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Storage and export of nutrient and oxyhydroxide elements across glaciated soils and watersheds in western Massachusetts, USA

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ABSTRACT

Quantifying the geologic, pedogenic, and human processes governing elemental release and transport in glaciated terrains is complex but has several important ramifications for nutrient storage, formation of secondary minerals, and protection of surface and groundwater resources.

Here, soils and river waters were studied in three subwatersheds of the Deerfield river from October 2018 to January 2020 to determine if nutrient (Ca, K, P) and oxyhydroxide elements (Al, Fe, Mn) were retained within the soil or exported from the watershed via river water at comparable rates in: Supra-glacial till Forested soils, Fluvial Agriculture soils, and Sub-glacial Till Hydric soils. This study found higher soil storage, soil water transport, and watershed export of nutrients in the Fluvial Agriculture subwatershed compared with the Supra-glacial Till subwatershed. The Supra-glacial Till subwatershed had the greatest overall river water nutrient export as it was the largest subwatershed but when considered with area-normalized basis, the Fluvial Agricultural soils exported 3x to 6x higher nutrients. When considering the oxyhydroxide elements, Al was not significantly different among geologic deposits and land covers. Iron concentrations in soils and soil water were not significantly different between hydric and forest soils, despite higher acidity, higher dissolved organic carbon, and lower electropotential in the former. Agricultural soils were enriched in Mn likely due to continuous agriculture since 1677 CE, which is unreported in agricultural fields of New England with potential impacts on soil C dynamics or microbial communities.

1. Introduction

Quantifying the geologic drivers and overlapping human processes on terrestrial biogeochemical cycles of elements in glaciated terrains is complex. Terrestrial biogeochemistry at the watershed-scale in New England, USA, remains poorly-constrained due to its heterogeneous composition of lithology and diverse geologic past affecting surface deposits. Surficial geology of New England is dominated by its glacial past that have created unique landforms and associated terrestrial ecosystem land cover. While there are additional glacial landforms and terrestrial ecosystems present, montane environments in New England can be generally characterized by three common examples: supra-glacial tills that are forested, sub-glacial tills that are commonly hydric with wetlands, and fluvial deposits of fine sands. The supra-glacial till (including melt out till, moraines, and flow till) is a heterogeneous mix of rock fragments from the Laurentide ice sheet, ranging from sand to boulders > 4 m diameter (Dyke and Prest, 1987). Supra-glacial till soils are very well-drained and typically Spodosols (Orthods) or Inceptisols (Dystrudepts) that support northern hardwoods except where mantled with boulders (Ciolkosz et al., 1989). Sub-glacial till (including lodgement till, deformation till) is a heterogeneous mix of rock fragments compressed beneath the Laurentide ice sheet. Sub-glacial till soils are poorly drained and commonly have Fragipans (Bx or Cd horizons see Lindbo and Veneman, 1993) and other near-surface impermeable layers within 1 m of the soil surface. Due to the commonly hydric conditions, sub-glacial till soils can be Spodosols (Aquods), Inceptisols (Aquepts), or Histosols (Saprists) and support wetland woody and herbaceous plants. Lastly, fluvial deposits (including outwash) is a well-sorted mix of fine rocks, sand, and coarse silt deposits in floodplains and low-lying areas formed from fluvial transport of glacial deposits between 16,500 and 9,400 years ago (Dyke and Prest, 1987; Ridge and Larsen, 1990; Uchupi et al., 2001). Mineralogy among these soils are similar but there are higher proportions of biotite and Fe-bearing silicates in glacial till and higher proportion of feldspars and quartz in fluvial deposits (Taylor and Blum 1995; Eberl 2004; Marek and Richardson, 2020).

Within each glacial landform, there are distinct terrestrial-aquatic

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biogeochemical cycles for each element, which vary according to their geochemical behavior and human alterations. Without human actions, nutrients (such as calcium (Ca), potassium (K), and phosphorus (P)) in temperate ecosystems are largely sourced from primary mineral weathering, with varying inputs from the atmosphere, and internally cycled by plants, stored in mineral soils through adsorption, and eventually leached to ground and surface waters. Nutrients within forests and wetlands developed on glacial till have been historically affected by deforestation (Richardson et al., 2017; Zetterberg et al., 2016), conversion to pastures (Hall et al., 2002), acid rain (Armfield et al., 2019) and development for homes (Levia, 1998). However, the fluvial deposits in valley bottoms and floodplains have remained in active cultivation for crops and pastures for centuries as the Connecticut River valley was colonized by European settlers in the first half of the 1600 s (McArdle, 1979).

Humans have enhanced soil abundance and mobility of nutrients, such as calcium (Ca), potassium (K), and phosphorus (P). First, humans have added nutrients as soil fertilizers and amendments to agricultural soils through animal manures, bone meal, liming agrominerals, and synthetic nutrient compounds (Potter et al., 2010; Osmond et al., 2015; Chen et al., 2018). Calcium, K, and P compounds vary in their solubility, depending on their form when added to agricultural soils such as highly soluble forms of $H_2PO_4^{-1}/HPO_4^{-2}$ contributing to eutrophication of surface waters, particularly lakes (Schindler et al., 2016). The Connecticut River, which is the largest river and watershed in New England USA, has suffered from eutrophication and toxic algae blooms (Garabedian 1998), primarily due to agricultural activities in soils. Garabedian (1998) estimated 11 million pounds (5000 Mg) of P entered the Connecticut River due to chemical fertilizer and manure leachate and runoff between 1992 through 1995 CE. Further, agroecosystem processes such as crop and tree removal are net removers of nutrients from terrestrial biogeochemical cycles (Richardson et al., 2017; Altieri et al., 2018).

Another group of important elements are oxyhydroxide elements (specifically aluminum (Al), manganese (Mn) and iron (Fe)), which are principally geogenic-elements sourced from the weathering of silicates (e.g. feldspars, ferrohornblende, spessartine) but can also be abundant in carbonates (e.g. siderite, rhodochrosite), or sulfide (e.g. pyrite, rambergite) minerals. In soils, the release of Al, Mn, and Fe from primary minerals allows for the formation of secondary oxyhydroxide minerals. In upland soils within the udic soil moisture regimes, Al commonly forms amorphous oxyhydroxide gibbsite or boehmite (Jolicoeur et al., 2000; Huang et al., 2002), Mn commonly forms birnessite, bixbyite, or hollandite (Dixon & White 2002), and Fe commonly forms ferrihydrite, goethite, and hematite (Bigham et al., 2002; Jiang et al., 2018). These reactive minerals develop a pH-dependent charge depending of their isoeletric point and surrounding pH, enabling Mn oxides to fix metal cations and (Al, Fe) oxides to fix both heavy metals and organic and inorganic oxyanions, either toxic or nutrient (Bigham et al., 2002; Dixon and White, 2002; Huang et al., 2002). Furthermore, Al, Mn, and Fe are coupled with carbon (C) cycling in soils as oxyhydroxides organo-mineral protections for organic C or serve as electron acceptors under oxygen limiting conditions (e.g. Possinger et al., 2020). Alterations to Al, Fe, and Mn biogeochemistry can affect microbial degradation of SOM (Colombo et al., 2014; Li et al., 2021; Neupane et al., 2023) and potentially promote immobilization of nutrients to through directly adsorbing compounds or facilitating precipitation Ca and P amorphous and crystalline phases (e.g. Spiteri et al., 2008; Weng et al., 2012).

The primary objectives of this study were to compare soil storage, soil water transport, river water transport, and watershed-scale export of nutrients and oxyhydroxide elements in supra-glacial till forest soils (Supra-till Forest), sub-glacial till Hydric soils (Sub-till Hydric), and fluvial Agriculture soils (Fluvial Farm). Here, soil physicochemical properties and macronutrient and oxyhydroxide elements were compared among Supra-till Forest, Sub-till Hydric, and Fluvial Agriculture subwatersheds of the Deerfield Watershed to determine potential linkages in storage in soil and transport via soil water to stream water exports for these three common glacial landforms. The Deerfield River is an excellent study area in northwestern Massachusetts with diverse subwatersheds with strongly glacial landforms that can serve as a testing ground for evaluating linkages between soils, land cover and their impact on river water quality. The first hypothesis was that the Fluvial Agriculture soils would have higher soil storage and river export of nutrients than Supra-Till Forest and Sub-Till Hydric soils due to nutrient additions by humans. The second hypothesis was that Sub-Till Hydric soils would have lower soil storage and highest river export of Mn and Fe due to greater reducing conditions than in Supra-Till Forest and Fluvial Agriculture soils. These are important considerations for Deerfield River Watershed management and also forest ecosystem researchers in New England and other glaciated, temperate forest regions globally.

2. Material and methods

2.1. Environmental setting and site descriptions

The Deerfield Watershed is located within northwestern Massachusetts and southern Vermont (Fig. 1). Overall, the climate of the watershed is humid continental mild to hot summers, no dry season, with coldest month averaging below − 0 °C. The climate does range from Dfa near its confluence with Connecticut River to Dfb in its headwaters in Vermont, using the Köppen climate classification. The Deerfield River Watershed has an area of 1720 km^2, a 210 km perimeter, and is currently 78 % forested with only 3 % of the watershed considered urbanized (United States Geological Survey, 2020, accessed February 11th, 2020). The Deerfield River has several dams controlling flow and is gauged and measured by the USGS at several locations: Somerset VT, Florida, MA, Buckland, MA, Shelburne Falls MA, and Deerfield MA.

The lithology of the Deerfield watershed is largely metamorphosed sediments part of the Connecticut Valley synclinorium (Zen et al., 1983), dominated by the Waits River formation and the Goshen Formation, both of which consist of schists and quartzite, with marble, granofels, and gneiss (Zen et al., 1983). Surface geology of the watershed is predominantly thin glacial till and thick glacial till on the uplands with stratified deposits in the river valleys. The upland soils in the watershed are young, rocky Inceptisols, especially in areas that have been previously deforested and/or converted to agricultural lands but fully developed Spodosols can be found in highest and steepest positions in the watershed. Upland watersheds are present in concave swales with poorly drained soils underlain with dense, fragipans derived from lodgement glacial till (e.g. Lindbo and Veneman, 1993). The soils on shoulder, footslopes, and valleys sides are relatively shallow, with thicker fluvial deposits in the valley bottoms at maximum depth at 117 m thick (Friesz, 1996; Marek and Richardson, 2020). Forests of the Deerfield are predominantly northern hardwoods: Sugar Maple (*Acer saccharum*), Red Maple (*Acer rubrum*), American Beech (*Fagus grandifolia*), Red Oak (*Quercus rubra*), and interspersed poplars (*Populus* spp), ash (*Fraxinus* spp.) and Basswood (*Tilia Americana*) on flat and gentle sloped landforms. Areas with steep slopes, outcrops from shallow soils, and bouldery areas are predominantly, White Pine (*Pinus strobus*), Eastern Hemlock (*Tsuga canadensis*), birch (*Betula* spp). Forested areas with hydric soils are dominated by poplars (*Populus* spp), Red Maple (*Acer rubrum*), Black Cherry (*Prunus serotina*), Black Gum Tupelo (*Nyssa sylvatica*) and wetland edges were dominated by sedges (*Carex* spp), reeds (*Phragmites* spp), Button Bush (*Cephalanthus occidentalis*), Leatherleaf (*Chamaedaphne calyculata*).

Three subwatersheds of the Deerfield Watershed were studied as representatives of specific glacial-landforms with co-varied land cover examples: Cold River subwatershed as the upland 'Supra-Till Forest' subwatershed, Schneck Brook as the flooded 'Sub-till Hydric' soil subwatershed, and Fuller Swamp Brook as the actively cultivated 'Fluvial Agriculture' subwatershed. Land cover across the subwatersheds was

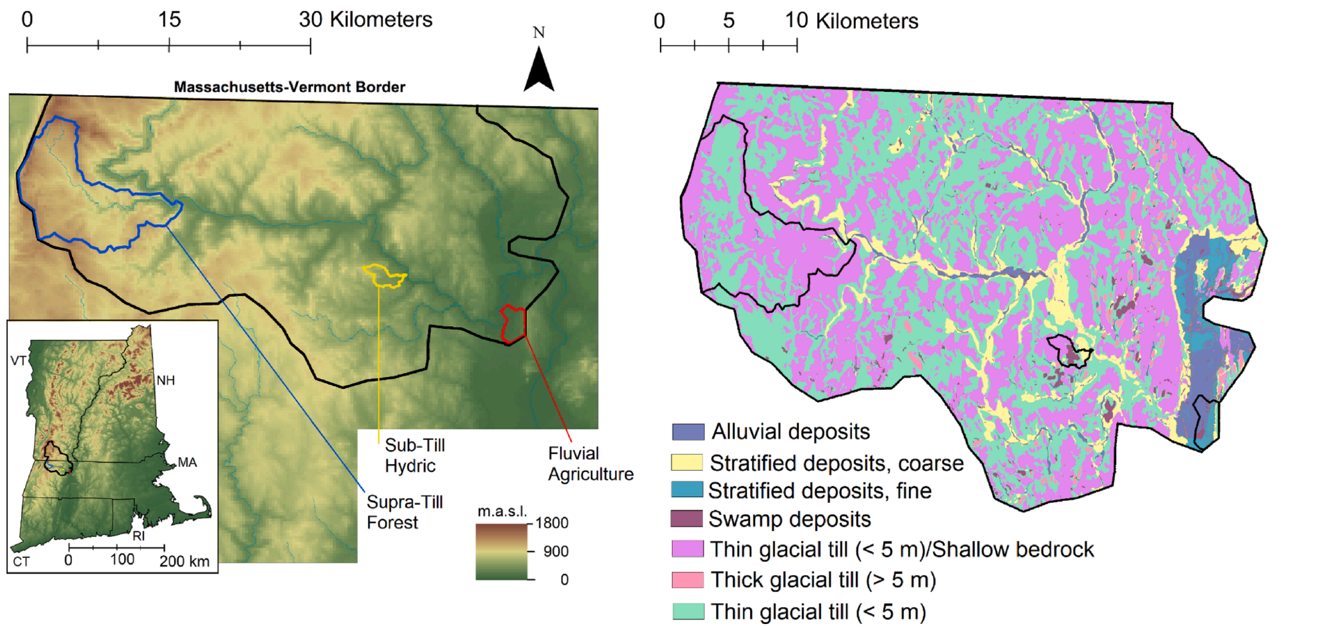

Fig. 1. (Left) Topographic map Map of the main Deerfield watershed (in black) and three subwatersheds: the Forest soil Cold River (in blue), Farmland soil Fuller Swamp Brook (in red), and Hydric soil Schneck Brook (in Yellow). (Right) USGS Surficial Geology map of glacial till, stratified glacial deposits, alluvial deposits, and swamp deposits based upon Stone et al (2018). Supra-glacial till and sub-glacial till were not separated when mapped by the USGS. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

characterized using spatial information from the National Land Cover Database (2016) (Jin et al., 2019). Upland forest soils were studied within the Cold River watershed, which is an 82.8 km^2 upland forested subwatershed, characterized by steep to rolling hill topography and protected forest lands. The Cold River watershed has 90 % forested land cover, 74 % thin glacial till and bedrock outcrops, and thus largely characteristic of a northern hardwood-dominated Forest developed on unconsolidated supra glacial till subwatershed (Table 1). Sub-till Hydric soils were studied within the Schneck Brook watershed, which is a small 3.9 km^2 subwatershed across hilly topography. Trees within Schneck brook are tolerant to hydric soils, such as Red Maple, Eastern Hemlock, and Black Cherry. Timber harvesting occurs throughout the Schneck Brook watershed and some farmland and pastures remain active. Schneck Brook has 31 % wetland land cover, 24 % swamp deposit surficial geology, and thus characterizes Sub-till Hydric soil dominated subwatershed (Table 1). Lastly, Fluvial Agriculture were studied within Fuller Swamp Brook, which is a small 5.4 km^2 floodplain subwatershed, with abundant agricultural lands on nearly level topography. The fields have been cleared before the incorporation of the Town of Deerfield Massachusetts in 1677 CE. Fluvial Agriculture soils in Fuller Swamp Brook watershed are active with staple row crops, goat and sheep pastures, dairy farms, and specialty seasonal crops. Fuller Swamp Brook has 36 % farmland land cover, 0 % glacial till, but 73 % stratified deposits of glaciofluvial deposits, and 27 % alluvial deposits. These characteristics are indicative of Fluvial Agriculture dominated subwatershed (Table 1). The Fluvial Agriculture soil sampling locations are currently used for row crops such as cabbage, kale, strawberries, tobacco, summer squash, winter squash, sweet potatoes, and eggplant under conventional agricultural practices.

2.2. Soil pits, soil lysimeters, and surface waters collection and sample preparation

At each subwatershed, a *catena* of three soil pits were sampled between June and August 2018. Each soil sampling location, three soil pits were excavated down to either refusal with compacted or pan horizons or lithic contact. Soil horizons were described following U.S. Soil Taxonomy (Schoeneberger et al., 2012) and collected in polyethylene bags. In total, 18 soil pits were excavated with 100 soil horizons described and sampled in this study. All mineral soil samples and organic horizons were oven-dried at 70 °C for 48 h and sieved to $\leq$ 2 mm.

Soil water was sampled at either above a restricting layer (example Cd fragipan) or at a maximum 1.5 m depth using lysimeters from Soil Moisture Equipment Co. (Santa Barbara, CA, USA) installed within each

Table 1
Description of land cover and surficial geology of the three subwatersheds studied. Land cover is based upon the National Land Cover Database (NLCD, 2016) and surficial geology is based upon USGS (Stone et al 2018).

Subwatershed	Glacial landform-land cover	Total area	Forest		Farmland		Wetland		Human Development	
		km^2	%	km^2	%	km^2	%	km^2	%	km^2
Cold River	Supra-Till Forest	81.8	90	73.9	1	1.1	5	3.8	3	2.8
Fuller Swamp Brook	Fluvial Agriculture	5.4	44	2.4	36	1.9	11	0.6	9	0.5
Schneck Brook	Sub-Till Hydric	3.9	59	2.3	5	0.2	31	31	4	0.2
			Thin Glacial till and bedrock		Alluvial deposits		Stratified deposits		Swamp deposits	
			%	km^2	%	km^2	%	km^2	%	km^2
	Supra-Till Forest		74	61	<1	0.0	25	21	<1	0.6
	Fluvial Agriculture		0	0	27	1.5	71	3.9	<1	0.1
	Sub-Till Hydric		70	2.7	5	0.2	0	0	24	0.9

catena within the three subwatersheds. One lysimeter was installed at the lowest elevation soil sampling site by digging a 1 × 1 m wide and deep hole and then augering to 1.5 m depth. The < 2 mm soil was replaced for the first 0.5 m followed by a 5 cm thick bentonite clay layer to seal the hole from vertical flow. Eight times during the study period, a vacuum of 85 kPa was applied to the lysimeter and soil water samplers collected water for 48 h. The first sample collection after 10 d after installation was discarded as a precaution of the soil materials settling. Soil water was collected as triplicate 100 mL acid-washed HDPE bottles.

Stream water samples were collected in 500 mL acid-washed polyethylene bottles using a pole sampler out 1 m from the stream channel at a depth of approximately 5 to 10 cm depth. Bottles were acid-washed with 10 % trace metal grade HNO_3, rinsed with stream water sample prior collection, and bottles filled with river water without gaseous headspace. Each stream water sampling was collected in triplicate.

2.3. Sample preparation and analyses

A 2:5 soil − water slurry was used to determine soil pH. Slurries were shaken for 1 h using a wrist-action shaker and vacuum extracted through a Whatman 40 filter. The pH of the supernatant extract was measured with a pH meter (8015 VWR). For organic-rich horizons, samples were filtered using a Whatman 1 filter. Loss-on-ignition (LOI) was used to estimate % soil organic matter (SOM) and measured by combusting a 4-g oven-dried subsample at 550 °C for 8 h. Every 20 samples included one blank and duplicate. To determine the soil particle size distribution, ~30 g of dried soil was weighed into 250 mL glass beaker. Organic matter was removed by LOI and added 100 mL of 1 M sodium hexametaphosphate (HMP) solution to the soil for at least 8 h to disperse soil particles. This HMP-soil slurry was washed out into a 1000 mL graduated cylinder with DI water. A modified Bouyoucos hydrometer method was used with hydrometer readings at 60 s and 1.5 h after mixing to the closest 0.5 g/L.

Soils were sequentially extracted for exchangeable elements and strong-acid digested for pseudototal concentrations. First, 0.50 g of soil was weighed into 50 mL centrifuge tubes and extracted with 30 mL of unbuffered 0.1 M ammonium acetate by shaking for 8 h and set still for an additional 16 h to reach a dynamic equilibrium. The soil slurry was then centrifuged at 3000 rpm for 1.5 h and the supernatant was collected. The remaining solid was digested using a strong acid, pseudototal digestion: with 5 mL of trace metal grade reverse aqua regia with a 9:1 ratio of 15.3 M HNO_3 to 12.1 M HCl acid, added to the remaining solids and heated to 90 °C for 45 min. This method allows for quantification of metals that are sorbed to organic matter and secondary Mn and Fe oxides not within crystalline silicates, providing an estimate of metals that are bioavailable or mobile (Chen and Ma, 1998). Soils were not ground to avoid creating fresh surfaces for dissolution of silicate minerals. With every 20 samples, a preparation blank, a duplicate, and a standard reference material (SRM) was included. Montana Soil 2711a and San Joaquin Soil 2709a from the National Institute of Standards and Technology (NIST) were used as SRMs. The digestates were then diluted to 50 mL using de-ionized water and a subsample was diluted further for instrumental analysis.

Soil water and stream waters were filtered to < 0.45 μm analyzed for pH, electrical conductivity (EC), and oxidation–reduction potential (ORP) using Atlas Scientific probes within the laboratory with 24 h of collection. Subsamples of soil water and stream waters were further analyzed for dissolved organic carbon (DOC) using a Shimadzu TOCV, which included blanks, duplicates, and spikes. Blanks had DOC below limit of detection, duplicates were < 3 % CV, and spikes had 94 to 101 % recovery rates. Soil water and stream waters were then digested using 1 to 5 g of 30 % H_2O_2 at room temperature for DOC removal and then acidified to pH 1 using 68 % HNO_3.

Soil extracts and soil digests, soil water, and stream waters were analyzed for elements (Al, Ca, K, Fe, Mg, Mn, P, Cu, Zn) with either an Agilent 5110 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) if concentrations were > 100 μg kg^{-1} or Agilent 7700x Inductively Coupled Plasma Mass Spectrometer (ICP-MS) if concentrations were < 100 μg kg^{-1} (Agilent Technology, Santa Clara, California, USA). Recoveries for pseudototal digests of soil Al, Ca, K, Fe, Mg, Mn, P, Cu, Zn were 82 – 111 % of their certified values. The metal concentration coefficient of variation between intra-sample duplicates was < 7 % and metal concentrations in the preparation blank samples were < 0.1 % of their analyte concentrations.

2.4. Statistical analyses

Throughout the manuscript, average values are presented in text and in figures ± 1 standard error. Descriptive statistics and nonparametric statistical tests were calculated in Matlab (Mathworks, Natick, MA, USA). Comparisons in soil properties, soil exchangeable and pseudototal concentrations, soil water concentrations, and river water concentrations among the three subwatersheds were compared using the nonparametric Kruskal-Wallis test with post-hoc Wilcoxon Rank Sign test. For statistical tests, homoscedasticity of sample variance was tested with Bartlett's test and α was set at 0.05.

2.5. Watershed discharge and elemental export

River water discharge for the Cold River was determined using data from the USGS NWIS system, as it is gauged as USGS sites 01,168,250 in Florida MA. However, river water discharge volume from the USGS is not available for Fuller Swamp Brook and Schneck Brook as they are substantially smaller watersheds. To estimate Fuller Swamp Brook and Schneck Brook discharge, monthly discharge data from other USGS gauged rivers was used: the Green River, North River, South River, Clesson Brook, and West Branch River. The watershed area and discharge rates were logarithmically transformed and a linear equation was fitted to the watershed area to discharge xy plot with a slope 1.031 and intercept of − 5.22 with an R^2 of 0.95. Using this equation, the monthly discharge for Fuller Swamp Brook and Schneck Brook was estimated (Supplemental Fig. 1). To estimate watershed export, total export from each of the three watersheds, the total discharge from Sept 18th 2018 through August 31st 2019 was determined from the summed monthly discharge rates. Average monthly concentrations were multiplied by the average monthly discharge and summed to determine an annual flux mass for each element (e.g. Richardson 2020). For months where water samples were not collected, the previous month's water chemistry was used. While not ideal due to missing stochastic events which cause large fluxes of materials via erosion, the data set provides for an estimate of typical export of nutrients without substantial outlier events such as tropical storms, hurricanes, and floods (see Chen et al., 2021). Fortunately, 2019 was a below average hydrologic year for western Massachusetts but without extreme precipitation events. Lastly, to account for differences in watershed size, total watershed export was divided by the watershed area to determine area-normalized export for the nutrient and oxyhydroxide elements.

3. Results

3.1. Soils physicochemical properties and elements across the catenas

Across the three soil catenas, there were significant differences in physicochemical properties as well as taxonomic features (Fig. 2). Supra-Till Forest soils were Spodosols of the Tunbridge soil series, with eluviated epipedons (E horizons) and spodic subsurfaces horizons (Bhs). Fluvial Agriculture soils were weakly developed Inceptisols of the Occum soil series with ochric epipedons with cambic subsurface horizons. Lastly, Sub-till Hydric soils were Inceptisols with ochric epipedons with a cambic subsurface and densic materials of the Woodbridge soil series. Supra-Till Forest and Sub-till Hydric soil catenas were significantly more acidic (pH 4.1 to 5.3) and had higher organic matter (SOM

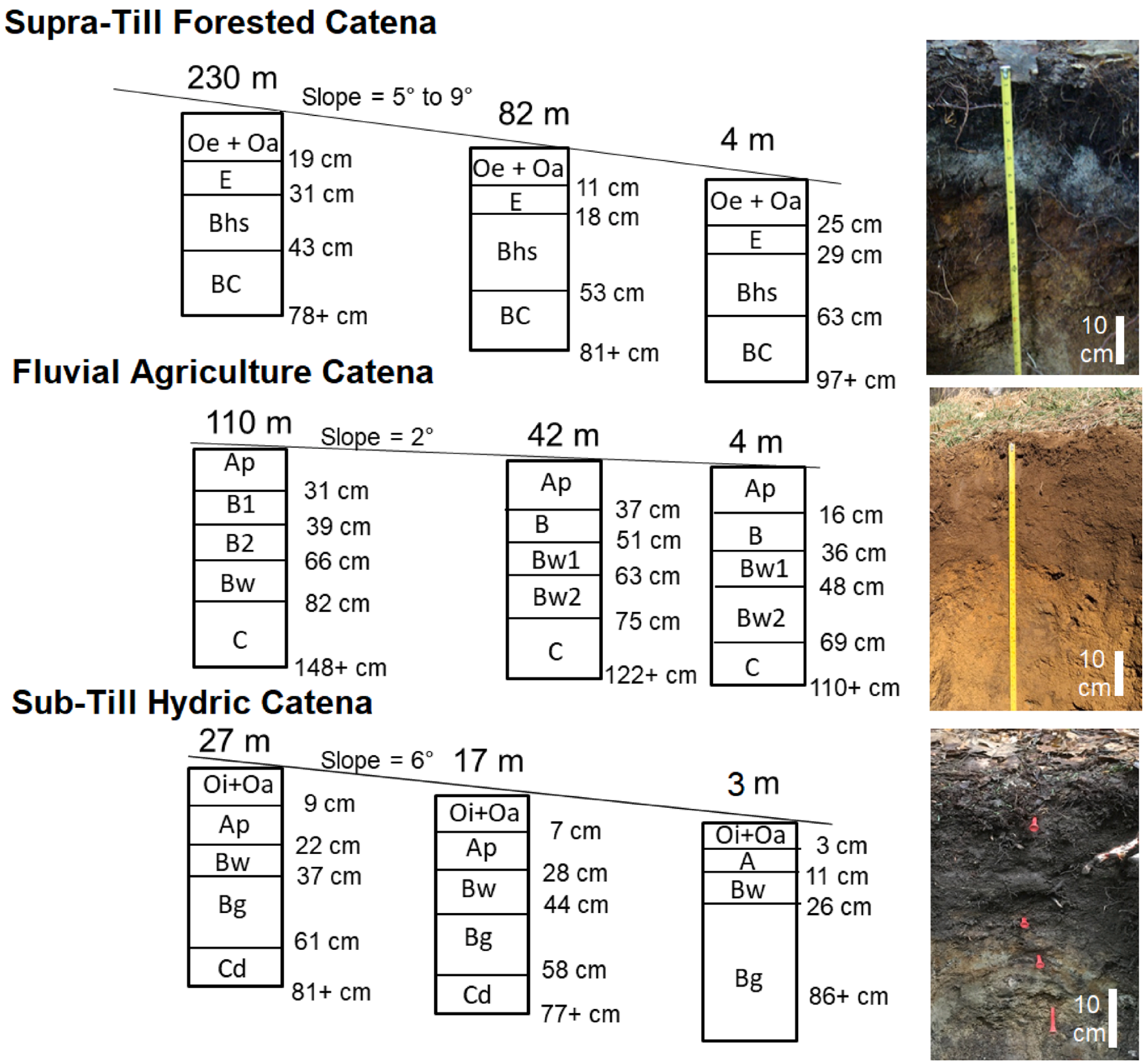

Fig. 2. Conceptualization of soils along the Supra-Till Forest *catena*, Fluvial Agriculture *catena*, and Sub-Till Hydric *catena* across the subwatersheds.

4 % to 11 %) than the Fluvial Agriculture soil *catena* (pH 6.1 and SOM 1 % to 4 %) ($p < 0.05$, Table 2). Generally, the Sub-till Hydric soils had significantly lower %Sand and higher %Silt and %Clay than the Supra-Till Forest and Fluvial Agriculture soils ($p < 0.05$, Table 2). The Fluvial Agriculture soil had the weakest aggregation and structure (1 and 2 coarse subangular blocky) of the three soils.

Examining exchangeable nutrient concentrations, there were some significant differences among the three catenas. Fluvial Agriculture soils had significantly higher exchangeable Ca in the Ap, B and Bw1 horizons than Supra-Till Forest soil E and Bhs horizons as well as Sub-till Hydric Ap and Bw horizons ($p < 0.05$, Table 3). Fluvial Agriculture Ap horizons had significantly higher K_{ex} than Supra-Till Forest E horizons, but B horizons were not significantly different among the three subwatersheds ($p < 0.05$, Table 3). Fluvial Agriculture Ap and B horizons had significantly higher P_{ex} than Supra-Till Forest E and Bhs horizons ($p < 0.05$, Table 3), but Ap and B horizons were not significantly different between Fluvial Agriculture and Sub-till Hydric soils ($p > 0.10$, Table 3). Examining oxyhydroxide elements, Supra-Till Forest Oe + Oa horizons had significantly higher Al_{ex} than Sub-till Hydric Oa horizons ($p < 0.05$, Table 3), but epipedon (Ap, E horizons) and subsurface (Bhs, Bw, B, Bg) had comparable exchangeable Al_{ex} horizons. Fluvial Agriculture and Sub-till Hydric Ap soils had significantly higher exchangeable Fe_{ex} in the Ap and Bw horizons than Supra-Till Forest soil E and Bhs horizons ($p < 0.05$, Table 3). Similarly, Fluvial Agriculture and Sub-till Hydric Ap soils had significantly higher exchangeable Mn_{ex} in the Ap and Bw horizons than Supra-Till Forest soil E and Bhs horizons ($p < 0.05$, Table 3).

Similar patterns were observed for the pseudototal nutrient concentrations. Fluvial Agriculture soils had significantly higher Ca_{ptotal} in the Ap, B and Bw1 horizons than Supra-Till Forest soil E and Bhs horizons, which were significantly higher than in the Sub-till Hydric Ap and Bw horizons ($p < 0.05$, Table 4). Interestingly, Fluvial Agriculture Ap horizons and Supra-Till Forest E horizons had similar K_{ptotal}, but were both significantly higher than Sub-till Hydric soils ($p < 0.05$, Table 4). Fluvial Agriculture Ap and B horizons had significantly higher P_{ptotal} than Supra-Till Forest E and Bhs horizons ($p < 0.05$, Table 4), but Ap and B horizons were not significantly different between Fluvial Agriculture and Sub-till Hydric soils ($p > 0.10$, Table 4). Evaluating oxyhydroxide elements, Supra-Till Forest Oe + Oa horizons had significantly higher Al_{ptotal} than Sub-till Hydric Oa horizons ($p < 0.05$, Table 4), but epipedon (Ap, E horizons) and subsurface (Bhs, Bw, B, Bg) had comparable Al_{ptotal} horizons. Fluvial Agriculture and Sub-till Hydric Ap soils had significantly higher Fe_{ptotal} in the Ap and Bw horizons than Supra-Till

Table 2
Average soil physicochemical properties concentration profiles. Values are ± 1 standard error.

Catena	Horizons	pH	SOM	% Sand	% Clay	Structure
		log units	mg/g	%	%	
Supra-Till	Oe + Oa	4.1 ± 0.6	6.2 ± 1.4	n/a	n/a	n/a
Forest	E	4.2 ± 0.5	0.4 ± 0.1	83 ± 6	6 ± 2	2 m Sbk
	Bhs	4.9 ± 0.8	1.1 ± 0.5	80 ± 3	6 ± 1	2 m Sbk
	BC	5.3 ± 0.3	0.4 ± 0.3	85 ± 5	4 ± 1	1 m Sbk
Fluvial	Ap	6.2 ± 0.1	0.5 ± 0.2	81 ± 8	3 ± 1	2 vc abk
Agriculture	B	6.1 ± 0.2	0.4 ± 0.1	78 ± 3	3 ± 1	2 co abk
	Bw1	6.1 ± 0.2	0.3 ± 0.1	83 ± 3	2 ± 0	2 co sbk
	Bw2	6.4 ± 0.3	0.1 ± 0.1	86 ± 4	3 ± 1	1 co sbk
	C	6.2 ± 0.2	0.1 ± 0.0	80 ± 4	4 ± 2	1 co sbk
Sub-Till	Oa	3.9 ± 0.4	1.4 ± 0.2	n/a	n/a	n/a
Hydric	Ap	4.3 ± 0.9	0.4 ± 0.1	73 ± 5	7 ± 3	2 g sbk
	Bw	4.8 ± 1.1	1.1 ± 0.5	71 ± 3	8 ± 2	2 m sbk
	Bg	4.6 ± 0.8	0.4 ± 0.3	77 ± 4	7 ± 3	2 m sbk
	Cd	4.8 ± 0.7	1.4 ± 0.2	78 ± 3	6 ± 2	1 co pl

Table 3
Average soil exchangeable concentrations of macronutrients and oxyhydroxide elements across the subwatersheds, determined using ammonium acetate extraction. Values are ± 1 standard error.

	Horizons	Ca_{ex}	K_{ex}	P_{ex}	Al_{ex}	Fe_{ex}	Mn_{ex}
		mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Supra-Till	Oe + Oa	152 ± 36	32 ± 6	1.3 ± 0.2	11.2 ± 1.2	35 ± 7	63 ± 10
Forest	E	51 ± 13	19 ± 7	0.7 ± 0.2	4.6 ± 1.8	28 ± 6	42 ± 7
	Bhs	18 ± 7	8 ± 2	0.4 ± 0.1	3.9 ± 0.6	23 ± 3	33 ± 9
	BC	14 ± 4	7 ± 1	0.4 ± 0.1	3.2 ± 0.3	20 ± 4	30 ± 6
Fluvial	Ap	278 ± 62	77 ± 18	1.7 ± 0.2	4.9 ± 1.2	49 ± 5	82 ± 9
Agriculture	B	177 ± 45	28 ± 13	1.0 ± 0.2	5.2 ± 1.0	56 ± 6	62 ± 7
	Bw1	158 ± 35	16 ± 6	0.7 ± 0.2	4.6 ± 0.7	40 ± 4	52 ± 6
	Bw2	73 ± 9	17 ± 2	0.6 ± 0.1	4.8 ± 0.4	37 ± 8	41 ± 2
	C	68 ± 5	21 ± 1	0.6 ± 0.1	5.3 ± 0.6	48 ± 5	36 ± 4
Sub-Till	Oa	27 ± 13	7 ± 3	0.4 ± 0.1	1.7 ± 0.5	18 ± 2	41 ± 7
Hydric	Ap	61 ± 16	43 ± 14	1.1 ± 0.3	10.0 ± 2.8	44 ± 5	55 ± 11
	Bw	32 ± 11	15 ± 4	0.5 ± 0.2	6.4 ± 1.7	32 ± 4	64 ± 13
	Bg	41 ± 16	18 ± 3	0.6 ± 0.1	6.0 ± 1.3	31 ± 4	71 ± 14
	Cd	51 ± 14	12 ± 3	0.4 ± 0.1	3.2 ± 1.4	34 ± 3	80 ± 12

Forest soil E and Bhs horizons ($p < 0.05$, Table 4). Similarly, Fluvial Agriculture and Sub-till Hydric Ap soils had significantly higher Mn_{ptotal} in the Ap and Bw horizons than Supra-Till Forest soil E and Bhs horizons ($p < 0.05$, Table 4).

3.2. Lysimeter soil water

Lysimeter soil water had significantly different pH, DOC, and ORP patterns. Average soil water pH was significantly higher in the Fluvial Agriculture soil (pH 5.90 ± 0.05) and was significantly lower for the Sub-till Hydric soils (pH 4.62 ± 0.09) and the Supra-Till Forest soil in between at (pH 5.01 ± 0.04). The differences among pH did not exhibit any seasonality. Average soil water DOC was significantly higher in the Sub-till Hydric soil (34 ± 10 mg kg^{-1}) than in the Fluvial Agriculture soils (17 ± 3 mg kg^{-1}) and the Supra-Till Forest soil in between at (10 ± 1 mg kg^{-1})($p < 0.05$, Fig. 3), which was primarily driven by high DOC concentrations during the growing season (April through September). Average soil water ORP was significantly higher in the Fluvial Agriculture soil (173 ± 3 mV) than in the Supra-Till Forest soils (150 ± 6 mV) and the Sub-till Hydric soil (95 ± 15 mV)($p < 0.05$, Fig. 3). There appear to be seasonality in low ORP for Sub-till Hydric soils during the winter season (November to March) but not for Fluvial Agriculture and Supra-Till Forest soils.

Soil waters had significantly different soil waters nutrient concentrations among nutrients and oxyhydroxide elements. Fluvial Agriculture soils had significantly higher average soil water Ca concentrations (171 ± 35 μg g^{-1}) than Sub-till Hydric soils (83 ± 11 μg g^{-1}) and Supra-Till Forest soils (43 ± 6 μg g^{-1}) ($p < 0.05$, Fig. 3). Fluvial Agriculture soils had significantly higher soil water K concentrations (26 ± 6 μg g^{-1}) than Sub-till Hydric soils (10 ± 1 μg g^{-1}) and Supra-Till Forest soils (9 ± 2 μg g^{-1}) (Fig. 3). Fluvial Agriculture soils had significantly higher soil water P concentrations (129 ± 21 ng g^{-1}) than Sub-till Hydric soils (37 ± 11 ng g^{-1}) and Supra-Till Forest soils (28 ± 5 ng g^{-1}) ($p < 0.05$, Fig. 3). Nutrient concentrations in soil water did not appear to have any seasonality, unlike Zabowski and Ugolini (1992). Examining oxyhydroxide elements, there were different patterns among the three subwatersheds. Lysimeter soil water Al concentrations were not significantly different among the subwatersheds ($p < 0.05$, Fig. 3). Sub-till Hydric soils had significantly higher soil water Fe concentrations (1684 ± 386 ng g^{-1}) than Fluvial Agriculture soils (946 ± 267 ng g^{-1}) and Supra-Till Forest soils (261 ± 45 ng g^{-1}) ($p < 0.05$, Fig. 3). Fluvial Agriculture soils had significantly higher soil water Mn concentrations (1249 ± 404 ng g^{-1}) than Sub-till Hydric soils (449 ± 63 ng g^{-1}) and Supra-Till Forest soils (199 ± 56 ng g^{-1}) ($p < 0.05$, Fig. 3). Soil water Fe and Mn appeared to have higher concentrations during the growing season (April to September).

3.3. River water concentrations

River water had significantly different pH and DOC patterns among the three subwatersheds. Average river water pH was not significantly different between the Supra-Till Forest soil watershed (pH 7.11 ± 0.11) and Fluvial Agriculture watershed (pH 6.90 ± 0.10) but was significantly lower for the Sub-till Hydric soils (pH 6.62 ± 0.13) ($p < 0.05$, Fig. 4). River water DOC was significantly higher in the Sub-till Hydric watershed (64 ± 22 mg kg^{-1}) than the Fluvial Agriculture watershed (13 ± 5 mg kg^{-1}) and the Supra-Till Forest watershed in between at (3.3 ± 0.6 mg kg^{-1})($p < 0.05$, Fig. 4). The differences among pH and DOC did not exhibit any seasonality.

River water nutrient and oxyhydroxide concentrations were significantly different among the three subwatersheds. Fluvial Agriculture watershed had significantly higher average Ca river water concentrations (24 ± 8 μg g^{-1}) than Sub-till Hydric watershed (13 ± 4 μg g^{-1}) and also Supra-Till Forest watershed (5 ± 2 μg g^{-1}) ($p < 0.05$, Fig. 4). Fluvial Agriculture watershed had significantly higher K river water concentrations (2.3 ± 1.2 μg g^{-1}) than Sub-till Hydric watershed (0.9 ± 0.4 μg g^{-1}) and Supra-Till Forest watershed (0.8 ± 0.3 μg g^{-1}) ($p < 0.05$, Fig. 4). Fluvial Agriculture watershed had significantly higher P river water concentrations (29 ± 16 ng g^{-1}) than Sub-till Hydric watershed

Table 4
Average soil pseudototal macronutrients and oxyhydroxide element concentrations across the subwatersheds, using strong acid digestion. Values are shown with ± 1 standard error.

	Horizons	Ca_{ptotal}	K_{ptotal}	P_{ptotal}	Al_{ptotal}	Fe_{ptotal}	Mn_{ptotal}
		g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}	mg kg^{-1}
Supra-Till	Oe + Oa	1.38 ± 0.24	0.98 ± 0.22	0.50 ± 0.09	11 ± 2	6 ± 3	0.13 ± 0.01
Forest	E	0.94 ± 0.34	1.28 ± 0.55	0.26 ± 0.11	10 ± 4	25 ± 6	0.17 ± 0.06
	Bhs	0.87 ± 0.24	1.83 ± 0.38	0.51 ± 0.08	16 ± 2	38 ± 7	0.18 ± 0.03
	BC	0.61 ± 0.19	1.53 ± 0.27	0.67 ± 0.06	14 ± 3	30 ± 2	0.19 ± 0.02
Fluvial	Ap	2.59 ± 0.77	1.75 ± 0.25	1.46 ± 0.16	16 ± 1	29 ± 2	0.61 ± 0.10
Agriculture	B	1.42 ± 0.22	1.57 ± 0.19	1.14 ± 0.13	16 ± 1	28 ± 4	0.59 ± 0.12
	Bw1	1.46 ± 0.13	1.77 ± 0.18	0.92 ± 0.12	15 ± 2	28 ± 2	0.41 ± 0.08
	Bw2	1.27 ± 0.11	1.73 ± 0.09	0.67 ± 0.04	13 ± 1	25 ± 4	0.26 ± 0.06
	C	1.22 ± 0.21	2.23 ± 0.31	0.62 ± 0.03	18 ± 3	34 ± 5	0.46 ± 0.05
Sub-Till	Oa	0.15 ± 0.08	0.09 ± 0.04	0.05 ± 0.03	5 ± 2	8 ± 5	0.08 ± 0.03
Hydric	Ap	0.32 ± 0.07	0.39 ± 0.14	0.22 ± 0.03	15 ± 2	28 ± 1	0.16 ± 0.04
	Bw	0.57 ± 0.06	0.42 ± 0.14	0.19 ± 0.01	24 ± 7	31 ± 5	0.15 ± 0.02
	Bg	0.52 ± 0.05	0.39 ± 0.11	0.18 ± 0.02	28 ± 5	32 ± 3	0.18 ± 0.02
	Cd	0.64 ± 0.02	0.92 ± 0.17	0.16 ± 0.01	16 ± 4	25 ± 7	0.17 ± 0.03

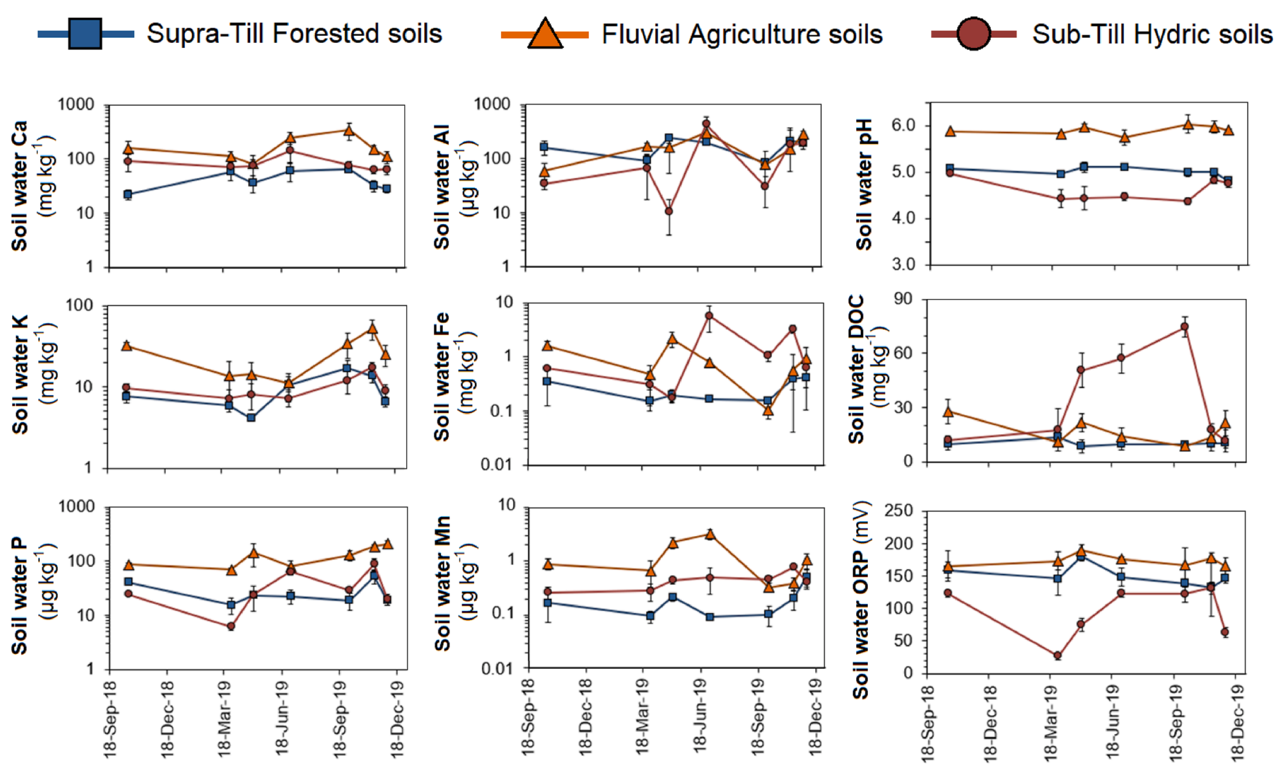

Fig. 3. Soil lysimeter ORP, pH, soil water nutrients, and soil water oxyhydroxide elements through time. Error bars are standard error of triplicate soil water samples from each lysimeter. Soil water samples were filtered < 0.45 µm.

(6.4 ± 3.5 ng g^{-1}) and Supra-Till Forest watershed (4.7 ± 2.3 ng g^{-1}) ($p < 0.05$, Fig. 4). Overall, river water nutrient concentrations did not appear to have clear seasonality. River water Al concentrations were not significantly different among the subwatersheds ($p < 0.05$, Fig. 4). Sub-till Hydric watershed had significantly higher Fe river water concentrations (171 ± 44 ng g^{-1}) than Fluvial Agriculture watershed (73 ± 30 ng g^{-1}) and Supra-Till Forest watershed (20 ± 11 ng g^{-1}) ($p < 0.05$, Fig. 4). Fluvial Agriculture river waters had significantly higher Mn concentrations (115 ± 54 ng g^{-1}) than Sub-till Hydric (16 ± 9 ng g^{-1}) and Supra-Till Forest (2 ± 1 ng g^{-1}) river waters ($p < 0.05$, Fig. 4). Oxyhydroxide elements concentrations trends did not appear to have clear seasonality.

3.4. River export

River water export for the watersheds were examined two ways, first on a mass per year basis to quantify total contributions of soils across the entire watershed and again as a mass per year per area basis to determine the relative role of soil on river water export but normalizing across watershed size. River water export of nutrient and oxyhydroxide elements scaled with the size of the watershed; DOC, Ca, K, P, Al, and Fe were greatest for the larger Supra-Till Forest watershed, which is over an order of magnitude larger than the other two watersheds (Table 5). Interestingly though, total river water DOC and Fe export was greater for the smaller Sub-till Hydric watershed than the larger Fluvial Agriculture watershed (Table 5). Further, total river water Mn export was greater the Fluvial Agriculture watershed than the Sub-till Hydric watershed or the Supra-Till Forest watershed (Table 5).

When scaled per unit area, area-normalized river water export yielded different results. First when considering nutrients, area-normalized river water Ca, K, and P export was greatest for the Fluvial Agriculture watershed (Table 5). Area-normalized river water Ca export was as great

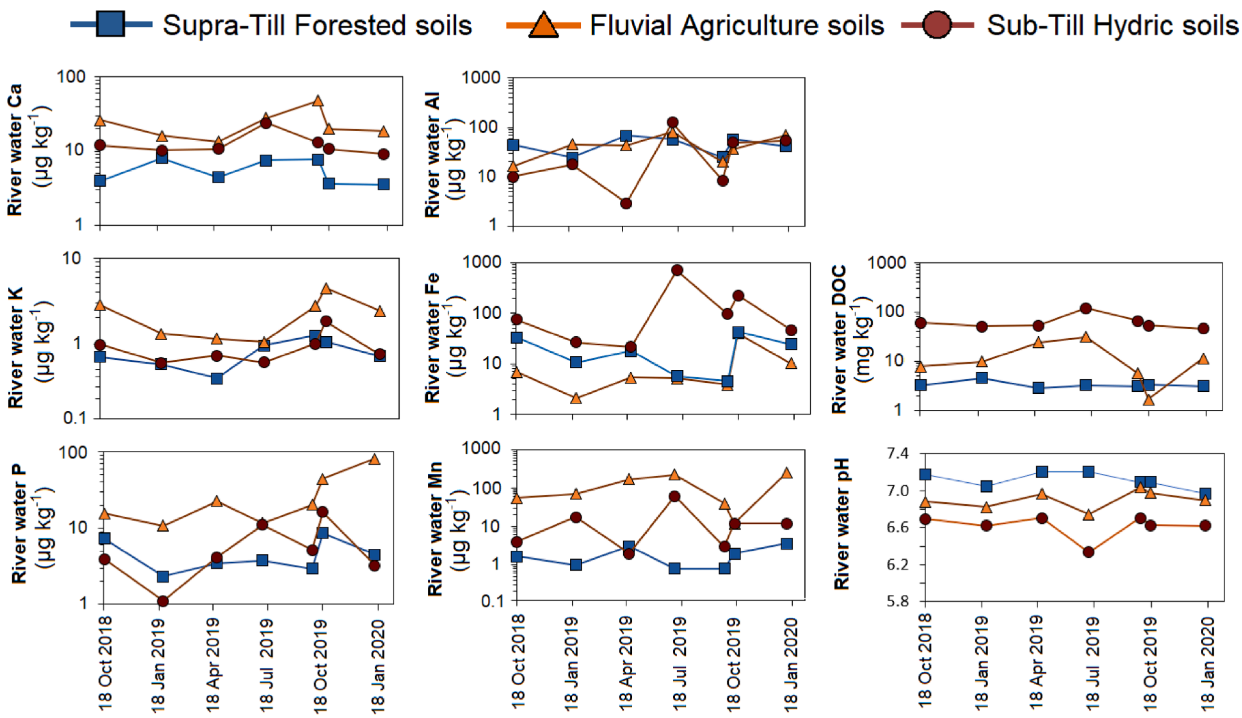

Fig. 4. River water pH, DOC, nutrients, and oxyhydroxide elements. River water samples were filtered < 0.45 µm.

Table 5
Total river water nutrient and oxyhydroxide element export rates from September 2018 to August 2019 using monthly average dissolved concentrations and monthly average discharge. Area-normalized river water export rates are also presented below, which were calculated using the total river water exports normalized to the total area for the watersheds.

Subwatershed	Total water Discharge	DOC	Ca	K	P	Al	Fe	Mn
	$km^3\ yr^{-1}$	$Mg\ yr^{-1}$	$Mg\ yr^{-1}$	$Mg\ yr^{-1}$	$Mg\ yr^{-1}$	$Mg\ yr^{-1}$	$Mg\ yr^{-1}$	$Mg\ yr^{-1}$
Supra-Till Forest	0.0559	187	309	45	0.26	2.5	1.12	0.10
Fluvial Agriculture	0.0034	45	83	10	0.10	0.15	0.25	0.39
Sub-Till Hydric	0.0024	154	31	2	0.02	0.09	0.41	0.04
	Total area	DOC	Ca	K	P	Al	Fe	Mn
	km^2	$Mg\ yr^{-1}\ km^{-2}$	$kg\ yr^{-1}\ km^{-2}$	$kg\ yr^{-1}\ km^{-2}$	$kg\ yr^{-1}\ km^{-2}$	$kg\ yr^{-1}\ km^{-2}$	$kg\ yr^{-1}\ km^{-2}$	$kg\ yr^{-1}\ km^{-2}$
Supra-Till Forest	81.8	2.3	3770	546	3.1	31	14	1.3
Fluvial Agriculture	5.4	8.2	15,230	1761	18.5	28	46	72.4
Sub-Till Hydric	3.9	39.7	7940	570	4.0	24	106	9.9

for Sub-till Hydric watershed than the Supra-Till Forest watershed (Table 5). The area-normalized Al export was similar among the three watersheds. However, area-normalized river water Fe and DOC export was greatest for the Sub-till Hydric watershed than Fluvial Agriculture watershed, which was also higher than Supra-Till Forest soil (Table 5). Lastly, area-normalized river water Mn export for the Fluvial Agriculture watershed was nearly an order of magnitude greater than the Sub-till Hydric watershed and nearly-two orders of magnitude greater than the Supra-Till Forest watershed (Table 5).

4. Discussion

4.1. Soil nutrient storage and export

The first hypothesis was that the Fluvial Agriculture soils would have the highest soil storage and river export of nutrients than Supra-Till Forest and Sub-till Hydric soils. The soil exchangeable and pseudototal concentrations results showed significantly higher nutrient concentrations in the epipedons and upper subsurface horizons in the Fluvial Agriculture soils than the Supra-Till Forest and Sub-Till Hydric soils. Considering the physicochemical properties of the Fluvial Agriculture soils, one would expect the low SOM (<1.0 mg g^{-1}) and clay content (<4%) to limit the accumulation of nutrients (Arshad and Coen, 1992). Thus, it is suspected the human addition of soluble nutrients via chemical fertilizers (see Chien et al., 2011), liming agrominerals (Tyler and Olsson, 2001; Murphy and Stevens, 2010), and the resulting higher soil pH surpassed levels obtained by natural soil development (e.g. Bauhus and Barthel, 1995) and biological uplift by forests and hydric plant communities (e.g. see Kraepiel et al., 2015). Terrestrial eutrophication and eutric soils has been long known, such as plaggen (see Blume and Leinweber, 2004), but the implications have been predominantly with respect to sustaining intensive agriculture (see Pospíšilová et al., 2011). The Fluvial Agriculture soils of this study have been cleared and farmed since 1677 CE. Plaggen soils are uncommon in modern intensive agriculture in the New England region.

Interestingly, the Sub-till Hydric soils had comparable or significantly higher exchangeable Ca, K, and P concentrations than the Supra-Till Forest soils but conversely had significantly lower pseudototal Ca, K, and P concentrations. It could be hypothesized the higher %Clay and % SOM may provide greater sorption capacity of exchangeable nutrients on exchange sites and weak organic complexes in the Sub-Till Hydric soils while Supra-Till Forest soils had nutrients in oxyhydroxides, strong organic complexes and other non-exchangeable phases irrespective of pH (Ross et al., 2008; Bourgault et al., 2017; Faulkner and Richardson, 2020). Furthermore, these results suggest that U.S. soil taxonomic systems for classifying low nutrient abundance using exchangeable nutrients may be missing the larger pool of non-silicate nutrients in forest soils. This is converse to common great group U.S. Taxonomic names given to many Spodosols and intensively weathered Inceptisols in the northeastern United States with low exchangeable nutrients (Dahlgren et al., 1989; Reuss et al., 1990), such as Typic Haplorthods and Dystrudepts that occur as map unit complexes and associations.

In the second part of the first hypothesis, it was presumed that Fluvial Agriculture soils would also have higher transport rate of nutrients from soils to river water due to human addition of soluble phases. The significantly higher soil water, river water concentrations, and area-normalized river water export of Ca, K, and P confirm this hypothesis. Comparing average Fluvial Agriculture soil water to average Supra-Till Forest soil water, intensive agricultural practices had higher soil water Ca by 3.0x, K by 1.9x, and P by 3.5x. Furthermore, Fluvial Agriculture river water nutrient concentrations further confirm the higher concentrations for Ca of 3.8x, K of 1.9x, and P of 5.2x compared with Supra-Till Forest river water. As previously mentioned, the addition of animal manures, bone meal, soluble chemical fertilizers, and liming agrominerals since 1677 CE have substantially increased the Fluvial Agriculture soils with inorganic nutrients compared to natural chemical weathering under forest environments. It was possible that the greater depth of the geologic deposits and potentially higher clay content of the deeper stratified glaciofluvial deposits in the Fluvial Agriculture watershed could increase nutrient capture compared with the thinner, coarser glacial till present in the Supra-Till Forests and Sub-Till Hydric subwatersheds but this was not the case. Moreover, the higher river water pH compared with soil water pH suggests potential consumption of the acidity by mineral weathering during water movement from the soil profile through shallow groundwater to the river (see Rhodes et al., 2001). In addition, the watershed area-normalized river export rates were greater for the Fluvial Agriculture soils than Supra-Till Forest soils for Ca by 3x, K by 2x, and P by 5x. On the basis of exchangeable soil concentrations, soil water concentrations, river water concentrations, and watershed area-normalized river export rates, Fluvial Agriculture soils are substantially larger stores of nutrients and mobile phases of nutrients and these human managed terrestrial agroecosystems may serve as major contributors to surface waters and aquatic ecosystems. These results are in strong agreement with previous studies noting humans enhancing terrestrial nutrient loading to aquatic ecosystems in temperate ecosystems of the northeastern U.S. (e.g. Rhodes et al., 2001; Piatek et al., 2009).

The mobility of the nutrients does not appear to be tied to DOC as higher DOC export in the thinner, Sub-Till Hydric soils than the Fluvial Agriculture soils. This disconnect between soil water, river water, and area-normalized export of nutrient and DOC further implies human land cover controls on nutrients in the Fluvial Agriculture subwatershed. Interestingly, soil water DOC was generally comparable between Supra-Till Forest and Fluvial Agriculture soils but river water DOC concentrations were much higher for Fluvial Agriculture than Supra-Till Forest. This disconnect suggests that additional soil to river transport or other river properties are limiting DOC export in forest soils. Potential processes include differences in internal decomposition/mineralization (unlikely according to Jandl and Sletten 1999), adsorption/complexation to soil minerals (more likely according to Sanderman and Amundson, 2008; Rumpel and Kögel-Knabner, 2011; Bourgault et al., 2017), or agricultural soils are more effective conduits from soil to river (which disagrees with Sanderman and Amundson, 2008 who found the opposite in California and Rhodes et al., 2001 who studied the smaller, adjacent Mill River watersheds in western Massachusetts). Furthermore, pH appeared to also be partly disconnected as soil pH was lowest in the Supra-Till Forest and Sub-Till Hydric soils between 4.4 and 5.1 pH but Supra-Till Forest river water had the highest pH between 6.8 and 7.2 and Sub-Till Hydric river water increased in pH up to 6.3 to 6.7. River water pH was expected to be highest in the Fluvial Agriculture subwatershed due to liming but the intensive weathering and low DOC content in the Supra-Till Forest likely drove the pH much higher. The pH increase in the Supra-Till Forest and Sub-Till Hydric river water may also reflect near surface of bedrock fracture dissolution of carbonate minerals present in Waits River formation and the Goshen Formation (e.g. Armfield et al., 2019; Jordan et al., 2019).

When considering total river water exports, the larger source of Ca, K, and P to the Deerfield watershed is the Supra-Till Forest subwatershed due to the larger volume of discharge water than the two other subwatersheds (Table 5). Since forest soils developed on glacial till are the most abundant land cover and not agricultural farmland atop fluvial deposits, this means that chemical weathering within forest soils at the watershed-scale is the dominant process in nutrient release to the Deerfield River. However, the high nutrient output from Fluvial Agriculture soils are likely to impact localized systems with lower flushing rates, such as ponds, lakes, reservoirs, and aquifers, but not affect larger rivers such as the Deerfield River. Excess nutrient export from Fluvial Agriculture soils has the potential to further degrade surface waters through eutrophication by PO_4^{-3}. River water P measured in this study was comparable or lower than values reported by Garabedian (1998) for the main Connecticut River in 1992 through 1995 of 10 to 100 μg kg^{-1}, suggesting improvements in nutrient capture, agricultural soil management, and wastewater management (see Faulkner and Richardson, 2020).

There are several limitations regarding the methods and findings linking nutrient storage and transport between soils and rivers. First, subsurface transport from soils to rivers were not quantified but qualitatively inferred. Thus, soil nutrients may have varying subsurface transport rates to rivers and the influence of deeper groundwater on rivers were not evaluated, despite their potential effects on nutrients in river water. Second, storage in soils was also qualitatively inferred from quantitative exchangeable and strong acid extractable concentrations. The mobility of nutrients within the strong acid extractable fractions may be transported from soils to rivers on the multi-annual or multi-decadal time scales. Lastly, the temporal and spatial resolution of soil sampling, soil water collection, and river water sampling were coarse and may have missed point sources and large events. Despite these limitations, we have assembled a first approximation on nutrient storage and movement within the watershed and its linkages with coupled surficial geology and land cover.

4.2. Oxyhydroxide elements storage and export

In the second hypothesis, it was postulated that Sub-till Hydric soils would have lower soil storage and highest river export of Mn and Fe due to more prevalent soil water reducing conditions than in Supra-Till Forest and Fluvial Agriculture soils. The results largely reject that Sub-till Hydric soils had lower soil storage of Mn and Fe. Exchangeable Mn and Fe soil concentrations were greater for Sub-till Hydric soils than for Supra-Till Forest soils and comparable with Fluvial Agriculture soils (Table 3). Moreover, pseudototal Fe soil concentrations were overall comparable across the three soil catenas but Mn was greater in Fluvial Agriculture soils compared to Sub-till Hydric soils and Supra-Till Forest soils. Sub-till Hydric soil water was more acidic, had higher DOC, and lower ORP values which should promoted greater Mn and Fe solubility and leaching but did not result in lower storage. One potential explanation is the formation of Mn and Fe oxyhydroxide nodules or sulfide phases in the Sub-till Hydric soils, allowing for comparable storage. As noted by Garrels and Christ (1965) and Vepraskas et al. (2012), reduced Fe^{+2} which is considered more mobile than oxidized forms of Fe^{+3} can be accumulated in nodules, concretions, masses, and pore linings due to oxygen from roots or isolated bubbles but can also be stored as FeS_2 or FeS in microsites within the profile (e.g. Hodges et al., 2019). Further, the formation of Mn and Fe oxyhydroxides may not have been as abundant in the Spodosols of Supra-Till Forest soils as hypothesized based upon its color.

A particular point of interest for Mn was the significantly higher exchangeable and pseudototal soil concentrations, soil water, and river water in the Fluvial Agriculture soils than the Supra-Till Forest and Sub-till Hydric soils. Fluvial Agricultures were expected to have lower Mn concentrations than Supra-Till Forest and Sub-till Hydric soils as Mn in soil is typically associated with clay content and SOM (Kabata-Pendias and Mukherjee, 2007; Santos and Herndon 2022). This study suggests that soil amendments, specifically liming agrominerals and synthetic fertilizers, have likely enhanced the abundance of Mn in the Fluvial Agriculture subwatershed either as a micronutrient on purpose or as a consequence of Mn substituted for Ca within carbonates used for soil liming (Prasad and Sinha 1982). One implication is that Mn is a micronutrient for plant photosynthesis, cellular respiration, fatty acid and protein synthesis, and enzyme activation (Li et al., 2019). The build-up of Mn in the soil suggests that crop nutritional needs are being met and excess Mn is being added to the soil. Manganese can become excessive and toxic for plants and disrupt many biochemical processes (Li et al., 2019), particularly when the ratio of Mn to Ca impedes Ca-based functions (Richardson, 2017). The other implication is that Mn may substantially alter how nutrients are retained, particularly P, and soil C may be sequestered in the soil. Manganese affects soil C storage by mediating reactions of litter decomposition and forming more recalcitrant organo-mineral interactions (Li et al., 2021).

Aluminum was not significantly different in the reservoirs of exchangeable and pseudototal soil concentrations and also not significantly different in comparisons of transport via soil water and river water concentrations among the three subwatersheds. It is hypothesized that the main processes governing Al biogeochemistry, weathering release, precipitation, and limited biological cycling (Cronan et al., 1990), were similar enough in the Supra-Till Forest soils, Sub-till Hydric soils, and Fluvial Agriculture soils that significant differences did not occur. This is particularly interesting as factors which control Al solubility in soil water and river water, such as acidity and DOC (Gruba and Mulder 2008), were nearly at or over a magnitude higher in the Sub-till Hydric soil than the Fluvial Agriculture and Supra-Till Forest. Lastly, this may imply that weathering of aluminosilicates were comparable in acidic forest and wetland soils as well as in agricultural fields and when examined at the watershed scale but could be impacted by unconstrained differences in soil parent material and hyporheic effects controlling soils to river transport of soluble Al compounds.

Similar to nutrients, there are several limitations regarding the methods and findings linking Al, Fe, and Mn storage and transport between soils and rivers. First, subsurface transport from soils to rivers were not quantified but qualitatively inferred. Second, the solubility and precipitation of oxyhydroxides were not evaluated and the transport of oxyhydroxide elements as colloids, nanoparticles, and organometallic complexes were not evaluated in this study and may greatly enhance the transport of Al, Fe, and Mn with respect to their expected overall solubility (e.g. Hassellov and von der Kammer 2008).

5. Conclusions and implications

This study found that agriculture in glaciofluvial soils had higher soil storage and river water export of nutrients (Ca, K, P) in the Fluvial Agriculture soil *catena* subwatershed compared with the Supra-Till Forest soils and Sub-till Hydric soils. The 1.9x to 5.2x higher in the Fluvial Agriculture soils of nutrients, particularly P, can lead to eutrophication in water bodies with low flushing rates, such as lakes, ponds, and aquifers. Conversely, the nutrient concentrations in the Spodosols of the Supra-Till Forest soils and the acidic, DOC-rich soil waters of the Sub-till Hydric soils suggest the ecosystems do not appear to be limiting for their respective forest canopies. Supra-Till Forest subwatershed is 16x larger than the, Fluvial Agriculture subwatershed and, when considered non-normalized to area, exported 5x the amount of Ca, 5x the amount of K, and 2.6x the amount of P as the Fluvial Agriculture subwatershed. When considered with area-normalized basis, it is clear the Fluvial Agriculture soils are exporting 3x to 6x the amount of nutrients than the Supra-Till Forest and Sub-Till Hydric soils. This is further evidence that small agricultural watersheds can have large impacts on the geochemistry and eutrophication of watersheds.

When considering the oxyhydroxide elements, there were several key points observed. First, Al was not significantly different in soils, soil water, and river water across the different land-uses. This implies that weathering rates and formation of solid Al phases are not substantially different or have not been increased by land-uses. Second, Fe was not significantly lower in the Sub-till Hydric soils and soil water than the Supra-Till Forest soils; thus, the higher acidity, higher DOC concentrations, and lower ORP did not cause lower soil storage of Fe. However, the Sub-till Hydric subwatershed also had higher acidity and higher DOC concentrations with higher river water Mn and Fe supporting the hypothesis of reducing conditions enhancing transport of Mn and Fe in the watershed. Shallow pathways or small soil volume allowing for Fe storage may have allowed for comparable Mn and Fe concentrations in the soil solid phase while generating higher Fe in soil water and river water across the subwatersheds. Lastly, Mn was enriched in the Fluvial Agriculture soils, potentially due to chemical fertilizers, animal manures, or liming agrominerals. The relatively high abundance of Mn in the agricultural soil was unexpected and unreported in agricultural fields of New England, with potential impacts on soil C dynamics or microbial communities.

Conflict of Interest.

This study was funded by the College of Natural Sciences at the University of Massachusetts Amherst to Dr. Justin Richardson (2018–001).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data is housed in a repository.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catena.2023.107174.

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