nps/success/state/nc_tar.html), but, as discussed, may not be the best measurement of excess nutrient load in all systems.

Creeks as wetlands during low flow and as streams during high flow

Many areas in coastal NC have a high water table, leading to poor natural drainage and many wetland areas (FINRMP 2006). The flat topography characteristic of coastal streams can create conditions that mimic wetlands during periods of low flow, allowing the stream to act as a material processor rather than a conduit (McMillan 2007). CJ-1, with an alternating pool-riffle sequence, illustrates an extreme example of how large amounts of material processing can occur in such streams. During low flow conditions sufficient nutrient and light availability spurs phytoplankton growth, as seen by an excessively large baseflow load of chl *a*, which is quickly washed out of the stream during high flow, shown by a minimal storm load. The phytoplankton community senesces and degrades, along with allochthonous organic matter, such as leaf litter, and releases NH_4 during low flow. Stagnant pools with plentiful organic matter create an autochthonous NH_4 source, which explains the large total load with a minimal storm component calculated for this stream.

It is clear from this example that in-stream processes resulting from the physical characteristics typical of coastal NC impact the volume of some materials found in streams, as well as the pattern of movement throughout streams during both base and storm flows. Detailed sampling in base-, but especially in stormflow, illustrates the pattern of movement of these materials, and can indicate whether sources are autochthonous or allochthonous.

Development alters hydrology

As watershed development increased across the ISCO sites, the storm proportion of material load for most parameters became more important. Changes in the relative importance of baseflow and stormflow material delivery can be a useful index of watershed development because it signifies altered hydrology due to increased IC associated with development. Impervious cover hinders percolation, can take the form of roads, rooftops, parking lots, and even compacted soil, and ultimately change the fate of rainwater (Arnold and Gibbons 1996). These minimally porous surfaces simultaneously alter the hydrology of both surface and groundwater by shunting rainwater directly to streams as overland flow, which diverts rainfall away from groundwater recharge via percolation, and reduces evapotranspiration potential (Harbor 1994). The difference in overland flow between a pristine and impacted watershed can be quite drastic. For example, in a typical pristine watershed with natural groundcover, 50% of rainfall will percolate into soil, 40% will return to the atmosphere via evapotranspiration, leaving only 10% to enter streams directly as overland flow. This relationship begins to shift with watershed development, so that in a typical watershed of 35-50% IC, percolation drops to 35%, evapotranspiration drops slightly to 35%, but the proportion that would enter the stream directly as overland flow increases 3 times to 30% (www.coastal.ca.gov/nps/watercyclefacts.pdf).

In this study it is likely that the hydrological cycle was altered by watershed development, which lead to increased discharge in general and of stormflow in particular. Residence time decreased which began to overwhelm processing capabilities, transforming streams within developed watersheds to act more as conduits, rather than processors. This can negatively implicate sensitive estuarine habitats, delivering greater amounts of nutrients that could spur eutrophication.

Development affects water quality, depending on the metric used

The use of raw concentration data served as a coarse indicator of impairment at low levels of watershed development in this study. Stormflow concentrations between all creeks were a very weak indication of land use change. It is doubtful that the lack of association was due solely to the minimal storm sampling regime at the LG sites, as the association was still week across the ISCO sites for which there was a complete storm record. Significant changes in concentration from base to storm values within a creek were found to be associated with development only for those materials that are less mobile and tend to be particle bound (NH_4 and PO_4). It was surprising that the same pattern was not seen for NO_X, a highly mobile material likely to be available for transport in a developed watershed. Close association of baseflow concentrations to development occurred only at very high levels of development (over 20% IC). Together, these patterns suggest that concentration data is not an appropriate indicator of land use change in this study site of low relief watersheds with minimal impairment.

A developed watershed transports a higher water volume than a pristine watershed to the lotic system, but also delivers an increased amount of material. Thus, the concentrations of material in base and stormflow may be similar (or, the concentrations from a pristine watershed to an impaired watershed), quantifying no change in watershed health, even though the amount of material transported to the fluvial system has obviously increased at stormflow (or in the impaired watershed) due to the increased water volume. The inherent characteristics of concentration as a measurement explain the weak association between both baseflow and stormflow concentrations with development across the entire range of watershed development in this study.

Holland et al. (2004) noted physical and chemical changes (e.g. altered hydrology, altered sediment characteristics) at 10-20%, and biological changes (e.g. decreased abundance of stress-sensitive macrobenthic taxa) at 20-30% IC cover in 23 HW tidal creeks of SC. Two creeks in this study (COG-5, TAR-6) are within the range in which physical and chemical changes would be anticipated. Because four creeks (CJ-1, FRN-2, GIL-3, TRP-4) are below this threshold of 10% IC, it is necessary to use a metric sensitive enough to reliably register water quality impairment before the ecological functioning of stream ecosystems is compromised.

We found correlations between total annual load and watershed development, even at low development levels (with a few exceptions as described previously). A significant correlation between watershed development and the total annual load of terrestrially derived materials (TSS, NO_X) suggests that load calculations are a viable indicator of land use change in this study system. Load is a measurement of the mass of a material in a sample, and can therefore act as a direct indication of watershed development by quantifying changes that occur in the amount of material that crosses the boundary from the terrestrial landscape to riverine networks.

During stormflow, material loads were more sensitive than raw concentration measurements to watershed development, especially for particle-bound materials (NH_4, PO_4). The greater volume of water delivered to a stream during stormflow can dilute concentration values and hide any association to development, but calculations of material load circumvent this effect. The relationship between development and stormflow load further indicates that material load in headwater streams can be a valuable tool in quantifying impacts of landscape alteration.

Importance of riparian wetlands

Total watershed development was strongly negatively correlated with total wetland area. It is therefore impossible to discern whether altered loads are due to increased development, decreased wetland area, or a combination of both. Wetlands are important mediators of stream water quality at the site scale by removing or retaining nitrate- N and P from through flowing surface and subsurface waters via denitrification of N, plant uptake of both N and P, or sedimentation of P (Zedler and Kercher 2005). Wetlands also store and slow floodwaters (Zedler and Kercher 2005), leveling spiky flow conditions spurred by IC of developed watersheds. Loss of wetlands has both physical and chemical effects on streams as the buffer between terrestrial development and streams is removed. However, research suggests that even very narrow widths of vegetation (~4m) directly adjacent to streams can remove up to 85-90% of nitrate, P, and sediments from runoff (Evans et al. 1996). The location and areal extent of removed wetlands is therefore important to maintaining stream water quality, but characterizing this was beyond the scope of this project. Even so, because of the known benefits to water quality imparted by wetlands (Verhoeven et al. 2006; Zedler and Kercher 2005), and the tight correlation between development and wetland area in this study, it is likely that the loss of wetlands negatively impacted water quality, and potentially magnified impacts that would have occurred from development alone.

Management implications

Coastal zone management is based on the assumption that altering land use in coastal watersheds will alter the magnitudes and patterns of delivery of nutrients, sediments and pathogens. This project tested the hypothesis that land use correlates with nutrient and sediment loads in small, flat, coastal watersheds. Results showed that material loads generally increased in association with a variety of indicators of watershed development in mixed-use watersheds. Furthermore, results suggest that HW streams are ideal locations to monitor increased material loads at even very low levels of development.

Mitigation of stormwater pollution requires an accurate understanding of the magnitude of pollution in storm as compared to base flow. Results of this study show that the stormwater component of total material load for most materials becomes more important with increased watershed development. Management efforts focusing on site level stormwater controls could mitigate increased loads associated with this portion of the hydrologic cycle. For example, retention ponds have been shown to decrease the influx of certain materials to streams, and riparian buffers help to dampen peak flows along with associated materials that occur with higher levels of IC.

Management efforts to stem large influxes of nutrient and sediments require continued monitoring of effected HW streams to make sure that implemented techniques are working properly. It is theoretically feasible that action taken to reduce the amount of sediment entering the lotic system starves downstream coastlines of necessary sediment to offset shoreline erosion and sea level rise.

Monitoring efforts of material load need to incorporate in-stream velocity measurements to calculate discharge, along with frequent water sampling that focuses on both base-, and throughout stormflow. Results of the method comparison study in this project showed significant variability in material load depending on the calculation method utilized.

Load Calculation Method Comparison

The derivation of estimated load from the "true" load is influenced by both the sampling frequency and the method used to estimate material load (Birgand et al. 2006; Stone et al. 2000; Longabucco and Rafferty 1998; Kronvang and Bruhn 1996; Dolan et al. 1981). Kronvang and Bruhn (1996) determined that linear interpolation yielded the least error and most reproducible load calculations for TN, TP, PP, and DP (13 total estimation methods compared) in small lowland streams in Eastern Denmark. Additionally, Longabucco and Rafferty (1998) found that event sampling was necessary to properly assess NPS contributions to annual loads. Therefore, when infrequent sampling hinders linear interpolation between concentration measurements, or when rain events are not fully represented, it is important to understand resulting impacts on estimated material load. It appears that currently there is no accepted standard method to calculate material load from HW streams (King et al. 2005; Birgand et al. 2006).

Budgetary restraints required installation of 2 types of sampling setups in the field to gather water quality information. Data from this study are valuable for a cost benefit analysis of stream monitoring approaches. A comparison of methods to calculate material load was performed on the three sites equipped with ISCO samplers: FRN-2, GIL-3, COG-5. The goal of this study was to examine the roles that three factors play in influencing load calculations: method of flow calculation (velocity of ISCO sites versus Manning Equation of Greenbox sites), method of extrapolating concentrations to 30-

minute intervals (concentration averages versus linear interpolation), and sampling frequency (throughout storm versus single grab typically on the falling limb).

Method #1 of load calculation is assumed to be the most rigorous because velocity is measured in situ, negating the necessity for calculating this metric from water depth and channel morphology, and therefore minimizing human error associated with these measurements. Additionally, the intensive sampling frequency throughout storms allows for interpolation of concentrations between sampling points. This maintains storm specific nuances in material concentrations, as opposed to averaging anomalies into blanket base and storm concentrations that are then applied to a wide variety of storms.

The magnitude and direction of over or underestimation using Method #2 as compared to Method #1 did not correlate with watershed development, and was not predictive based on the characteristics of a particular material. However, it is possible that the extrapolation technique is more important for creeks or parameters with spikier storm concentrations. Utilizing Method #1, a single extreme value remained storm specific via linear interpolation, but in Method #2, this extremely high value was taken into account for a seasonal average and artificially raised the storm concentration for that season. This trend was noted empirically in a drastic overestimation in NH_4 load of COG-5 in Method #2 as compared to Method #1. This result suggests that material loads of developed watersheds that were subjected to substantial changes in material concentrations could be misrepresented to a greater degree than pristine watersheds that are not subject to extreme changes in material concentrations. Generalizing trends based on extrapolation method is complex, as highlighted by comparing TSS loads between Method #1 and #2; as described previously, the increase in storm load of TSS was expected because of its spiky nature, but the large increase in base load for the same parameter was not expected.

Method #3 reduced sampling frequency to explore the importance of the sampling regime on the outcome of load calculations. Method #3 was compared to Method #2 across all three creeks, thereby singling out effects that a minimized sampling frequency had on base and storm loads by maintaining the extrapolation technique. This sampling regime effectively eliminated samples representing rising and peak concentrations of storms, which eliminated the high concentrations associated with a first flush of terrestrially derived materials (i.e. TSS), and also eliminated reduced concentrations associated with the dilution of stream derived materials (i.e. NH_4). In addition to storm samples, the minimal sampling method eliminated the last baseflow sample before a storm.

It was hypothesized that the storm load calculated with Method #3 would result in an underestimation of terrestrially derived materials, and an overestimation of in-stream derived materials as compared to a method that incorporated samples that represented all parts of a hydrograph. Baseflow load was also expected to change but because this ‘before’ sample was essentially a random elimination of a baseflow sample, the magnitude and direction of change that this elimination could cause was unclear, but was expected to be minimal.

Typically, the direction that storm load was over or under estimated was predictable based on the sampling frequency and the source of material. Results showed the expected reduction in storm load of some terrestrially derived materials (TSS and NO_X), and the expected overestimation of storm load of in-stream derived materials (NH_4). However, the difference in magnitude of change between base and storm loads was unexpected. For example, the substantial decrease in TSS storm load was understandable given the extreme values observed in rising and peak parts of the hydrograph that were not included in the load calculation using Method #3. However, TSS base load decreased almost as much as the decrease calculated in storm load, which was quite a drastic and unexpected response for eliminating only the ‘before’ samples of base load. Load change in TSS is an illustrative example of an extreme case (the most extreme in this study), but serves to highlight the importance of frequent sampling to obtain a complete representation of the range of concentrations throughout both base and storm flows. Many studies that calculate load rely on a few samples that are extrapolated to a larger time scale. This study is evidence of the potential extreme misrepresentation of load that can stem from the seemingly random elimination of baseflow samples, and the purposeful elimination of certain stormflow samples.

The magnitude of derivation from the true base and storm calculated with Method #3 increased with amount of watershed development only for NH_4, and possibly for PO_4. This was surprising as all parameters, not just NH_4 and PO_4, showed a general increase in load with increased development in this study. Method #3 overestimated NH_4 load to a greater extent in developed watersheds than in pristine watersheds. This suggests that for autochthonous materials, misrepresentations in load that occur from sampling frequency may be more severe in developed watersheds. Of all terrestrially derived materials, the trend was only seen in PO_4, with the greatest decrease in load found in COG-5. Although this same pattern was not seen in this study in other allochthonous materials (NO_X, TSS), the same principals hold true; the more altered or developed the landscape is, the more material there is available to be dislodged and delivered to streams with rainfall. So in highly developed watersheds, the concentration spikes associated with the initialization of rainfall could be larger, and missing this sample would result in an even greater decrease in load estimate. It is possible that the levels of development found in this study were not enough to influence an association with development for allochthonous materials.

Method #4 was compared to Method #3 to single out changes in flow calculation, while maintaining the method to extrapolate concentration. The magnitude and direction of change in total annual discharge and material load that resulted from using the Manning Equation varied to a large degree between streams, but stormflow load was altered to a greater degree than baseflow load in all three streams. These patterns were not predictable and had no apparent correlation to watershed development. Because the Manning Equation drastically altered discharge measurement from the ‘true’ discharge, materials that overland flow and groundwater carry will necessarily be impacted by a change in water volume, thus magnifying (or dampening) any misrepresentations in load that stemmed from changes in sampling frequency. An understanding of the mechanisms behind the Manning Equation may explain this inequality.

The slope-area method utilizing the Manning Equation to calculate discharge has been widely used (Gordon et al. 2004), but can give substantial error in stream discharge, usually due to incorrect estimates of flow resistance (*n*) (Marcus et al. 1992). It is based on the assumption of uniform flow from unchanging channel cross-section and velocity (Chow 1959). Determining most of the physical characteristics (area, wetted perimeter, and Manning's *n*) of the three ISCO streams used for this study was simplified by the culvert pipes in which depth sensors were placed, making it unlikely that these characteristics caused errors in the equation. The exception to this was streambed slope, in which even very small errors in measurements can magnify errors in the slope value, and increase errors in calculated discharge. Results therefore suggest that using the Manning Equation in coastal plain watersheds of extremely minimal slope is not appropriate, and must be taken with caution. However, the Manning Equation has been shown to be valid for low-gradient, tranquil streams (Jarrett and Malde 1987), even though errors in peak discharge can be 10-50% or more depending on conditions (Gordon et al. 2004).

Errors in flow estimates of the ISCO sites using the Manning Equation are likely exacerbated in the LG sites due to complexities of measuring stream characteristics for parameters in the equation. The LG sites in this study were anything but uniform channels, rife with riffles, pools, and non-uniform channel width, bank height and slope.

Attempts were made to circumvent errors in misrepresenting stream characteristics of LG sites by multiple measurements along a stream reach, however, deviations from the assumptions of the Manning Equation could have been a source of error in flow calculations.

There seemed to be a pattern in the direction and magnitude of total load when using Method #4 compared to Method #3, with a large increase occurring in the most pristine (FRN-2), minimal change in the next highest developed (GIL-3), and negative change in the most developed (COG-5). However, it is unclear how the Manning Equation would affect load in a predictable direction or magnitude based on development. Therefore, I suggest that this pattern is simply due to random coincidence, and that the magnitude and direction in change of material load when calculated with the Manning Equation is not predictable based on watershed development.

It is important to be wary of the potential for over or underestimates in total load, as well as the proportion of base to storm loads, depending on whether the site was an ISCO or LG. The load of the 3 LG sites (CJ-1, TRP-4 and TAR-6) cannot be taken as absolute values, but can still offer information regarding general trends within the data.

Conclusions

Studies have shown that changes in water quality can be quantitatively measured when IC of the watershed exceeds about 10-20%, and ecological characteristics responded, generally adversely, at 20-30% IC (Sanger et al. 2008). Our study suggests that water quality alteration begins in response to less than 5% IC, corresponding to roughly 10% developed watershed area. Comprehensive load calculations in this study enabled cross-watershed comparisons of the impacts of watershed development on HW streams at very low levels of IC (<10%) and development (<30%). Impacts resulting from watershed development were documented in HW streams in this study in terms of physical changes as increased discharge, chemical changes as increased levels of nutrients, and biological changes as increased chl *a* loads.

The baseflow component of material load was generally the dominant source of material load to creeks in this study. However, as watershed development increased, the stormflow component became increasingly more important in terms of material delivery. This implies that management efforts should focus on stormwater controls in developing watersheds. Additionally, material loads from minimally developed watersheds surpassed background levels of material loads that would be expected from pristine watersheds, suggesting the necessity of implementing a comprehensive watershed management plan before development actually takes place.

Results of the method comparison study suggested that the Manning Equation is an inappropriate method for calculating water velocity in streams of minimal water surface slope, such as coastal plain watersheds of NC, because of the difficulties in accurately measuring this parameter. Therefore, it is imperative that a direct measurement technique be employed, such as the in-situ ultrasonic Doppler velocimeters used in this study.

Additionally, material load calculations utilizing a complete concentration record that includes base- and storm-flows, allowing for linear interpolation, is a more robust method than a sampling regime that does not characterize material concentrations throughout rain events.

APPENDIX

1a. Summary chart for each creek displaying annual load calculated via each method.

COGDELS

Material	Units	Designator	Method 1	Method 2	Method 3	Method 4
		Base	2045.66	2041.67	2041.67	2028.75
Discharge	m^3	Storm	1562.85	1562.24	1562.24	741.32
		Total	3608.59	3603.99	3603.99	2770.07
		Base	23.61	28.23	12.87	12.45
TSS	kg	Storm	36.31	43.69	8.34	3.81
		Total	59.92	71.92	21.20	16.26
		Base	0.04	0.05	0.04	0.04
NO_X	kg	Storm	0.03	0.03	0.02	0.01
		Total	0.07	0.07	0.06	0.05
		Base	0.06	0.08	0.12	0.10
NH_4	kg	Storm	0.03	0.06	0.10	0.04
		Total	0.09	0.15	0.22	0.14
		Base	0.01	0.01	0.01	0.01
PO_4	kg	Storm	0.01	0.01	0.01	0.00
		Total	0.02	0.02	0.02	0.01
		Base	0.55	0.60	0.58	0.56
TN	kg	Storm	0.40	0.46	0.45	0.21
		Total	0.95	1.06	1.03	0.77
		Base	0.45	0.47	0.42	0.42
ON	kg	Storm	0.35	0.37	0.33	0.16
		Total	0.79	0.84	0.75	0.58
		Base	0.005	0.010	0.012	0.010
Chl *a*	kg	Storm	0.003	0.010	0.012	0.005
		Total	0.009	0.019	0.024	0.015

1b. Summary chart for each creek displaying annual load calculated via each method.

FRENCH

Material	Units	Designator	Method 1	Method 2	Method 3	Method 4
		Base	1144.15	1144.15	1142.62	1575.24
Discharge	m^3	Storm	525.84	480.08	480.08	809.39
		Total	1669.99	1624.23	1622.70	2384.63
		Base	3.79	5.12	2.18	2.69
TSS	kg	Storm	1.98	2.65	0.96	1.57
		Total	5.77	7.77	3.14	4.25
		Base	0.02	0.02	0.01	0.02
NO_X	kg	Storm	0.01	0.00	0.00	0.01
		Total	0.02	0.02	0.01	0.03
		Base	0.02	0.01	0.02	0.02
NH_4	kg	Storm	0.01	0.01	0.01	0.01
		Total	0.02	0.02	0.02	0.03
		Base	0.01	0.01	0.01	0.02
PO_4	kg	Storm	0.01	0.00	0.00	0.01
		Total	0.02	0.02	0.02	0.03
		Base	0.37	0.35	0.34	0.39
TN	kg	Storm	0.21	0.21	0.19	0.21
		Total	0.59	0.57	0.53	0.60
		Base	0.34	0.32	0.31	0.35
ON	kg	Storm	0.20	0.20	0.18	0.19
		Total	0.54	0.52	0.49	0.53
		Base	0.0009	0.0008	0.0006	0.0007
Chl *a*	kg	Storm	0.0004	0.0005	0.0004	0.0003
		Total	0.0012	0.0012	0.0010	0.0010

1c. Summary chart for each creek displaying annual load calculated via each method.

GILLETS

Material	Units	Designator	Method 1	Method 2	Method 3	Method 4
Discharge	m^3	Base	2095.00	2095.00	2095.00	2510.27
		Storm	1125.15	1125.15	1125.15	851.11
		Total	3220.15	3220.15	3220.15	3361.38
TSS	kg	Base	7.83	12.52	5.03	5.91
		Storm	10.19	12.41	3.97	3.08
		Total	18.05	24.93	9.00	8.99
NO_X	kg	Base	0.02	0.03	0.02	0.02
		Storm	0.02	0.02	0.02	0.02
		Total	0.05	0.05	0.04	0.04
NH_4	kg	Base	0.06	0.05	0.06	0.07
		Storm	0.03	0.02	0.03	0.03
		Total	0.08	0.07	0.08	0.10
PO_4	kg	Base	0.02	0.02	0.02	0.03
		Storm	0.01	0.01	0.01	0.01
		Total	0.03	0.03	0.04	0.04
TN	kg	Base	0.82	0.81	0.89	0.84
		Storm	0.56	0.61	0.61	0.28
		Total	1.38	1.42	1.50	1.11
ON	kg	Base	0.74	0.73	0.81	0.75
		Storm	0.51	0.57	0.56	0.24
		Total	1.25	1.30	1.37	0.99
Chl *a*	kg	Base	0.002	0.002	0.001	0.001
		Storm	0.001	0.001	0.001	0.000
		Total	0.002	0.003	0.002	0.002

2a. Summary charts for each creek displaying % change in annual load comparing each method.

% Change
COGDELS

Material	Designator	method 1:2	method 2:3	method 1:3	method 3:4	method 1:4
Discharge	Base	0	0	0	-1	-1
	Storm	0	0	0	-53	-53
	Total	**0**	**0**	**0**	**-23**	**-23**
TSS	Base	20	-54	-45	-3	-47
	Storm	20	-81	-77	-54	-89
	Total	**20**	**-71**	**-65**	**-23**	**-73**
NO_X	Base	13	-22	-11	6	-6
	Storm	-16	-20	-33	-52	-68
	Total	**1**	**-21**	**-20**	**-15**	**-32**
NH_4	Base	42	39	97	-12	73
	Storm	145	53	274	-58	57
	Total	**73**	**45**	**151**	**-33**	**68**
PO_4	Base	29	-22	0	3	3
	Storm	1	-31	-30	-48	-64
	Total	**15**	**-26**	**-16**	**-19**	**-32**
TN	Base	9	-4	5	-3	2
	Storm	15	-3	11	-53	-48
	Total	**11**	**-4**	**7**	**-25**	**-19**
ON	Base	5	-10	-5	-1	-6
	Storm	8	-12	-5	-51	-54
	Total	**6**	**-11**	**-5**	**-23**	**-27**
Chl *a*	Base	76	27	125	-17	87
	Storm	196	22	261	-57	57
	Total	**121**	**25**	**176**	**-36**	**76**

2b. Summary charts for each creek displaying % change in annual load comparing each method.

FRENCH

Material	Designator	method 1:2	method 2:3	method 1:3	method 3:4	method 1:4
	Base	0	0	0	38	38
Discharge	Storm	-9	0	-9	69	54
	Total	**-3**	**0**	**-3**	**47**	**43**
	Base	35	-57	-42	23	-29
TSS	Storm	34	-64	-52	64	-21
	Total	**35**	**-60**	**-46**	**35**	**-26**
	Base	15	-43	-35	94	27
NO_X	Storm	-39	-48	-68	357	47
	Total	**2**	**-44**	**-43**	**132**	**32**
	Base	-12	12	-1	35	33
NH_4	Storm	-10	-5	-15	68	43
	Total	**-11**	**7**	**-6**	**45**	**36**
	Base	-2	7	6	39	46
PO_4	Storm	-11	-2	-13	95	69
	Total	**-5**	**5**	**0**	**53**	**53**
	Base	-5	-4	-9	14	4
TN	Storm	-1	-11	-11	10	-3
	Total	**-4**	**-6**	**-10**	**13**	**2**
	Base	-6	-2	-8	10	2
ON	Storm	1	-10	-9	4	-6
	Total	**-3**	**-5**	**-8**	**8**	**-1**
	Base	-11	-15	-25	1	-24
Chl *a*	Storm	19	-17	-1	-13	-13
	Total	**-2**	**-16**	**-17**	**-4**	**-20**

2c. Summary charts for each creek displaying % change in annual load comparing each method.

GILLETS

Material	**Designator**	**method 1:2**	**method 2:3**	**method 1:3**	**method 3:4**	**method 1:4**
Discharge	Base	0	0	0	20	20
	Storm	0	0	0	-24	-24
	Total	**0**	**0**	**0**	**4**	**4**
TSS	Base	60	-60	-36	18	-24
	Storm	22	-68	-61	-22	-70
	Total	**38**	**-64**	**-50**	**0**	**-50**
NO_X	Base	18	-24	-11	15	3
	Storm	-2	-4	-6	-27	-32
	Total	**7**	**-15**	**-9**	**-6**	**-14**
NH_4	Base	-15	16	-1	24	22
	Storm	-18	23	1	-5	-3
	Total	**-16**	**18**	**-1**	**14**	**13**
PO_4	Base	-4	10	6	24	32
	Storm	-6	18	11	-12	-3
	Total	**-5**	**13**	**7**	**12**	**20**
TN	Base	-2	10	9	-6	2
	Storm	10	-1	9	-55	-51
	Total	**3**	**5**	**8**	**-26**	**-20**
ON	Base	-1	11	10	-8	2
	Storm	12	-2	10	-56	-52
	Total	**4**	**6**	**9**	**-28**	**-21**
Chl *a*	Base	12	-43	-36	8	-31
	Storm	29	-31	-10	-45	-51
	Total	**17**	**-38**	**-28**	**-13**	**-37**

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