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Accumulation and transport of nutrient and pollutant elements in riparian soils, sediments, and river waters across the Thames River Watershed, Connecticut, USA

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ABSTRACT

Understanding drivers of nutrient and pollutant elements (NPEs) in soils, sediments, and river water is important for protecting water resources and aquatic ecosystems. The objectives of this study were to quantify accumulation and transport of NPEs (P, As, Cd, Cu, Ni, Pb, and Zn) in riparian soils, sediments, river water, and watershed-scale exports within seven post-industrial subwatersheds of the Thames River, Connecticut, USA. Suspended sediments and river water samples were collected from February 2019 to January 2020. Arsenic concentrations in soil (6 to 18 mg kg^{-1}) and sediments (8 to 85 mg kg^{-1}) generally exceeded state and federal EPA quality targets but not river water. Elevated Pb 'hot spots' occurred in some riparian soils (>2000 mg kg^{-1}) and sediments (>200 mg kg^{-1}), but the other NPEs concentrations were below toxic thresholds. Riparian soil concentrations and watershed land cover were generally weak predictors for NPE concentrations in bottom sediments, suspended sediments, and river water. DOC, Mn, and Fe concentrations were important predictors for area-normalized dissolved and sediment-bound export of NPEs across the seven watersheds. Dissolved export was greater than sediment export for Mn, P, As, Cd, Cu, and Ni but not for Fe, Pb, and Zn. Watersheds with higher farmland had higher P river water concentrations, but the larger, more urbanized watershed had the highest total and area-normalized P export. An estuarine sediment core that captures sediment from the whole watershed and spans pre-industrial conditions through present shows that export of most NPEs has decreased since its peak, but all remain above baseline throughout the Thames River watershed. Future constraints on surface soil-river exchange and erosion inputs are needed to investigate rates of NPE sourcing to the watersheds.

1. Introduction

Nutrient and pollutant elements (NPEs) such as As, Cd, Cu, P, Pb, Ni, and Zn have been enriched in terrestrial and aquatic ecosystems due to anthropogenic activities beyond background natural weathering. Understanding their abundance and mobility is important for protecting water resources and freshwater and marine ecosystems. NPE pollution from terrestrial systems can negatively impact the health and growth of fish and bivalves in aquatic ecosystems, especially if the elements are enriched in water or sediments or if they are able to bioaccumulate through the food web (e.g. Wang et al., 2013; Zhang et al., 2020; Haghnazar et al., 2023). For example, shellfish aquaculture in SW England has been negatively impacted by Cu from historical pollution and natural deposits (Webber et al., 2021). In addition, excessive nutrients such as P can stimulate eutrophication, resulting in algae bloom, oxygen depletion, killing organisms, and causing thousands to millions of dollars in damages and lost economic opportunities (Dodds et al., 2009; Casey et al., 2014; Beusen et al., 2022). Most infrastructure, domestic use, and regulatory work to limit NPE has focused on limiting point source pollution (e.g. Ribaudo, 2001) or areas where modern trace element pollution is occurring such as cities and industrial parks (e.g. Marsalek and Chocat, 2002; Sen et al., 2013; Feng et al., 2020). However, areas with historical legacy or non-point sources of element pollution can also drive potentially hazardous concentrations of trace

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elements in aquatic ecosystems. As a neighboring example, the Blackstone river has elevated As and Pb from pesticides and metal smelting and excessive point source P from agriculture that exceeded 200,000 kg yr^{-1} in 2004 (Mangarillo et al., 2005). For example, Mussels and oysters in the North and South Bays in Santa Catarina, Brazil had accumulated As, Cu, and Ni concentrations despite limited point sources within proximity to the mariculture, but were below maximum regulatory limits (De Souza et al., 2016).

Riparian soils and river bottom sediments provide ecosystem service of sequestration of toxic elements (Harris, 1997; N'Guessan et al., 2009; Audry et al., 2010; Haghnazar et al., 2023). Organic matter (OM) and macroelements in the form of oxyhydroxides (e.g. Fe and Mn) can increase the capacity for capturing and sequestering NPE pollution in riparian soils and river bottom sediments (e.g. Tessier, 2003; N'Guessan et al., 2009; Audry et al., 2010; Jiann et al., 2013; Yan et al., 2022). As a prime example, Pavlović et al. (2016) found riparian soils, particularly in forested areas, had sequestered As and other trace elements sourced from natural weathering, industrial pollution, and mining activities. Overland flow from and erosion of riparian soils in agricultural and peri-urban areas can mobilize NPE (Zhang and Wang, 2020; May et al., 2023), contributing to the contaminant load of the river. Thus, considering the current land-use is potentially a key factor for evaluating terrestrial soils as sources. In addition, NPEs can be released from temporary storage within wetlands, riparian soils, or impoundments following dam removal (Dow et al., 2020) and also can result from changes in natural and human-driven flow rate and shifts in sedimentation (Ashley et al., 2006; Chon et al., 2012; Tripathi et al., 2014; Yan et al., 2022). Furthermore, leaching and subsurface lateral flow act to transport dissolved trace elements from riparian zones to streams but is difficult to quantify as hyporheic flow and transport of trace elements due to variable flow direction and quantity (Boano et al., 2014; Liu et al., 2020; May et al., 2023). Water parameters such as dissolved organic carbon (DOC) and acidity can promote the soluble transport of NPEs, which can vary due to land-use within a watershed (Vidon et al., 2008). Furthermore, sediments can be important mechanisms for nutrient transport, specifically P, from agricultural sources and is dependent on precipitation runoff and subsurface inputs from soils and riparian zones (e.g. May et al., 2023).

The Thames River and its watershed of eastern Connecticut and southern Massachusetts is one of three major inputs of NPE to Long Island Sound (Breault and Harris, 1997; Richardson et al., 2022), which is home to economically and culturally important fisheries that provide the regional economy millions of dollars in revenue from bivalves, decapods, and fish (CT DEEP, 2019). The Thames River, like many rivers of the eastern United States, has historical point sources as well as and modern non-point sources of trace element pollution. During the 1700s to 1800s, the Thames River watershed had tanneries and paper mills, which have been historical sources of a suite of metals (Larned, 1899; Klotz, 1977; Colombo et al., 2004). More recently, trace elements have been sourced from non-point sources such as automobiles, roadways, industrial activities, metal smelting, waste water, septic fields, and large agricultural operations (Klotz, 1977; Nikolaidis et al., 1994; Colombo et al., 2004; Gilbert and Clausen, 2006; Richardson et al., 2015).

The three primary objectives of this study were: (1) quantify trace elements sequestered in riparian soils and river bottom sediments, (2) assess current trace element transport in dissolved phases and on suspended sediments, (3) evaluate watershed-scale NPE exports within the Thames subwatersheds to evaluate potential land-cover controls. Our three objectives were examined with respect to three potential drivers: (A) physicochemical properties (pH, organic matter, Fe, Mn) driving sequestration or transport, (B) current land cover (examined through development, farmland, wetland, and forest land cover) driving accumulation of higher concentrations, and (C) higher NPE concentrations in soils and bottom sediments driving higher river water transport and watershed-scale export. For our suspected driver of NPE contamination, we hypothesized that riparian soils and bottom sediments sequestration of trace elements would be related to physicochemical properties such as organic matter, Fe, Mn, or particle size driving variations in NPE concentrations. For the second hypothesis, it was assumed that dissolved and suspended sediment transport of NPEs is driven by current land cover of urban, developed areas but could potentially be related to forested catchments with historical pollution, or from agricultural areas. Lastly, we expected that watershed scale NPE export would be controlled by river water properties (specifically dissolved organic carbon (DOC) and OM, Fe concentrations, and concentrations of the element of interest) and linked again with current land cover properties of the watershed. The information can be used to help evaluate the need for greater riparian soil management and for evaluating the ecotoxicological threat of historical and modern pollution sources to the Thames River watershed and Long Island Sound.

2. Material and methods

2.1. Subwatersheds of the Thames River

The Thames River Basin (3817 km^2) covers eastern Connecticut (CT) (79 % of the total watershed), southcentral Massachusetts (17 % of the total watershed), and a small portion of western Rhode Island (4 % of the total watershed) (Fig. 1). Although the Thames River drains a large area, the Thames River itself is only 24 km long and entirely comprised of a bedrock-bound tidal estuary with brackish waters. Thus, we focused on the freshwater subwatersheds that drain much of the Thames River basin: the Shetucket, Yantic, and Quinebaug rivers. The terrain of the three watersheds is generally hilly, with glacial features of eskers, drumlins, and kettle lakes as well as surface geologic deposits of outwash plains, glacial till, and deltaic deposits. According to the Köppen climate classification, the climate in the Thames River watersheds straddles the border for Dfb and Dfa, which is humid continental, with hot summers and consistent precipitation throughout the year. The Thames River watersheds' bedrock geology are generally metamorphic rocks of the Merrimack synclinorium, comprised of the Hebron gneiss, Brimfield schist, and Tatnic Hill formations (Rodgers, 1980). Upland soils are predominately shallow, rocky glacial till, while lowlands are coarse and fine stratified drift, or modern fluvial materials in current and prior drainage paths. Most soils are Inceptisols derived from glacial till or reworked glaciofluvial materials with weak to moderate surface horizon development due to historical deforestation and agricultural conversion to pastures or croplands. Spodosols are uncommon but present in rocky, less disturbed forests. Land cover, urbanization, and historical industry vary among the various subwatersheds of the Thames River. We focused on some of these subwatersheds to examine the role of these extant and historical impacts on the watershed to evaluate the drivers of NPE and P abundances. We studied the two largest subwatersheds: Quinebaug and Shetucket, and five smaller subwatersheds that were higher proportions of specific land-covers: forested (Still River), human developed (French River), or agricultural (Bartlett and Exeter, Little River and Yantic River).

The Shetucket River is the largest subwatershed in the Thames River Basin at 1362 km^2 and is located in the central portion of the basin (Table 1). It contains four hydroelectric dams, within the urban center of Willimantic CT. Based upon the NCLD 2016 land cover data (Homer et al., 2020), it is largely forested at 969 km^2 (71 %), and moderately impacted by humans with 55 km^2 (4 %) developed land (See Supplemental Fig. 1 for NLCD 2016). We studied the Still River subwatershed in the northwestern portion of the Shetucket River to evaluate the NPE export from a representative largely unimpacted watershed. Of the subwatersheds in this study, the Still River was the least impacted, with only 1 % developed and 4 % farmland, and the remainder mostly in forest and wetland (Table 1).

The Quinebaug River is the second largest of the subwatersheds of the Thames River, spanning the entire eastern section of the basin, covering 1932 km^2. At 6 % developed, it is one of the more impacted

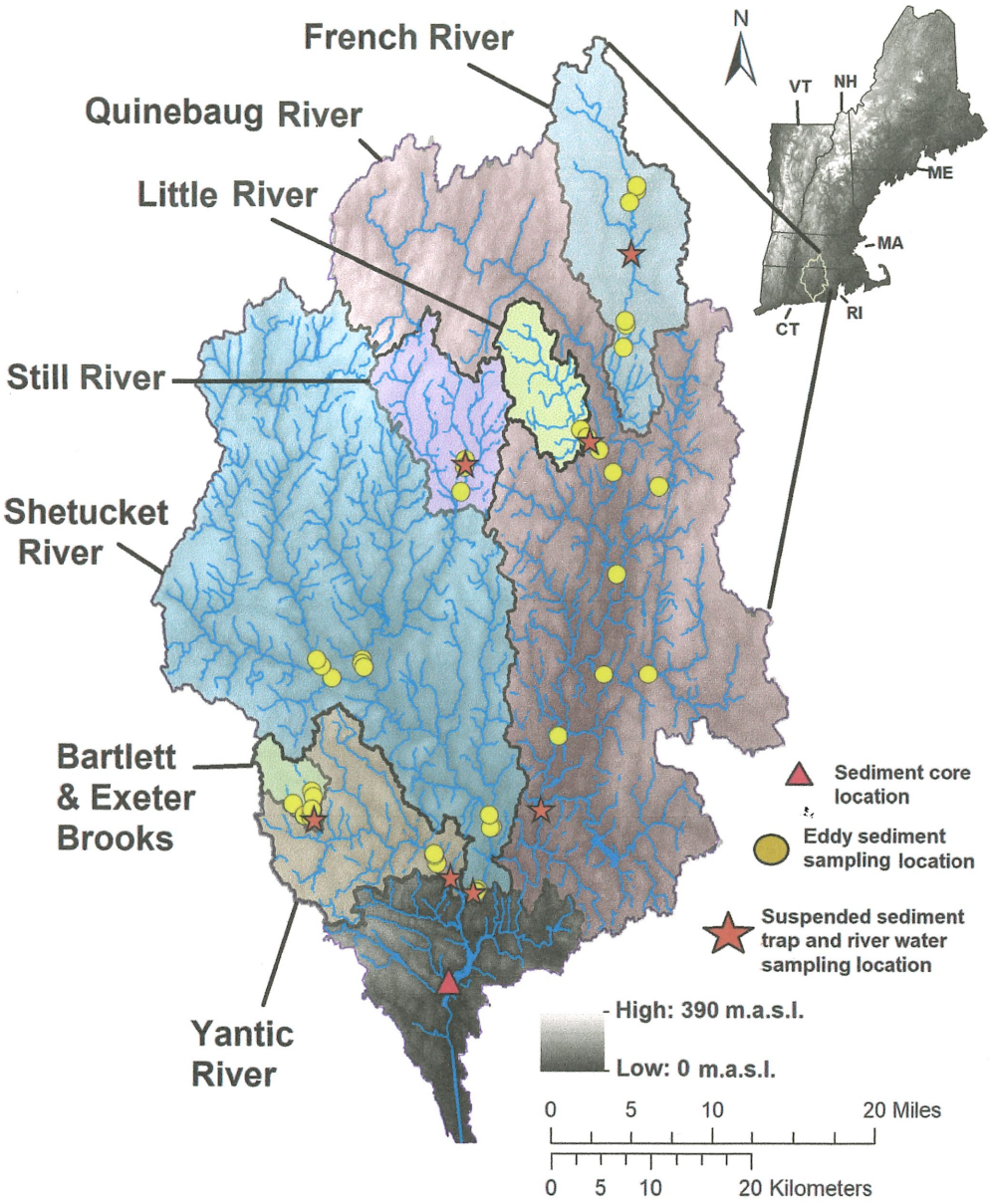

Fig. 1. Subwatersheds studied in Thames River watershed and locations of Eddy sediment, sediment trap, river water sampling, and sediment core collection locations.

Table 1
Subwatershed land covers based upon NLCD 2016 dataset (Homer et al., 2020). Forest includes deciduous, evergreen, and mixed forests. Farmland includes cultivated crops and pastures. Wetland includes woody and emergent herbaceous wetlands. Developed includes low intensity, medium intensity, and high intensity but not open space.

River	Total Area	Forest		Farmland		Wetland		Developed		Wastewater facilities
	km^2	%	km^2	%	km^2	%	km^2	%	km^2	
Bartlett and Exeter	37	67	25	10	4	13	5	2	1	0
French	261	58	151	7	11	12	30	11	28	2
Little	78	60	47	16	13	13	10	2	2	0
Quinebaug	1932	63	1217	7	135	14	270	6	116	12
Shetucket	1362	71	969	6	76	10	135	4	55	3
Still	143	75	108	4	6	11	16	1	1	0
Yantic	263	63	166	12	31	10	25	5	14	1

subwatersheds within our study area. Major impacts in the watershed include nine hydroelectric dams, and the urban centers of Plainfield CT, Putnam CT, Danielson CT, Oxford MA, Webster MA. Two subwatersheds of the Quinebaug were studied, the Little River and French River. The Little River has ongoing industrial activity and agricultural pollution. It has the lowest forested percentage (60 %) of our study's subwatersheds.

Conversely, the French River has historical industry and tanneries, but limited industry at present and only 7 % agricultural land. The Little River had the highest proportion of farmland (16 %). The French River had the highest proportion of development at 11 % and highest proportion of open water (6 %) from its ample ponds and lakes.

The Yantic River subwatershed is 263 km^2 and located in the southwestern portion of the Thames River basin. Based upon the NCLD 2016 land-use data, it is largely forested and moderately developed (Table 1). The Yantic subwatershed has the second highest proportion of farmland at 12 %. To investigate the impact of agriculture, we studied the Bartlett and Exeter Brooks in the northwestern corner of the Yantic watershed. Although Bartlett and Exeter Brooks have proportionally similar farmland as the overall Yantic watershed, they drain large agricultural operations, including the largest poultry farm of New England (Oyewumi et al., 2017).

2.2. Riparian soil, bottom sediment, and estuarine sediment core sampling and processing

Riparian areas were sampled at 27 locations within each of the seven watersheds by watercraft or land in the summer of 2019 (see Supplemental Fig. 2). In brief, forested areas in lowland depositional areas were selected along the main river channel using 2014 orthosatelite imagery. Riparian soil sampling sites were river banks that are or appeared to be controlled by river deposition and sites with human modifications present such as riprap, embankment rock, or concrete were rejected. Further, sites were forested with riparian trees and shrubs. Sites along ponds, lakes, reservoirs, and other standing water that allowed emergent macrophytes were not sampled as they are unlikely to be mobilized in non-extreme events. Soils were hand-augered down to six depth intervals: 0–5 cm, 5–10 cm, 10–15 cm, 15–20 cm, 20–25 cm, and 25 to 30 cm. Depths were checked using a custom levelling rod.

Bottom sediments were collected from 39 river pools across the seven watersheds in the summer of 2018 (3–7 samples per subwatershed). Pools were mapped for bottom sediments using 2014 orthosatelite imagery and confirmed in-person. A composite sample of three push probes (Inner Diameter 2.1 cm) down the top 10 cm was collected. As we were interested in NPE transport in association with mineral sediment, areas within abundant emergent, floating, and submerged macrophytes were avoided and samples with peat or other predominantly organic-rich material were rejected.

In order to place our modern observations in a longer historical context, we analyzed a sediment core from a low energy backwater location within the Thames River Estuary, which should contain a continuous record of sediment deposition. The sediment core was taken in Horton Cove in 1.7 m water near Uncasville (41.444256 N, −72.100877 W) using a vibracore on June 30, 2022. The top most unit (0–11 cm) had noticeable odor (H2S). The sediment core was sampled every 2 cm to a depth of 146 cm below the surface for percent organic content, grain size, and NPE abundance. Percent organic content was determined by loss on ignition (LOI) following procedures in Dean (1974), after which subsamples were run for grain size distribution on a Coulter Laser Particle Size Analyzer following procedures in Yellen et al. (2021).

All soil samples and sediment samples were air-dried. Mineral soil samples were then weighed and sieved to ≤2 mm and then re-weighed. A 2:5 soil–water slurry was used to determine soil pH. Slurries were shaken for 1 h using a wrist-action shaker and filtered with 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 was used to estimate percent organic matter (%OM) and measured by combusting a 4-g oven-dried subsample at 550 °C for 8 h. To determine the soil particle size distribution, we weighed ~30 g of dried soil into 250 mL glass beaker. Organic matter was removed and we 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. We utilized a modified Bouyoucos hydrometer method with hydrometer readings at 60 s and 1.5 h after mixing to the closest 0.5 g L^{-1}. River waters were filtered to <0.45 μm and analyzed for dissolved organic carbon (DOC) using a Shimadzu TOCV (Shimadzu Corporation, Kyoto, Japan), which included blanks, duplicates, and spikes. Blanks had DOC below limit of detection, duplicates were <4 % CV, and spikes had 92 to 103 % recovery rates.

2.3. River water sampling

River waters were sampled upstream of confluences from February 2019 January 2020. River waters were sampled approximately every two weeks until November 2019, then monthly for December 2019 and January 2020. For each sample, approximately 1 L of water was collected about 3 m from the riverbank using a telescopic dipstick and stored in acid-washed high density polyethylene bottles. Water sampling followed USGS 2006 *Collection of Water Samples* protocols, which includes that each bottle was rinsed with sample and bottles were filled with no headspace (USGS, 2006). Within 24 h after sampling, the pH values were measured and samples were filtered through 0.2 μm Whatman™ Nylon membranes. The filter membranes were frozen, freeze-dried, and weighed to determine sediment mass within river water. The filtered water subsamples were stored at 4 °C while 1-L was dried down on hotplates to 50 mL at 120 °C in a fume hood over 10 h. Preparation blanks were also performed to quantify and assess contamination.

2.4. Suspended sediment traps

Suspended sediment traps were deployed during the spring, summer, and fall of 2019 in each of our study subwatersheds adjacent to riparian soil sampling locations (locations in Supplemental Fig. 2). Suspended sediment traps were created following designs and descriptions from Tessier (2003); Kayvantash et al. (2017) and Patault et al. (2019). The sediment traps consist of polyethylene bottles, perforated at 5 cm from the top with two opposite holes (diameter 5 cm) bottle cap (Supplemental Fig. 3). A fin was attached to the straight side of the bottle cylinder below one of the holes to ensure the trap inlet faced upstream. The traps were suspended by rope from a tree branch. Flow conditions at our sampling locations were generally subcritical, laminar flow within pools (not riffles). A 2.3 kg steel ballast was attached to the sediment trap to keep it submerged and oriented correctly. The samples are qualitative suspended solids transported within the river water and were deposited within the trap due to a decrease in velocity and turbulent forces. Further details about the development of this trap can be found in Tessier (2003) and Kayvantash et al. (2017). Suspended sediment traps were deployed approximately 2 m from the stream bank in the main river channel.

2.5. Strong acid digestions and instrumental analysis

Soil and sediments were assessed for the strong acid digestible fraction to determine trace element abundance without overestimating metals within the silicate mineral fraction using a modified USEPA 3050B method with closed vessel hot plate digestion. First, 2 g of soil or sediment was weighed into 50 mL centrifuge tube. Next, 5 mL of 9:1 ratio of trace metal grade nitric acid to hydrochloric acid (15 M HNO_3 + 10 M HCl, Fisher Scientific) of reverse aqua regia was added to each tube. The solution was heated to 90 °C for 45 min using a hot plate and diluted to 50 mL using 18.2 MΩ cm deionized water. For every 20 samples, a preparation blank, duplicate sample, and standard reference material (SRM) of either Montana Soil 2711a or NY/NJ sediment 1944 SRM from the US National Institute of Standards and Technology were included. Digests were further diluted using 18.2 MΩ cm deionized

water and analyzed for trace elements with an Agilent 5110 Inductively Coupled Plasma-Optical Emission Spectrometer (Agilent Technologies, Santa Clara, California, USA). The same soil and sediment extracts and digests dilutions were analyzed for macro elements (Ca, K, Mg, Fe, Mn, Cu, Zn) with an Agilent 7700× Inductively Coupled Plasma Mass Spectrometer (Agilent Technology, Santa Clara, California, USA). Standard Reference Material recoveries of As, Cu, Fe, Mn, Ni, Pb, and Zn were 81–107 % of their certified values. The metal concentration coefficient of variation between intra-sample duplicates was <8 % and metal concentrations in the preparation blank samples were <0.1 % of their analyte concentrations.

2.6. Dissolved and suspended sediment NPE export

We utilized sediment masses in river water samples, NPE concentrations in trapped suspended sediment samples, and USGS river discharge data to estimate export rates of NPE from each watershed. First, total monthly discharge was determined from the summed discharge amounts through the sampling period obtained from the USGS stations for each watershed (see Richardson, 2020). Next, monthly discharge of dissolved NPE was determined using the average river water concentrations from each month with the monthly watershed discharge. The monthly discharge of sediment NPE was calculated using the mass of sediment within the 1-L bottle, the total monthly discharge of river water for each watershed, and the NPE concentrations from trapped suspended sediment for each month. Trapped suspended sediments were used as a better estimate of the integrated NPE concentrations due to their multi-week deployment. The monthly dissolved river water and sediment were summed to estimate an annual export rate. Our method likely underestimates export rates of dissolved and sediment sorbed NPEs during storms events or other stochastic large influxes but provides an empirical approximation that is consistent across our study subwatersheds.

2.7. Statistical analyses

Statistics were applied to riparian soil, river water, and sediment data to determine averages and relationships among physicochemical properties and NPEs. Descriptive and comparative statistics were calculated in Matlab (Mathworks, Natick, MA, USA). Average values are presented in text and in figures ±1 standard error. Data were tested for normal distribution using the Kolmogorov-Smirnov test and logarithmically transformed when necessary to establish normality. NPE concentrations in suspended sediments and river water were compared among the subwatersheds using an ANOVA with post hoc *t*-test. NPE concentrations in riparian soils and bottom sediments were compared among the subwatersheds using the nonparametric Kruskal-Wallis test with post hoc Mann-Whitney *U* test. We utilized a stepwise linear regression and multiple linear regression to examine cause-effect relationship among watershed properties, physicochemical properties, and element concentrations in soil, sediments, and river water. First, data were tested for normality, logarithmically transformed when necessary. Next, we used the following explanatory variables: Variables tested include watershed properties (%Forest, %Wetland, %Developed, % Farmland), soil properties (%OM, pH, Fe, Mn, response element), bottom sediment properties (%OM, pH, Fe, Mn, response element), suspended sediment properties (%OM, Fe, Mn, response element), and river water properties (DOC, pH, Fe, Mn, response element). Lastly, explanatory variables that were significant and a dummy test variable were included in a multiple regression to explain the variation in a single response element, which was one of the area-normalized export rates for NPEs (As, Cd, Cu, Ni, Pb, and Zn).

Since the stepwise regression and multiple regression were structured to examine explanatory variables with specific mechanisms, relationships among the different elements and some physiochemical properties (pH, %OM or DOC) were explored separately using a normalized principal component analysis. In the principal component analysis (PCA), riparian soil, suspended sediment, bottom sediment, or river water data were normalized with their respective standard deviations to remove the weighted effect of data with larger numerical values. Biplots of the two principal components (PCs) with the highest explanatory power were generated. Since riparian soil and bottom sediment sampling are spatially independent and river water and suspended sediment sampling were temporally different, each of the environmental media needed to be compared with a separate PCA.

3. Results

3.1. Riparian soils

Concentrations of NPEs in riparian soils generally did not exceed Connecticut's Department of Energy and Environmental Protection (CT-DEEP) planning for either residential or commercial limits for direct exposure from soil (Fig. 2). Average riparian soil As exceeded the 10 mg kg^{-1} limit for French, Little, Shetucket, and Yantic soils. Average riparian soil Pb exceeded the 400 mg kg^{-1} limit only for Yantic soils below 15 cm depth. Average riparian soil Cd, Cu, Ni, and Zn did not exceed the CT-DEEP's residential regulator limits of 34 mg kg^{-1}, 2500 mg kg^{-1}, 1400 mg kg^{-1} and 20,000 mg kg^{-1}, respectively.

Considering NPEs variation among watersheds, overall riparian soils As concentrations were significantly higher in the Shetucket and Yantic soils than Bartlett + Exeter, Quinebaug and Still soils (Fig. 2). Overall riparian soils Cu concentrations were significantly higher in the Shetucket and Yantic soils than Quinebaug and Still soils, while Cd concentrations were significantly higher in the French and Quinebaug soils than Bartlett + Exeter, Little, and Still soils (0.7, 0.9, and 0.9 mg kg^{-1}) Further, overall riparian soils' Zn concentrations were significantly higher in the Shetucket and Yantic soils than Bartlett + Exeter, Quinebaug and Still soils. Riparian soil Ni was significantly higher in the 0 to 5 cm depth in the Shetucket sampling sites than all other watersheds but there were no other significant differences for the other depths. Riparian soil Pb concentrations were significantly higher in the 15 to 30 depths at Yantic sampling sites compared with the other watersheds. In addition, riparian soil Pb concentrations were significantly higher for Quinebaug and Shetucket than Bartlett + Exeter and Still River watersheds. From the riparian soil PCA in Fig. 3, we can observe that As, Cu, Pb, Zn and Fe were all strongly associated. Soil pH, %OM, and Mn were separately associated. Lastly, Ni and Cd were associated together.

While there were many differences in riparian soil physicochemical properties among the watersheds, there were few general trends (Fig. 2). Riparian soils had significantly higher %SOM across depths for Little River soils than all other watershed soils, except for Bartlett + Exeter soils (Fig. 2). Overall, riparian soils pH were significantly higher in Bartlett + Exeter and Yantic soils than Quinebaug, Shetucket, and Still soils (Fig. 2). Riparian soil P concentrations for 0 to 15 cm depths were significantly higher for Bartlett + Exeter and Little soils than the other watershed soils (Fig. 2). Overall riparian soil Fe was significantly higher for Shetucket, Still, and Yantic soils than French and Quinebaug soils (Supplemental Fig. 4). Riparian soil Mn was significantly higher in the French and Still soils than Little and Quinebaug rivers (Supplemental Fig. 4).

3.2. Bottom sediments

To evaluate the potential toxicity, we compared NPE concentrations in bottom sediment concentrations with USEPA sediment quality targets Level II for the protection of freshwater sediment-dwelling organisms (see Crane et al., 2002; Crane et al., 2021). Bottom sediment As concentrations exceeded the SQT Level II target of 33 mg kg^{-1} at all watersheds, except the Still River (Fig. 4). Bottom sediment Cd and Cu concentrations did not exceed SQT Level II targets of 5 mg kg^{-1} and 150 mg kg^{-1}, respectively, at any watersheds. Bottom sediment Pb and Ni

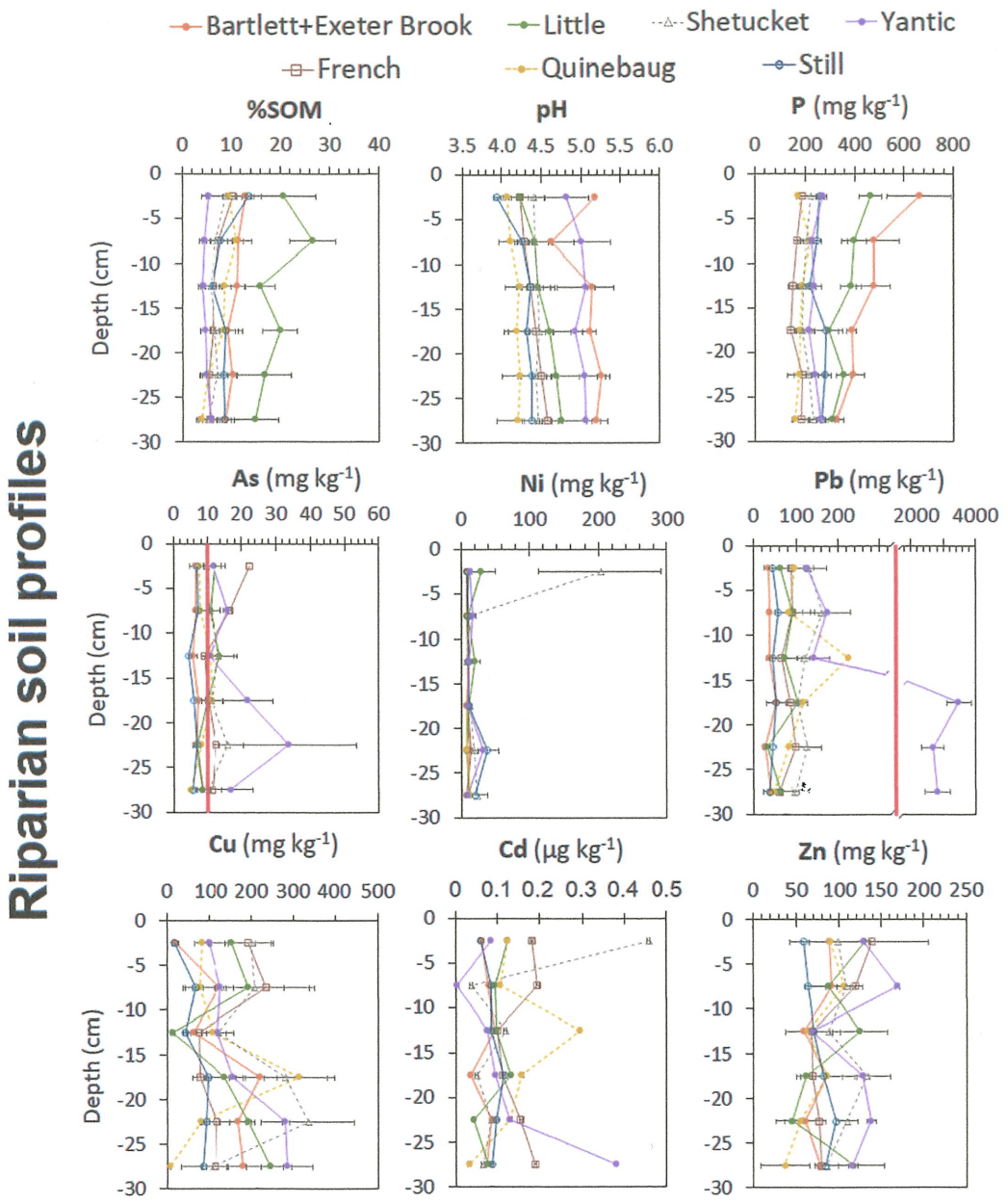

Fig. 2. Riparian soil trace metal concentrations collected from 27 stream banks across the seven subwatersheds. Error bars represent standard error among the riparian soils sampled in each watershed. Red lines for As and Pb indicate CT-DEEP limits for direct exposure for humans; limits for Ni, Cu, Cd, and Zn are not visible at the provided scale.

concentrations at Yantic River exceeded SQT Level II targets of 130 mg kg^{-1} and 49 mg kg^{-1}, respectively, but were below for all other watersheds. Bottom sediment Zn concentrations exceeded SQT Level II targets of 460 mg kg^{-1} at French and Yantic rivers, not the other watersheds.

Generally, the bottom sediments within river pools in French and Yantic rivers had higher %OM, Fe, and Mn that promote NPE accumulation (Fig. 4, Supplemental Fig. 5). Bottom sediments %SOM was higher in Bartlett + Exeter and French river than all other watersheds (Fig. 4). Overall bottom sediment pH were not different, except French river bottom sediments had a lower pH of 5.4 ± 0.2 compared with the others. Bottom sediment P concentrations for were significantly higher for Bartlett + Exeter and Quinebaug than the other watersheds. Bottom sediment Fe was significantly higher for French and Yantic than the other watersheds (Supplemental Fig. 5). Bottom sediments Mn was significantly higher in the French and Yantic rivers than the other rivers (Supplemental Fig. 5).

Generally, NPE concentrations in bottom sediments were significantly higher in the French River and/or Yantic River (Fig. 4). Bottom sediment As concentrations were comparable among rivers, but was significantly lower for Little and Still rivers. Bottom sediment Cu and Cd concentrations were significantly higher in the Bartlett + Exeter and Yantic soils than the other rivers. Bottom sediment Zn concentrations were significantly higher in the French, Shetucket, and Yantic soils than the other rivers. Bottom sediment Ni was significantly higher in the Yantic river than all other watersheds. Bottom sediment Pb concentrations were significantly higher at French river and Yantic river compared with the other watersheds. From the bottom sediments PCA in Fig. 3, we can observe that As, Cd, Mn and Fe were all strongly associated with a weak association with %OM. Copper and Zn were separately

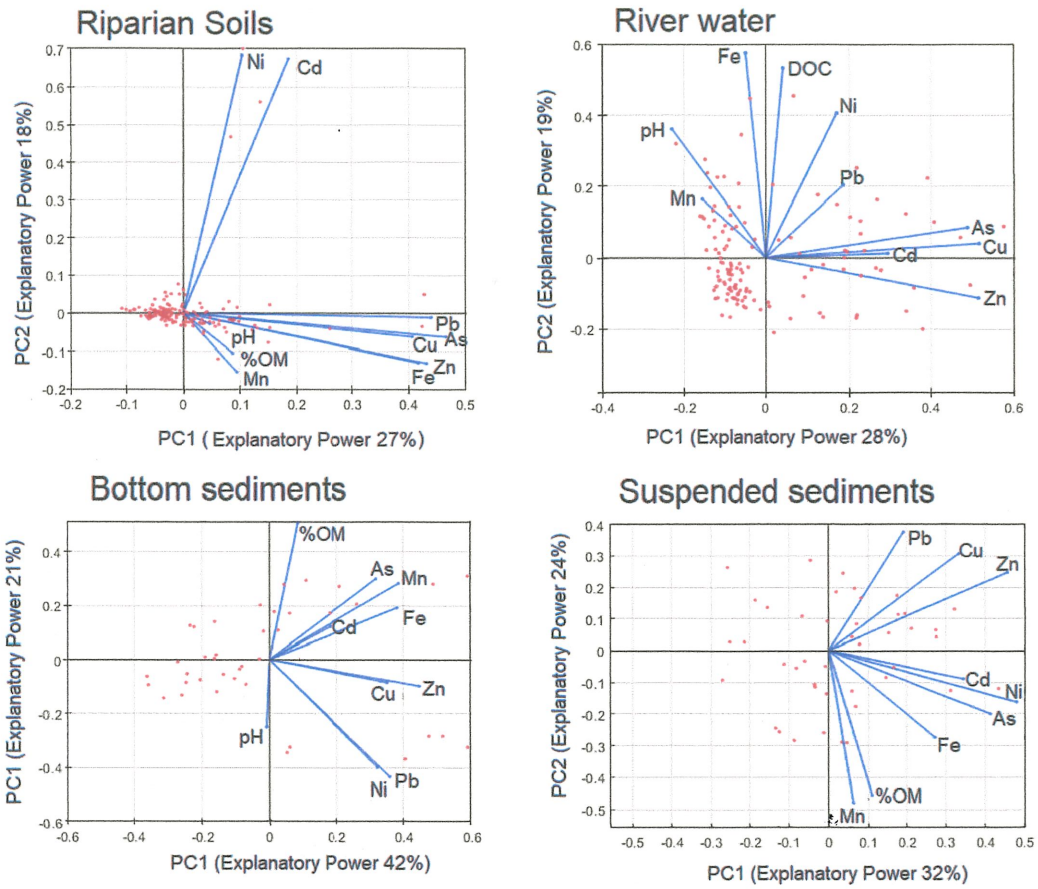

Fig. 3. Principal component analysis of physicochemical properties (pH, %OM for soil and sediments or DOC for river water) of sample concentrations (Mn, Fe, P, As, Cd, Cu, Ni, Pb, Zn) for riparian soils, river water, bottom sediments, and suspended sediments among the seven watersheds.

associated. Lastly, Ni and Pb were associated together, also with a weak association with pH.

We compared our measured bottom sediment physicochemical properties and NPE concentrations with 1992–1994 published bottom sediment data from Harris (1997) for the French, Quinebaug, and Yantic Rivers. Bottom sediments from Harris (1997) had much higher %OM, Fe, and Mn concentrations than in our study. Bottom sediment As concentrations were 3 to 10 times higher than those reported in Harris (1997), but our observed bottom sediment Cd concentrations lower by a similar factor. Bottom sediment Cu, Pb, Ni, and Zn were mixed, with French and Quinebaug rivers having lower concentrations than Harris but higher in the Yantic river.

3.3. Suspended sediments

To evaluate the potential hazard for aquatic organisms, we compared NPE concentrations in suspended sediment concentrations with USEPA Level II sediment quality targets for the protection of freshwater sediment-dwelling organisms (Fig. 5) (see Crane et al., 2002; Crane et al., 2021). Average suspended sediment As concentrations exceeded the SQT Level II target of 33 mg kg^{-1} at Bartlett + Exeter and French river. Average suspended sediment Cd, Cu, Pb, and Ni concentrations did not exceed SQT Level II targets of 5 mg kg^{-1} (Cd), 150 mg kg^{-1} (Cu), 130 mg kg^{-1} (Pb), and 49 mg kg^{-1} (Ni), at any watersheds. Suspended sediment Zn concentrations exceeded SQT Level II targets of 460 mg kg^{-1} at French and Yantic rivers, but not the other watersheds.

Generally, the suspended sediments of Bartlett + Exeter, French river and Yantic river had high amounts of properties that promote NPE accumulation. Suspended sediments %OM was highest in Bartlett + Exeter compared with all other watersheds (Fig. 5, Supplemental Fig. 6). Suspended sediment P and Mn concentrations were higher for Bartlett + Exeter brooks than other watersheds. Generally, NPEs in suspended sediments were higher in the French and/or Yantic Rivers (Fig. 5). Suspended sediment As concentrations were significantly higher for Bartlett + Exeter Brooks and French River than the other rivers. Also, suspended sediment Cu concentrations were significantly higher in the Yantic river than the other rivers, while suspended sediment Cd concentrations were significantly higher in the Quinebaug river (than the other rivers, Fig. 5). However, suspended sediment Ni was not significantly different among the watersheds (Fig. 5). Suspended sediment Pb concentrations was significantly higher at Shetucket and Yantic Rivers compared with the other watersheds. Suspended sediment Zn concentrations were significantly higher in the French and Yantic than the other rivers. From the suspended sediments PCA in Fig. 3, we can observe that Pb, Cu, and Zn were all associated, while Cd, Ni, As, and Fe were separately associated. Lastly, Mn and %OM were associated together.

3.4. River water concentrations

Most NPE concentrations in river water samples did not exceed CT-DEEP Water Quality Criteria for aquatic life or human health criteria (Fig. 6). Copper did not exceed the human health criteria limit of 1300 μg L^{-1} nor the freshwater aquatic life criteria of 4.8 μg L^{-1}. River water Ni and Zn were far below both aquatic life criteria (29 μg L^{-1} and 65 μg L^{-1}, respectively) and human health criteria (610 μg L^{-1} and 7400 μg L^{-1}, respectively). River water As did not exceed the aquatic life criteria but exceeded the human health criteria 0.021 μg L^{-1} limit for all rivers.

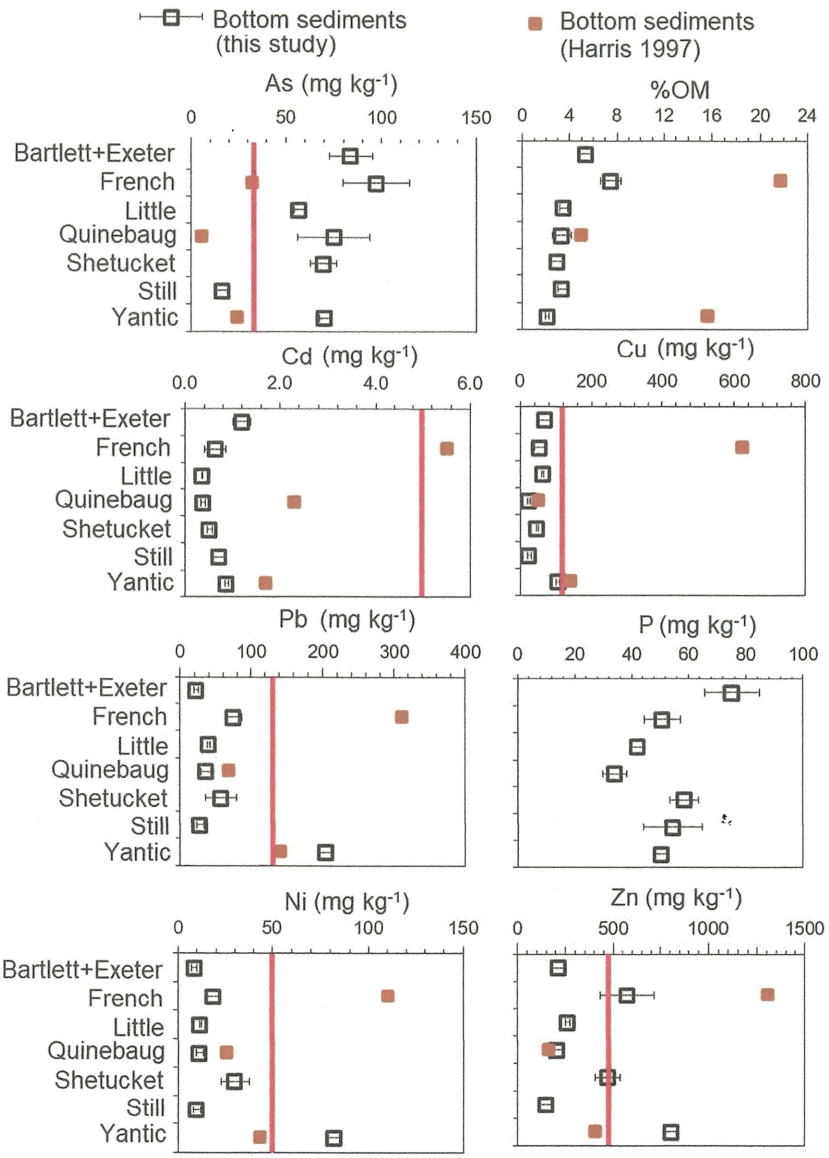

Fig. 4. Bottom sediments from pools across the seven watersheds. The red line indicates USEPA Level II sediment quality targets (SQT).

Cadmium did not exceed the human health criteria of 5 μg L^{-1} limit but did exceed the freshwater chronic aquatic life criteria of 0.125 μg L^{-1} for all rivers. River water Pb concentrations were far below the human health criteria of 140 μg L^{-1} but exceeded the freshwater chronic aquatic life criteria of 1.2 μg L^{-1} for one sampling interval for Shetucket and Quinebaug rivers. River water P were below US EPA regional ambient water quality criteria of 31 μg L^{-1} (see USEPA, 2000).

River water pH and concentrations of Fe, Mn, and P were not different among the rivers (Supplemental Fig. 7, Fig. 6). However, river water DOC was consistently lower in Quinebaug and Yantic Rivers relative to our other sampling locations. River water Cu, Cd, Ni, and Zn were not significantly different among the rivers. River water As was significantly lower for Bartlett + Exeter brooks compared with the other rivers. River water Pb was significantly higher for Quinebaug and Shetucket rivers compared with the other rivers. From the river water PCA in Fig. 3, we can observe that As, Cu, Cd, and Zn were all closely associated. Also, Pb, Ni, DOC were separately associated and partly associated with Fe, pH, and Mn indicated by PC2.

3.5. *Dissolved and sediment-bound NPE watershed export*

Total annual trace elements exports for dissolved and sediment-bound NPE were determined using monthly discharge rates from the USGS stream gauges (Fig. 7), except for Still River and Bartlett + Exeter Brooks which were determined by its watershed area and data from other adjacent watersheds (see Richardson, 2020 and Section 2.6). Total dissolved export of DOC, macroelements (Fe, Mn), and NPEs (As, Cd, Cu, P, Pb, Ni, and Zn) were greatest for the Quinebaug and Shetucket rivers and generally lowest at the smallest watersheds, Bartlett + Exeter and Little rivers (Fig. 8, Supplemental Table 1). However, there were some exceptions. Dissolved export of DOC, P, As, Fe, Cd, Cu, and Ni for Still River was similar or less than export from the Little River, despite the Still River having twice the area as the Little River (Fig. 8, Supplemental Table 1). Total sediment-bound NPE export was also greatest for the Quinebaug and Shetucket rivers and generally lowest at the smallest watersheds, Bartlett + Exeter and Little Rivers (Fig. 8; Supplemental Table 2). Total sediment-bound export of As for the French River was greater than the much larger Shetucket River (Fig. 8; Supplemental Table 2). Also, total sediment-bound export of OM, P, As, and Cu for Still

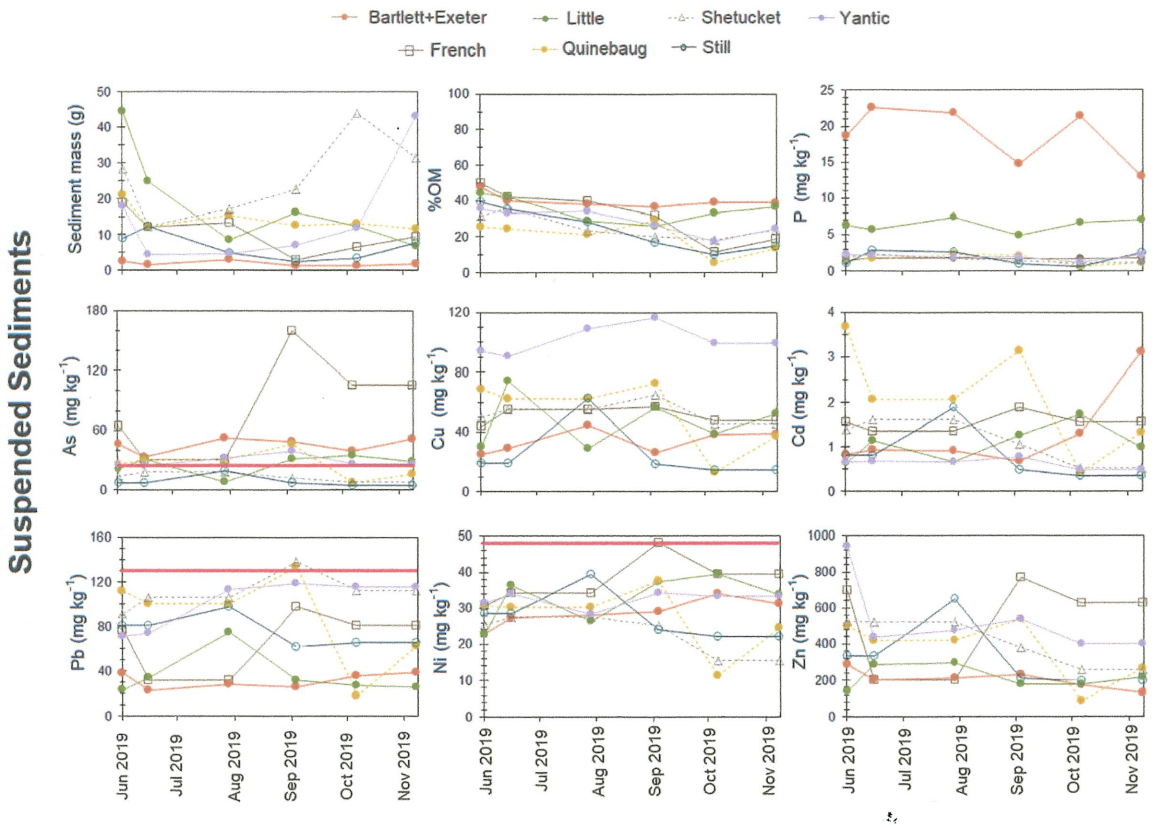

Fig. 5. Suspended sediment NPE concentrations approximately once a month across the seven subwatersheds from June 2019 to November 2019. The red line indicates USEPA Level II sediment quality targets (SQT); SQT goals for Cd, Cu, and Zn are much higher than our observed data and not visible at the provided scale.

River was less than the smaller Little River (Fig. 8; Supplemental Table 2).

To understand differences in land-use and soils, the dissolved and sediment export rates were normalized to their respective watershed area for comparisons across small and large watersheds. For dissolved export rates, the Quinebaug River still had the highest area-normalized export of Mn, Cd, Pb, and Zn (Table 2). However, Bartlett + Exeter and Little River had higher dissolved P and As than other watersheds. Area-normalized dissolved export of DOC, Fe, Cu, and Ni were generally comparable, with less than a factor of two variation among the watersheds. The Still River watershed had lower area-normalized dissolved export of As and Zn than the other watersheds and the Still and Yantic River watersheds had the lowest area-normalized dissolved Cd exports. Considering area-normalized sediment-bound export, the French and Littler Rivers had the highest OM, P, Fe, As, Ni, and Zn than the other watersheds (Table 2). The highest sediment-bound export of Cd was the Quinebaug River and Pb was the Shetucket River. The Yantic River had the highest sediment-bound export of Mn and Cu. Lastly, Bartlett + Exeter had the lowest sediment-bound export of OM, Fe, As, Cd, Cu, Pb, Ni, and Zn of all the watersheds.

3.6. Stepwise and multiple regressions for dissolved and sediment-bound NPE export

Stepwise and multiple regressions were used to determine which explanatory variables were most important between watershed properties and area-normalized dissolved and sediment-bound export of NPEs across the seven watersheds (Table 3). We utilized land-cover (National Land Cover Database 2016, see Homer et al., 2020) and average physicochemical properties and NPE concentrations for riparian soils, bottom sediment, and suspended sediment across the watersheds.

Across the stepwise regressions for area-normalized dissolved export rates, we most commonly found river water DOC, river water Fe, river water Mn, and river water concentrations of the respective element were positively correlated variables for area-normalized dissolved export of Cd, Ni, Pb, and Zn (Table 3). Surprisingly, we found %Wetland cover as an important explanatory variable for dissolved As export. Next, we found riparian soil Mn negatively correlated with area-normalized dissolved exports of P, Cu, and Zn. The only element in which riparian soil P was positively correlated with area-normalized dissolved export was P. Suspended sediment was only important for dissolved As; suspended sediment %OM was positively correlated with area-normalized export of dissolved As. Bottom sediments were only important for dissolved As, Pb and P.

For area-normalized sediment-bound export rates, stepwise regressions we most commonly found suspended sediment Mn, Soil OM, bottom sediment Fe, and suspended sediment concentrations of the respective element were correlated variables for area-normalized sediment-bound export of As, Cd, Cu, Ni, and Zn (Table 3). We found % Developed cover as an important explanatory variable for sediment-bound As and Pb export. Next, we found %Forest and bottom sediment OM negatively correlated with area-normalized sediment-bound exports of Cu. Soil pH was negatively correlated with sediment-bound Pb export.

3.7. NPE historical transport from sediment core profiles

The estuarine sediment core from Horton Cove shows substantial changes in NPE export from the watershed based upon changes in NPE concentrations with depth. A clear onset for industrialization can be seen at approximately 50 cm depth (red lines in Fig. 9), which has been dated regional estuaries to 1850–1900 (Woodruff et al., 2013; Yellen et al., 2023). There are sharp peaks for Cd, Cu, Pb, and Zn between 30 and 36 cm in depth which correspond to an increase in organic content

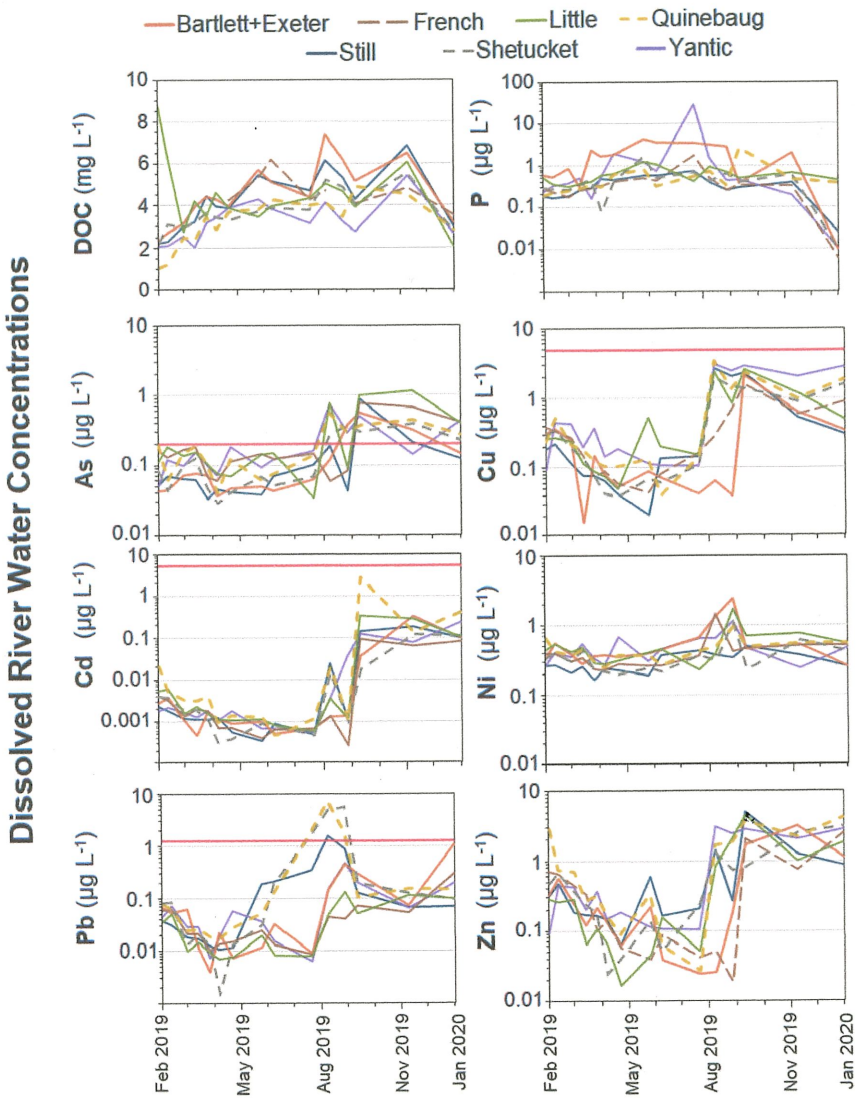

Fig. 6. River water concentrations measured approximately twice a month across the seven subwatersheds from February 2019 to February 2020, except Nov 2019, Dec 2019, and Jan 2020. Red line indicates CT-DEEP Water Quality Criteria or US EPA regional ambient water quality; water quality guidelines for Ni and Zn are much higher than the data provided and not visible at the provided scale.

and decrease in grain size. This is possibly due to high affinity of these elements to organic matter fraction, as well as their partitioning to fine grain sizes in the sediment. However, elevated concentrations of As and Ni before the onset of industrialization, suggested alternative sources for these elements within the watershed. As observed, NPE concentrations in the sediment through the present remain above pre-industrial levels, with the possible exception of Ni, and S. The sediment core shows P had increasing concentrations to the surface, following the % OM but different than the metal pollutant and particle size profiles.

4. Discussion

4.1. Abundant As throughout the Thames River watershed

Arsenic was the most widespread and elevated NPE across the seven watersheds. We observed riparian soil As concentrations exceeding CT-DEEP limits of 10 mg kg^{-1} limit for French, Little, Shetucket, and Yantic soils. Concentrations of As in bottom sediments exceeded the EPA limit of 33 mg kg^{-1} in all watersheds except the Still River. Suspended sediment As concentrations exceeded the SQT Level II target of 33 mg kg^{-1} at Bartlett + Exeter and French river. River water dissolved As exceeded the human health criteria 0.021 µg L^{-1} limit for all seven rivers. These findings highlight active transport of As in bottom sediments, suspended sediments, and river water across all watersheds. Dissolved As was the largest export mode for most watersheds by a factor of 2 for most watersheds, except the French River (Fig. 8). The Quinebaug watershed had the highest total dissolved and total sediment-bound As due to its larger watershed area (Fig. 8). The second largest dissolved and sediment-bound As was the large Shetucket and the much smaller French River, respectively, indicating size was not the dominating factor for As laden-sediment transport. However, area-normalized dissolved As export was greatest in the smallest watershed of Bartlett and Exeter Brooks and sediment-bound As was greatest for the French River (Table 2). These results highlight As was not controlled by the size of the watershed, supporting our hypothesis that other factors such as land-use, geology, or historical pollution may be governing As abundance and transport at the watershed scale.

We expected As to be found in hot spots due to historical mills, tanneries, and industrial pollution (such as Larned, 1899; Klotz, 1977; Colombo et al., 2004), but found As to be widely dispersed. Bottom sediment As concentrations have increased in the French, Quinebaug, and Yantic rivers since 1992–1994 (Harris, 1997). The export of As in

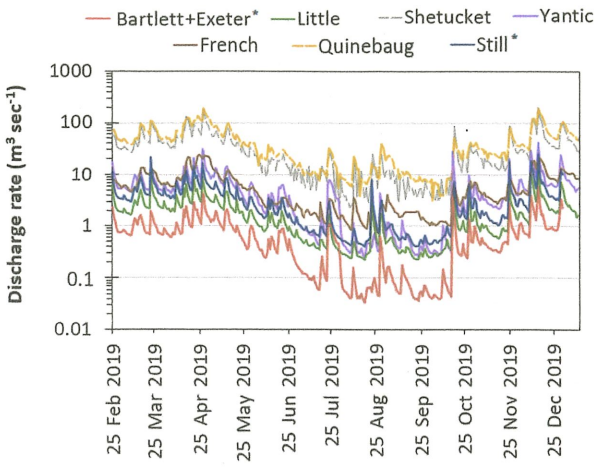

Fig. 7. River discharges for the seven watersheds over the 1 year of sampling. Discharge rates for French, Little, Quinebaug, Shetucket and Yantic were measured by the USGS. (*) indicates that Bartlett + Exeter and Still River were estimated by building a regression with watershed area from similar sized watersheds gauged in central and eastern Connecticut by the USGS. See Richardson (2020) for detailed methods.

the Thames River watershed, as interpreted from our estuarine sediment core, did not occur as only a clear peak (Fig. 9). Instead, nonnegligible As export occurred since pre-industrial times reflecting the abundant natural As in the region (Ayotte et al., 2003). Modern As export remains above pre-industrial conditions within the sediment, suggesting continued excess export from the watershed.. We hypothesize that this may be mobilization from historical As from industrial pollution (e.g. tanneries Landrot et al., 2012), but may be associated with current human development and industrial activities (Davis et al., 1994; Adriano, 2001) and municipal fuel combustion (Shi et al., 2012).

The abundance of human development was not associated area-normalized dissolved As export but was correlated with area-normalized sediment-bound As export. The high dissolved As export from Bartlett and Exeter Brooks and Little River is likely associated with agriculture and historical As use as a pesticide (e.g. Peryea and Creger, 1994; Oyewumi et al., 2017). As described by Ayotte et al. (2003), the metamorphosed sediments of the Merrimack syncline have generated elevated As concentrations in groundwater including the northern parts of the Thames River watershed. Thus, the bedrock could be impacting river water As concentrations throughout the watershed, particularly the French and Quinebaug watersheds. Similar conclusions were made for the Zarjoub River in Iran (Haghnazar et al., 2023) and the Saskatchewan River, Canada (Stone et al., 2022) of geologic influences with anthropogenic pollution further increasing sediment concentrations. From the sediment core data, it is clear that natural As export is non-negligible and human activities appear to have only doubled As export within the Thames River watershed.

PCA results shown in Fig. 3 also support that riparian soil, bottom sediment, river water, and suspended sediments As concentrations have some anthropogenic linkages due to associations with Cu, Fe, Ni, Pb, and Zn were commonly found in anthropogenic pollution (Adriano, 2001; N'Guessan et al., 2009; Audry et al., 2010; Oyewumi et al., 2022). Further, geochemical controls of DOC and pH were not important with riparian soil, bottom sediment, river water, and suspended sediments As concentrations. Continued monitoring of As in the Thames River watershed is needed, particularly for projects and developments that may mobilize historical As from soils and sediments.

4.2. 'Hot spots' and 'diffuse accumulation' of Pb

Across the Thames River watershed, Pb storage was at background concentrations in the riparian soils, bottom sediments, and suspended sediments in several subwatersheds (Bartlett + Exeter, Still, Little). However, the subwatersheds with higher, non-background concentrations of Pb show two stories: 'hot-spot' linkages in the Yantic River, and 'diffuse accumulation' in the French, Shetucket, and Quinebaug rivers. The Yantic river had elevated Pb in riparian soil, exceeding 3000 mg kg^{-1} (Fig. 2) and bottom sediment Pb exceeding 200 mg kg^{-1} (Fig. 4). The spatial proximity for the riparian soil and bottom sediment suggest a direct cause-effect link of a 'hot spot' leading to elevated accumulation. Since the elevated riparian soil Pb was primarily below 15 cm depth in the Yantic watershed, we hypothesize that Pb was deposited decades ago from pollution and buried with new sediments containing lower NPE concentrations. Yantic bottom sediment Pb concentrations have slightly increased since the 1992–1994 sampling by Harris (1997). This finding highlights that despite increases in environmental regulation on Pb entering surface waters, the legacy effects of these pollutants are still seen today. Our sediment core data show that Pb transport greatly increased from baseline up to 500 mg kg^{-1} but have since decreased down to 106 mg kg^{-1} (Fig. 9).

Contrary to the Pb 'hot spot' in the Yantic watershed, the French, Quinebaug, and Shetucket rivers were broadly elevated in Pb (Fig. 6). Similarly, riparian soils with Pb concentrations approaching or exceeding the CT-DEEP 400 mg kg^{-1} regulator limit were observed in the French, Quinebaug, and Shetucket rivers, with four soil samples in the 350 to 650 mg kg^{-1}. River water Pb exceeded the freshwater chronic aquatic life criteria of 1.2 μg L^{-1} for one sampling interval for Quinebaug and Shetucket rivers. It is important to note that sediment-bound export was larger than dissolved export (Fig. 8), by a factor of 2 to 10, which agrees with its low solubility. Suspended sediment Pb concentrations exceeded the USEPA SQT Level II during the late-summer dry conditions in September 2019 for the three rivers. Since bottom sediment Pb have decreased for the French and Quinebaug rivers in Harris (1997) sampling in 1992–1994, bottom sediment Pb appears to have been exported or buried over the past three decades. Watershed %Developed was not correlated with area-normalized dissolved export of Pb but was correlated with sediment-bound Pb. Furthermore, the Quinebaug and Shetucket watersheds had the highest areas of human development overall (55 and 116 km^2) and the greatest river area-normalized dissolved and sediment-bound Pb export. These result links human activities to sediment bound Pb export. Previous studies that made use of Pb stable isotopes have shown soil Pb concentrations have been largely impacted by human inputs (e.g., Richardson et al., 2014) and in river sediments through enrichment factors (Oyewumi et al., 2022) but natural weathering can influence Pb in stream bed sediments (N'Guessan et al., 2009).

Lastly, Quinebaug and Shetucket rivers were the largest total dissolved and sediment-bound exporters of Pb (Table 2). Area-normalized sediment-bound Pb export was significantly correlated with %Developed area among the watersheds. These results highlight that the larger, more urbanized Quinebaug and Shetucket watersheds were the most important governing Pb export in the broader Thames River watershed. Despite the lack of a clear correlation, we hypothesize the Pb was sourced from the large number of metropolitan areas via historical releases beginning in the 1800s and continuing through 1970s with the passage of the Clean Air Act (42 U.S.C. §7401 et seq. 1970) and Clean Water Act (33 U.S.C. §1251 et seq. 1972).

We expected to observe physicochemical properties enhancing or driving NPE accumulation in riparian soils and bottom sediments as found in previous studies (e.g. Audry et al., 2010; Yan et al., 2022). The Pb 'hot spots' in the Yantic river were independent of physicochemical properties. Our PCA results suggest that DOC and Fe were promoting Pb accumulation in riparian soils and bottom sediments as well as transport in river water and suspended sediments. This is further evident in the stepwise and multiple regressions in Table 3 linking area-normalized dissolved export of Pb with river water Fe. This matches previous findings that have shown stream bed sediment Pb controlled by physicochemical parameters (N'Guessan et al., 2009; Jiann et al., 2013). River

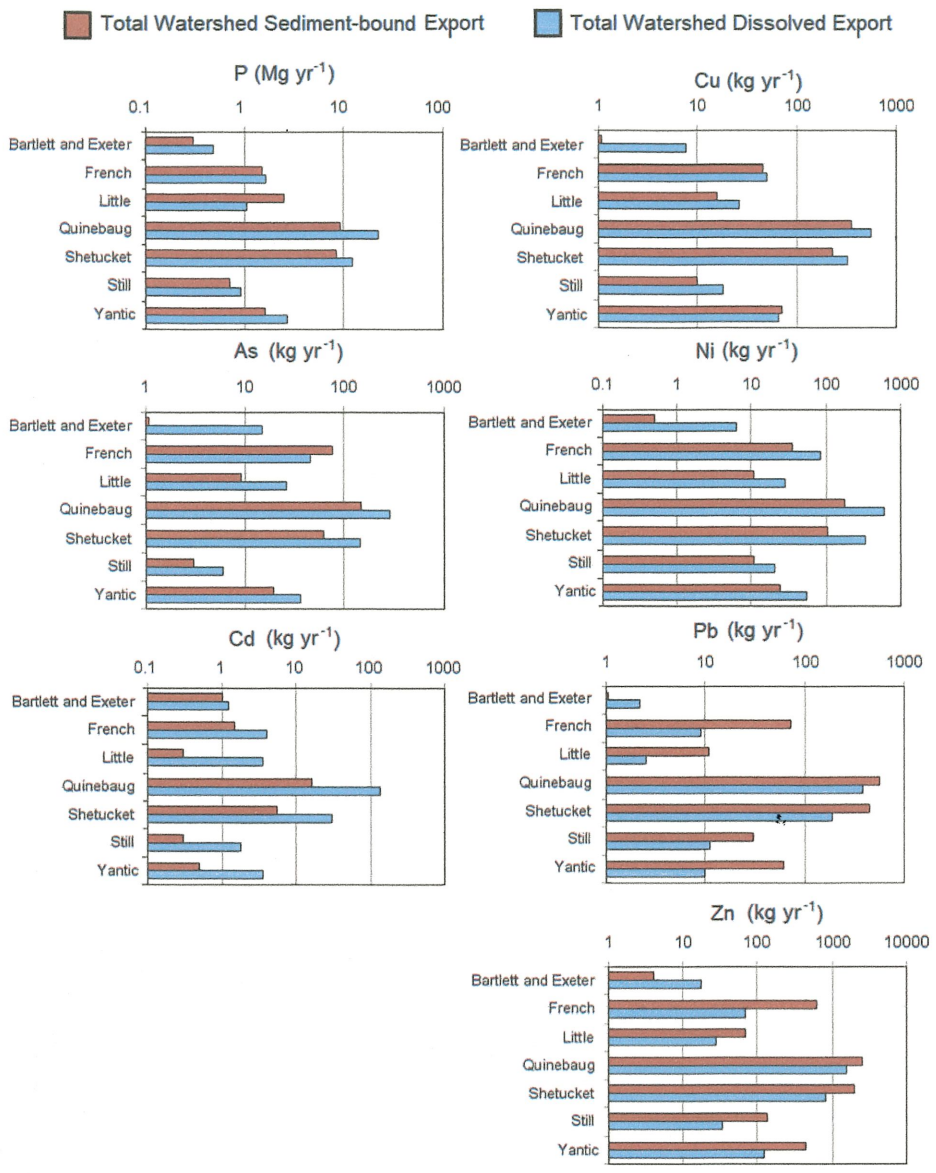

Fig. 8. Estimated total watershed export dissolved in river water or sediment-bound on an annual basis. Dissolved water export rates were determined using average monthly concentrations and river discharge rates (see Fig. 7). Sediment-bound export rates utilized trapped suspended sediment concentrations, filtered sediment masses, and river discharge rates.

water DOC and Fe are likely important for increasing Pb solubility and decreasing adsorption (Audry et al., 2010; Jiann et al., 2013). Area-normalized sediment-bound Pb export was correlated with suspended sediment Pb concentrations, which were used to determine the export rate and negatively correlated with soil pH. Thus, we can further conclude river water Fe and DOC helps control dissolved Pb transport at the watershed-scale while sediment-bound Pb export is controlled by suspended sediment concentrations rather than properties of the suspended sediment.

4.3. Limited storage and transport of Cd, Cu, Ni, and Zn

Our riparian soils and bottom sediments showed limited storage of sediment-bound Cd, Cu, Ni, and Zn. Their concentrations were below levels known to negatively impact terrestrial or aquatic ecosystems across the seven watersheds according to CT-DEEP values and USEPA SQT Level II. The only exceptions were bottom sediment Ni and Zn concentrations, which exceeded SQT Level II targets, and were associated with historical metalworks in the watershed. Further, bottom sediment Cd, Cu, Ni, and Zn concentrations are comparable or lower than 1992–1994 concentrations measured by Harris (1997). Furthermore, the estuarine sediment core data show that Cd, Cu, Ni, and Zn export in the Thames River watershed increased more than an order of magnitude from baseline but have since decreased down to a multiple of baseline concentrations over time. (Fig. 9). Observed low concentrations of these metals in riparian soils and bottom sediments within our study subwatersheds are consistent with lower NPE production and export within the watershed, with remaining export likely from relic sources as has been seen in similar local watersheds (Dow et al., 2020). Additionally, the sediment concentrations are at or are approaching background concentrations for soils and sediments in other studies (e.g. Richardson, 2020), which showed significant decreases through time (e.g. Pouyat and McDonnell, 1991; Breault and Harris, 1997; Richardson et al., 2015). Higher Cd, Cu, Ni, and Zn concentrations in riparian soils and bottom sediments were somewhat associated with Fe, but not associated with %OM or pH as evident in the PCAs in Fig. 3. Also, elevated riparian

Table 2
Estimated annual dissolved export and sediment-bound export of NPE masses on area-normalized annual basis (kg yr^{-1} km^{-2} or Mg yr^{-1} km^{-2}). Export rates were determined using average monthly concentrations and discharge rates.

River	Area-normalized dissolved export								
	P	Fe	Mn	As	Cd	Cu	Pb	Ni	Zn
	kg yr^{-1} 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}	kg yr^{-1} km^{-2}
Bartlett and Exeter	16	0.05	0.9	0.40	0.03	0.21	0.06	0.17	0.48
French	6	0.09	3.9	0.18	0.02	0.19	0.03	0.31	0.27
Little	18	0.07	1.6	0.33	0.05	0.34	0.03	0.35	0.37
Quinebaug	11	0.10	6.5	0.15	0.07	0.29	0.20	0.31	0.81
Shetucket	9	0.07	2.2	0.11	0.02	0.24	0.14	0.25	0.60
Still	6	0.07	4.8	0.04	0.01	0.13	0.08	0.14	0.24
Yantic	10	0.10	5.5	0.14	0.01	0.25	0.04	0.20	0.46

River	Area-normalized sediment-bound export								
	P	Fe	Mn	As	Cd	Cu	Pb	Ni	Zn
	kg yr^{-1} 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}	kg yr^{-1} km^{-2}
Bartlett and Exeter	8	0.03	0.03	0.03	0.00	0.03	0.03	0.01	0.11
French	6	0.17	0.07	0.29	0.01	0.18	0.28	0.13	2.33
Little	32	0.13	0.09	0.12	0.00	0.21	0.14	0.14	0.90
Quinebaug	5	0.11	0.06	0.08	0.01	0.18	0.30	0.09	1.30
Shetucket	6	0.15	0.08	0.05	0.00	0.16	0.33	0.08	1.45
Still	5	0.14	0.08	0.02	0.00	0.07	0.22	0.08	0.96
Yantic	6	0.10	0.10	0.07	0.00	0.26	0.23	0.09	1.61

Table 3
Stepwise-regressions and multiple regression model outputs for area normalized dissolved and sediment-bound export for NPEs across the seven watersheds. Variables tested include watershed land cover (%Forest, %Wetland, %Developed, %Farmland), soil properties (%OM, pH, Fe, Mn), bottom sediment properties (%OM, pH, Fe, Mn), suspended sediment properties (%OM, Fe, Mn), and river water properties (DOC, pH, Fe, Mn) as well as the respective element for sediments, soil, and river water. (+) indicates a positive correlation while (−) indicates a negative correlation.

	Area-normalized dissolved export				Area-normalized sediment-bound export			
	Significant variables from stepwise regression	Multiple regression R^2	Multiple regression F statistic	Multiple regression P value	Significant variables from stepwise regression	Multiple regression R^2	Multiple regression F statistic	Multiple regression P value
P	Bottom sed OM (−) Soil Mn (−) Soil P (+)	0.98	51	0.01	Bottom sed Fe (+) River water Fe (+) Soil OM (+)	0.98	92	0.01
As	%Wetland (+) Bottom Sed pH (+) Suspended sed OM (+)	0.99	73	0.00	Developed (+) Soil OM (+) Suspended sed Mn (+)	0.98	60	0.00
Cd	River water Fe (+) River water Mn (+) River water Cd (+)	0.96	24	0.01	Bottom Sed Fe (+) Suspended sed Mn (+) Suspended sed Cd (+)	0.99	75	0.00
Cu	Soil Mn (−) Bottom Sed Mn (−) Soil OM (−)	0.95	19	0.02	Forest (−) Bottom sed OM (−) Suspended sed Mn (+) Suspended sed Cu (+)	0.98	216	0.00
Ni	River water DOC (+) River water Fe (+) River water Mn (+)	0.93	14	0.03	Soil OM (+) Suspended sed Mn (+) Suspended sed Ni (+)	0.99	103	0.00
Pb	River water Fe (+) Bottom sed Pb (+)	0.85	29	0.00	Developed (+) Soil pH (−) Suspended sed Pb (+)	0.98	51	0.00
Zn	River water DOC (+) River water Zn (+) Soil Mn (−)	0.79	5	0.04	Soil OM (+) Suspended sed Zn (+)	0.94	19	0.02

soil accumulation of Cd and Ni appear independent of geochemical parameters, suggesting localized human pollution sources (Fig. 3).

Overall, our suspended sediments and river water show that Cd, Cu, Ni, and Zn concentrations were below levels known to negatively impact terrestrial or aquatic ecosystems across the seven watersheds. The results suggest that Cd, Cu, Ni, and Zn were either not elevated in the Thames watershed or they were sequestered in areas not studied such as upland soils, wetlands, and deeper bottom sediments. On the basis of current and historical riparian soil and bottom sediment concentrations, a mix of the two processes is likely the case. Changes between 1992 and 1994 bottom sediments in Harris (1997) and our study for French, Quinebaug, and Yantic Rivers emphasize decreases or no change in Cd and Cu or no change and increases for Ni and Zn. These findings agree with Oyewumi et al. (2022), who found the central Connecticut Farmington River had moderate to no enrichment for Cd, Cu, Ni, and Zn.

The Quinebaug and Shetucket rivers were the largest total dissolved and sediment-bound exporters of Cd, Cu, Ni, and Zn, but without a significant correlation with %Development of the watersheds, our evidence for current urban developed areas as primary sources is limited. Land cover was generally not correlated with area-normalized export

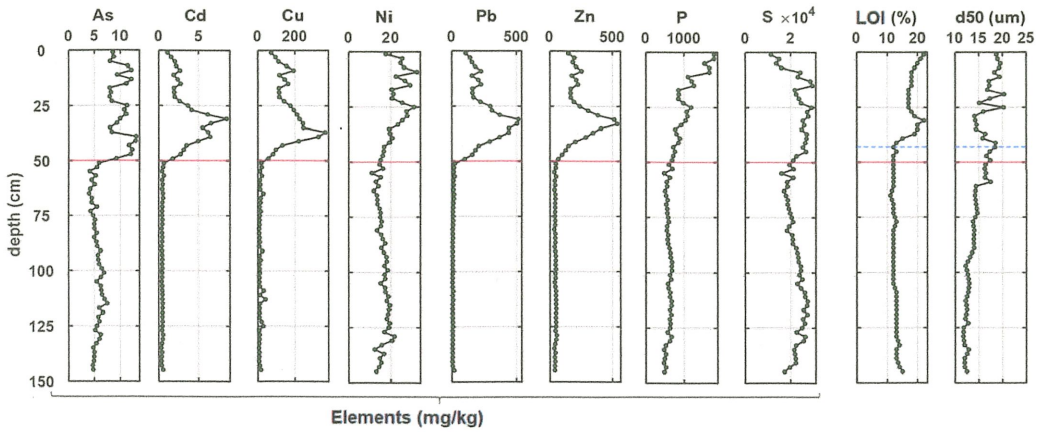

Fig. 9. Down-core profiles from our estuary sediment core showing concentrations of metals (As, Cd, Cu, Ni, Pb, Zn), phosphorous, sulfur, percent organic (LOI), and median grain size (d50). The depth at which metals increase above background is indicated by a red line, and corresponds to the onset of industrialization in the region.

likely due to the spatial and temporal intricate human impacts on the rivers and complex hydrogeochemistry controlling the NPEs. Thus, we were limited in our conclusions that urbanization or agriculture affected Cd, Cu, Ni, or Zn area-normalized exports at the watershed scale. Instead of land cover, river water DOC, Mn, and Fe concentrations were important for area-normalized dissolved and sediment-bound exports of Cd, Cu, Ni, and Zn (Table 3). The correlations between Fe and Mn with Cd, Cu, Ni, and Zn suggests that organic complexation and inorganic complexation are controlling export. River water DOC and Fe are likely important for increasing metal solubility and preventing adsorption to immobile sediments, as observed in Audry et al. (2010) and Jiann et al. (2013). Lastly, riparian soil Mn and %OM were negatively correlated with river water Cu, implying that either Mn and OM were promoting Cu sequestration in riparian soil or that riparian soils with higher Mn and OM (such as more hydric or wetland soils) were poor sources of Cu. Copper sorption to Mn oxides is well-known and actively used in removal of metals in waste waters (e.g. Han et al., 2006). However, our sediment core shows the temporal export of Cd, Cu, Pb, and Zn in Thames River watershed to be strongly linked but weak linkages with % OM (Fig. 9) and poor linkages with Mn (Supplemental Materials).

4.4. Phosphorus storage and transport

We expected P in riparian soils, bottom sediments, river water, suspended sediments, and watershed-scale export to be greatest in watersheds with higher %Farmland, which was only partially confirmed. Riparian soils and suspended sediments P concentrations were second highest for the Little River, whose watershed has the highest proportion of farmland. However, riparian soils, bottom sediments, suspended sediments, and river water had higher mean P concentrations in Bartlett + Exeter brooks than all other watersheds, despite a high %Forest and intermediate %Farmland. Area-normalized dissolved and sediment bound P export was greatest for the Little River and Bartlett + Exeter Brooks. These results show that the watershed with the first and third highest proportion agriculture had the highest storage and higher transport of P than the other watersheds. Thus, we did not find a strong linkage in agricultural enriching soil, sediment, and river water concentrations.

When considered at the watershed-scale, watershed P export was greater for dissolved than sediment export rates for most watersheds, by a factor of 1.1 to 1.7, highlighting that dissolved P is the key factor at the watershed scale. However, total dissolved and sediment-bound P export was greatest for the Quinebaug river due to having the largest water discharge, followed by Little River and Bartlett + Exeter Brooks. Thus, the watersheds with high %Farmland had high P river water concentrations, but the largest, most urbanized watershed had the highest total and area-normalized P export. Fortunately, river water concentrations were below the ambient water quality criteria of 31 μg L^{-1} for New England (see USEPA, 2000). In addition, watershed export of P in our study (6 to 14 kg yr^{-1} km^{-2}) was within or below the lower range of Connecticut watershed P export of (10 to 170 kg yr^{-1} km^{-2}) described by Norvell et al. (1979), but was higher than forested watersheds (~3 kg yr^{-1} km^{-2}), and much lower than urban watersheds (24.5–83.7 kg yr^{-1} km^{-2}) in the Chesapeake Bay between 1998 and 2007 (Duan et al., 2012). With major changes to P pollution management, we observe that there are measurable decreases in P export but P pollution is still present and remains a serious issue limiting long-term societal sustainability (Farmer, 2018; Metson et al., 2022). The sediment core shows P export has continued increasing, which may be tied to %OM dynamics in the Thames River watershed. However, it is clear that unlike the metal pollutants, policies have not substantially decreased its export. Furthermore, siliclastic sediments do not appear to be driving P export as particle size profiles do not have similar changes with depth.

Our stepwise and multiple regressions show that area-normalized dissolved P was negatively correlated with bottom sediment %OM and riparian soil Mn. These results imply that riparian soil Mn and bottom sediment OM may be directly promoting P sorption or areas with high Mn and OM accumulation may be poor sources of P (such as hydric soils). Sediment-bound P was correlated with river water and bottom sediment Fe concentrations, suggesting sediment Fe is important for the colloidal transport of P. Additionally, PCA analyses show that P consistently varied with Mn, %OM, and pH across riparian soils, bottom sediments, suspended sediments, and river water samples, albeit along PC2 with lower explanatory power. The high capacity of wetland and riparian soils for removal of P is well known (see Skinner, 2022) and our findings agree with previously observed mechanisms of Mn and Fe oxide and OM complexation and removal of P from river waters (e.g. House and Denison, 2000; Hoffmann et al., 2009; Kim et al., 2011). Since the highest P concentrations were observed in the riparian soils, preventing their erosion and maximizing their sorption capacity through Mn and Fe oxides and OM supports the argument for maintain and improving their P removal efficiency between 0.01 and 1.3 kg yr^{-1} km^{-2}(see Hoffmann et al., 2009).

4.5. Study limitations

Our study had limitations in methods used to investigate soils, sediments, and addressed the full heterogeneity observed at the watershed scale. For soils, we focused on only soil solid phase samples and did not

include dissolved soil water, which can be more effective in understanding mobility of NPEs from soil. In addition, we examined soils and bottom sediments from only a small set of river and stream locations and not every major tributary or confluence within the watersheds. Further, there were limitations in spatial and temporal river water and suspended sediment sampling. Our water sampling did not occur in high enough frequency to capture the effect of major storms and high flow conditions, in which elements that exhibit positive concentration-discharge flushing would be underestimated. However, trace elements such as Pb are commonly diluted under high discharge (e.g. Bradley and Lewin, 1982). Also, our suspended sediment passive samplers and 1 L bottle samples were limited in our assessment of suspended sediments. Our passive sampling method captured organic-rich suspended particles and thus would underestimate analytes associated with sorption to siliciclastic sediment transport within the Thames River watershed. Additionally, we did not measure NPE concentrations on sediments from the 1 L bottles as the masses were often too small for several of the rivers and we instead used trapped sediment concentrations. We did not collect suspended sediments during a major storm event (e.g. tropical storm), when low order watersheds transport a large percentage of their suspended load. Thus, our passive suspended sediment samplers likely reflect low and moderate flow conditions, potentially biasing our results (Yellen et al., 2016). Despite these limitations, our results at the watershed scale confirm that physicochemical properties and land-use are not simple cause-effect systems and thus process-based models require additional field measurements, such as subsurface flow and internal river storage to understand watershed-scale biogeochemistry.

5. Conclusions and implications

Our study highlights that the soil–sediment–river water linkages for NPEs are complex: riparian soil NPE concentrations were generally weak predictors for sediments and river water NPE concentrations and human development and agriculture land covers were not weakly linked with soil, sediment, and river water NPEs. Physicochemical properties, specifically DOC, Fe, and Mn concentrations were important predictors for watershed dissolved and sediment export of NPEs.

Arsenic was the most abundant NPE and generally exceeded soil CT-DEEP and sediments and river water EPA SQT Level II targets. The other NPEs were limited in the enrichment. These results show that the Thames watershed has impairments relating to As and occasionally Pb but other NPEs concentrations are low. Either historical enrichment of NPEs have been sequestered in upland soils, trapped within wetlands, buried in lake and reservoir bottom sediments, or have been exported to Long Island Sound.

While our methods were able to generate estimates of dissolved solute exports and estimates for NPE stocks in riparian soil, bottom sediment of pools, and suspended sediments across the Thames River watershed, there are several important limitations. First, our riparian soil and bottom sediments are limited spatially and with depth. Our sediment core shows that export of NPEs through time has widely varied and mobilization of deep bottom sediments could yield higher NPE fluxes. Second, large flushing events moving NPEs through the watershed were not captured. This has been shown to be important for capturing large stochastic fluxes but was not measured in our study. Third, our suspended sediments were from low to medium baseflow conditions of the rivers, likely underestimating sediment-bound export of NPEs that occur during large storm events that are important for large erosion events. Lastly, we hypothesize that groundwater transport, hyporheic exchange, and erosion likely control transport of NPEs to surface waters and additional studies are needed to investigate these effects.

CRediT authorship contribution statement

Mark J. Butler: Conceptualization, Methodology, Investigation, Writing – Original Draft, Writing – Review and Editing, Data Visualization.

Brian C. Yellen: Methodology, Conceptualization, Writing – Original Draft, Writing – Review and Editing.

Oluyinka Oweyumi: Methodology, Conceptualization, Writing – Original Draft, Writing – Review and Editing.

William Ouimet: Methodology, Sample Collection, Writing – Review and Editing.

Justin B. Richardson: Conceptualization, Methodology, Supervision, Project Administration, Investigation, Writing – Original Draft, Data Visualization.

Declaration of competing interest

The authors state that work was conducted without any personal, professional, or financial relationships that could potentially be construed as a conflict of interest. This study was funded by the College of Natural Sciences at the University of Massachusetts Amherst.

Data availability

Data is available at UMass Scholarworks: https://doi.org/10.7275/hqcy-3y46

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.165630.

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