

RESEARCH ARTICLE

Comparing catchment hydrologic response to a regional storm using specific conductivity sensors

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Abstract

A better understanding of stormwater generation and solute sources is needed to improve the protection of aquatic ecosystems, infrastructure, and human health from large runoff events. Much of our understanding of water and solutes produced during stormflow comes from studies of individual, small headwater catchments. This study compared many different types of catchments during a single large event to help isolate landscape controls on streamwater and solute generation, including human-impacted land cover. We used a distributed network of specific electrical conductivity sensors to trace storm response during the post-tropical cyclone Sandy event of October 2012 at 29 catchments across the state of New Hampshire. A citizen science sensor network, Lotic Volunteer for Temperature, Electrical Conductivity, and Stage, provided a unique opportunity to investigate high-temporal resolution stream behavior at a broad spatial scale. Three storm response metrics were analyzed in this study: (a) fraction of new water contributing to the hydrograph; (b) presence of first flush (mobilization of solutes during the beginning of the rain event); and (c) magnitude of first flush. We compared new water and first flush to 64 predictor attributes related to land cover, soil, topography, and precipitation. The new water fraction was positively correlated with low and medium intensity development in the catchment and riparian buffers and with the precipitation from a rain event 9 days prior to Sandy. The presence of first flush was most closely related (positively) to soil organic matter. Magnitude of first flush was not strongly related to any of the catchment variables. Our results highlight the potentially important role of human landscape modification in runoff generation at multiple spatial scales and the lack of a clear role in solute flushing. Further development of regional-scale in situ sensor networks will provide better understanding of stormflow and solute generation across a wide range of landscape conditions.

KEYWORDS

citizen science, first flush, new water, solute generation, stormflow, tracer

1 | INTRODUCTION

Understanding the hydrology of extreme events is vital to predicting how flooding might change in response to climate change. Climate change scenarios predict more extreme rain events (Allan & Soden, 2008), which would likely lead to increased flooding. Recent increases in high flows have already been detected in the northeastern United States. For example, a 75-year analysis of 28 gauges in New England showed "increased frequency and intensity of events in the upper 10th percentile of the daily precipitation distribution" (Collin, 2009). Rainfall-runoff dynamics are nonlinear (e.g., Detty & McGuire, 2010), thus, more information that traces runoff generation during extreme

precipitation events is needed. Tracing source waters for flooding events will improve our ability to predict when and where storms will result in floods. Further, many contaminants are transported during stormflows, particularly in catchments with human-dominated land uses, thus, better predictions about their transport can protect human and aquatic health (Aucharova & Khomich, 2006; Brown & Peake, 2006; Mason & Sullivan, 1998; Yuan, Hall, & Oldham, 2001).

Land cover change alters hydrologic pathways, which has strong implications for flooding. Urbanization increases the intensity and the amount of overland runoff generated (Burns et al., 2005; Leopold, 1968; Leopold, 1991; Vicars-Groening & Williams, 2007; Miller et al., 2014; Hawley & Bledsoe, 2011; Gremillion, Gonyeau, & Wanielista,

2000; Sheeder, Ross, & Carlson, 2002). Chemical and isotopic hydrograph separation techniques have demonstrated that storm runoff generally consists of more pre-event water than “new water” (NW) in forested catchments, suggesting that displacement of stored water is the major runoff generation mechanism (Buttle, 1994; Kirchner, 2003; Peters, Freer, & Aulenbach, 2003; Shanley, Kendall, Smith, Wolock, & McDonnell, 2002; Waddington, Roulet, & Hill, 1993). In more urbanized settings, tracer studies have demonstrated that runoff pathways generate more NW (Buttle, Vonk, & Taylor, 1995; Jefferson, Bell, Clinton, & McMillan, 2015; Pellerin, Wollheim, Feng, & Vorosmarty, 2008; Soulsby, Birkel, & Tetzlaff, 2014). For example, in the northeastern U.S., Pellerin et al. (2008) found higher NW contributions to peak flows (up to 97% NW) in a small urban catchment than what had been previously demonstrated in forested catchments in the region (e.g., 25% NW from Hooper and Shoemaker, 1986). These hydrograph separation studies have employed stable water isotopes and major ions as their water tracer; however, specific electrical conductance (SC) has proven to be similarly useful (Ahmad & Hasnain, 2002; Laudon & Slaymaker, 1997; Matsubayashi, Velasquez, & Takagi, 1993; Pellerin et al., 2008; Pinder & Jones, 1969).

Watershed development can impact water quality during storms, particularly the timing of solute or pollutant flushing, as observed with the first flush (FF) phenomenon. An FF is defined as a disproportionate increase of particulate or dissolved materials in the rising limb of a runoff event (Obermann, Rosenwinkel, & Tournoud, 2009). Many studies have found FF to be associated with highly impacted areas, such as urban catchments with large areas of impervious surface including roofs, streets, drainage ditches, and storm drains (Deletic, 1998; Lee, Bang, Ketchum, Choe, & Yu, 2002; Sansalone & Buchberger, 1997; Sansalone & Cristina, 2004). Pollutant loads were shown to increase as development intensity increased, with high density residential watersheds producing the highest loads (Lee & Bang, 2000). FF has also been observed during storms in rural catchments (Zhuanxi, Tao, Meirong, Jialiang, & Bo, 2012) and forested catchments (Inamdar, Rupp, & Mitchell, 2009). Solutes exported in the FF can vary depending on catchment land cover.

This study utilized a citizen science model to capture the hydrologic response to a regional precipitation event. The citizen science approach allowed the project to increase the number of stations collecting data that also increased geographic coverage, which was crucial to this study. Citizen science projects have increased in many science fields as a cost-effective method of collecting high-resolution data. Community-oriented science has been utilized in the aquatic science field since the 1930s and has gained popularity in the past decade, resulting in datasets otherwise unattainable (Buytaert et al., 2014; CoCoRaHS; Datry, Pella, Leigh, Bonada, & Hugueny, 2016; Gallart et al., 2016; Le Coz et al., 2016; Lottig et al., 2014; Lowry & Fienen, 2013).

The objectives of this research were to use data collected by citizen scientists to (a) identify patterns of storm response across catchments of varying land cover; (b) determine the spatial variation of FF and NW; and (c) identify spatial patterns of topographic, soil, land cover, and precipitation-related attributes that correlate with FF and NW. We hypothesized that FF and the fraction of NW would have a stronger correlation with human-influenced factors relative to

topographic and soil catchment attributes. These response metrics are correlated with spatial patterns of land cover, soil organic matter, and antecedent conditions. Associations among these variables emphasized the importance of human impacts to land cover to NW and soil organic matter to FF.

2 | METHODS

Measurements of SC ($\mu\text{S}/\text{cm}$) and stage of streamwater were made during the tropical storm Sandy event between October 29, 2012, and October 31, 2012. These data were collected using a citizen science water-sensing network, the Lotic Volunteer for Temperature, Electrical Conductivity, and Stage sensing network (LoVoTECS). Trained members of the LoVoTECS network maintained sensors at their local site(s), downloaded data from the sensors, and made independent SC measurements for quality assurance (Plymouth State University, go.plymouth.edu/lovotecs, n.d.). The citizen science model allowed the network to cover a broad spatial domain, providing a unique opportunity to investigate the regional hydrologic response to this event. Twenty-nine catchments (Figure 1) were analyzed by using chemical hydrograph separation and descriptive analysis of the SC time series (hereafter referred to as the chemograph).

2.1 | Site descriptions

The 29 study catchments ranged in size from 1.0 to 2,626 km^2 , with a median size of 22 km^2 (Table 1; Figure 1). Elevation of the study sites ranged from 7 to 822 m with a median elevation of 342 m. Median soil depth in the catchments, according to Natural Resources Conservation Service (NRCS) State Soil Geographic (STATSGO) data, was 145.0 cm, which varied by about 20% across sites (USDA–NRCS, 1994). The catchments were dominated by forest cover (median of 84%), consistent with New Hampshire's dominant land cover. Development generally covered less than 10% of the catchments (median of 4.6%). Only two sites were intensely developed, meaning combined open space, low, medium, and high intensity development was greater than 90%. The median low, medium, and high intensity development in the study sites was 1%, 0.3%, and 0%, respectively. New Hampshire's climate is humid continental. Summers are warm and humid with an average temperature of 18.5 °C, and winters are cold and wet with an average temperature of −6.2 °C (NOAA, <https://www.ncdc.noaa.gov/cdo-web/>, n.d). Precipitation is evenly distributed throughout the year, ranging from 82 mm/month in winter to 99 mm/month in fall (NOAA, <https://www.ncdc.noaa.gov/cdo-web/>, n.d). Post-tropical depressions and cyclones typically impact this region in the late summer and autumn.

Catchment characteristics were calculated to explore lotic response to this event across sites. Catchment delineations were created using the Hydrology Tool Box in ESRI's ArcGIS, version 10.2. Ten-meter resolution elevation data were obtained from the United States Geological Survey National Elevation Dataset for catchment delineation and to extract mean elevations for each catchment. Land cover data were extracted from the National Land Cover Dataset (Homer et al., 2015), which used Landsat Thematic Mapper imagery

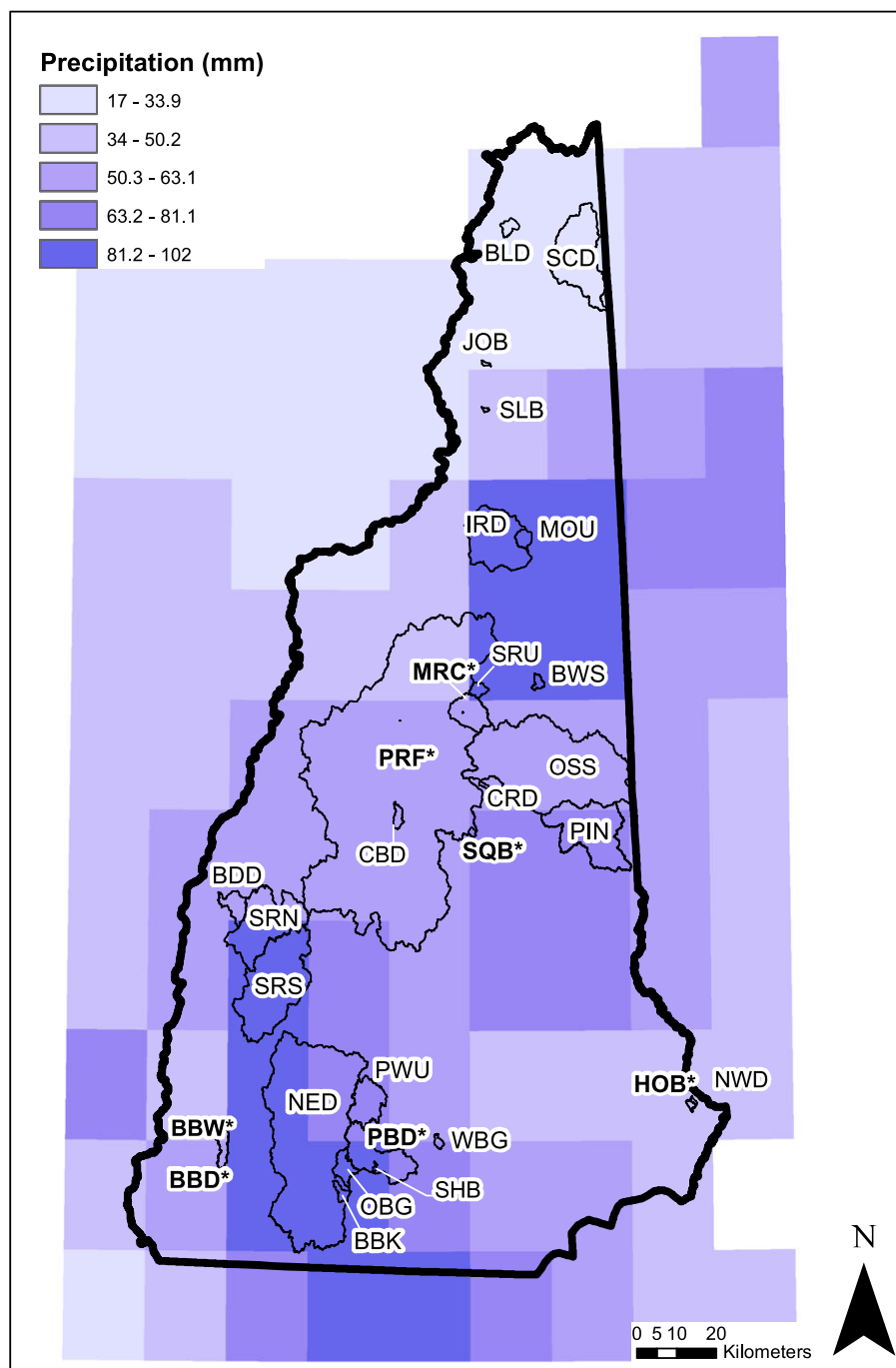


FIGURE 1 Twenty-nine study site delineations with three letter IDs and gridded precipitation (mm) data from the post-tropical cyclone Sandy event between October 29, 2012, and October 31, 2012. Precipitation data is from NOAA Climate Prediction Center (Daily US UNIFIED). Bold and asterisked sites showed a first flush

(Table 2). The National Land Cover Dataset is a dataset often used to assess changes in land cover overtime; however, in this study, it was used to represent 2012 land cover in each catchment. The NRCS STATSGO soil data were used to extract soil characteristics of each basin (Table 2). The STATSGO data included the following variables: available water capacity of the soil, percent clay in the soil, the actual k-factor used in the water erosion component of the Universal Soil Loss Equation, soil organic content, soil permeability, cumulative thickness of all soil layers, hydrologic group soil index, drainage quality, surface slope, liquid limit of the soil, percent hydric soils, and annual flood

frequency category (according to NRCS, annual flood frequency of 1 = frequent [$>50\%$ chance], 2 = occasional [5% to 50% chance], and 3 = rare [$<5\%$ chance]). Hydrologic group soil index variables are classified as 1 = well drained to 4 = poorly drained. Drainage quality is defined as 1 = well drained to 7 = very poorly drained. A weighted mean of each soil variable was calculated for each catchment. Distance to upstream road and road density within a 500-m buffer were calculated from the NH GRANIT Public Roads data (University of New Hampshire, <http://www.granit.unh.edu/data>, n.d.). Distance to closest upstream road was measured from the sensor location to the first road

TABLE 1 Site descriptions, locations, and highlighted catchment attributes for the 29 study sites

Site	Lat.	Long.	River	Area (km ²)	Precip. sandy (mm)	Precip. 10/20/12 (mm)	Low dev. (%)	Med. dev. (%)	OM (%)	Open water (%)
BBD*	42.9233	-72.2726	Beaver Brook	24.14	78.02	9.40	5.83	4.25	2.76	0.09
BBK	42.9077	-71.9221	Bogle Brook	10.72	105.83	10.61	0.05	0.00	2.68	0.39
BBW*	42.9307	-72.2714	Beaver Brook	21.89	78.02	9.40	5.00	2.55	2.75	0.05
BDD	43.5500	-72.2678	Blood Brook	33.39	77.49	9.11	0.76	0.06	0.97	0.06
BLD	45.0506	-71.3857	Back Lake Brook	6.35	24.50	8.63	1.95	0.22	1.32	11.30
BWS	44.0605	-71.2929	Louisville Brook	7.51	101.14	24.48	0.00	0.00	0.36	0.00
CBD	43.7706	-71.7295	Clay Brook	11.01	63.92	6.26	0.08	0.00	1.76	0.00
CRD	43.8009	-71.4375	Creamery Brook	2.15	65.20	6.75	2.19	0.56	0.70	0.00
HOB*	43.0821	-70.7960	Hodgson Brook	5.23	49.97	17.13	25.30	19.23	5.17	0.00
IRD	44.4116	-71.4960	Israel River	186.38	87.17	20.48	0.98	0.07	1.41	0.06
JOB	44.7582	-71.4270	Johnson Brook	1.74	33.47	6.36	0.00	0.00	1.53	0.00
MOU	44.3734	-71.2986	Moose River	15	87.17	20.48	2.19	0.26	0.84	0.00
MRC*	43.9404	-71.5112	Mad River	65.16	69.60	11.83	1.20	0.48	2.25	0.06
NED	43.1738	-71.8168	Contoocook	976.28	95.15	8.32	1.54	0.46	2.30	3.21
NWD	43.0812	-70.7979	Newfields Ditch	3.62	49.97	17.13	26.06	18.21	0.50	0.00
OBG	42.9175	-71.9161	Otter Brook	30.04	105.83	10.61	1.60	0.27	2.76	3.35
OSS	43.7924	-70.9925	Ossipee River	904.5	63.87	6.45	0.89	0.30	16.10	3.59
PBD*	42.9697	-71.6979	Piscataquog	140.98	91.94	10.41	0.91	0.13	1.99	0.88
PIN	43.7620	-71.1349	Pine River	227.3	68.54	6.30	0.85	0.46	3.52	2.63
PRF*	43.4378	-71.6523	Pemigewasset	2646.46	60.38	7.26	0.96	0.32	2.06	2.62
PWU	43.1090	-71.7620	Piscataquog (North)	86.66	86.83	7.35	0.52	0.03	2.04	4.27
SCD	44.8828	-71.0720	Dead Diamond River	217.17	37.99	6.57	0.01	0.00	1.57	0.06
SHB	42.9547	-71.7934	School House Brook	1.5	105.83	10.61	0.00	0.00	1.47	0.00
SLB	44.6654	-71.4574	Slide Brook	1.0	43.67	7.29	0.00	0.00	1.37	0.00
SQB*	43.7036	-71.5013	Unnamed	3.13	72.17	6.29	0.00	0.00	3.00	0.20
SRN	43.3915	-72.1863	Sugar River	210.98	74.77	9.13	1.97	0.27	2.11	2.05
SRS	43.3895	-72.1946	Sugar River	325.3	105.94	8.46	2.61	0.63	1.98	7.61
SRU	44.0236	-71.4357	Swift River	12.02	101.14	24.48	1.23	0.04	2.04	0.09
WBG	43.0165	-71.6013	Piscataquog (Main)	5.34	76.09	12.09	3.09	1.54	0.72	0.13

Note: Precip. Sandy is the total precipitation (mm) from the post-tropical cyclone Sandy event, obtained from the CPC US Unified Precipitation database provided by NOAA. Precip 10/20/2012 is the total precipitation (mm) from the rain event on October 20, 2012, obtained from the CPC US Unified Precipitation database provided by NOAA. Low dev. is the percent of low intensity-developed land cover in each catchment, as defined by the National Land Cover Database (2011). Med. dev. is the percent of medium intensity developed land cover in each catchment, as defined by the National Land Cover Database (2011). Organic matter (OM) is the average percent by weight across soil layers in each catchment (NRCS STATSGO). Open water is the total percent of open water in each catchment, as defined by the National Land Cover Database (2011).

*Indicates site that demonstrated a first flush.

that crossed the main stem (Table 2). When extracting and calculating percent land cover in the riparian zone, 100- and 800-m buffers were also included. Overall, a total of 64 metrics describing the catchment characteristics were assembled (Table 2).

2.2 | New water

New water SC was assessed from precipitation collected in an open area in Plymouth, New Hampshire, using a low-density polyethylene bag, which lined a clear glass wide-mouthed jar. SC was analyzed with a calibrated Oakton ECTestr11+ meter, which has an accuracy and precision of $\pm 1\%$ full scale (Oakton Instruments). Because we measured SC at only one site, we evaluated spatial variability using previous rainfall SC values measured at nearby National Atmospheric Deposition Program (NADP) sites: Hubbard Brook, New Hampshire (NH02), and the coastal site at Casco Bay, Maine

(ME96; NADP Program Office, 2007). We expected that the precipitation SC would not vary much spatially given the regional nature of the Sandy event. However, the NADP comparison supported this expectation. Gridded precipitation data were obtained from the Climate Prediction Center US Unified Precipitation database provided by NOAA to estimate the spatial variation of the total precipitation from the event (CPC US Unified Precipitation, NOAA). Daily precipitation raster data from October 29, 30, and 31, 2012, were combined and summarized. A mean precipitation was then extracted from each catchment. Calculations were made by using the following R packages: rgdal, raster, RNetCDF, and foreign (Bivand et al., 2016; Hijmans et al., 2016; Michna and Woods, 2016; R Core Team et al., 2015, respectively).

In streamwater, electrical conductivity (EC, $\mu\text{S}/\text{cm}$), temperature ($^{\circ}\text{C}$), and absolute pressure (kPa) were measured with HOBO U24-001 and U20-001 data loggers (Onset Computer Corporation) and

TABLE 2 Catchment variables used in data analysis

Catchment attributes	Unit	Source
100 m barren	Percent of 100-m riparian buffer	USGS, NLCD, 2011
100 m crops	Percent of 100-m riparian buffer	USGS, NLCD, 2011
100 m deciduous	Percent of 100-m riparian buffer	USGS, NLCD, 2011
100 m evergreen forest	Percent of 100-m riparian buffer	USGS, NLCD, 2011
100 m herbaceous	Percent of 100-m riparian buffer	USGS, NLCD, 2011
100 m herbaceous wetland	Percent of 100-m riparian buffer	USGS, NLCD, 2011
100 m high developed	Percent of 100-m riparian buffer	USGS, NLCD, 2011
100 m low developed	Percent of 100-m riparian buffer	USGS, NLCD, 2011
100 m med developed	Percent of 100-m riparian buffer	USGS, NLCD, 2011
100 m mixed Forest	Percent of 100-m riparian buffer	USGS, NLCD, 2011
100 m open space developed	Percent of 100-m riparian buffer	USGS, NLCD, 2011
100 m open water	Percent of 100-m riparian buffer	USGS, NLCD, 2011
100 m pasture	Percent of 100-m riparian buffer	USGS, NLCD, 2011
100 m shrubland	Percent of 100-m riparian buffer	USGS, NLCD, 2011
100 m woody wetland	Percent of 100-m riparian buffer	USGS, NLCD, 2011
800 m barren	Percent of 800-m riparian buffer	USGS, NLCD, 2011
800 m crops	Percent of 800-m riparian buffer	USGS, NLCD, 2011
800 m deciduous	Percent of 800-m riparian buffer	USGS, NLCD, 2011
800 m Evergreen Forest	Percent of 800-m riparian buffer	USGS, NLCD, 2011
800 m herbaceous	Percent of 800-m riparian buffer	USGS, NLCD, 2011
800 m herbaceous wetland	Percent of 800-m riparian buffer	USGS, NLCD, 2011
800 m high developed	Percent of 800-m riparian buffer	USGS, NLCD, 2011
800 m low developed	Percent of 800-m riparian buffer	USGS, NLCD, 2011
800 m med developed	Percent of 800-m riparian buffer	USGS, NLCD, 2011
800 m mixed Forest	Percent of 800-m riparian buffer	USGS, NLCD, 2011
800 m open space developed	Percent of 800-m riparian buffer	USGS, NLCD, 2011
800 m open water	Percent of 800-m riparian buffer	USGS, NLCD, 2011
800 m pasture	Percent of 800-m riparian buffer	USGS, NLCD, 2011
800 m shrubland	Percent of 800-m riparian buffer	USGS, NLCD, 2011
800 m Woody wetland	Percent of 800-m riparian buffer	USGS, NLCD, 2011
Annual flood frequency	1, 2, or 3	NRCS, STATSGO
Area	km ²	USGS, NED
Available water capacity	inch/inch	NRCS, STATSGO
Barren	Percent of watershed area	USGS, NLCD, 2011
Clay	Percent of soil (<2 mm in size)	NRCS, STATSGO
Crops	Percent of watershed area	USGS, NLCD, 2011
Deciduous	Percent of watershed area	USGS, NLCD, 2011
Distance to upstream road	Meter	NH GRANIT: NH Public Roads
Drainage	Continuous scale 1–7	NRCS, STATSGO
Evergreen	Percent of watershed area	USGS, NLCD, 2011
Herbaceous	Percent of watershed area	USGS, NLCD, 2011
Herbaceous wetland	Percent of watershed area	USGS, NLCD, 2011
High developed	Percent of watershed area	USGS, NLCD, 2011
Hydrologic group	Continuous scale 1–4	NRCS, STATSGO
If hydric soil	1 if hydric	NRCS, STATSGO
KF factor	Erodibility F-factor	NRCS, STATSGO
Low developed	Percent of watershed area	USGS, NLCD, 2011
Mean basin elevation	Meter	USGS, NED
Mean basin slope	Degrees	USGS, NED
Med developed	Percent of watershed area	USGS, NLCD, 2011
Mixed forest	Percent of watershed area	USGS, NLCD, 2011

(Continues)

TABLE 2 (Continued)

Catchment attributes	Unit	Source
Open space developed	Percent of watershed area	USGS, NLCD, 2011
Open water	Percent of watershed area	USGS, NLCD, 2011
Organic matter	Percent by weight	NRCS, STATSGO
Pasture	Percent of watershed area	USGS, NLCD, 2011
Permeability	inch/hour	NRCS, STATSGO
Precipitation 10/20/12	Basin mean, mm	NOAA Climate Prediction Center
Precipitation Sandy	Basin mean, mm	NOAA Climate Prediction Center
Road density	km/km ²	USGS, NLCD, 2011
Road density 500-m buffer	km/km ²	NH GRANIT: NH Public Roads
Shrubland	Percent of watershed area	USGS, NLCD, 2011
Slope of soil	Percent of watershed area	NRCS, STATSGO
Soil thickness	inch	NRCS, STATSGO
Woody wetland	Percent of watershed area	USGS, NLCD, 2011

Note: USGS = United States Geological Survey; NLCD = National Land Cover Database; nrsc = Natural Resources Conservation Service; NOAA = National Oceanic and Atmospheric Administration; NH = New Hampshire.

logged at 3-minute intervals. Stage was calculated as the difference between the absolute pressure from a transducer placed on the stream bottom and the nearest barometric station. Fourteen barometer stations were measuring at the time of the event and had a broad spatial distribution across the state. Each water pressure sensor and barometer were corrected for temperature and standardized to mean sea level, and the nearest barometer to each water pressure sensor was used for stage calculation. EC values were converted to SC by $SC_{25} = EC / (1 + 0.02 [T - 25])$, where SC_{25} is the corrected EC value adjusted to 25 °C; EC is the measured conductivity; and T is the water temperature (°C) at time of EC measurement (Radtko et al., 2005). The SC values were then used for chemical hydrograph separation using a two-component mixing model, separating new and old water (Pinder and Jones, 1969):

$$NW = C_i - C_o / C_n - C_o, \quad (1)$$

where NW is the event fraction of streamflow, C is SC (μs/cm), and subscripts i, o, and n indicate instantaneous, old, and NW, respectively. NW extracted at minimum SC is referred to as NW_{SC} and NW extracted at peak stage height is referred to as NW_H from this point forward (Figure 2). Specific conductivity data were quality-controlled and assured by comparing the logger measurements to calibrated Oakton ECTestr11+ meters. Hand measurements were taken monthly by the volunteers and partners when data loggers were downloaded. There was a median difference of 2 μs/cm in October 2012 ($n = 29$) and 4 μs/cm in November 2012 ($n = 29$). The accuracy of the HOBO U24-001 is 3% or 5 μs/cm.

2.3 | First flush

A feature in some SC chemographs was an initial spike in SC, associated with an FF dynamic (Figure 2). In order to quantitatively determine whether or not an FF was present, pre-event levels, peak SC, and the end of the FF were determined. The start of the event was site-specific and defined visually as the point on the SC curve before dilution or an FF began. Pre-event water was assigned the median

SC value from October 25, 2012, at 0:00 hours to October 29 at 17:00 hours. The Sen slope of the trajectory of pre-event SC was also determined for this period. The Sen slope is defined as the median slope of lines through pairs of sample points (Sen, 1968). If SC rose to 10% above the projected Sen slope line at the start of the event, it was considered an FF. The FF magnitude was defined as the percent increase from pre-event levels. The FF was defined as complete when the SC dropped to 10% below the Sen slope line (Figure 3).

2.4 | Analysis of catchment controls

NW_{SC} , NW_H , and FF magnitude were compared to catchment attributes using a Spearman correlation. Statistical significance was set as $p < .1$. The presence of FF was compared to catchment attributes using the nonparametric binary correlation test, Somers' D (Somers, 1962). Somers' D is a measure of the strength and direction between ordinal dependent and ordinal independent variables. The Somers' D test was chosen over the Goodman and Kruskal's gamma because the latter does not make a distinction between the two ordinal variables. Statistical significance was set as $Dxy > 0.6$. Regression trees were used to analyze multivariate relationships between NW and the 64 catchment variables using the rpart algorithm (Therneau et al., 2015; Table 2). Because of the small sample size of FF sites, a regression tree for magnitude of FF could not be created. A classification tree was produced for the presence of FF only.

3 | RESULTS

The variation in storm response of streamwater SC and stage shows a stage increase and subsequent SC dilution (Figure 4). The dilution of SC occurred at all 29 sites producing NW fraction ranging from 0.02 to 1.0. At most sites, SC recovered to pre-event levels a week after the Sandy event. The highly developed site (HOB) and forested sites SQB and PBD showed FF behavior and the other forest-dominated site SCD did not (Figure 4).

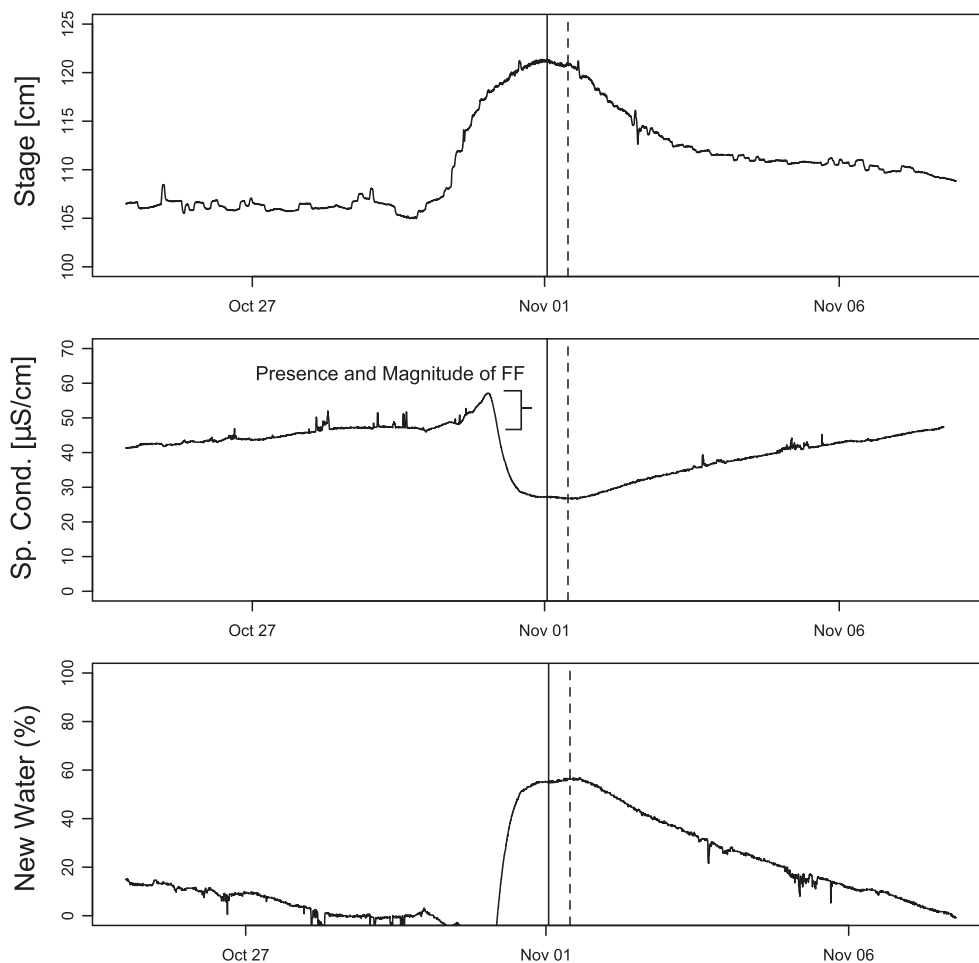


FIGURE 2 Storm metrics: Fraction of new water at peak stage (NW_H), new water at minimum specific conductance (SC; NW_{SC}), and presence and magnitude of first flush (FF) from post-tropical cyclone Sandy in Franklin, NH, October 2012 (Site PRF)

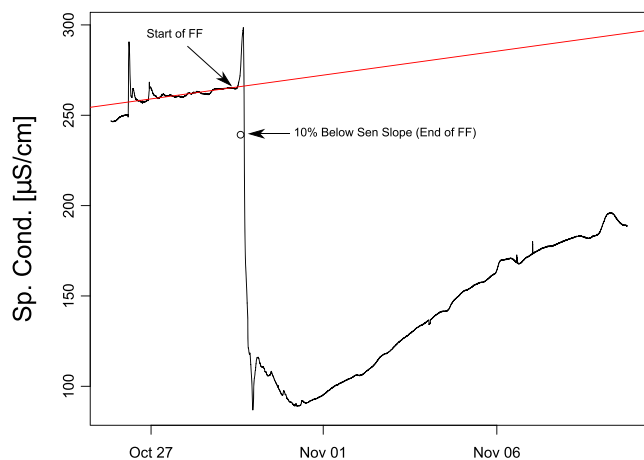


FIGURE 3 Chemograph of specific conductance during the Sandy event on October 29, 2012. The black line shows the specific conductance at Beaver Brook (BBW) in Keene, NH. The red line represents the Sen slope calculation of the pre-event water. FF = first flush

3.1 | NW fraction

Precipitation during Sandy ranged from 17 to 102 mm with a median of 76 mm (Figure 1). The measured SC of precipitation for the event in Plymouth, New Hampshire, was 11 $\mu\text{S}/\text{m}$. SC values from the Sandy

event at the NADP sites were not available, thus, we looked at the previous years to assess the variability of SC in precipitation. From 2007 to 2013, the range of weekly SC was 6.1 to 19.5 $\mu\text{S}/\text{cm}$ (median = 8.4 $\mu\text{S}/\text{cm}$) at NADP NH02 and 6.3 to 17.6 $\mu\text{S}/\text{cm}$ at ME96 (median = 10.1 $\mu\text{S}/\text{cm}$). The strong similarity in SC at these two different sites (one coastal and one mountainous) suggested that our measured precipitation SC would be applicable across all of our sites. Thus, we used our measured value of 11 $\mu\text{S}/\text{cm}$ as C_n value for Equation 1.

Across the 29 sites, NW_{SC} fractions ranged from 0.02 to 1.00 with a median of 0.51 and an inter-quartile range of 0.36 to 0.74. The site with the largest amount of NW_{SC} was the Mad River Campground site, draining the White Mountain National Forest and impacted by the small-town drainage infrastructure of Waterville Valley. The top five sites with the most NW_{SC} were either located in the central mountainous region of the State or in the city of Portsmouth, which is located in the southeastern corner of New Hampshire. The site that had the least amount of NW_{SC} was the Piscataquog River in south central New Hampshire, which was approximately 760 m downstream of a reservoir. The five sites with the least amount of NW_{SC} were distributed across the state with no apparent spatial pattern. A significant positive correlation was found between NW_{SC} and the following attributes: low intensity development in the 100- and 800-m riparian buffers, low and medium intensity development in the catchment, medium

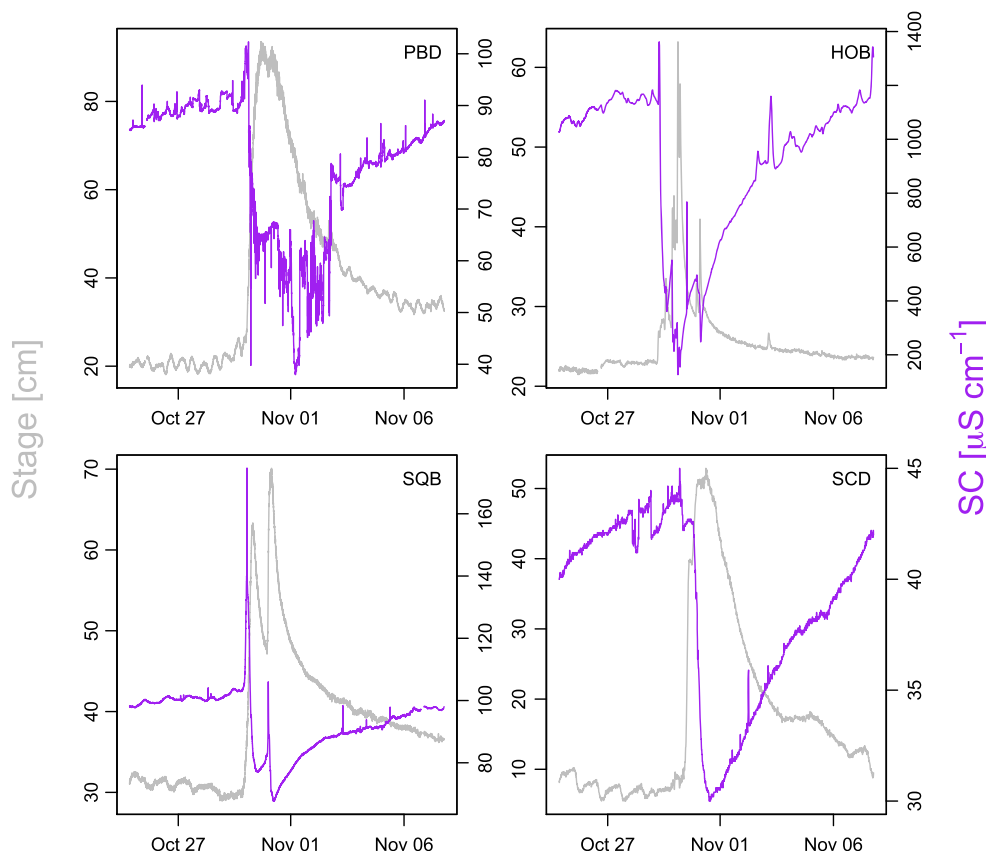


FIGURE 4 Examples of paired stage graphs and chemographs from four sites of varying land cover during the post-tropical cyclone Sandy event in October 2012. Developed site, HOB and forested sites, SQB, and PBD show a first flush. Forested site SCD does not show a first flush. SC = specific conductance

development in the 800-m buffer, soil permeability, and the precipitation from the rain event 9 days prior to Sandy (Table 3).

The regression tree for NW_{SC} was strongly predictive ($r^2 = 0.75$, $p < .0001$, Figure 5). The primary branch in the tree was determined by low intensity development in the catchment. The secondary branches were driven by open water and shrub cover in the 800-m riparian zone. If shrub cover was greater than 1.5%, NW_{SC} was predicted to be 0.19. If shrub cover was less than 1.5%, NW_{SC} increased to 0.56. If open water was greater than or equal to 0.11%, NW_{SC} was predicted to be 0.52 but if less than 0.11%, NW_{SC} increased to 0.84.

NW_H fractions ranged from 0.02 to 0.94 with a median of 0.36 and an interquartile range of 0.27 to 0.72. The NW_H was typically

90% of the NW_{SC} based on the relationship between the two variables. The site with the largest amount of NW_H was the Swift River, SRU, a headwater site draining the White Mountain National Forest. As with NW_{SC} , the top five sites with the most NW_H were located in the White Mountain region and on the seacoast, in the city of Portsmouth. The site that had the least amount of NW_H was again the Piscataquog River. No clear spatial pattern could be drawn for the five sites with the least amount of NW_H . A significant positive correlation was found between NW_H and the following attributes: low intensity development in the 100- and 800-m riparian buffers, medium intensity development in the 800-m riparian buffer, low and medium intensity in the catchment, and precipitation from the rain event 9 days prior to Sandy (Table 4). A significant negative correlation was found between NW_H and open water and mixed forest cover (Table 4).

Similar to the NW_{SC} regression tree, the NW_H multivariate analysis showed that the primary branch was also driven by low intensity development in the catchment ($r^2 = 0.83$, $p < .0001$, Figure 5). The secondary branches were driven by pasture and open water cover in the catchment. Shrub cover in the 800-m buffer drove a tertiary split beneath the secondary split due to pasture cover. If pasture cover in the 100-m riparian buffer was less than 3.6% and shrub cover in the 800-m buffer was less than 1.5%, NW_H was predicted to be 0.08. However, if shrub cover was less than 1.5%, NW_H increased to 0.28. If pasture cover was greater than 3.6%, NW_H increased to 0.47. If open water was greater than 0.11%, NW_H was predicted to be 0.44 but if less than 0.11, NW_H increased to 0.76.

TABLE 3 Spearman's correlation results for NW_{SC} and catchment attributes in ascending order

Catchment attribute	Spearman's rho	p
800 m low developed	0.573575	.001761
Low developed	0.491918	.005762
100 m low developed	0.518069	.006707
Precipitation 10/20/12	0.42917	.02017
800 m med developed	0.443828	.02039
Med developed	0.421055	.0205
Permeability	0.36068	.05459

Note: Significant variables have a $p < .1$.

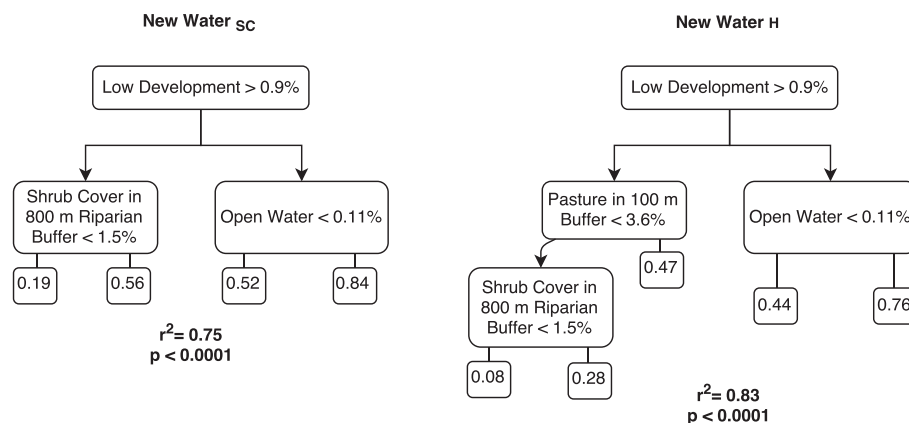


FIGURE 5 Regression tree analysis for the fraction of new water calculated with minimum specific conductance (NW_{sc}) and peak stage height (NW_H) during post-tropical cyclone Sandy and correlated attributes. Numbers at the end of the leaves are predicted fractions of new water

TABLE 4 Spearman's correlation results for NW_H and catchment attributes in ascending order

Catchment attribute	Spearman's rho	p
Low developed	0.703458	.00001
800 m low developed	0.622783	.0005216
Med developed	0.561269	.001251
100 m low developed	0.563725	.002708
800 m med developed	0.456439	.0167
Precipitation 10/20/12	0.414941	.02521
Mixed forest	-0.33841	.06737
Open water	-0.3369	.07392

Note: Significant variables have a $p < .1$.

3.2 | FF presence

Seven of the 29 sites showed an FF response to precipitation. The FF sites were located in the White Mountain region of New Hampshire or in the low-lying terrain in the southern portion of the State. The Somers' D test showed that FF presence was most correlated with soil organic matter (OM). Other variables had a much lower Dxy value, low enough to suggest minimal correlation. The primary branch in the classification tree for the presence of FF was also driven by soil OM. If soil OM was less than 2%, the regression predicted that there would be no flush. If OM was greater than 2% in the catchment, evergreen cover in the 800-m riparian buffer drove a secondary branch. If evergreen cover was less than 20.9%, no FF was predicted. If evergreen cover was greater than 20.9%, then woody wetlands caused a tertiary branch. If woody wetlands were less than 0.21%, no FF was predicted but if woody wetlands were greater than 0.21%, an FF was expected to occur (Figure 6).

3.3 | FF magnitude

Of the seven sites that showed an FF, magnitude ranged from a 0.71 to 0.88 increase from pre-event conditions. The site that had the largest FF was Beaver Brook (BBW), located in downtown Keene, which is developed on what used to be extensive floodplain wetlands in the southeastern part of New Hampshire. The site with the smallest FF was SQB, a small tributary to Squam Lake in central New Hampshire.

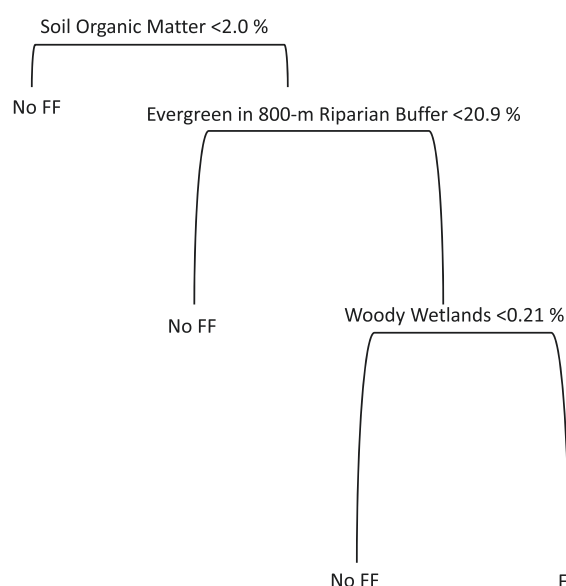


FIGURE 6 Classification tree for presence of first flush (FF) at the 29 study sites during post-tropical cyclone Sandy

The Spearman's test showed no significant positive or negative relationships between FF magnitude and catchment variables. FF was correlated with herbaceous and woody wetlands in the 800-m riparian buffer but not significantly ($p = .14$ for both; Table 6).

4 | DISCUSSION

4.1 | Controls on NW generation

Developed land uses both in the riparian buffers, and at the catchment level had the strongest influence on fraction of NW that entered the 29 catchments during the Sandy event. This result was expected given the known role of development in increasing runoff generation efficiency, particularly infiltration excess runoff from impervious surfaces (Horton, 1933; Pitt et al., 2003). Further, our results are consistent with other studies that have applied chemical hydrograph separation in urbanizing catchments (Buttle 1994; Jefferson et al., 2015; Pellerin et al., 2008). However, our study domain is broader than previous

studies, demonstrating that human impacts on NW generation persist across many differently sized catchments and across many topographic positions. Additional study of more storms or locations will help understand the relative importance of land use versus other catchment or climatic factors in catchment NW generation.

Antecedent moisture emerged as an important factor to NW generation according to the univariate correlations for NW_{SC} and NW_H . Precipitation during the storm event on October 20, 2012, ranged from 6.3 to 24.5 mm and had a median of 9.13 mm. Reduced soil moisture deficit from this prior rain event would have increased the possibility of saturation excess runoff during Sandy. The humid, forested northeast United States is prone to saturation-excess runoff from variable source areas (Dunne and Black, 1970; Easton et al., 2008; Schneiderman et al., 2007), which is also a likely source of NW from this event, even in urban areas.

The regression tree algorithm selected the amount of open water as a damping factor for NW generation. This was likely due to the mixing—and thus masking—of any NW inputs from tributaries and direct precipitation with existing stored water in lakes, ponds, and reservoirs. Jefferson et al. (2015) traced runoff in urban catchments that contained storm retention ponds and found a similar storage effect impacting runoff generation.

4.2 | Controls on FF

Soil OM was the variable most significantly related to the presence of an FF (Table 5); however, it is not clear how OM would control the flush. We anticipated that OM was indicating a role of wetlands in FF control, but this was not apparent in the data except for the presence in the classification tree (Figure 6). For example, Hodgsons Brook had the highest soil OM of the 29 sites (5.2%), but wetlands covered only 5.5% of the catchment and this catchment was heavily urbanized (91.2%). This site had an FF and also one of the highest FF magnitudes of 81%. At the landscape scale, soil OM accumulates in valleys and depressions at lower elevations (Doetterl et al., 2016; Gregorich et al., 1998; Lal, 2003; Rumpel et al., 2006), therefore, soil OM may be indirectly indicative of landscape position. New Hampshire is more densely populated in the lower elevations or non-mountainous areas, suggesting that soil OM and developed land may covary. However, other sites that had high soil OM, such as the Pine River in Ossipee, did not demonstrate an FF. The Otter Brook site (OBG: 2.7% OM, 42% evergreen in the 800-m buffer and 12.7% woody wetland) should have had an FF according to the classification tree, but it did not. This suggests that our study may be missing factors (or a combination of factors) that are driving the FF process. Urbanization did not emerge as an important factor in FF control, which is counter to the literature addressing FF from urban infrastructure (Deletic, 1998; Lee et al., 2007; Bolstad and Swank, 1997; Qin et al., 2010). However, much of the FF literature addresses specific pollutants,

which may demonstrate an FF without a significant change in SC, which is a more general indicator.

Alternatively, soil OM is associated with near-stream areas where biologically derived solutes are generated. Soil OM is well known to have high-cation exchange capacity and thus could provide a greater pool of base cations available for flushing. Buffam et al. (2001) found that dissolved organic matter had a quick response to stormflow, which suggests a near-stream or in-stream source of dissolved organic matter during storm events. Creed and Band (1998) concluded that nitrogen flushing was related to the rate of change of the expanding source area, which is strongly driven by topography. The cyclic drying and rewetting of the source area could affect the available solutes available for release. The Buffam et al. (2001) study highlights our need to include antecedent moisture content information to better capture local connectivity, available flow paths, and contributing area during storm events. More sites are needed to better understand where, when, and why FF behavior occurs. Future work should also include an assessment of which solutes are contributing to this FF phenomenon.

4.3 | Role of citizen science

The citizen science model used in our network allowed us to increase the number of stations collecting data and their geographic coverage. The travel and labor cost of visiting all 29 sites one time was approximately \$700, which was eliminated by means of volunteer efforts. Volunteers typically visited the sites every month from April to November, which saved the project roughly \$5600 per field season. The benefits of using such a model are in collecting data efficiently, reducing costs, and enhancing citizen scientist knowledge of the local areas of interest. We see strong potential for citizen science networks that use robust sensors to monitor water resources.

4.4 | Implications of study

The community-supported data collection proved to be a cost-efficient method of collecting high-quality stream data with in situ sensors. Because of our volunteers' efforts, we have a data covering a broad set of catchments to demonstrate the human impact on NW. Chemical hydrograph separation has typically involved a single or small set of catchments. By increasing the number of study catchments, we are able to produce relationships between catchment conditions and NW generation. Land development was the most important watershed feature in producing NW. Such information can be applied to regional assessment of basin runoff generation and predict areas susceptible to floodwater impacts on human and aquatic health. Our study suggests that soil OM is important to FF generation—across many catchment conditions. This work highlights that FF is not specific to developed catchments. The FF requires further attention to better understand which solutes are causing these flushes and tests our study predictions that soil OM is a driver of FF.

TABLE 5 Somers' D results for the presence of a first flush compared to watershed attributes

Catchment attribute	C	Dxy
Organic matter	0.817857	0.635714

Note: Significant variables have a Dxy > 0.6.

5 | CONCLUSION

Chemical hydrograph separation analysis was performed at 29 sites throughout New Hampshire during the post-tropical cyclone Sandy

event in October 2012. The fraction of NW was most closely correlated to human-disturbance attributes and less so to topographic and landscape characteristics. Seven out of the 29 sites showed the presence of an FF. FF was most correlated with soil OM, suggesting a possible role of OM in solute retention or generation in near-stream areas. Our results suggest that data from citizen science networks could help hydrologists and watershed managers to better understand stormflow generation and solute transport in diverse watersheds, especially in preparation for future land-use changes. The efforts of our volunteers increased capacity to collect data, reduced overall project costs, and provided citizen scientists with valuable information about their local streams.

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