

Assessing organic contaminant fluxes from contaminated sediments following dam removal in an urbanized river

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Abstract In this study, methods and approaches were developed and tested to assess changes in contaminant fluxes resulting from dam removal in a riverine system. Sediment traps and passive samplers were deployed to measure particulate and dissolved polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in the water column prior to and following removal of a small, low-head dam in the Pawtuxet River, an urbanized river located in Cranston, RI, USA. During the study, concentrations of particulate and dissolved PAHs ranged from 21.5 to 103 $\mu\text{g/g}$ and from 68 to 164 ng/L , respectively. Overall, temporal trends of

PAHs showed no increases in either dissolved or particulate phases following removal of the dam. Dissolved concentrations of PCBs were very low, remaining below 1.72 ng/L at all sites. Particulate PCB concentrations across sites and time showed slightly greater variability, ranging from 80 to 469 ng/g , but with no indication that dam removal influenced any increases. Particulate PAHs and PCBs were sampled continuously at the site located below the dam and did not show sustained increases in concentration resulting from dam removal. The employment of passive sampling technology and sediment traps was highly effective in monitoring the concentrations and flux of contaminants moving through the river system. Variations in river flow had no effect on the concentration of contaminants in the dissolved or particulate phases, but did influence the flux rate of contaminants exiting the river. Overall, dam removal did not cause measurable sediment disturbance or increase the concentration or fluxes of dissolved or particulate PAHs and PCBs. This is due in large part to low volumes of impounded sediment residing above the dam and highly armored sediments in the river channel, which limited erosion. Results from this study will be used to improve methods and approaches that assess the short- and long-term impacts ecological restoration activities such as dam removal have on the release and transport of sediment-bound contaminants.

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Introduction

Restoration of rivers, their associated watersheds, and ecosystems is a growing priority for government agencies (e.g., USDA, NOAA, USEPA), as well as conservation organizations (e.g., American Rivers, Trout Unlimited). Historically, dams have provided a range of diverse and tangible benefits to society such as power generation, flood control, water supply, navigation, and recreational use (Whitelaw and Macmullan 2002). These benefits, however, have come at a cost in the form of ecologically impaired watersheds and river systems (Poff and Hart 2002). Dams have negatively impacted the water quality of many rivers (e.g., water temperature, nutrient alterations) (Gregory et al. 2002; Stanley and Doyle 2002) and have been associated with reductions in the diversity and populations of aquatic and benthic organisms (Bednarek 2001). Dams also interrupt the natural transport of sediments through river systems, resulting over time in changes to the river's hydrology, sedimentation, and geomorphology (Baish et al. 2002). Consequently, dam removal has been identified as an important activity in the overall effort to restore riverine habitats and ecosystems.

In the USA, dams range widely in size and design, depending on the human needs being served (e.g., power generation, irrigation). Recent data from the National Inventory of Dams (NID) shows more than 84,000 large dams currently listed (USACE 2013) in the USA, with estimates of more than two million when including smaller structures with a height of 5 ft or less (Graf 1993). Many of these low-head dams are owned by individuals, small companies, or municipalities without the financial resources to either properly maintain or remove the structures.

The fact that many existing dams have outlived their primary, specified use is alone justification for removal of these structures (Pohl 2002). Also relevant is that many impoundments have exceeded their design or service life, adding concerns of dam safety to the rationale for removal. Arguably, one of the most important and frequently cited justifications for dam removal has been the interruption of fish migration, which has resulted in reduced populations of commercially and ecologically important species (Gregory et al. 2002). Finally, economic issues such as repair and potential liability costs along with the opportunity to restore fish runs, protect endangered species, improve water quality, and recreational uses have been often cited as reasons

for removal (Bowman 2002). As a result of these factors, rates of dam removal have increased in the USA, with 63 dams removed in 2012, and just under 600 since 1999 (American Rivers 2013).

As the number of dams being considered for removal has increased, so too has the need for methods and approaches to monitor conditions and assess recovery and restoration efforts following removal. Some progress has been made with respect to post-removal assessments of ecological recovery and development of approaches (e.g., Stream Functions Pyramid) to measure functional improvement of physical, chemical, and biological processes (Harman 2008). Responses to dam removal vary greatly depending on dam and watershed characteristics, with little information existing on impacts resulting from small dam removal (Hart et al. 2002). Sediment-related issues resulting from post-removal erosion, transport, and subsequent redeposition are among the most important physical factors concerning dam removal today (Heinz Center 2002). Currently, most sediment management plans associated with dam removal projects do not have any post-removal monitoring component to measure changes in the behavior and flux of sediment-bound contaminants. There is an increasing need to better understand how contaminated sediments in river systems respond following dam removal to better assess the ecological impacts and recovery of these projects. This is particularly relevant for many rivers in New England that were dammed as far back as the start of the American Industrial Revolution and which still contain historically contaminated sediments behind the dam and in the river.

To date, few studies (e.g., Ashley et al. 2006; Evans and Gottgens 2007) have investigated changes in the concentrations of sediment-bound contaminants following dam removal. None to our knowledge have measured dissolved and particulate fluxes of contaminants before and after dam removal, instead relying exclusively on bulk sediment measurements, which limits information necessary to make informed management decisions. There have been instances where dams with contaminated sediment issues were removed, resulting in significant environmental damage. One example is the Niagara Mohawk dam in Fort Edward, New York, USA originally used to generate hydroelectric power. This dam spanned a portion of the upper Hudson River and contained enormous quantities of polychlorinated biphenyl (PCB)-contaminated sediment accumulated from long-term discharge. When removed in 1973, PCB-laden sediment

was released and ultimately transported throughout much of the Hudson River system. As a result, portions of the river were designated as an USEPA Superfund site (Sloan et al. 2005). Consequently, remediation and monitoring efforts at this location are still taking place today (<http://www.epa.gov/udson/>).

Our objective for this study was to develop and evaluate novel methods and approaches not previously employed to measure contaminant fluxes in riverine systems prior to and following dam removal. To accomplish this, we measured polycyclic aromatic hydrocarbons (PAHs) and PCBs in the dissolved and particulate phases in the water column of the Pawtuxet River before and after dam removal to better understand how contaminant mobility and fate were affected.

Passive samplers were deployed during this study and evaluated for their ability to measure subtle changes in dissolved phase contaminant concentrations in the water column over time and space. Sediment traps were co-deployed alongside the passive samplers to measure particulate contaminant concentrations. The dam in this study was a low-head impoundment located at the mouth of the lower Pawtuxet River, a moderately contaminated, urbanized river in Cranston, RI, USA, which had been continuously dammed in a range of configurations since 1638 (USDA 2006). The Pawtuxet River system is typical of many in New England where dam locations contain contaminated sediments, a major issue impeding the overall removal process.

Materials and methods

Study area and deployments

The Pawtuxet River watershed covers an area of approximately 590 km² (Fig. 1). The Pawtuxet River has an overall length of approximately 19.8 km, measured at the confluence of the North and South branches of the Pawtuxet (USGS 2013). For this study, the lower Pawtuxet River is identified as the river segment starting at the USGS gauging station in Cranston extending downriver to the site of the Pawtuxet Falls dam: an overall length of approximately 7 km. River width in this segment ranges between approximately 15 to 60 m with depths ranging from approximately 1 to 3 m in channel locations. In this segment, the river exhibits very little vertical gradient, dropping approximately 1 m over its 7 km length (Kleinschmidt 2005).

The lower Pawtuxet River started receiving domestic and manufacturing wastes in the 1800 s, and late into the century, water quality had become an issue (Kleinschmidt 2005). During this period, human population and manufacturing activities on the lower parts of the river and within the watershed had steadily grown. In the 1930s, domestic WWTPs were constructed that discharged effluents to the river, with three secondary level plants currently discharging to the river above the study area. More recently, manufacturing facilities and chemical operations had discharged a broad array of organic chemicals and heavy metals to the river (Lopez-Avila and Hites 1980; Quinn et al. 1985). There have been remedial actions in the 1990s to remove sediment-bound contaminants (e.g., PCBs) from a location above sampling site 1 in the study area (Fig. 1). Despite these efforts, contaminants remain distributed throughout the sediments of the lower river. Among the major sediment-bound contaminants present are PAHs and PCBs (Quinn et al. 1985) along with heavy metals such as cadmium, copper, lead, and zinc (Ciba Geigy Corporation 2003). Also present at high concentrations are numerous specialty chemicals, such as plastic additives and antimicrobial compounds, that are not listed as priority pollutants and for which no sediment criteria guidelines exist (Lopez-Avila and Hites 1980).

Using historical data, on-site surveys, and the dam removal feasibility study (Kleinschmidt 2005), three sites were selected for deploying sediment traps and passive samplers for the study (Fig. 1). Two sites were selected in the river; site 1 was 1.9 km upriver from the dam location in approximately 3 m of water far enough upriver so it would be free from major changes in morphology (e.g., erosion, bed, or bank) other than small decreases in water level (<1 ft). This location is also below most of the known industrial discharges to the river (Lopez Avila and Hites, 1980; Quinn et al. 1985). Site 2 was located 760 m above the dam in approximately 2.5 m of water and was identified as a potential location which would register any upriver effects resulting from erosion or remobilization of contaminated sediment. Site 3 was located approximately 50 m below the dam location in Pawtuxet Cove in approximately 4 m of water. This site was situated as close as possible to the dam location without exposing the samplers to excessive turbulence and mixing at high water flows. This location is tidally influenced, but salinities were extremely low, generally ≤ 0.5 psu at a river flow of 14.1 m³/s. The dam was classified as a run

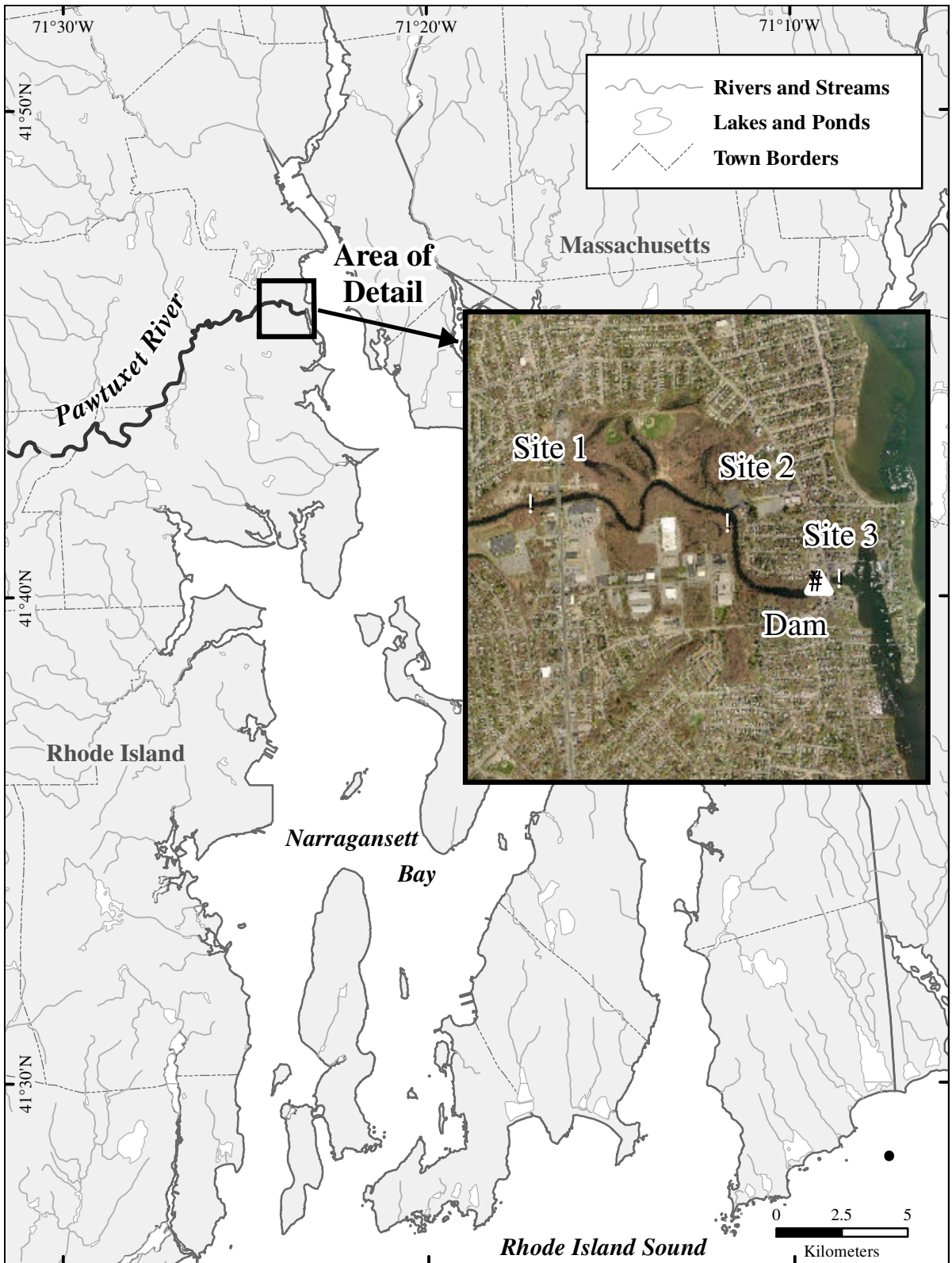


Fig. 1 Map of the study area

of river structure, constructed of concrete, 52 m in length, approximately 1.5 m in height and replaced an existing timber dam in 1924. Physical removal of the dam started on August 9, 2011, and major operations were completed in approximately 3 weeks. Sediment trap and sampler deployments occurred at four periods during the study: once before dam removal and three times following removal (Table 1; Supplemental Materials (SM)). In addition, sediment traps were deployed continuously at site 3 (below dam) during the study to provide a long-term record of particle fluxes from the river.

River flow data for this study was collected from the USGS gauge site (USGS 01116500 Pawtuxet River). This field gauge is located on the Pawtuxet River 7.2 km above the location of the dam and has been in operation since 1939. One small tributary, the Pocasset River, contributes flow to the Pawtuxet below the gauging station. Raw reported flow data from the gauging station was corrected for the Pocasset input using the watershed ratio correction factor approach which has been used previously for such purposes (Emerson et al. 2005). In order to better understand particle transport trends and to estimate contaminant fluxes through and exiting from the river, a model of total suspended solids (TSS) versus flow was constructed. Water samples ($n=13$) were collected at site 3 at a range of flows and were filtered

through Whatman GF/F glass fiber filters (0.7 μm nominal retention) and TSS calculated gravimetrically. Further information on the flow model can be found in the SM section.

Sediment extraction

PAHs and PCBs were extracted from a sediment core collected in 2007 and the fine fraction ($<63 \mu\text{m}$) of the sediment trap contents by way of accelerated solvent extraction (ASE) using a Dionex ASE model 200 (Thermo Scientific, Chelmsford, MA, USA). Stainless steel extraction cells were loaded with approximately 0.5 g of freeze-dried sediment mixed with approximately 3 g diatomaceous earth prior to the addition of PAH internal standard (IS) and CB 198 as IS for PCB analysis (Table S1). Samples were extracted using a 1:1 mixture of hexane/acetone over three 5-min static cycles at 150 °C and 1,800 psi. Extracts were evaporated to approximately 2–5 mL and solvent exchanged to hexane prior to being loaded onto silica solid phase extraction cartridges (Waters Corporation, Milford, MA, USA) topped with approximately 1 g each of sodium sulfate and activated copper. Extracts were eluted with 12–15 mL of a 90:10 mixture of hexane/dichloromethane (DCM), exchanged to hexane, reduced to 1 mL and stored at $-5 \text{ }^\circ\text{C}$ until analysis by GC/MS.

Table 1 Summary of PAH and PCB data

	Before			After 1			After 2			After 3		
	28 July 2011–9 August 2011			5 December 2011–19 December 2011			28 February 2012–13 March 2012			10 July 2012–24 July 2012		
	Site 1	Site 2	Site 3	Site 1	Site 2	Site 3	Site 1	Site 2	Site 3	Site 1	Site 2	Site 3
$\sum\text{PAH}_d$ (ng/L)	164	135	92.9	68	–	69	146	154	93	143	150	71
$\sum\text{PCB}_d$ (ng/L)	0.51	0.86	0.64	0.91	–	0.59	0.35	0.38	0.58	0.59	1.43	1.72
$\sum\text{PAH}_p$ ($\mu\text{g/g}$)	76.4	68.6	40.5	28.8	21.5	25.1	87.5	42.6	40.5	103.0	78.0	27.4
$\sum\text{PCB}_p$ (ng/g)	168.0	202.3	203.4	173.9	231.1	190	80.1	116.6	133.7	248.0	468.8	169.7
Flux $\sum\text{PAH}_d$ (g/day)	–	–	56.0	–	–	229	–	–	101	–	–	22
Flux $\sum\text{PCB}_d$ (g/day)	–	–	0.39	–	–	1.95	–	–	0.63	–	–	0.53
Flux $\sum\text{PAH}_p$ (g/day)	–	–	88.0	–	–	1531	–	–	221	–	–	16
Flux $\sum\text{PCB}_p$ (g/day)	–	–	0.4	–	–	11.6	–	–	0.73	–	–	0.1
Avg daily flow (m^3/s)	–	–	7	–	–	37.1	–	–	11.1	–	–	3.7
Bulk surficial sediments 0–2.5 cm^a	Site 1			Site 2			Site 3					
$\sum\text{PAH}$ ($\mu\text{g/g}$)	18.1			315.5			52					
$\sum\text{PCB}$ (ng/g)	8.2			12.8			17.5					

^aSurficial sediments collected during “After 2” deployment

PE sampler preparation and extract processing

Low-density polyethylene (PE; 25 μm thick; Covalence Plastics, Minneapolis, MN, USA) was cut into strips of 15 cm \times 40 cm. Strips of PE were pre-cleaned by soaking for 24 h sequentially in acetone, DCM, and Milli-Q water. Strips of PE were then soaked in a performance reference compound (PRC) solution (80:20 methanol/water) containing deuterated PAHs and ^{13}C -labeled PCBs for 21–28 days on an orbital shaking table (Table S1). Neat deuterated PAHs and ^{13}C -labeled PCBs in nonane were purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Deuterated PAHs in DCM were purchased from Sigma-Aldrich (St. Louis, MO, USA). Each PRC jar contained four sampler strips and 900 mL aqueous PRC solution. Strips of PE were removed from the PRC solution; one strip was taken from each PRC solution jar and cut in half for pre-deployment PRC concentrations, and the remaining strips were attached to stainless steel wire inside galvanized extended minnow trap cages. Passive sampler cages were deployed for 12–14 days at the three site locations in the Pawtuxet River. Samplers retrieved from the field were wiped clean of water and epiphytes before extraction. Passive samplers were weighed and extracted by soaking sequentially in acetone and DCM for 24 h with PAH and PCB IS (Table S1). Acetone and DCM extracts were combined, solvent exchanged to hexane, and volume reduced to 1 mL.

Analysis

For this study, 21 individual PAHs and 26 PCB congeners were measured (Table S1). In this paper, summed concentrations of PAHs and PCBs are reported and indicated by “ Σ ”, while dissolved and particulate concentrations are presented using the subscript “d” and “p,” respectively. Analysis of PAHs and PCBs were performed on an Agilent 7890 gas chromatograph equipped with a 5975 mass selective detector (GC/MSD) (Agilent Technologies, Wilmington, DE, USA) operated in select ion monitoring mode. Analytes were quantified with five- and six-point calibration curves for PAHs and PCBs, respectively, with calibrations (with a linear coefficient of determination of $r^2=0.99$ or better as minimum acceptance criteria) performed prior to each analysis. All sediment extractions were extracted along with process blanks and standard reference materials (SRM). Blank values were below the limit of

quantitation, while National Institute for Standards and Technology (NIST) SRM 1944 recoveries averaged 105 and 97 % for PAHs and PCBs, respectively. Continuing calibration verification standards were measured as part of each instrument run and were within 10 % of stated concentrations. Dissolved water concentrations of PCBs and PAHs were calculated using passive sampler concentrations, chemical-specific passive sampler partition coefficients, and mass transfer coefficients obtained from PRC equilibration. Deuterated PAHs and ^{13}C -labeled PCBs were used as PRCs for PAHs and PCBs, respectively. Calculations and other information regarding PE samplers are described in more detail in the SM and Perron et al. (2013). For total organic carbon (TOC) analysis, certified standards produced calibration curves with an r^2 of 0.99 or better, and a manufacturer-supplied SRM was frequently analyzed and within 10 % of certified value. All samples were run in duplicate and had an average relative standard deviation of 6.3 %, while blanks were below the level of detection. Grain size analysis was conducted using a Malvern Mastersizer 2000 laser particle size analyzer (Worcestershire, UK) with results reported using the Udden Wentworth scale.

Results

River conditions

During the study (July 28, 2011–July 24, 2012), river flow varied from 2.9 to 75.2 m^3/s with a mean of 14.4 m^3/s (Fig. 2). Average flows during three of the four sampler deployments were much lower (3.7–11.1 m^3/s) than the first post-removal deployment (37.1 m^3/s), which coincided with a major wet weather event in December 2011 and registered the peak flows (e.g., 75.2 m^3/s) observed during the study (Table 1, Fig. 2). During this deployment, flow ranged between 18.5 and 75.2 m^3/s , and the PE sampler at site 2 was lost. Overall, the average flow during the study (14.4 m^3/s) is slightly higher than the previous 5 years of recorded average flow (12.7 m^3/s). The data used in the TSS model were sampled over a wide range of flow (5.8–34.9 m^3/s) following dam removal, and overall levels were low, ranging from 0.9 to 27 mg L^{-1} , with TSS increasing with flow. Data were fit using linear regression with a coefficient of determination (r^2) of 0.75 (Fig. S1). The resulting model was used to predict

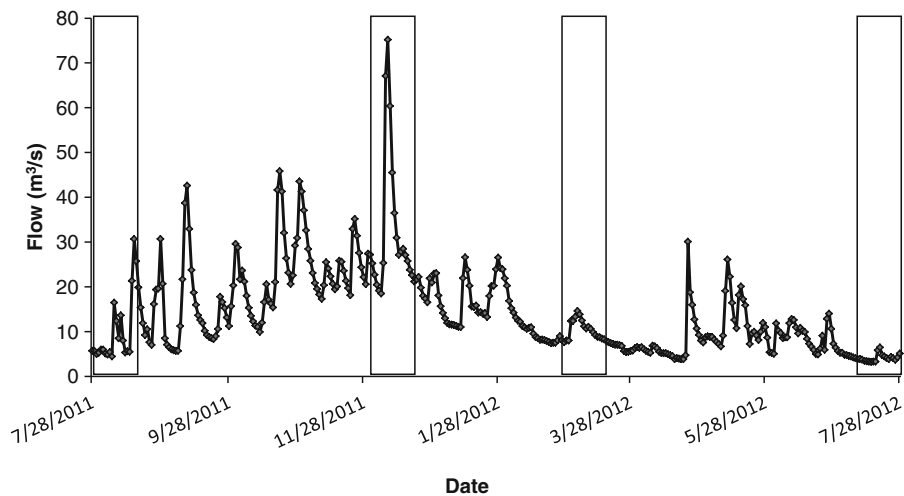


Fig. 2 Pawtuxet River flow rates

particulate-bound contaminant fluxes at different river flows during the study period. Suspended sediment fluxes over the course of the study were also estimated, with daily sediment transport at the mouth of the river (site 3) ranging from 0.66 to over 250 MT per day (dry weight) depending on river flow. During the 1-year period of this study, an estimated 5,000 MT of suspended sediment was predicted to have exited the river. Grain size analysis was performed on sediment trap contents at site 3 and provides a continuous record of change in particle size that may be attributable to post-dam removal morphological adjustments in the river. The percent of sand in the trap at site 3 increased from 47 % to a high of 68 % following dam removal, with a corresponding decline in the silt fraction (Fig. S2). This shift in distribution remained present for several deployments before reverting back to pre-removal values.

Dissolved PAHs and PCBs

Before dam removal and throughout the three post-removal deployments, $\sum\text{PAH}_d$ ranged from 68 to 164 ng/L at each of the sites (Fig. 3a). Higher concentrations were generally observed at sites 1 and 2 in the river than at site 3 below the dam site, where concentrations ranged from 69 to 93 ng/L. $\sum\text{PCB}_d$ were present at much lower concentrations, ranging from 0.35 to 1.72 ng/L across all sites for both pre- and post-removal deployments (Fig. 3b). $\sum\text{PCB}_d$ concentrations were very consistent for the pre-removal and post-removal deployments (≤ 0.9 ng/L); however, increases

to 1.43 and 1.72 ng/L were noted during the final deployment at sites 2 and 3, respectively.

Suspended particulate PAHs and PCBs

$\sum\text{PAH}_p$ from sediment traps ranged in concentration from 21.5 to 103 $\mu\text{g/g}$ across all sites and deployments (Fig. 4a). Excluding post-removal deployment 1, post-removal concentrations at site 1 were higher than pre-removal. At sites 2 and 3, post-removal concentrations were either equal to or less than those observed pre-removal. Between sites, there was a declining trend in concentration from sites 1 to 3 in three of the four deployments, with concentrations at site 1 always the highest (Fig. 4a). $\sum\text{PCB}_p$ concentrations ranged from 80 to 469 ng/g across all sites and deployments (Fig. 4b). At sites 1 and 2, post-removal concentrations were higher than pre-removal values with the exception of post-removal deployment 2. At site 3, $\sum\text{PCB}_p$ levels were slightly higher in the pre-removal deployment compared to all the post-removal deployments. There was a consistent increase in concentration noted from sites 1 to 2, suggesting that particles enriched in $\sum\text{PCB}_p$ were being entrained into the water column below site 1.

Sediment PAHs and PCBs

A sediment core collected in 2007 near site 2 provided a temporal record of $\sum\text{PAH}$ and $\sum\text{PCB}$ levels residing within the sediments of the lower Pawtuxet river. For $\sum\text{PAH}$, concentrations exceed 200 $\mu\text{g/g}$ at the bottom of

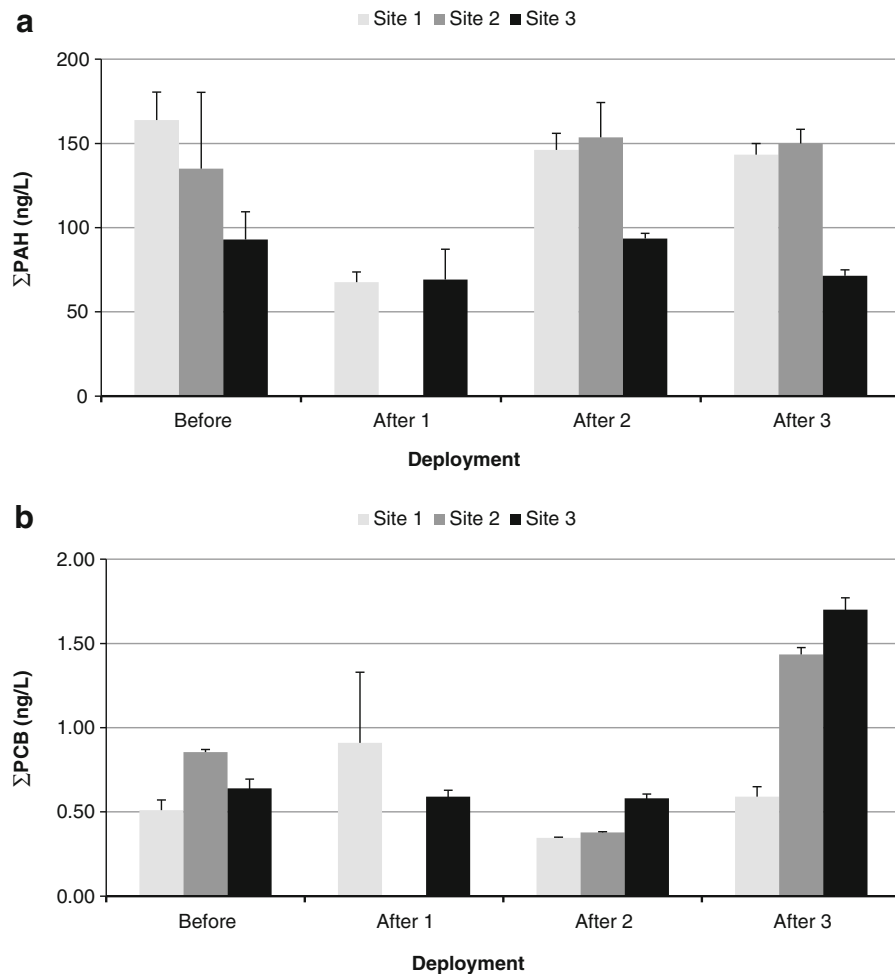


Fig. 3 **a** Dissolved Σ PAH concentrations; **b** dissolved Σ PCB concentrations

the core, showing an irregular declining trend towards the top of the core with an average concentration of $33 \mu\text{g/g}$ in the top 5 cm (Fig. 5). For Σ PCB, concentrations remain fairly constant at or near $1 \mu\text{g/g}$ from the bottom of the core to 40 cm depth. Above 40 cm, the concentrations climb rapidly to over $30 \mu\text{g/g}$, suggesting an event occurred which resulted in the discharge or release of PCBs upriver of this location (Fig. 5). Concentrations decline rapidly from this maxima, but remain above $3 \mu\text{g/g}$ in the top 5 cm. Surficial sediments were collected at each sampling site to provide a spatial perspective of the current contaminant levels at each location. For Σ PAH, sediment concentrations ranged from 18 to $315 \mu\text{g/g}$, with the highest levels at site 2 (Table 1). Sediment concentrations of Σ PCB ranged from 8.2 to 17.5 ng/g , with the highest levels recorded at site 3 below the dam.

Discussion

Effects of dam removal on Σ PAH and Σ PCB dissolved and particulate concentrations

A major focus of this study was to monitor water column conditions before and after dam removal to determine if this process resulted in increased chemical concentrations or fluxes to the river. Concentrations of Σ PAH_d during the first post-removal deployment were the lowest measured during the study, coinciding with a prolonged rain event (7.5 cm in 48 h) which resulted in a peak flow of $75.2 \text{ m}^3/\text{s}$ and elevated flows for much of the deployment (Fig. 3a). The other post-removal deployments had flows ranging from 29 to $16.5 \text{ m}^3/\text{s}$, exhibiting similar trends in concentration between all sites including the pre-removal deployment (Fig. 2).

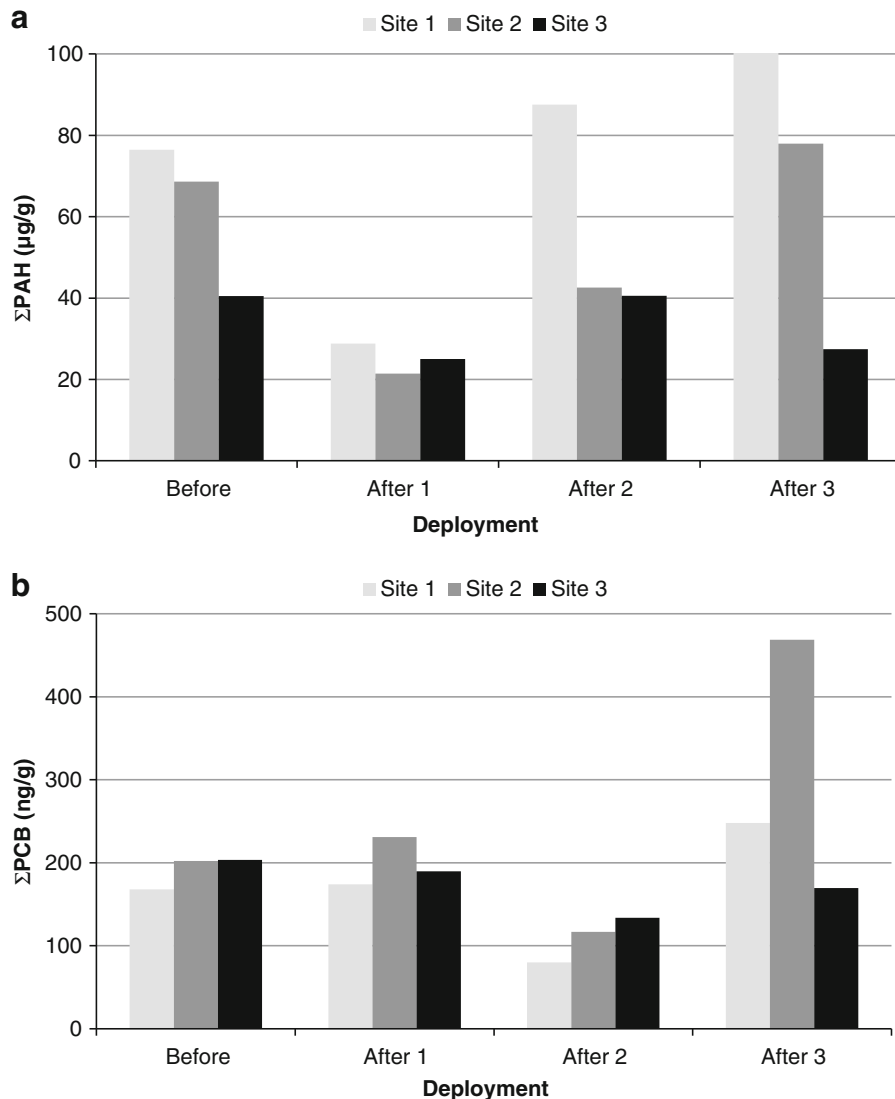


Fig. 4 **a** Particulate ΣPAH concentrations; **b** particulate ΣPCB concentrations

Concentrations of ΣPAH_d remained remarkably consistent between site 1 in the upper part of the study area and at site 2 just above the dam across all deployments. This indicates that removal of the dam was not affecting ΣPAH_d concentrations immediately above the dam and up to site 1 (Fig. 3a). Concentrations at site 3 were generally lower than the river sites and were very consistent across all pre- and post-removal deployments.

Concentrations of ΣPCB_d were much lower than ΣPAH_d, remaining below 1.0 ng/L during pre- and post-removal until the final post-removal deployment, with sites 2 and 3 showing the highest concentrations recorded during the study at 1.43 and 1.72 ng/L,

respectively (Fig. 3b). There were no clear spatial trends reflected in these data, and the only temporal feature was the slightly higher levels noted at sites 2 and 3 during the final deployment. The lower concentration of ΣPCB_d relative to ΣPAH_d is due to the large disparity in particulate concentrations observed in the sediment traps and river sediments, which is the source of the dissolved phase contaminants via partitioning between the two environmental phases (Table 1). Further, PAHs are arguably the most ubiquitous organic contaminants because there are so many sources in developed areas including releases from petro-chemical industries, burning of fossil fuels, and spills of petroleum during

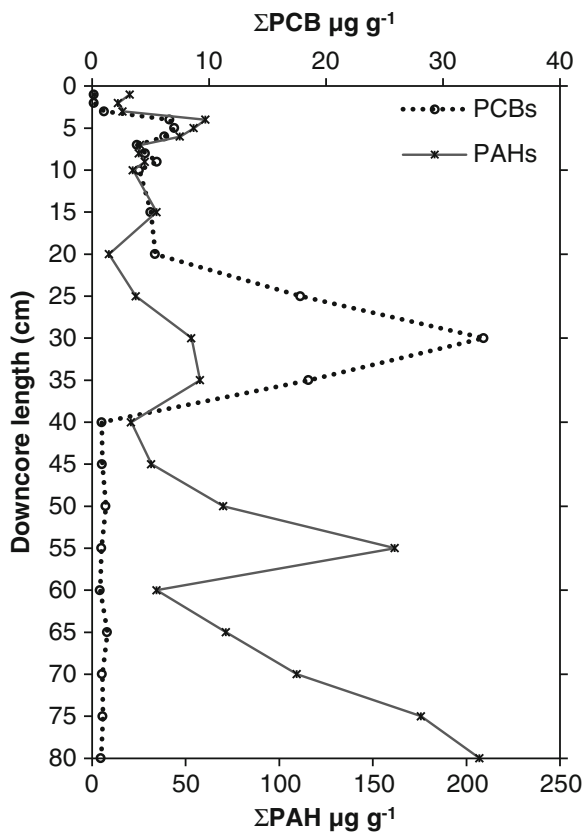


Fig. 5 Σ PCB and Σ PAH concentrations in the sediment core

transport (Burgess et al. 2003). In contrast, PCBs are far more limited including the historical leakage by transformers and heat transfer fluids (Erickson 1992). Spatial behavior of the two compound groups was somewhat different in that the lowest concentrations of Σ PAH_d across sites were observed at site 3 where Σ PCB_d are more variable. What was not observed is either a large or sustained increase in either Σ PAH_d or Σ PCB_d at any of the sites following dam removal. This is remarkable, particularly for site 3 (below the dam), which is where any effects of dam removal would be expected to be seen. A benefit of using passive samplers for measuring water column concentration is that they sample the dissolved phase, which is a good surrogate for the bioavailable concentration of the PAHs and PCBs (Gschwend et al. 2011). The absence of large increases in either Σ PAH_d or Σ PCB_d concentrations indicates that their bioavailability had not changed as a result of dam removal. It is important to recognize that passive sampler measurements reflect average concentrations during these deployments (Huckins et al. 2006). Although the

samplers are extremely sensitive and efficient monitoring devices over time, sudden spikes in concentration would not be detected. Based on the overall spatial and temporal responses of the Σ PAH_d and Σ PCB_d data, there is no evidence of increased concentrations during the deployments that can be attributed to removal of the dam.

During the four deployments, Σ PAH_p showed a declining trend in concentration from sites 1 to 3 (Fig. 4a). It is unlikely that this was due to in situ dilution as there are no source inputs such as large streams or discharges to the river below site 1, and at site 3, measured salinities during the study were less than 0.5 psu, confirming substantial dilution by seawater is not occurring at this site. The declining trend was also observed in the dissolved phase; therefore, the particulate and dissolved values from their corresponding sites and deployments were analyzed and a Pearson product coefficient (r) was determined. A strong correlation and significant relationship between particulate and dissolved PAHs across sites and times were observed ($r=0.81$; $p=0.002$). In contrast, Σ PCB_p behaved differently from Σ PAH_p spatially, with concentrations increasing from sites 1 to 2, and concentrations at site 3 remaining below those of site 2 values for all post-removal deployments (Fig. 4b). The correlation between dissolved and particulate Σ PCB was weaker than that for PAHs ($r=0.55$; $p=0.07$), but both phases were again linked to each other.

The similar interphase (i.e., particulate-dissolved) responses observed for Σ PAH_p and Σ PCB_p reflect their uniform behavior in the water column, while their difference in concentrations between sampling locations is likely site specific. Spatial variability in their respective sediment concentrations within the river is likely the major influence. These differences could be related to the source of the contaminants. PAHs enter the Pawtuxet system through varied sources (e.g., runoff, industrial discharges atmospheric deposition) (Quinn et al. 1985), while data from the sediment core suggests that much of the PCB present is from a single source. This is supported by strikingly different concentrations of Σ PAH_p and Σ PCB_p at each of the sampling sites (Table 1). The relationship between the particulate and dissolved phases could cause increases in contaminant bioavailability, especially in rivers where resuspension and erosion of sediment may occur. In summary, our findings show that (1) neither Σ PAH_p nor Σ PCB_p concentrations increased below the dam site following removal, and (2) the sampling devices and monitoring approaches being

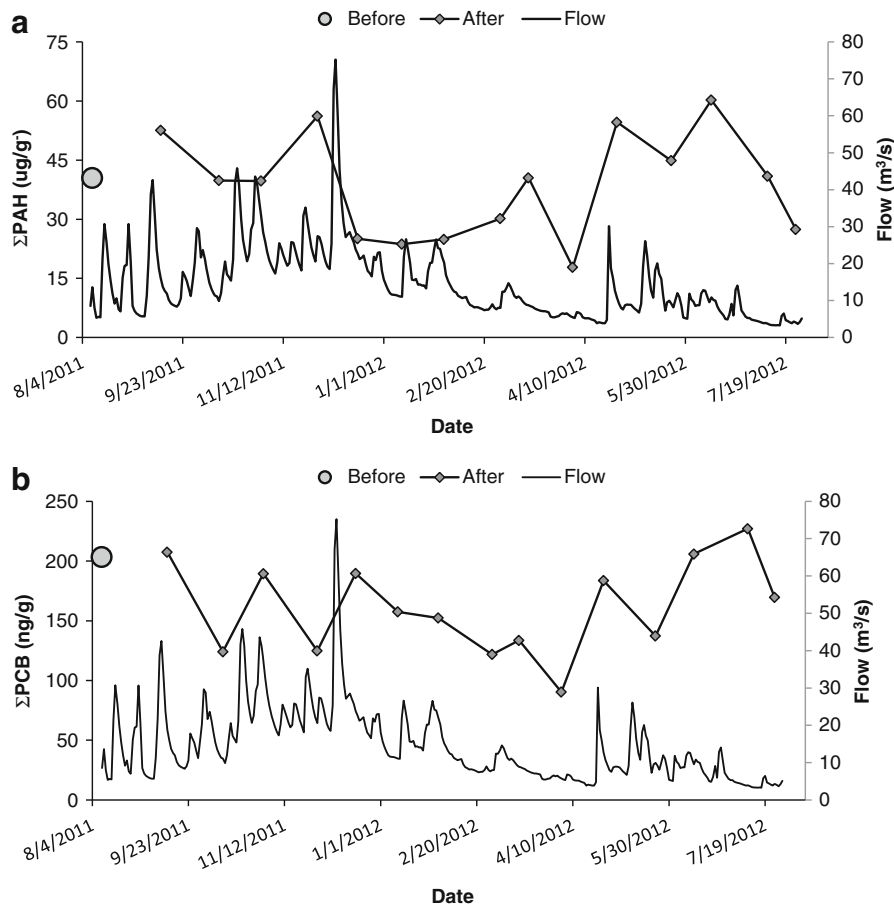


Fig. 6 **a** Sediment trap Σ PAH (below dam); **b** sediment trap Σ PCB (below dam)

tested were sensitive to small changes in contaminant behavior through time and space in this river. We suspect that in this system the site-specific sediment concentrations of the PAHs and PCBs are more significant than the effects of the dam removal.

Transport of particulate PAHs and PCBs

To determine if increases in contaminant concentrations occurred at any point following dam removal, Σ PAH_p and Σ PCB_p were measured throughout the study below the dam at the mouth of the river (site 3) by continuous deployment (one pre-removal, 15 post-removal) of sediment traps. The pre-removal trap concentration of Σ PAH_p was 40.5 μ g/g, while post-removal values ranged from 17.8 to 60.3 μ g/g during the study with a mean of 38.6 μ g/g and a standard deviation (SD) of 13.4 (Fig. 6a). In the deployment immediately following dam removal, Σ PAH_p increased slightly, but declined to

below pre-removal values in the next several deployments. The pre-removal value was exceeded five times during the post-removal deployments, with most of the concentrations falling within 1SD of the mean post-removal values. At site 3, there was no correlation nor relationship found between average daily river flow for each of the sediment trap deployments and their respective Σ PAH_p concentrations ($r < 0.001$; $p = 0.7$). The variability of Σ PAH_p concentrations following dam removal was minimal despite the great range of river flow during this period. This is further supported by the mean post-removal value (38.6 μ g/g), which was slightly lower than the pre-removal value (40.5 μ g/g).

During the same period, Σ PCB_p concentrations ranged from 121 to 227 ng/g. The pre-removal concentration was 203 ng/g, with slightly higher levels observed in 4 of the 15 post-removal deployments (Fig. 6b). Σ PCB_p concentrations in the deployments

following dam removal averaged 169.7 ng/g, more than 30 ng/g lower than the pre-removal value of 203 ng/g. As observed with the $\sum\text{PAH}_p$, there was no correlation or relationship between $\sum\text{PCB}_p$ concentration and the average daily flow ($r < 0.001$; $p = 0.84$), indicating that $\sum\text{PCB}_p$ levels were also insensitive to variability in river flow during the study. It is clear that the concentrations of $\sum\text{PAH}_p$ and $\sum\text{PCB}_p$, as well as their temporal trends during the study, were quite different. What is similar, however, is their narrow range of post-removal variability, which is also close to their respective pre-removal values. This consistency is remarkable given the range of river conditions (e.g., flow, TSS) recorded during the study period. It is also worth noting that all $\sum\text{PAH}_p$ and $\sum\text{PCB}_p$ values during this study exceeded the summed effect range low ($\sum\text{ERL}$) values of $\sum\text{PAH} = 4.0 \mu\text{g/g}$ and $\sum\text{PCB} = 50 \text{ ng/g}$, respectively (Long et al. 1995). The continuous data from this site provides compelling evidence that neither removal of the dam or any subsequent morphological adjustments occurring within the river caused increased transport of particulate contaminants or the release of either of these particulate phase contaminants to the water column.

Contaminant fluxes

Using the average daily flow, the suspended solids model, and measured dissolved and particulate PAH and PCB concentrations, dissolved and particulate fluxes at site 3 were calculated for each deployment period. Contaminant flux can be used to evaluate potential effects during the different stages of dam removal and estimate contaminant masses transiting through and exiting a river during discrete time intervals. Daily fluxes of $\sum\text{PAH}_p$ at site 3 varied between deployments from 16 g/day to over 1,531 g/day during the study, with an annual flux of more than 160 kg of $\sum\text{PAH}_p$ estimated to have exited the Pawtuxet River during the study (Table 1). $\sum\text{PCB}_p$ fluxes ranged from 0.1 to 11.6 g/day at site 3, with a total flux during the study estimated at 683 g. For dissolved fluxes, daily $\sum\text{PCB}_d$ fluxes were much lower than daily $\sum\text{PAH}_d$ fluxes. Daily $\sum\text{PAH}_d$ fluxes ranged from 22 to 229 g/day (Table 1). The flux of $\sum\text{PAH}_d$ during the pre-removal deployment was 56 g/day, increasing to a maximum of 229 g/day during the first post-removal deployment before dropping to 22 g/day by post-deployment 3. Daily $\sum\text{PCB}_d$ fluxes ranged from 0.39 g/day before removal, rising to 1.95 g/day in

the first post-removal deployment before dropping to 0.63 and 0.53 g/day in the second and third deployments, respectively (Table 1). Flux rates of PAH_d and PCB_d differed by a factor of 10 and 5, respectively, during the study, while the particulate fluxes were approximately a factor of 100 for both contaminants. As expected, river flow was the driving variable regulating flux rates, with the differential response between phases due to the increased sediment entrainment with greater flow (i.e., during the first post-removal sampling), as supported by the data used in our empirical TSS flow model (Fig. S1). The corresponding yet smaller increase in the dissolved phase is also attributed to higher solids in the water column, which most likely resulted in increased partitioning to dissolved phases.

Physical effects of dam removal

For the present study, dam removal had minimal effects overall on sediment disruption and contaminant transport in the lower Pawtuxet River based on visual observations along with chemical and physical data. It is well documented that the major impacts of dam removal are increased erosion and transport of sediment throughout river systems (Hart et al. 2002; Cui et al. 2006). Factors affecting sediment transport are discharge rate and duration, along with grain size, type, and volume (Cheng and Granata 2007). Engineering studies performed during the dam removal feasibility process revealed that sediment accumulation upriver was minimal, with estimates of approximately 1,700 m³ primarily along banks and a small point bar ~100 m upriver (Kleinschmidt 2005). For many small, low-head dams like the Pawtuxet, it is likely that some of the sediments trapped above the dam are periodically flushed during high flow events, limiting long-term storage. Trap efficiency of the dam was also calculated with minimal retention of sediment predicted. This was confirmed by on-site observations that showed little fine-grained sediment present behind the dam (Kleinschmidt 2005). In addition, little noncohesive sediment was present in the areas that would be susceptible to erosion, and the slope angle of the Pawtuxet River is extremely low (1 m drop over 7 km). In the lower river, the channels are well armored and many of the banks vegetated. Overall, conditions were such that large post-removal increases in sediment transport were highly unlikely. A small increase in grain size distribution was observed in sediment traps below

the dam for several deployments following removal, suggesting that there may have been a small adjustment to the river's morphology and/or hydraulic features (Fig. S2). There were, however, no observed changes in channel geometries following removal, only decreases in water level which may or may not explain the temporary shift in grain size. The decline in water level did, however, result in increased riparian vegetation in newly exposed areas, particularly in and around site 2.

Summary

The effects of dam removal on contaminant remobilization in the Pawtuxet River were evaluated by monitoring water column conditions above and below the dam site using novel sampling techniques over a 1-year period. Prior to the dam removal, dissolved and particulate PAHs and PCBs were measurable in the water column due to previous long-term discharge to the Pawtuxet River and were still present in sediments throughout much of the river. Following dam removal, concentrations of PAHs and PCBs in both particulate and dissolved phases varied slightly between sites, due mainly to spatial variability in their distribution within river sediments. No increases in particulate and dissolved Σ PAHs or Σ PCBs were noted that could be associated with removal of the dam. The linked behavior between particulate and dissolved concentrations does have implications for bioavailability, particularly in rivers where large-scale erosion and resuspension of sediment may occur. This may result in elevated dissolved chemical concentrations that could impart adverse effects to biota.

Passive samplers were employed to monitor dissolved chemicals, and to our knowledge, this is the first time they have been used for assessing the effects of dam removal. Results demonstrate that they were highly effective in monitoring dissolved organic contaminants during dam removal. Of particular benefit was their high sensitivity, their ability to be used for monitoring contaminant bioavailability, and their capability to assess potential changes in contaminant toxicity. Sediment traps were also employed and proved to be of enormous utility for sampling suspended sediments in the river during this study. They permitted continuous collection of sediment particles in the water column under a range of conditions and were able to be co-deployed with PE

samplers, allowing simultaneous collection of particulate and dissolved phase data. Passive samplers and sediment traps, as supported by the results, were the best sampling option to meet data objectives and will likely meet future monitoring needs for dam removal projects where organic contaminants are a concern. In the future, consideration should be given to deploying samplers early on during the "feasibility study" to establish baseline conditions, understand river behavior, and identify potential problems that may assist in the overall dam removal and subsequent restoration process. In addition, monitoring conducted during and post-removal provides information on the conditions of the river, which is highly valuable information to project managers. Further, if budgets allow, the use of greater passive sampler and sediment trap replication is encouraged to support more extensive hypothesis testing between sampling sites and time periods.

Surficial sediment and sediment core data show that high levels of contaminants persisted in the river sediments despite cessation of chemical releases, periodic flood events, and long-term sediment transport. Dissolved and sediment-bound chemical flux rates were calculated for Σ PAHs and Σ PCBs, with evidence that river flow volume, not removal of the dam, regulated the rate these chemicals moved through the river during the study period. Overall findings from monitoring the Pawtuxet River indicate that dam removal did not adversely impact the rate of contaminated sediments or dissolved chemicals exiting the river. This is due in large part to the absence of sediment upriver prone to transport following removal, as well as site-specific attributes that helped minimize dam removal effects (e.g., low river slope angle, well-armored channels, and vegetated banks). Although large impacts were not observed in this project, measurement of contaminant fluxes at key locations and periods before, during, and after dam removal in projects where contaminated sediments are an issue (e.g., Superfund sites) can be performed to identify and better understand spatial and temporal trends as well as monitor river restoration events that are at critical junctures.

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