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Flowpath influence on stream acid events in tropical urban streams in Singapore

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Abstract

We investigated processes contributing to periodic acidification events in headwater streams of Nee Soon Forest Catchment (NSFC) in Singapore by monitoring hydrochemical changes in response to rainfall inputs. Stream chemistry response to most rainfall events was characterized by decreases in pH from means ranging from 5.1 to 5.3 to below 4.8–5.0 and corresponding increases in specific electrical conductivity from baseflow values of 15–30 to 50–80 μS cm^{-1}, indicative of low-total dissolved solids in stormflow. The decreases in pH in the streams, which are typically acidic year-round, were related to occasional highly acidic rainfall inputs (pH ~4.05) and likely the flushing of organic acids into the stream by shallow subsurface flow interacting with surface litter and/or organic-rich soil horizons. The interaction of rainwater runoff with organic matter in the soil matrix possibly alters the chemical composition of stormflow, influencing pH. Decomposition of instream organic matter also reduces stream water pH. Leaching experiments revealed that the overland flow passing through organic matter and A horizon material has the potential to lower stream water pH by approximately a half unit or more, in part, by flushing nitrates that were produced by microbial decomposition of organic matter and/or precipitated sulphur that enterred the forest by wet or dry atmospheric deposition. The observed periodic acid events are a natural phenomenon in the stream system in this urban environment because of naturally acidic rainfall and granitic soils with low buffering potential. However, acid events are likely amplified in frequency and magnitude by anthropogenic pollution emissions of sulphur and nitrogen species (e.g., SO_2 and NO_x) from local and regional sources that lower rainfall pH. Although, acid runoff events are typically short-lived (<12–24 h), further longitudinal monitoring and experimental studies are needed to investigate the long-term implications on sensitive taxa in the NSFC streams. Finally, understanding the flow pathways of stormflow water in the nested system was critical for deciphering the mechanisms driving stream acid events at the site.

KEYWORDS
acid rain, buffering capacity, freshwater swamp forest, *Johora singaporensis*, *Parathelphusa reticulata*, runoff pathways

1 | INTRODUCTION

Many freshwater streams are naturally acidic because of the geochemical composition of the in situ rock, the presence of organic material, and the pathways through which precipitation flows as it moves through the coupled hillslope-stream network over various time scales (Dangles et al., 2004; Lohse et al., 2009). Stream acidification can result from chemical weathering of soils, production of dissolved organic carbon from decaying vegetation, the dissociation of carbonic and humic acids, input of marine aerosols, and oxidation of previously reduced sulphur and nitrogen (Galloway, 2001). From an ecosystem perspective, managers and ecologists are now often concerned about the anthropogenic acidification that stems from acid rain produced by anthropogenic emissions of SO_2 and NO_x gasses (Driscoll et al., 2001; Laudon & Bishop, 1999; Renberg et al., 1993; Rosemond et al., 1992; Schindler, 1988). The negative effects of acid rain are often superimposed on the natural pH signal in some streams, particularly when the chemistry of the local soil-geological complex does exhibit substantial acid buffering capacity (Dangles et al., 2004).

Human activity has been largely responsible for the exit from the Holocene and into the Anthropocene (Steffen et al., 2011). In addition to changes to the carbon cycle, humans are significantly altering the element cycles such as sulphur, nitrogen and phosphorus – with adverse effects on a broad range of ecosystem services (Steffen et al., 2011). Acid rain has been a pertinent driver of contemporary degradation of terrestrial and aquatic ecosystems worldwide for at least half a century (Camargo & Alonso, 2006; Grennfelt et al., 2020; Oden, 1968; Ulrich et al., 1980; Whelpdale & Kaiser, 1996). Acid rain was first articulated following the Industrial Revolution (Smith, 1872). International efforts aimed at reducing atmospheric emissions of acid-forming gasses have led to a marked decrease of sulphate (SO_4^{2-}) deposition in both North America and Europe by the turn of the 21st century (Evans et al., 2001; Likens et al., 2001). Further, data indicate that NO_x emissions reduced by about 50% from 1990 to 2014 in the USA, yet anthropogenic emissions still greatly outweigh those from natural sources because of the prevalence of vehicles and industry (EPA, 2018).

In comparison, efforts to reduce emissions of acid-forming gases in Asia have been slow to develop (Bhatti et al., 1992; Duan et al., 2016; Nowlan et al., 2014). For example, Dentener et al. (2006) estimated that substantial portions of natural vegetation in many areas of Asia were still receiving nitrogen deposition in excess of a critical annual threshold of 1000 mg(N) m^{-2} after the turn of the century in South Asia (60% of vegetation), Japan (50%), East Asia (40%), and South-East (SE) Asia (30%). Further, high-deposition rates of SO_4^{2-} are routinely found in East Asia (specifically in southeastern China, northeastern India and Bangladesh (Aas et al., 2019; Dentener et al., 2006)). High-deposition rates of sulphuric and nitric acids are largely concentrated in East Asia (China, South Korea), South Asia (Pakistan, India, Bangladesh), and Myanmar, Thailand, and Laos of mainland SE Asia (Vet et al., 2014). The potential for acidification and eutrophication in freshwater bodies in these "hotspot" areas is therefore a lingering concern for managing freshwater ecosystems and preserving biodiversity (Duan et al., 2016; Vet et al., 2014). However, available data on the impacts of acid deposition in many Asian countries are limited (Jeon & Nakano, 2001; Komai et al., 2001; Cao et al., 2013). Although stream acidification in Singapore, which is an island nation, located on the end of the Malaysian peninsula in SE Asia, is not considered a chronic threat, low stream pH values have been reported for some natural streams over the last decade (Oon, 2012; Nguyen et al., 2019).

Singapore is a densely populated SE Asian city of 5.5 million people with an elaborate transportation network supporting nearly a million vehicles operating on more than 3400 km of roads (Land Transport Authority, 2014). It also has a productive industry sector. Combustion of fossil fuels for industry and transportation are a recognized local pollution concern, in addition to other anthropogenic emissions from neighbouring nations (Malaysia, Indonesia), transboundary air pollutants from seasonal wildfires in the SE Asia region, emitted pollutants from cargo ships along the Singapore Strait, and marine aerosols (Quah & Boon, 2003; Velasco & Roth, 2012). This setting contributes to acid rain and consequentially, acid events in sensitive streams of Singapore (Bouwman et al., 2002). For example, Nguyen et al. (2018) reported low mean pH values for springs in the upper portion of Nee Soon catchment of Singapore: 4.49 ± 0.18 to 4.88 ± 0.33. Harmful effects on aquatic ecosystems are typically expected if stream pH falls below 5.0 (Baker & Christensen, 1991). Despite some monitoring efforts of freshwater species, detailed work quantifying the biogeochemical, hydrological and hydrochemical responses of streams during rainstorms has not been investigated thoroughly in Singapore. Nor is the influence of storm water flow pathways on stream chemistry known.

Our focus in this study was characterizing stream acid events in the Nee Soon Swamp Forest in Singapore, which is the home of two endemic crab species, *Parathelphusa reticulata* and *Irmengardia johnsoni*. Both are endemic to Singapore and are threatened with extinction - with *P. reticulata* classified as critically endangered and *I. johnsoni* classified as vulnerable in the International Union for Conservation of Nature (IUCN) Red List (Esser & Cumberlidge, 2008; Chua et al., 2015; Ng et al., 2015). Building on the knowledge from prior work by Cai et al. (2018) and Nguyen et al. (2018), we had three aims: (i) describe stream chemistry

responses to rainfall events; (ii) distinguish the biogeochemical processes that contribute to low stream pH, *viz* acidification or buffering; and (iii) develop a simple conceptual model linking geophysical processes, including runoff flow pathways, with changes in stream acidity. Our study combines hydrometric and hydrochemical measurements with stable water isotopic compositions to provide new insights into the dynamics of possible human impacts on the urban hydrological cycle as well as stream water quality in a remnant forest of high-conservation value. Acidification of inland waters with widespread impacts on the hydrochemistry and ecology of streams, rivers, and lakes, is a critical issue related to urbanization in Asia (Vogt et al., 2007; Hamid et al., 2020). Further, the linkage between stream acidification and hydrological flow paths is arguably an understudied topic in tropical systems worldwide.

2 | STUDY AREA AND METHODOLOGY

2.1 | Study area

Singapore is a small island city-state (~722 km^2) located at the southernmost part of the Malay Peninsula, 1.35° N from the equator. It has a tropical rainforest climate (Köppen: Af), characterized by small diurnal temperature variation (daily highs: 31–33°C; lows: 23–25°C), high-relative humidity (annual average: 84%), and abundant rainfall with annual average of 2166 mm (1981–2010) (MSS: Meteorological Service Singapore, 2017). Rainfall is typically acidic (mean pH = 4.2), with SO_4^{2-} concentrations comparable to other industrialized locations in the region (Balasubramanian et al., 2001). Similarly, the low pH precipitation is also related to the dissolution of NO_x in cloud and rain droplets; the industrial sector is the main contributor of NO_x (Balasubramanian et al., 1999; Molina et al., 2019).

Having once been nearly completely covered in dense forest, Singapore now only has small, fragmented forests protected in reserves, such as the Bukit Timah Nature Reserve (BTNR) and the Central Catchment Nature Reserve (CCNR). Generally, the shaded forest streams are shallow with relatively cool, mildly acidic water flowing over sand, clay, or mud substrates, with many sections having an accumulation of leaf litter (Clews et al., 2018; Ho et al., 2018). It is within such reserves that perennial streams supporting sensitive species can be found including three endemic freshwater crab species and 15 nationally endangered/critically endangered fish species (Yeo et al., 2010; Li et al., 2016). In low-lying areas of moderately broad valleys, subsurface water returns to form shallow swamps that may partially desiccate during dry spells. When flooded, saturation overland flow is generated.

The Nee Soon Forest Catchment (NSFC; Figures 1, 2) is located within the CCNR and contains the only remaining freshwater swamp forest in the country, Nee Soon Swamp Forest (NSSF, Murphy, 1997; O'Dempsey & Chew, 2011; Cai et al., 2018). The areal extent of NSFC is 4.8 km^2, of which NSSF occupies 91 ha. Nee Soon catchment is underlain by deeply weathered (<30 m), Triassic-age Bukit Timah Granite, which includes granite, adamellite, and granodiorite (Zhao et al., 1994). The lower portion of NSFC is likely in contact with the Kallang sedimentary formation. Nguyen et al. (2018) found that the soil mineralogy in the upper part of the catchment was composed largely of quartz (79%), followed by kaolin (17%) and small amounts of gibbsite (3%) and goethite (1%). These acidic (pH 3.5–4.0) and nutrient-poor Ultisols result from strong weathering in the hot and humid climate of Singapore (Ives, 1977; Chia et al., 1991).

In this study, we focus on the less-disturbed, upper part of NSFC, where two headwater streams (U1 and U2) flow into M1, which is a second-order stream (Strahler classification). Their respective drainage areas are 0.67, 0.71, and 1.45 km^2 (Figure 1). All three stream reaches are perennial. In the prior study that determined the two first-order streams had mean pH values in the range of 4.5–4.9 (Nguyen et al., 2018), the pH of shallow groundwater in the vicinity of the streams ranged from 4.93–5.06, substantially lower than the sampled surface and groundwater at sites in the lower part of the catchment (5.69 ± 0.48). While naturally-acid rainfall inputs (from sea salts, CO_2, dust) are likely responsible, in part, for some of the low pH values that have been observed in Nee Soon streams (Nguyen et al., 2018), other surficial processes almost certainly interact as reported elsewhere (Gee & Stoner, 1989; Driscoll et al., 2001). For example, some degree of low stream water pH is expected because of the low buffering capacity of the granites underlying streams in the central part of Singapore. Other plausible factors include: (1) low neutralizing capacity of subsurface waters; (2) decomposition of organic matter producing natural organic acids that lower the water pH; (3) deposition of anthropogenic sulphuric and nitric acids; (4) hillslope drainage through acidic soils; and (5) increased transfer of carbonic acids from the atmosphere (related to increasing levels of CO_2). In most instances, stream acidification occurs because of a number of these processes (Gee & Stoner, 1989; Driscoll et al., 2001).

3 | METHODS

3.1 | In-situ sampling and measurements

We collected stream water and shallow groundwater from the U1, U2, and M2 in NSSF from May 2017 to December 2018 (Figure 1; Table 1, Table S1, Table S2). We measured stream discharge at each collection time from flow velocities recorded with Hach FH950 Portable Velocity Meter at seven equally distanced measuring points across the streams and at 0.4 of the water column depth. Stream widths were < 2 m; and they rarely vary. We collected shallow groundwater samples from 1-m deep wells that were augered on both sides of the streams. The wells were lined with a 3-inch PVC pipe and sealed to prevent contamination. The groundwater samples were retained after initial purging of the wells to ensure collection of well-mixed groundwater. As the groundwater table was typically near the surface, the

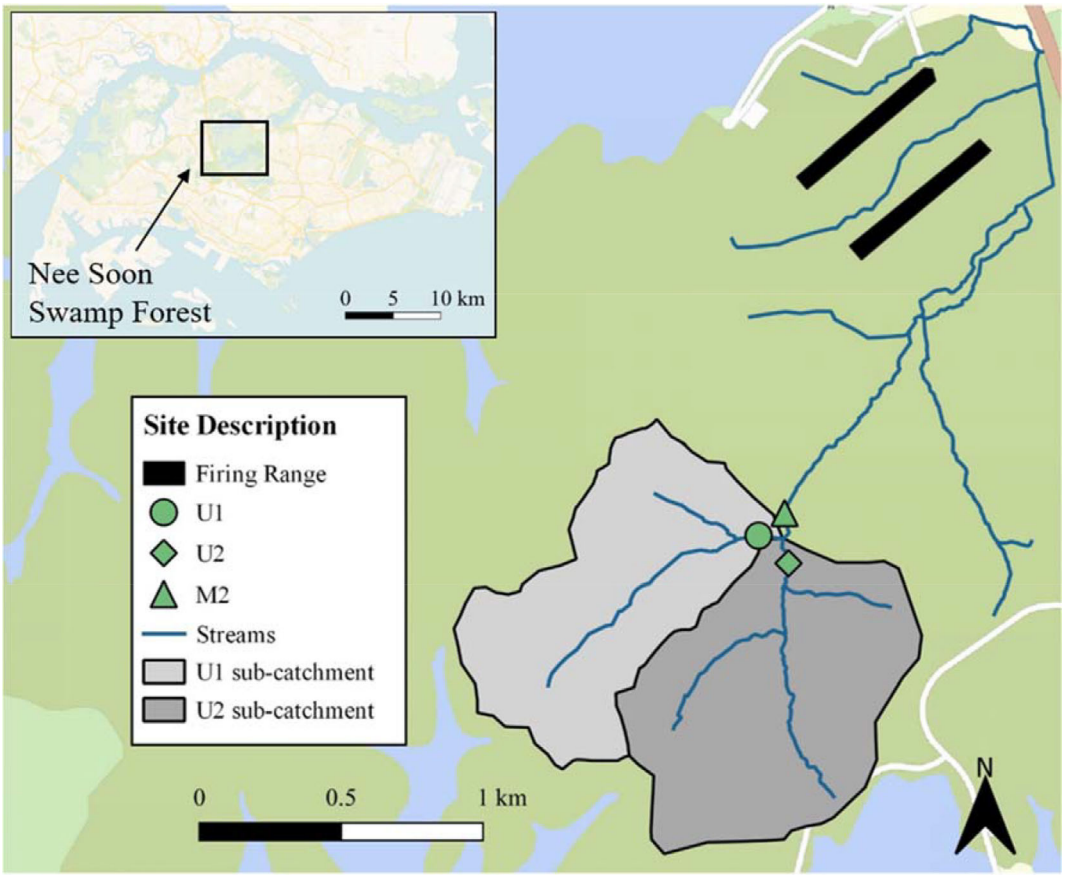

FIGURE 1 Location of study sites in the Nee Soon Forest Catchment, and (inset) location of the Nee Soon Freshwater Swamp Forest within the island of Singapore

FIGURE 2 (a) Nee Soon Forest Catchment, stream M2; (b) Monitoring station typical set-up: Each sensor is located in a perforated pipe, protected from falling leaves and wildlife by a fine mesh (stream U2)

depth of the wells was only 1.2 m. We collected both the stream and groundwater grab samples (~200 mL) on a regular bi-weekly basis over the study period. We measured in-situ pH, specific electrical conductivity (σ), total dissolved solids (TDS), salinity (S) and temperature (T) with handheld Extech ExStik EC500 meter at the time of water sampling.

TABLE 1 Statistical summary (median ± MAD; and range) of pH, specific electrical conductivity (σ), cations and anions in rainfall, stream water (Q) and groundwater ells (W)

	pH	σ (μS cm^{-1})	H^+ (μeq l^{-1})	Mg^{2+} (μeq l^{-1})	Ca^{2+} (μeq l^{-1})	Na^+ (μeq l^{-1})	K^+ (μeq l^{-1})	NH_4^+ (μeq l^{-1})	SO_4^{-2} (μeq l^{-1})	NO_3^- (μeq l^{-1})	Cl^- (μeq l^{-1})	F^- (μeq l^{-1})
Rainfall	4.90 ± 0.40 [4.28–6.39] (22)	26.9 ± 7.4 [9.1–73.2] (22)	12.62 ± 8.31 [0.41–52.48] (22)	41.78 ± 6.05 [33.83–109.55] (22)	60.07 ± 16.91 [40.21–268.30] (22)	24.45 ± 7.66 [13.24–76.86] (22)	63.23 ± 25.63 [28.63–389.23] (22)	0.84 ± 99.84 [BDL-3.91] (5)	89.17 ± 39.00 [11.91–279.48] (22)	22.75 ± 9.82 [BDL–43.78] (21)	32.20 ± 18.95 [5.15–204.50] (22)	2.11 ± 0.38 [BDL–5.33] (19)
M2 Q	5.24 ± 0.24 [4.83–5.87] (22)	12.9 ± 2.6 [2.7–47.1] (25)	5.75 ± 3.58 [1.35–14.79] (27)	27.97 ± 1.38 [26.19–47.91] (27)	36.20 ± 5.04 [27.80–88.20] (27)	55.38 ± 5.59 [30.33–85.48] (27)	13.44 ± 1.60 [11.47–24.06] (27)	21.33 ± 20.77 [BDL-54.29] (18)	17.51 ± 2.36 [BDL–39.1] (26)	20.04 ± 8.31 [BDL–48.16] (24)	48.70 ± 2.03 [43.88–62.04] (27)	16.32 ± 2.53 [BDL–35.79] (19)
M2 W1	4.65 ± 0.13 [4.52–5.39] (11)	28.2 ± 4.1 [15.3–61.8] (11)	22.39 ± 7.81 [4.07–30.2] (11)	40.71 ± 1.99 [33.99–53.09] (11)	46.79 ± 8.74 [37.36–98.80] (11)	58.35 ± 19.45 [34.43–86.64] (11)	25.04 ± 1.04 [23.93–34.1] (11)	16.62 ± 115.62 [BDL-33.79] (3)	87.73 ± 31.50 [19.76–127.48] (11)	6.86 ± 2.74 [BDL–21.38] (10)	54.23 ± 7.34 [41.3–73.66] (11)	17.32 ± 2.53 [BDL–26.84] (8)
M2 W2	5.08 ± 0.18 [4.60–5.99] (27)	24.8 ± 10.3 [12.9–54.3] (25)	8.32 ± 4.27 [1.02–25.12] (27)	30.59 ± 4.30 [24.01–54.41] (27)	39.5 ± 9.66 [28.66–91.07] (27)	60.22 ± 6.63 [BDL-36.78] (27)	18.81 ± 5.55 [11.70–50.07] (27)	33.24 ± 132.24 [BDL–44.32] (11)	28.21 ± 8.81 [BDL–92.68] (25)	11.05–9.39 [BDL–43.95] (16)	55.17 ± 4.95 [49.1–104.06] (27)	13.42 ± 112.42 [BDL–41.75] (10)
U1 Q	5.11 ± 0.18 [4.53–5.81] (26)	13.7 ± 3.3 [3.4–62.4] (23)	7.85 ± 3.20 [1.55–29.51] (26)	28.74 ± 2.60 [25.71–49.13] (26)	35.83 ± 6.92 [26.78–65.68] (26)	55.60 ± 4.67 [31.69–80.52] (26)	15.90 ± 4.44 [11.44–44.57] (26)	19.39 ± 118.39 [BDL-44.32] (12)	15.9 ± 2.00 [BDL–27.8] (25)	22.44 ± 11.21 [BDL–50.26] (23)	46.61 ± 2.23 [42.07–77.99] (26)	16.11 ± 2.93 [BDL–20.47] (16)
U1 W1	4.65 ± 0.23 [4.37–5.98] (11)	42.8 ± 8.5 [13.3–85.4] (11)	22.39 ± 9.23 [1.05–42.66] (11)	44.61 ± 6.03 [26.25–71.95] (11)	65.61 ± 11.68 [43.21–97.70] (11)	43.33 ± 9.46 [32.41–68.50] (11)	40.03 ± 11.42 [13.69–112.54] (11)	21.46 ± 120.46 [BDL–48.70] (4)	99.72 ± 23.69 [13.21–181.2] (11)	44.82 ± 24.35 [BDL–70.78] (9)	68.1 ± 3.63 [46.67–95.55] (11)	24.11 ± 10.90 [BDL–35.01] (7)
U1 W2	4.63 ± 0.10 [4.36–6.11] (26)	27.1 ± 7.9 [8.2–121.2] (24)	23.73 ± 5.78 [0.78–43.65] (26)	31.32 ± 4.75 [20.94–52.45] (26)	34.99 ± 8.42 [21.59–89.37] (26)	41.79 ± 6.47 [12.43–64.73] (26)	21.65 ± 8.42 [11.16–166.95] (26)	21.33 ± 12.83 [BDL–145.41] (20)	17.20 ± 5.11 [BDL–138.9] (19)	51.50 ± 5.45 [BDL–63.92] (23)	47.16 ± 3.09 [40.13–211.20] (26)	15.63 ± 114.63 [BDL–51.47] (7)
U2 Q	5.25 ± 0.16 [4.835–5.8] (27)	16.1 ± 5.8 [7.3–61.6] (25)	5.62 ± 1.97 [1.58–14.79] (27)	29.13 ± 2.65 [24.35–40.01] (27)	36.58 ± 7.58 [16.32–94.31] (26)	55.23 ± 6.37 [37.10–84.65] (27)	16.59 ± 5.09 [11.22–23.78] (27)	23.7 ± 16.06 [BDL–49.86] (15)	16.41 ± 2.27 [9.43–34.22] (27)	18.98 ± 9.87 [BDL–39.93] (25)	48.94 ± 2.75 [39.82–75.07] (27)	15.42 ± 3.00 [BDL–19.68] (15)
U2 W1	5.58 ± 0.19 [5.29–5.96] (10)	23.7 ± 10.4 [12.5–61.8] (10)	2.70 ± 1.19 [1.10–5.13] (10)	41.47 ± 1.98 [37.73–46.04] (10)	184.41 ± 66.67 [74.06–282.11] (10)	64.49 ± 11.77 [52.72–171.53] (10)	24.66 ± 1.85 [22.81–46.59] (10)	28.92 ± 127.92 [BDL–95.44] (5)	28.38 ± 5.84 [3.47–69.06] (10)	7.21 ± 4.25 [BDL–20.60] (7)	50.58 ± 3.18 [45.65–62.46] (10)	13.00 ± 112.00 [BDL–35.79] (5)
U2 W2	5.47 ± 0.18 [4.79–6.82] (27)	18.7 ± 8.2 [9.9–85.2] (25)	3.39 ± 1.15 [0.15–16.22] (27)	29.49 ± 2.25 [21.94–46.43] (27)	56.60 ± 19.75 [28.92–744.81] (26)	56.61 ± 7.05 [10.34–80.95] (27)	17.79 ± 6.08 [11.30–49.08] (27)	22.08 ± 11.71 [BDL–52.08] (20)	12.82 ± 1.87 [BDL–74.74] (22)	11.32 ± 8.35 [BDL–29.98] (20)	49.34 ± 4.21 [7.17–81.06] (27)	13.37 ± 112.37 [BDL–31.05] (10)
Detection Limit (mg/L)	NA	NA	NA	NA	NA	<0.2	<0.5	<0.15	<0.15	<0.1	<0.1	<0.05

Note: Values are medians ± median absolute deviations (MAD); ranges are reported in "[]"; the number of samples are reported in "()".
Abbreviation: BDL, below detection limit.

We established an automated hydrometric station at each of the three stream locations to log water level, pH, σ, and turbidity readings to create continuous time series (Figures 1, 2). Instruments at each station included a Campbell Scientific (CS, Logan Utah) CR1000 data logger, a CS451 pressure transducer, a CS547A water conductivity and temperature probe, an Aqualabo (Champigny sur Marne, France) pH probe, and an Analyte NEP5000 turbidity probe (Observator Instruments, Ridderkerk The Netherlands). The loggers were programmed to take readings every minute, with values stored every 20 min, but also for each minute when any of the measured parameter values changed by more than 10% since the last logged value. The loggers recorded data from April to December 2018.

We collected a total of 22 rain samples from September to December 2018 in an open area at the visitor centre of the nearby BTNR. Samples could not be collected on site because of overhead obstruction by the forest canopy, and importantly, interference by inquisitive long-tailed macaques. The rainfall samples were accumulated by funnelling water into 500-ml acid-washed Nalgene HDPE bottles. The funnel was covered with a fine cloth mesh to minimize sample contamination from falling leaves and living organisms. After sampling, we washed the funnel and collection bottle thoroughly, then dried them before replacing them for additional measurements.

We collected soil samples at 10-cm intervals from nine 1.5 to 2 m deep profiles using either a Russian auger (for waterlogged soils) or standard open-face screw auger (hillslope soils) to extract the soil. We also used a 98-cm^3 stainless-steel sampling ring to collect the top 5 cm of streambed sediment samples from 11, 20-m long reaches at each of the U1, U2, and M2 streams in NSFC. All sediment and soil samples were sealed in Ziploc® bags and transported to the lab for processing on the same day.

3.2 | Water analyses

We analysed all water samples in the National University of Singapore (NUS) Geography laboratory for dissolved organic carbon (DOC), pH, and major ions. Dissolved oxygen was determined in the field. We first filtered the samples into 50-ml sterilized polypropylene tubes using 0.45-μm syringe filters and stored them at 4°C. For analysis that required water samples to be acidified, we added 2% HNO_3 before storing. We determined laboratory pH with a Thermo Scientific Orion 3 Star pH meter and DOC using an Elementar Vario TOC cube analyser. We determined major anions and cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^-, SO_4^{2-}, NO_3^-) using a Dionex™ ICS-5000 Thermo Scientific™ high-pressure ion chromatography system. For these analyses, we placed 5-ml filtered samples into 20-ml glass vials that had been acid washed with 5% HNO_3 and placed in a furnace at 550°C for complete removal of organic matter and other contaminants.

3.3 | Streamflow characterization

To characterize the sources of water to streamflow, isotopic analysis (δ^2H and $\delta^{18}O$) of rainfall ($n = 109$), shallow soil water ($n = 20$), stream water ($n = 67$), and groundwater ($n = 24$) samples were performed using isotope ratio infrared spectroscopy (LGR OA-ICOS CA, USA) at the University of Saskatchewan. Laboratory precision was ±1‰ and ± 0.2‰ for δ^2H and $\delta^{18}O$, respectively. To quantify the similarities or differences between water samples, we calculated the offset of a stream water and groundwater sample from the local meteoric water line (LMWL) using the line-conditioned (LC) excess (Landwehr & Coplen, 2004). The LC-excess describes the difference in the isotopic composition of environmental waters from that of local precipitation, which has, by definition, an LC-excess of zero.

We compared two rainfall δ^2H and $\delta^{18}O$ datasets in Singapore to inform our use of the slope and intercept parameters in LMWL, and thus, the calculation of LCE. One rainfall isotope dataset, which was from Nanyang Technological University (NTU) (Munksgaard et al., 2019) resulted in a LMWL with slope (±SE) of 7.41 (±0.09) and intercept of 7.68 (±0.57) (Adj. R^2 0.955, n = 280); the data were collected between 03 Jan 2014 and 31 Oct 2015 (666 days). The other rainfall isotope dataset, which was from the National University of Singapore (NUS), resulted in a LMWL with slope (±SE) 7.23 (±0.12) and intercept 3.98 (±0.74) (Adj. R^2 0.969, n = 109). As a precursor to this study, it was collected between 11 Nov 2014 and 31 Oct 2015 (380 days). We then compared the two LMWLs to test if their slope and intercept parameters were different by fitting a standard least-squares model with interaction. The slopes were not statistically different ($p = 0.2706$), whereas the intercepts were ($p < 0.0001$). The statistically different intercepts between the two datasets meant that we needed to choose one of the two datasets. We used the NTU dataset for two reasons: (1) longer record length than the NUS dataset; and (2) the NTU dataset came with rainfall amount information, which enabled us to calculate the amount-weighted isotopic composition of precipitation.

To identify flow path contributions to runoff generation at the M2 stream reach below the two sub-basins, we represented streamflow as a mixture of three components: shallow subsurface flow (SSF; 0–30 cm), shallow groundwater (GW), and saturation excess overland flow (SOF; amount-weighted isotopic composition of precipitation). The components were based on observations of overland flow generation, return flow through occasional small pipes, and a consistent baseflow. We employed a three-component isotope mixing model and calculated the following fractions in M2 stream water:

$$f_{soil} = \frac{(\delta^{18}O_{rf} - \delta^{18}O_{gw})(\delta^2H_{stream} - \delta^2H_{gw}) - (\delta^2H_{rf} - \delta^2H_{gw})(\delta^{18}O_{stream} - \delta^{18}O_{gw})}{(\delta^{18}O_{rf} - \delta^{18}O_{gw})(\delta^2H_{soil} - \delta^2H_{gw}) - (\delta^2H_{rf} - \delta^2H_{gw})(\delta^{18}O_{soil} - \delta^{18}O_{gw})} \quad (1)$$

$$f_{gw} = \frac{(\delta^2H_{stream} - \delta^2H_{rf}) - (\delta^2H_{soil} - \delta^2H_{rf})f_{soil}}{\delta^2H_{gw} - \delta^2H_{rf}} \quad (2)$$

$$f_{rf} = 1 - f_{soil} - f_{gw} \quad (3)$$

where f_{soil}, f_{gw}, and f_{rf} are the fraction of soil water (i.e., the shallow subsurface flow), groundwater (via percolation) and amount-weighted isotopic composition of rainfall (rainfall in the channel and saturation excess overland flow), respectively (Equations 1, 2, 3). Note, again, that the stable water isotope samples were collected at different times ($n = 20$) between November 2014 and December 2015 from our stream chemistry samples. The use of these isotope samples, therefore, is meant to simply inform on the predominant flowpath contributions to M2 stream water generation and gain insights into episodic acid events of streams at our study sites.

3.4 | Soil and sediment analyses

We analysed soil and streambed samples for organic matter (OM), pH, and major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}). Prior to chemical analysis, we dried all samples at a low temperature of 60°C for 96 h to preserve OM stability (Pansu & Gautheyrou, 2006). We then sieved the dry samples through 2-mm screens; then we further lightly ground the <2 mm fraction by hand using a pestle and mortar. We determined soil pH in a soil suspension of ultrapure water (10 ml) and 5 g of finely ground soil (Burt and Soil Science Division Staff, 2014). The soil suspension was mixed for 30 min on a shaker and the soil suspension was left to settle for 15 min before measuring pH with a calibrated Thermo Scientific Orion 3 star pH probe. We determined OM content via Loss-On-Ignition (LOI) by placing 2 g of finely ground soil into acid-washed crucibles and incinerating it in a muffle furnace for 4 h at 550°C.

We extracted major cations from soil samples using un-buffered ammonium acetate (NH_4OA_c), (Burt and Soil Science Division Staff, 2014); potassium chloride (KCl), for the Al extraction. We added separate stock solutions of 1 M-NH_4OA_c and 1 M-KCL (12.5 ml each) to 3 g of soil sample. We then shook the analyte before leaving it to settle for 15 min, then centrifuging at 2500 rpm for 5 min to form a supernatant that was then decanted and stored. We repeated the process until 50 ml of supernatant analyte was accumulated. Only samples extracted with NH_4OA_c require the first extraction to be left overnight for maximum contact and exposure to the soil. We then filtered all supernatant analytes through 0.45-μm syringe filters and transferred them into 15 ml polypropylene tubes to be further analysed with a PerkinElmer Optima 8300 Inductively-Coupled Plasma Optical Emission Spectrometry (ICP-OES) machine. Filtered KCl-extracted analytes were diluted by a factor of two by adding 2.5 ml of analyte to 2.5 ml of ultrapure water before ICP-OES analysis.

Exchangeable base cations (EBC), effective cation exchange capacity (ECEC), and base saturation (BS) for soils were calculated as:

$$EBC = sum\left(Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}\right) \quad (4)$$

$$ECEC = EBC + Al^{3+} \quad (5)$$

$$BS = EBC/ECEC * 100\% \quad (6)$$

where EBC and ECEC have units of cmol (+) kg^{-1}; BS is expressed in %.

The exchange base cations (Equation 4) is an indicator of the soil capacity to hold and exchange cations and to provide buffering effect against changes in the soil pH. To classify the soil resistance to changes in soil chemistry caused by land use or other influences, we used the buffering capacity classifications outlined by Hazelton and Murphy (2016; p.64 after Metson, 1961). Equation 5 is an estimator for "actual" cation exchange capacity (CEC), which normally includes the summation of the four base cations (Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}) and two acid ions (H^{+} and Al^{3+}). Sumner and Miller (1996) stated that Equation 5 is acceptable for determining CEC at "field pH" in all soils but those containing salts and carbonates even though H^{+} is excluded. In general, the exchange capacity of a soil is a measure of its ability to hold and release various elements and compounds; it is related to the presence of clay particles and organic matter that tend to be negatively charged. Both clay-rich and organic-rich soils can have high CEC, because in the first case, the negative charge of clays attract and retain cations. In the latter case, the dissociation of organic acids causes a net negative charge in soil organic matter; and this negative charge is balanced by cations in the soil (Ketterings et al., 2007). Because organic acid dissociation depends on the soil pH, the CEC of a soil will increase with an increase in pH (Moore et al., 1998).

Equation 6 determines BS as the percent cation exchange capacity (ECEC) that is saturated by Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}. In this study, the soil leaching extent (i.e., base cation depletion) is based on the criteria established by Hazelton and Murphy, (2016; p.64 after Metson, 1961).

3.5 | Leaching experiments

We conducted a leaching experiment to examine the effect of rainfall and shallow-subsurface flow on releasing organic acids from the organic matter on the forest floor and the A horizon soil (referred herein as OM-soil media). The experiment was performed using stream water collected from the NSFC streams. Briefly, in 500-ml acid-washed plastic containers, we placed 10 g of leaf litter and 95 g of soil. We then allowed 100 ml of stream water to drain through the soil-litter at a rate of 100 ml/30 min. We analysed the leachate for pH, σ, and cations. We used stream water, rather than rainwater, because this particular experiment was performed during a dry spell.

3.6 | Data analysis

For data analyses, we used non-parametric approaches as the data were not normally distributed. Values below detection limit (BDL) were substituted with ½ the value of the detection limit. Median absolute deviation (MAD) is used as a robust measure of variability. For single pair comparison of sites (U1, U2 and M2), we used Kruskal-Wallis rank sum test. For pairwise comparison between multiple sites, we used the Wilcoxon Rank Sum tests. For the latter, we used p-

value-adjustment ('fdr' Benjamini & Hochberg, 1995) for multiple testing. Due to ties present in the datasets, the p-value-estimation was set to normal approximation (i.e. exact p-values could not be calculated). Statistical significance was assessed at $\alpha = 0.05$. All statistical summaries and tests were performed in the R version 3.5.0 (2018–04–23) aka Joy in Playing (R Core Team, 2017).

4 | RESULTS

4.1 | Rainwater, stream, and groundwater chemistry

The 22 rainfall samples had a median (± MAD) pH of 4.90 ± 0.40 (Table 1). The range of pH values was below neutral at 4.28 to 6.39. Median specific conductivity was low (26.85 ± 7.4 μS cm^{-1}), ranging from 9.10 to 73.2 μS cm^{-1}. Calcium (60.07 ± 16.91 μeq l^{-1}) and K^+ (63.23 ± 25.63 μeq l^{-1}) were the dominant cations; the highest concentrations exceeded 260 and 380 μeq l^{-1}, respectively. Median values for Mg^{2+}, Na^+, and H^+ were 41.78 ± 6.05, 24.45 ± 7.66, and 12.62 ± 8.31 μeq l^{-1}, respectively. The median concentration for NH_4^+ was below detection limit. Anions with the highest median concentrations were SO_4^{2-} (89.17 ± 39.0 μeq l^{-1}), Cl^- (32.2 ± 18.95), and NO_3^- (22.75 ± 9.82) (Table 1). The chemistry of the measured rainfall samples was different from that reported by Hu et al. (2003) in that the volume-weighted mean pH in their study was lower (mean of 4.25 ± 0.22) and NH_4^+ was variable (mean of 20.51 ± 6.58 μel/l). However, we would expect differences because their collection site was nearer to industrial estates.

The hand-collected stream water samples represent either baseflow or low-flow conditions associated with the tail end of the recession phase of the storm flow hydrograph for rainfall events occurring on the preceding day. The median pH values of these stream water samples were all low and similar at the three NSFC sites (Table 1): U1 (5.11 ± 0.17), U2 (5.25 ± 0.16), and M2 (5.24 ± 0.24). In contrast, the ordering of pH in shallow groundwater differed: U1 (two medians of the two wells ranged from 4.63 to 4.65) < M2 (4.65 to 5.08) < U2 (5.47 to 5.65). The specific conductivity values for streamflow at all three sites are also similar (medians ranging from 13 to 28 μS cm^{-1}); and the range of groundwater values were only slightly higher (Table 1): U1 (27–43 μS cm^{-1}) > U2 (19–24 μS cm^{-1}) > M2 (25–28 μS cm^{-1}). Sodium and calcium were the cations occurring in the highest concentrations in most streams and shallow groundwater samples, with medians ranging from 42 to 65 μeq l^{-1} for Na^{2+} and 36 to 184 for Ca^{2+}, respectively. Sulphate (13–100 μeq l^{-1}), Cl^- (47–68 μeq l^{-1}), and NO_3^- (7–52 μeq l^{-1}) were the most prevalent anions in both stream and groundwater (Table 1). Furthermore, stream water samples with higher NO_3^- concentrations were typically associated with lower pH values ($R^2 = 0.56$; Figure S1). Comparing the sum of cations and anions showed higher concentrations of cations in throughfall samples compared to the rainfall and stream water samples (Figure S2).

4.2 | Time series of pH, σ and water level

The time series of pH, σ, and water level for the streams at sites M2 (Figure 3a), U1 (Figure 3b), and U2 (Figure 3c) in NSFC all show seasonal and synoptic (rain event) variation. The patterns are similar for the three streams, but with nuanced differences in pH. Across the measurement period, median pH (of >15 000 logged values) in section U1 was lower (5.03) than at U2 (5.24) or M2 (5.17). This ranking is in line with the low-flow, hand-sample pH data reported above, but the time series values are slightly lower because they include many logged measurements made during high flows—which includes acid events. The M2 stream section has greater seasonal variation: at times, it was more acidic than tributary U2; at other times, less acidic.

All streams were more acidic during the relatively dry April–June period; pH then increased from August until the end of the year. A lowering of pH during the drier period, although not statistically significant, supports the notion that rainfall chemistry alone is not the key driver of low stream pH. Stream water during the dry period would largely be sourced from groundwater or slow-moving lateral subsurface flow in the hillslope.

4.3 | Storm response

The stream chemical response to individual rainfall events was characterized by an increase in σ and a decrease in pH (Figure 4). During the 21 April 2018 event, stream pH dropped from initial values >5.25 to about 5.00 at U2 and 4.50 at M2. Meanwhile, σ rose slightly from <20 μS cm^{-1} to >30–40 μS cm^{-1} in the three streams. Following the event on 21 April 2018 (Figures 4a, b) stream water pH and σ recovered to approximately pre-storm signatures over the next 24 h, but without fully reaching them. During the 20 September 2018 event, the pH at U1 dropped from ~5.2 to almost 4.3 in less than 2 h, then recovered to about 5.0 over a 24-hour period (Figure 4c). The drop in stream pH was about 0.8 pH units at U1 and 0.7 pH units at M2. These declines in pH are some of the largest in the observation period; most others were less dramatic. Increases in stream σ in response to rainfall were on the order of 2–8 fold, from lows of 5–20 μS cm^{-1} to highs of 25–45 μS cm^{-1} (Figures 4c, d) with a few instantaneous spikes >50 μS cm^{-1}, which might have been caused by instrument measurement error as they were not sustained for more than a minute. All these low conductivity values are characteristic of a system influenced by granitic geology, which is composed of many inert materials that do not readily dissolve into ions in water.

The rapid and contrasting response of pH (decrease) versus σ (increase) suggests a potential dual role of rainfall and surface runoff in producing acid events in all three streams. The finding that the pH value at U1 can be different from that at U2 and M2 by one half pH unit, at the same time during an event, further supports the idea that site-specific processes related to runoff pathways, for example shallow subsurface flowing through organic-rich layers, are contributing to the stream water signature - but perhaps differently even at the sub-catchment scale. Here we assume the throughfall chemistry is

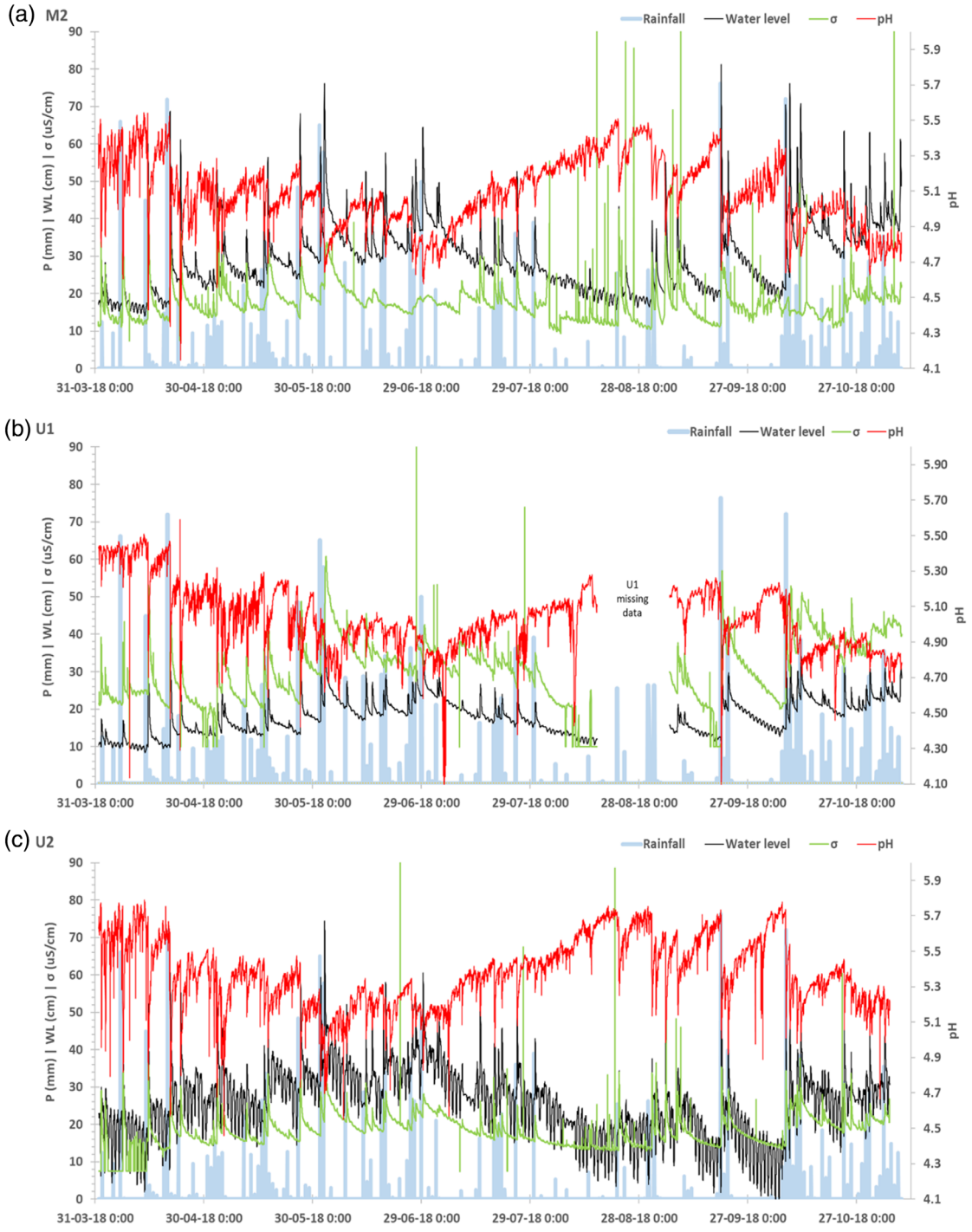

FIGURE 3 Time series of rainfall (P), water level (WL), specific electrical conductivity (σ) and pH at NSFC sites M2 (a), U1 (b), and U2 (c)

similar at the three closely situated sites (differences related to throughfall variation could produce differences).

4.4 | Soil and streambed sediment chemistry

The soils in sub-catchments U1 and U2 were similar in most geochemical characteristics (Table 2). For example, median pH was strongly acidic at 4.62 and 4.64, respectively. The corresponding exchangeable base cations (EBS = 0.77 vs. 0.65 cmol (+) kg^{-1}) and effective cation exchange capacity (ECEC = 1.05 vs. 1.60 cmol (+) kg^{-1}) were not greatly different, nor were K^+ and Mg^{2+} concentrations. The main differences were for the following: higher base saturation in U1 (78.9%) than U2 (42.6%); higher Al^{3+} in U2 than U1 (0.91 vs. 0.22 cmol (+) kg^{-1}); and higher organic matter (based on LOI proxy) in U2 than in U1 (LOI = 10.3 vs. 4.0%). Further, Ca^{2+} and Na^+ concentrations are different in U1 versus U2 (Table S3).

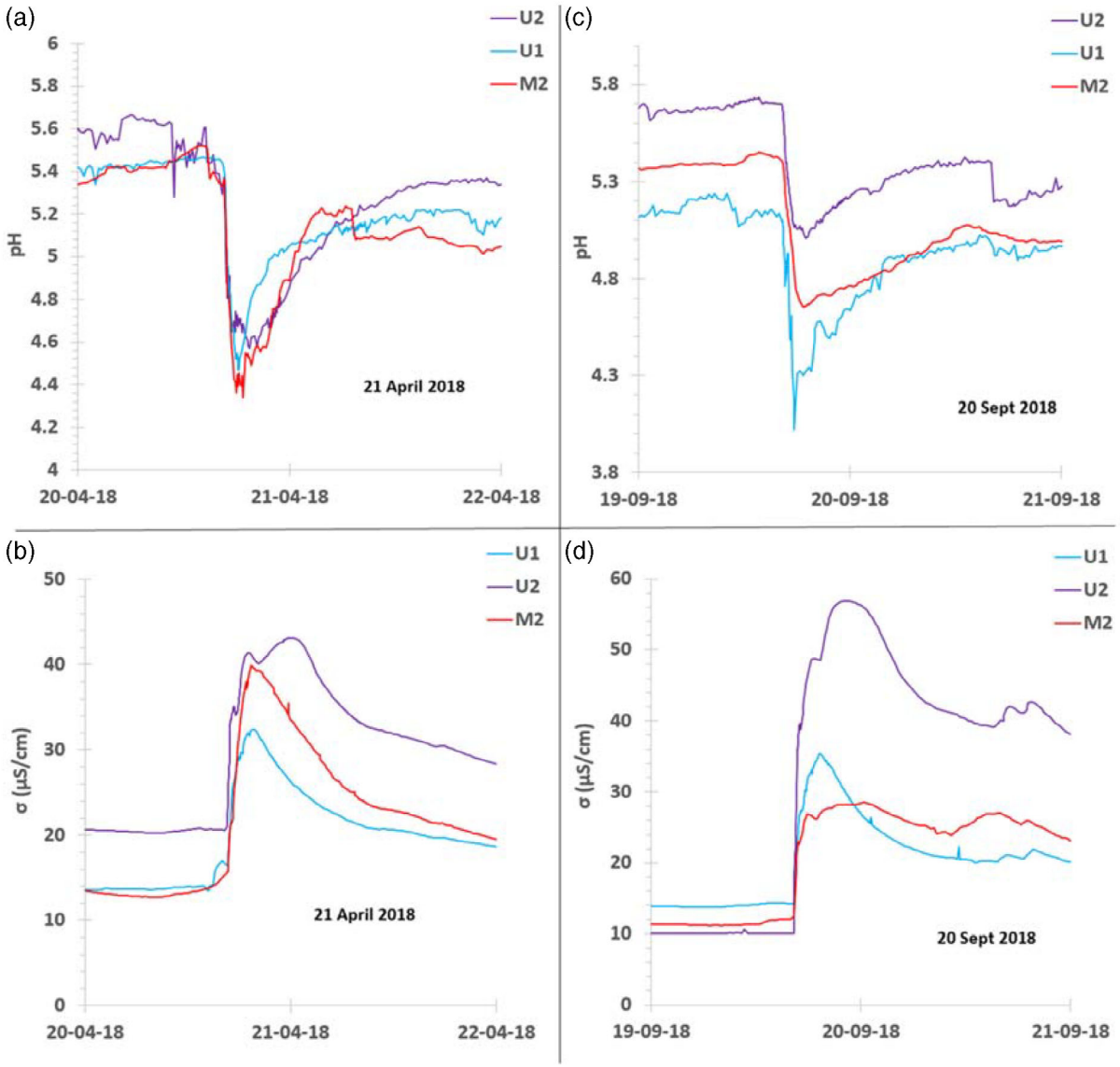

FIGURE 4 Response of pH and specific electrical conductivity (σ) during events on 21 April 2018 (a, b) and 20 September 2018 (c, d) at NSFC sites M2, U1, and U2. Rainfall pH on 20 September 2018 was 4.18; on 21 April, it was not determined

The low ECEC values <2.0 cmol (+) kg^{-1} are in line with those expected of acidic sandy soils that have limited organic matter (Holmgren et al., 1993; Hazelton & Murphy, 2016; p.64 after Metson, 1961). The range of median sand content of soil profiles is somewhat high at 58 to 67% (raw data not shown). Organic matter is moderate at about 5–10% (based on LOI). The low BS values at U2 (42.6%) support the idea that base cations are reduced relative to acid ions (namely Al^{3+}), indicating that the soils are leached (Hazelton & Murphy, 2016; p.66 after Metson, 1961). Collectively, these acid soils have low buffering capacity that would not allow them to neutralize acidic rainfall inputs (Soil Survey Staff, 2017). However, a contrasting lowering of pH in stormflow could occur through leaching organic acids from soil layers containing substantial organic material.

The streambed sediment geochemistry in tributaries U1 and U2 is similar, but differs from the downstream M2 site, despite being located very nearby (Table 2). For example, the median pH values were lower (4.75–4.87 vs. 5.04), LOI was higher (32–34 vs. <5%), Al^{3+} was higher (1.7–2.2 vs. <0.32 cmol (+) kg^{-1}), and ECEC was higher (2.6–3.0 vs. 0.63 cmol (+) kg^{-1}) for U1 and U2 vs. M2 (Table 2). The median base saturation of U1 sediments (37%) was only slightly higher than the U2 and M2 medians (23 and 30%), respectively. The low ECEC at M2 is indicative of a sandy environment with limited organic material. In comparison, high-accumulation rates of organic matter exist in the smaller U1 and U2 tributary streams with low flow velocities and low sediment transport capacities. As with soil, the streambed sediments have limited capacity to buffer against inputs of acidic water. As water passed through the OM-soil media (30 min contact time in the leaching experiment), pH was reduced by 10%, or about 0.5 pH units = ~5.2 to 4.7 (raw data not shown). Associated with these pH reductions were a significant 3.5-fold increase in

TABLE 2 Summary (median ± MAD; and range) of pH, organic matter (OM (LOI)), major cations, exchangeable base cations, effective cation exchange capacity, and base saturation for soils and streambed material in Nee Soon Forest Catchment

Location	pH	OM (LOI)	Ca^{2+}	K^{+}	Mg^{2+}	Na^{+}	Al^{3+}	EBC	ECEC	BS
		(%)	Cmol (+) kg^{-1}	Cmol (+) kg^{-1}	Cmol (+) kg^{-1}	Cmol (+) kg^{-1}	Cmol (+) kg^{-1}	Cmol (+) kg^{-1}	Cmol (+) kg^{-1}	%
Soils										
U1 (n = 46)	4.62 ± 0.27 [3.99–5.62]	3.95 ± 1.32 [1.11–32.77]	0.270 ± 0.119 [0.135–2.496]	0.084 ± 0.010 [0.069–0.260]	0.273 ± 0.055 [0.211–1.224]	0.154 ± 0.006 [0.144–0.277]	0.219 ± 0.068 [0.109–4.985]	0.766 ± 0.172 [0.562–4.257]	1.046 ± 0.241 [0.689–7.644]	78.93 ± 6.21 [30.06–90.26]
U2 (n = 54)	4.64 ± 0.12 [4.21–5.09]	10.34 ± 2.77 [3.36–23.36]	0.181 ± 0.047 [0.128–0.639]	0.083 ± 0.005 [0.069–0.113]	0.230 ± 0.016 [0.206– 0.366]	0.149 ± 0.005 [0.139–0.172]	0.908 ± 0.334 [0.155–3.343]	0.647 ± 0.070 [0.556–1.279]	1.602 ± 0.385 [0.711–4.510]	42.60 ± 8.96 [19.07–78.21]
Stream bed material										
M2 (n = 33)	5.04 ± 0.21 [4.56–5.53]	4.88 ± 2.96 [0.97–26.78]	0.092 ± 0.041 [0.025–0.553]	BDL [BDL–1.744]	0.060 ± 0.034 [0.011–1.042]	0.019 ± 0.005 [0.01–0.092]	0.315 ± 0.190 [BDL–1.703]	0.180 ± 0.090 [0.054–1.880]	0.631 ± 0.340 [0.095–2.546]	29.57 ± 13.38 [14.34–100.00]
U1 (n = 33)	4.75 ± 0.15 [4.49–5.29]	31.19 ± 5.41 [13.33–47.45]	0.723 ± 0.233 [0.218–4.614]	BDL [BDL–0.272] NA = 1	0.291 ± 0.127 [0.097–0.603]	0.058 ± 0.017 [0.024–0.105]	1.696 ± 0.610 [0.024–3.419]	1.130 ± 0.330 [0.538–5.290] NA = 1	3.013 ± 0.670 [1.163–5.309] NA = 1	36.68 ± 11.35 [21.39–99.56] NA = 1
U2 (n = 33)	4.87 ± 0.15 [4.40–5.44]	33.67 ± 9.15 [2.58–53.31]	0.211 ± 0.112 [0.048–1.424]	0.057 ± 0.057 [BDL–0.565] NA = 2	0.146 ± 0.109 [0.015–0.448]	0.024 ± 0.015 [0.004–0.072]	2.166 ± 0.680 [0.109–5.201]	0.410 ± 0.260 [0.071–2.21] NA = 2	2.630 ± 0.931 [0.349–5.851] NA = 2	23.32 ± 11.16 [5.60–78.64] NA = 2
Detection Limit (mg/L)	NA	NA	NA	<0.5	NA	<0.2	NA	NA	NA	NA

Note: Values are medians ± median absolute deviations (MAD); ranges are reported in "[]";
Abbreviation: BDL, below detection limit; NA, not available; MAD, median absolute deviation; Loss-On-Ignition (LOI)

SO_4^{2-} (from <0.8 to ~3.0 mg l^{-1}), a 75% increase in K^+ (from 2.5 mg l^{-1}) and a 25% increase in Cl^- (from 3.0 mg l^{-1}). Furthermore, nitrate concentrations in the water passing through the OM-soil media was 18–61% higher, compared to the deeper soils (> 20 cm): from 22.6 μeq/L^{-1} (U1); 58.6 μeq/L^{-1} (U2) and 147.4 μeq/L^{-1} (M2).

5 | DISCUSSION

5.1 | Baseline determinants

Firstly, a wide range of pH can be expected in Singapore's rainfall depending on the monsoon season (e.g., Northeast or Southwest Monsoon), location of cloud formation, and storm tracking over the ocean and lands of variable pollution emissions. These geographical aspects affect the atmospheric chemistry that determines rainwater pH (e.g., Camarero & Catalan, 1996; Murray et al., 2013). For example, the differences in ions in the rainwaters with one of the highest (6.35; 27 December 2018 at BTNR) and lowest (4.06; 23 October 2018 at NUS campus location) recorded pH values are substantial (yet always acidic). The low pH rain water was dominated by sulfate and nitrate: SO_4^{2-} (134 μeq l^{-1}) > NO_3^- (61 μeq l^{-1}) > > {Cl^-, Ca^{2+}, Mg^{2+}, Na^+, K^+ (ranging from 24 to 44 μeq l^{-1})}. In contrast, the high pH event water contained much higher concentrations of cations: K^+ (389 μeq l^{-1}) > SO_4^{2-} (279 μeq l^{-1}) > Ca^{2+} (268 μeq l^{-1}) > Cl^- (204 μeq l^{-1}) > Mg^{2+} (109 μeq l^{-1}) > Na^+ (77 > μeq l^{-1}) > NO_3^- (32 μeq l^{-1}).

In a prior work, Balasubramanian et al. (2001) determined the sources accounting for most of the variance of rainfall ion chemistry in Singapore were soil particles (Ca^{2+}, K^+), acidification processes (NSS-SO_4^{2-}, NO_3^-, NH_4^+, H^+), biomass burning ($HCOO^-$, CH_3COO^-), and sea-spray (Na^+, Cl^-, Mg^{2+}). Using their work as a guide, we recognize that some of our lowest pH values likely result from enrichment of acids as rain clouds passed over local air pollution sources. At the other extreme, the rainfall of events with relatively higher pH likely contain higher concentrations of ions from soil/dust particles, including those from long-range sources, and potentially sea spray for storms approaching the island of Singapore from the ocean, again as reported by Balasubramanian et al. (2001). Future work could address this issue of ion sources in more detail.

Although high-rainfall pH variability was observed, we recognize that our measurements are determined from bulk sample (whole-event) calculations that mask inter-storm extrema. Instantaneous pH values during a rainfall event could be lower, on the order of 3.4, which is the lowest value we measured in 2016 prior to the study at the National University of Singapore, 15 km away. Furthermore, the difference in the distribution of rainfall pH values measured onsite at BTNR and NUS demonstrate how rainfall chemistry is, in part, affected by the location where rainfall events form and by the path over which clouds move - even spatially close areas in Singapore can have substantial chemistry differences (Balasubramanian et al., 1999). The direct contribution of nitrogen through precipitation is partly responsible for the low pH events and the combination of processes such as nitrification, are some of the potential major causes for the changes in stream water pH (see discussion below). In the case of storm runoff at the site, one must keep in mind that the incoming water chemistry will also be modified as the rainfall passes through the canopy as throughfall (Figure S2) (Filoso et al., 1999; Germer et al., 2007) - but there has been very little work on this aspect in Asia.

In other work from the region, pH values in rainwater samples from urbanized Kuala Lumpur and Petaling Jaya, Malaysia were between 4.84 and 6.95, and rainfall constituents were mostly contributed by terrestrial sources rather than sea spray (Yusop et al., 1989). Similar to our findings, Yusop et al. (1989) observed high-concentrations of Ca^{2+} and Mg^{2+} in their rainfall samples and this was due to local dust input. Periodic acid rain events (median pH of 4.6 to 5.5) have also been observed in Hong Kong (Peart et al., 1995). Unlike our study, the surface waters observed in Ma On Shan Country Park in Hong Kong were near-neutral (pH of 6.3 to 7); and this may be due to the mineralisation and/or occurrence of sedimentary carbonate rocks such as limestone and dolomites in the area (Peart et al., 1995).

The soils of NSFC are acidic (median pH ~4.6) by nature because of the granite parent material, millennia of input of slightly acidic rainfall (from the natural presence of CO_2, NO_x, and SO_2 in the troposphere), acid release as vegetation uptakes nutrients as a part of plant growth (Jalota et al., 2018), and organic acid release when vegetation is decomposed. The low occurrence of base (nutrient) cations, as reflected by ECEC values ranging from 1–2 cmols (+) kg^{-1}, is typical of sandy loam soils (median sand content ~60 to 65%) that are not particularly high in organic matter (LOI ~ 7 to 11%) and have undergone substantial leaching over time in an intense tropical climate regime. Similar findings have been observed in other parts of Singapore (e.g., Leitgeb et al., 2019) and in other tropical systems (e.g., Shamshuddin et al., 1995; Osman, 2013), suggesting soil element depletion may occur at a rate faster than they can be replenished by slow mineral weathering or deposition from the atmosphere (e.g., Sollins et al., 1988; Matson et al., 1999; Driscoll et al., 2003).

The low pH also likely lowers ECEC, which is more associated with organic acids from decomposition than from the small fraction of clay (7%–8%; largely kaolinite) that is present in the soils in NSFC. Again, the low BS values in the soils in U2 (38 to 43%) support the idea that base cations are reduced relative to acid cations (namely H^+ and Al^{3+}). The high-BS values >75% at U1 and M2 are likely elevated because of the low presence of acid cations (note that we only measured Al^{3+}). Care is needed in interpreting the BS values because they are sensitive to small changes because of the low concentrations of all cations. For the current state, where rain acidity is amplified by anthropogenic sources of NO_x (internal combustion) and SO_2 (fossil fuel combustion), the low base cation content of the soil does not offer much buffering potential while acidic rainfall infiltrates into the soil and percolates downwards to subsurface material with low permeability. Furthermore, future scenarios with higher deposition of reactive nitrogen (NO_x) and sulphate could magnify future acidification events at the site and in SE Asia in general (Dentener et al., 2006).

5.2 | Potential roles of runoff pathways

The relationships between pH and σ during high- and low-flow conditions provides insight on differences among streams and potentially, dominant runoff pathways. The tendency for σ to be relatively high and pH relatively low for high flows is apparent in the scatter plot of the two variables (Figure 5). In the figure, the low-flow values were chosen as the lowest 10% of recorded water level values (grey colour); the high-flow values are the highest 10% (orange); and the remainder are the intermediate 80% of recorded values (blue). When the groundwater grab samples are compared, the signatures at U1 mostly plot within the range of high and intermediate flows (Figure 5c). The groundwater signatures at U2 are shifted to the right in the diagram, but align more with low-flow values (Figure 5b). The groundwater signatures at M2 have greater spread, with many values plotting below the low-flow signatures. In contrast, the streamflow grab samples plot

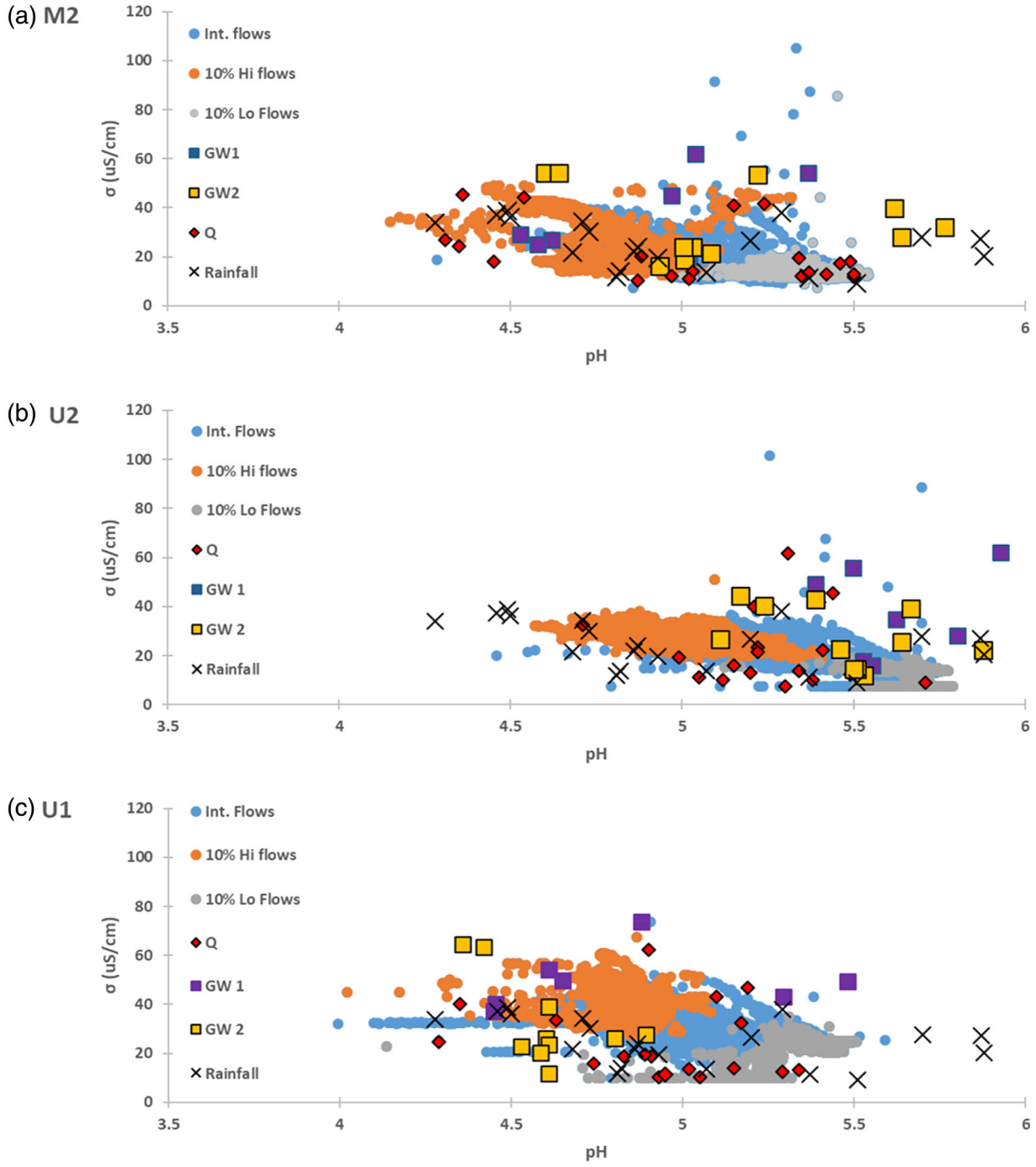

FIGURE 5 Scatter plots of pH versus specific electrical conductivity (σ) for the streams at the three NSFC sites M2 (a), U2 (b) and U1 (c). The data are compared with the groundwater signatures from each site (2–6 wells combined). Also included are values for rainfall collected at Bukit Timah Nature Reserve. The discharge data are from the automated recording sensors; all other are from laboratory analysis

within the range of low and intermediate values at all sites (i.e., their signatures are often different from those of the groundwater). Many of the rainfall values plot to the right of streamflow values at U1 and M2 because of their high pH values.

Fundamentally, the patterns in Figure 5 support the idea that both groundwater and stream water at M2 (below the confluence of U1 and U2) contain unequal mixes of source water from the upslope U1 and U2 sub-catchments. The ranges of both M2 groundwater and stream water pH and σ values plot together with the ranges of values for U1 and U2 (Figure 5). The tendency for stream pH to stay below 5.25 may reflect a greater contribution from water from the U1 sub-catchment. The drop in stream pH well below that of local groundwater suggests that the latter does not greatly buffer inputs of new water from the low pH rainfall. Furthermore, the values of stream water pH that are lower than rainfall supports the possibility that organic acids are being washed into the streams via runoff water during rainfall events; this response aligns with our leaching experiments. The difference in stream water and rainfall pH can also be explained by the different timing and nature of the measurements: while stream water pH is measured continuously (at least once per 20 min), the rainfall sample is an aggregate for an entire event and collected usually the day following the event.

Tracer work in nearby Bukit Timah in Singapore (Chappell & Sherlock, 2005) and unpublished data from Nee Soon show a dramatic decrease in high saturated hydraulic conductivity (from a median of ~500 mm/h at the surface to 25 mm/h at 50 cm) of a magnitude that could restrict vertically infiltrating water, deflecting it horizontally downslope (Kho, 2016). This anisotropy is relevant to the mechanisms that alter stream water chemistry in some tropical locales. For example, Small et al. (2012) demonstrated that local subsurface water flows contributed to acidification events in several watersheds in Costa Rica. Further, Johnson et al. (2007) documented elevated carbonic acid ($H_2CO_3^-$) concentrations in a forested Amazonian stream following increases in water table height during the wet season. Supporting this assertion are the results from our leaching experiments showing that organic acids are potentially released by water moving through the subsoil and/or near the surface in contact with the litter layer. The increasing concentration of nitrate and decrease in stream water pH (Figure S1) indicate increased decomposition of organic matter and possibly nitrification. Similar responses have been observed in other tropical soil and stream ecosystems (e.g., Gonçalves et al., 2006; Sayer & Tanner, 2010; Fujii et al., 2012).

Further, the results from our stable water isotope mixing model support both field observations and leaching experiments. Over the 17 time points that span almost a year for which we have stable water isotope data, saturation excess overland flow (43% ± 29%; mean ± 1SD) tended to contribute more to stormflow response than shallow subsurface flow (29% ± 23%) or deeper, slow moving flow (5% ± 15%). Rainfall intensity (Figure 6a) is somewhat positively correlated with shallow subsurface flow contributions to streamflow at M2 (Pearson's R = 0.48). We observed saturation overland flow occurring in locations in the stream riparian zone where the local water table has risen, and/or where subsurface flow converges from upslope sub-

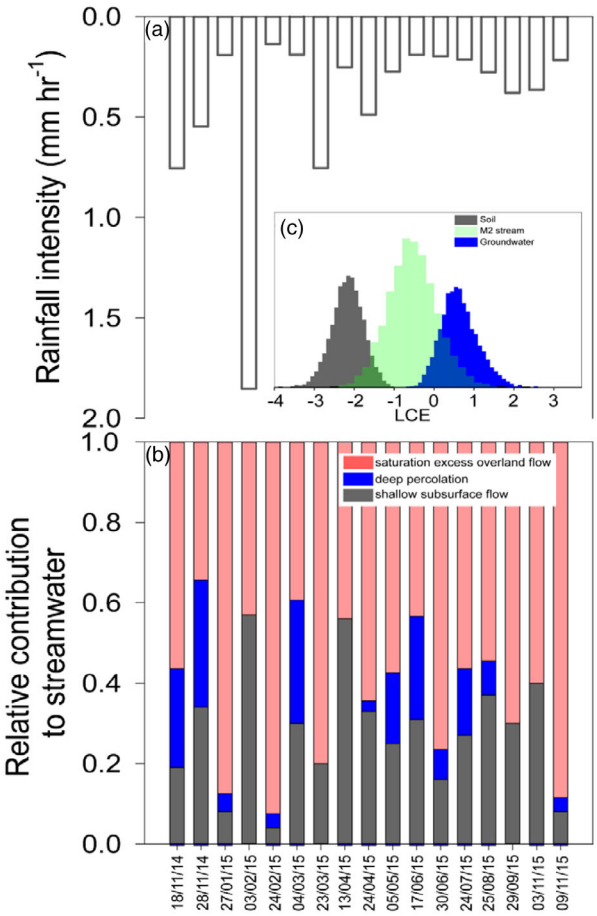

FIGURE 6 Stable isotope mixing model. (a) Rainfall intensity (mm hr^{-1}); (b) three-component isotope source apportionment of M2 stream water; (c) histograms of line-conditioned excess (LCE) of M2 stream water, soil water end-member (representing shallow subsurface flow), and groundwater end-member (representing deep percolation) obtained by resampling the calculated LCEs of respective waters. Precipitation amount-weighted $\delta^{18}O$ and $\delta^{2}H$ represent saturation excess overland flow. The correlation coefficients of shallow subsurface flow, deep percolation, and saturation excess overland flow with precipitation intensity are 0.48, −0.30, −0.01, respectively

catchments—often in non-sloping, low-lying locations, particularly in the swamp forest. We were not however able to distinguish between these two mechanisms and assume they are connected.

The calculated line-conditioned excess (LCE) values (Figure 6C) present another way of summarizing the insights from the stable water isotope mixing model results. That is, the theoretical distribution of streamflow at M2 (mean ± 1SD) (−0.5 ± 0.6) overlaps more with shallow subsurface flow (0–30 cm soil with LCE -2.2 ± 0.4) and saturation excess overland flow (amount-weighted rainfall with LCE ~0) than with shallow groundwater (LCE -0.6 ± 0.5). Because these insights were derived from resampling the calculated LCE values of respective waters, we consider the probability density in Figure 6C as indicative of the likely outcomes had we been able to obtain stable water isotope samples more frequently than we did over the same

period. Important for acid events in Nee Soon is that SSF and the generation of SOF on the valley floor are more likely to lower pH by leaching organic acids than the return of GW via a water table rise following interaction with generally inert granite substrate.

5.3 | Conceptual model of stream pH response for the Nee Soon Swamp stream system

A conceptual model of stream acid events in Nee Soon Swamp Forest requires understanding streamflow generation processes as well as characteristics of rainfall inputs and the underlying soils and geology. Based on past works (Chappell & Sherlock, 2005; Kho, 2016; Teo, 2016; Nguyen et al., 2018; Koh, 2019) and our observations/data (Figure 6), we infer that the key processes that contribute to streamflow are: (a) shallow subsurface flow (SSF) along the soil-bedrock (saprolite) interface and/or above flow-restricting subsoil; (b) saturation overland flow (SOF) in the valley bottom where the water table rises to form the swamp or SSF converges; (c) subsurface flow that returns to the stream and/or riparian zone (return flow); and (d) a shallow groundwater component that is deeper and (somewhat) older than SSF, and contributes baseflow by maintaining a high-water table (Figure 7). Other types of overland flow are possible but cannot be separated because they are rare and isolated, including (a) Horton overland flow (HOF; or infiltration excess overland flow) generated on the walking paths; and more rarely (b) saturation overland flow forming where a substantial reduction in saturated hydraulic conductivity occurs at moderately shallow depths (> 25–50 cm; vertical anisotropy), creating a bottleneck to infiltrating water during very large, high-intensity events, under wet catchment conditions (Figure S3; probably rare). More likely, however, the water at this bottleneck may flow through the soil profile as SSF through macropores and/or small pipes (see video)—but pipeflow does not occur to the extent observed at other nearby locations that are somewhat analogous in geography, for example Bukit Tarek in Peninsular Malaysia (Negishi et al., 2007). Given the small area of the catchment, and tendency for stream flow to become very low during extensive dry periods, the mean age of the water in the stream is probably on the order of a few months (this age cannot be calculated from our data). Thus, rainfall will interact variably in time and space with organic matter (canopy, leaf litter, organic surface layer) and the soil matrix as it moves to the stream system and possibly changes in chemical composition, influencing stream pH.

Again, a wide range of rainfall chemistry is expected at Nee Soon depending on where the storm clouds form–for example, over the ocean, directly over the urban-industrial complex, or a long-distance mainland location. The chemistry will be modified further as it passes through the canopy (e.g., particular cations may be removed; others may be enriched by flushing dry deposition from leaves) before it comes in contact with the swamp/stream or the leaf litter of the forest floor before entering the soil matrix. The rainfall regime in Singapore is typically sufficient to keep the soil profile moist year round such that hydrological pathways through which water moves do not require excessive wetting to be active. As such, most rain events trigger stormflow, but the response is dependent on the total rainfall depth and intensity. Thus, the processes contributing to stormflow likely vary from event to event (as indicated in Figure 6). Nevertheless, on aggregate, based on the $\delta^{18}O$ and $\delta^{2}H$ isotope analysis, the median (± MAD) annual streamflow contributions were 59%

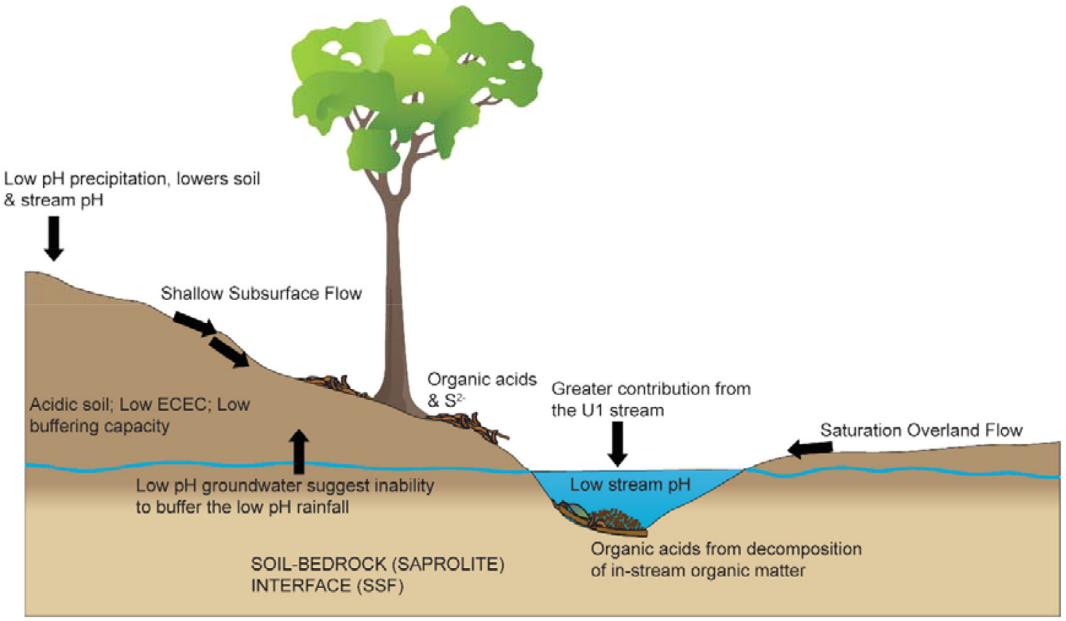

FIGURE 7 Conceptualization of the key pathways contributing to a stream acid event in the NSFC. The stream acid events are manifested by low pH rainfall and groundwater, organic acids and a greater contribution of low pH stream water from the U1 sub-catchment. Transport pathways, such as saturation excess overland flow and shallow subsurface flow further affect the magnitude of the acid events

± 16% from SOF forming in the valley in the riparian zone (event water); 31% ± 11% from SSF that returns typically into the channels or riparian zone (event water mixed with soil water); and 4% ± 4% from shallow groundwater that moves on a slower time scale than SOF and SSF. With regard to the latter, which was sometimes not detected (Figure 6), the buffering of acidic waters by the granite bedrock should be minor. Deep and very slow flow pathways are not likely at these "headwater" sites.

The pH of the stream at most times will largely reflect the chemistry of either or both: (a) the pH of throughfall, either falling directly in the stream/swamp or as SOF forming on saturated areas near the riparian zone; or (b) event SSF water containing leached organic acids from the surface litter layer or shallow hillslope soil profile. Both types of water would be modulated by the chemistry of rainfall, which varies greatly in pH from event to event (on the order of pH 4–7). The very low pH values we have observed in rainfall are almost surely the result of local-to-regional anthropogenic sources, although ocean salts and long-range sources likely contribute at some times. The elevated concentrations of sulphate, nitrate, and ammonium are indicative of anthropogenic sources of acid rain (Zhang et al., 1999), which both our study and others have reported for Singapore (Balasubramanian et al., 2001; Hu et al., 2003; Molina et al., 2019).

6 | CONCLUSION

We describe the characteristics of periodic acidification events in headwater streams in the NSFC in urban Singapore. Our findings show that the acid events in general are a natural phenomenon (owing to highly weathered and naturally low buffering potential of granite-derived soils and acidic rainfall), but are amplified by anthropogenic emissions of sulphur and nitrogen species (e.g., SO_4^{2-} and NO_x) that lower the pH of rainfall entering the catchment. The observed decreases in stream pH during the acid events were related to inputs of acidic rainfall and likely the flushing of organic acids into the stream system by water moving through the subsurface soil and surface litter layers in response to storms. Furthermore, decomposition of instream organic matter also likely contributed to a reduction in stream water pH. Although the acid events we observed were typically short-lived (<12–24 h), events triggered by larger inputs of acid rain, for example during very wet periods or rare extreme storms, could potentially equate to more severe implications on sensitive freshwater decapod and macroinvertebrate communities. With respect to catchment hydrology, we were able to establish a working model of streamflow generation pathways involving shallow subsurface flow, shallow groundwater flow, and saturation overland flow in the riparian zone. Further, the insights gained into the understanding of hydrological pathways in this tropical system through mixed traditional and isotopic tracer methods were critical for understanding the mechanisms contributing to stream acid events.

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DATA AVAILABILITY STATEMENT

Raw data used for making the graphs and table are available at https://www.adziegler.com/data/. If you use the data please reference or cite this paper.

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