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Reconstruction of Contaminant Trends in a Salt Wedge Estuary with Sediment Cores Dated Using A Multiple Proxy Approach

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metals

Abstract

The Taunton River is a partially mixed tidal estuary in southeastern Massachusetts (USA) which has received significant contaminant inputs, yet little information exists on the history of discharge and the subsequent fate of these contaminants. Three sediment cores taken along a transect were analyzed, reconstructing the spatial and temporal trends of pollution in the estuary. A combination of radiometric dating, contaminant markers, and storm layers from major hurricanes were used to establish age models and sedimentation rates. Age estimates obtained from the different dating methods compared well, establishing an accurate history of contaminant release to the estuary. Polycyclic aromatic hydrocarbons (PAHs) were present in one core at depths corresponding to the early 1860s, earlier than previously established dates of introduction. Temporal and spatial trends of Cr, Cu, Hg and Pb indicated multiple sources of varying input to the river. Polychlorinated biphenyls (PCBs) were present in each of the cores from the 1930s onward, with elevated levels still present in surficial sediments at several sites. A unique organic compound, Topanol, which was produced locally was used as a tracer to track contaminant transport in the river. Tracer data indicates that contaminants are still being transported and deposited to surficial sediments at high concentrations well after their discharge. This reconstruction demonstrates the utility of using multiple dating proxies where often the sole use of radiometric dating techniques is not an option and provides insights into the fate of contaminants discharged decades ago but continue to represent environmental risks.

Introduction

Estuaries are sinks for numerous classes of anthropogenic contaminants. In depositional areas, sediments become "chemical archives" which can be used to reconstruct the history of contamination (Valette-Silver, 1993

). Successfully developing sediment chronologies in estuaries can be challenging due to sediment resuspension, erosion and bioturbation. Radiometric dating using ^{137}Cs and ^{210}Pb have been used extensively to establish sediment chronologies in estuaries (Valette-Silver, 1993   . On the other hand, anthropogenic organic compounds or "anthro-markers" which have known dates of introduction or termination into the environment have been used to a lesser extent (Zegers, Lewis, Booij, Smittenberg, Boer, De Boer, et al., 2003; Hartmann, Quinn, Cairns, & King, 2005). In some locations, marked changes in sediment lithology (i.e., layers) occur from documented events such as hurricanes or dredging that can also be used as dating markers

). Combined, these different dating methods provide strong lines of evidence for determining sedimentation rates and can be used for developing accurate reconstructions of estuarine depositional history.

The key concerns with contaminants such as metals, PCBs and PAHs are their toxicity at low concentrations and their persistence in the estuarine environment (Long & Morgan, 1990). Their ultimate fate in estuaries is controlled to a large extent by processes

(Vertical margin citations: Goldberg, Gamble, Griffin, Hodge, & Koide, 1977; Appleby, 2001) ... Goldberg et al. 1977 ... Goldberg)

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which regulate their presence in the water column. These processes involve both physico-chemical phenomena like solubility and sorption (Karickhoff, Brown & Valsaraj, Thibodeaux, Lin, Dikshit t) and transport mechanisms including diffusion, resuspension and bioturbation (Gevao, Hamilton-Taylor, Murdoch, Jones, Kelly & Tabner, 1997; Ko & Baker, 2004; Reible Popow, Ridgway & Shimmeld, 2002). Previously buried contaminated sediments can be advectively transported and redeposited considerable distances from their origin (   ).

The Taunton River, located on the east side of Narragansett Bay in southeastern Massachusetts, was settled by European colonists in the early 1600s. Land clearing and agricultural activities were initially established, rapidly followed by early colonial industry such as bog iron mining in the 1650s and ship building in the 1700s. By the 1830s, numerous textile mills were operating downriver in the city of Fall River. Industrial development flourished, moving upriver to the town of Somerset, where pottery mills, foundries and other metal-working industries were well established by the 1850s (Hart, 1946).

Part of the legacy of this early industrialization is the accumulation of contaminants in the estuarine sediments. The contaminant history in much of Narragansett Bay has been well documented (Goldberg et al., 1977; Santschi, Nixon, Pilson & Hunt, 1984; Nixon, 1995) while little is known about severity or extent of contamination in the Taunton River estuary. Boucher (1991) investigated nutrient chemistry while Hartmann (2001) provided data on organic contaminants. In this study, we present sediment core profiles from three sites in the Taunton River, which provide spatial and temporal information on PAHs, PCBs and toxic heavy

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metals. Age models and sedimentation rates for the sites were generated using a combination of anthro-markers and radiometric dating tools along with measuring the depth of sand layers which represent major storms (i.e., hurricanes).

Experimental Section

Study Site. The Taunton River estuary is located in Narragansett Bay, within the state of Massachusetts (USA) (Figure 1), with an overall length of 70 km.

at Mount Hope Bay, with saltwater intrusion reaching as far as 20 km upriver.[2] Tidal influences extend 29 km to the city of Taunton, draining a watershed area

The lower Taunton River is highly urbanized with manufacturing, power generation plants and other industrial activities dominating the waterfront. Above the town of Somerset, the river edge is less developed with a low density of residential dwellings and long stretches of wood and grasslands adjacent to the shoreline. Water depth decreases significantly at this point in the river and narrows with no navigable channel present past Segregansett Point. Previous work at this location (Hartmann, 2001; King, unpublished data) has documented elevated concentrations of PCBs and Hg in sediments. Industrial discharges in the towns of Dighton and Somerset have been suspected as a source of metals and organic contaminants to the river.

The objective of this study was to reconstruct the history of contamination to the lower Taunton River, which is classified as a salt wedge estuary. To accomplish this, a series of sediment cores were collected along a transect from three locations representing the upper, middle and lower points of the salt wedge within the estuary (Table 1). Near the upper point

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of the salt wedge is the mouth of the Segregansett River, located between Dighton and the city of Taunton (Figure 1). The Segregansett River site (SR) is in a small cove approximately 4 ha in area with a water depth of 1-2 m and is tidally influenced with an average salinity of approximately 5. Discharge to the Taunton River is minimal and limited by a 10-m wide railroad overpass. The second site is located in Muddy Cove (MC), a small embayment of approximately 2 ha in area which is surrounded by wetlands and residential properties. Depth ranges from 1-2 m and the embayment receives freshwater input from Muddy Cove Brook, a stream which passes through the site of a closed chemical manufacturing facility in the town of Dighton. A hurricane barrier stands upstream of Muddy Cove, preventing tidal surges from flowing into town. The third site, Somerset Jetty (SJ) is next to a former railroad jetty 5 km below MC adjacent to the town of Somerset on the east side of the river in 2-3 m of water. Salinities at SJ average approximately 25 with an average tidal range of approximately 1.5 m for all three sites (Boucher 1991).

Sampling Sediment cores were collected from each site (Figure 1) using a 10-cm diameter piston corer with an acid-cleaned polycarbonate barrel approximately 2.5 meters in length. Once on deck, cores were capped and kept vertical during transport with 10 cm of overlying water on top of the core to minimize mixing. Cores were split in half lengthwise within 1 week of collection and were sampled at 1 cm resolution using either teflon or titanium sampling tools. Sediments for organic analysis were stored in solvent-rinsed and oven baked (450°C) glass jars with teflon liners while sediments for metals analysis were stored in acid cleaned polyethylene containers. All cores and samples were stored at 4°C in the dark.

Sediment Properties

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Analysis-Metals and Physical Properties Sediments sampled for metals were processed using a CEM model MDS 2000 microwave oven (Matthews, NC) and closed teflon digestion vessels. A combination of concentrated acids, 3 ml hydrofluoric, 2 ml hydrochloric and 5 ml nitric, was added to each sample and microwaved. Hg was analyzed using a Leeman Labs (Hudson, NH) model PSII Hg analyzer. The other metals were analyzed on an Applied Research Laboratories (Valencia, CA) model 3410 inductively coupled plasma atomic emission spectrometer (ICP-AES) or a Perkin Elmer SIMAA 6000 Graphite Furnace Atomic Absorption Spectrophotometer (Norwalk, CT). Detection limits for the study metals were $Cr > 0.1$, $Cu > 0.02$, $Hg > 0.001$, $Pb > 0.02$ ug/g. Chemical analyses were conducted following rigorous quality control standards. Calibrations were performed using National Institute for Standards and Technology (NIST) traceable calibration standards and multi-point calibrations. Cr, Cu, Hg, and Pb were analyzed utilizing blank and duplicate samples in order to assess precision and accuracy. Duplicate samples were within 5% relative percent deviation while blanks were below detection limit. Standard reference material (SRM) MESS-2 (National Research Council, Ottawa, Canada), an estuarine sediment with certified metal values was digested and analyzed along with samples. SRM recoveries for the metals in this study ranged between 80% and 115%. Grain size analysis was conducted using a Malvern Mastersizer 2000 particle size analyzer (Worcestershire, UK) with results reported using the Udden Wentworth scale. Sediment porosity was determined using methods described by Berner (1971).

Analysis-Organic Compounds Prior to extraction, sediment samples were spiked with internal standards d-10 phenanthrene, d-12 benz[a]anthracene and d-12 perylene for PAHs

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and congener 198 (IUPAC no. 198) for PCBs. Sediments were extracted three times

sequentially in 100 ml glass centrifuge tubes using 1:1 hexane:acetone and sonicated for 15

minutes followed by centrifugation at 1000 x g on a IEC (Needham Hts, MA) model 8R

centrifuge. Extracts were combined and volume reduced under nitrogen, exchanged to

hexane and purified using Sep Pak silica cartridges (Waters Corp, Milford, MA). For PCB

analysis, an aliquot was taken and treated with concentrated sulfuric acid followed by

addition of activated copper to remove sulfur. SPAH concentrations are the sum of 13

compounds: (fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene,

chrysene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3,cd]pyrene,

dibenz[ah]anthracene and benzo[ghi]perylene). PAHs were analyzed using an Agilent 6890

gas chromatograph equipped with a 5973 mass selective detector and a DB-5 MS 60 meter

capillary column (Agilent Technologies, Wilmington, DE). Twenty four PCB congeners

(IUPAC nos. 8, 18, 28, 52, 44, 66, 101, 99, 110, 151, 118, 153, 105, 138, 187, 183, 128, 180,

170, 194, 195/208, 206 and 209) and two pesticides, Aldrin and p,p'-DDE were measured.

 Total PCB is reported as two times the sum of the congeners measured based on the

congener analysis of Aroclor standards 1242, 1254 and 1260 (Ultra, North Kingstown, RI).

PCBs were quantified using a Hewlett Packard series II 5890 gas chromatograph (Hewlett

Packard, Avondale, PA) equipped with an electron capture detector and a 30 m DB-5

capillary column. Both instruments were calibrated with NIST traceable calibration standards

and multi-point calibrations. Quality control of the extraction and quantification procedures

were evaluated using NIST SRM 1944 for PAHs and PCBs. Mean recoveries for PAHs were

81% and for PCBs 91% (n=6). Duplicate samples were generally within 10% RSD while

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procedural blanks (n=6) were below detection limit (1.0 ng/g PCB, 10 ng/g PAHs) for analytes reported in this study.

A phenolic antioxidant compound 1,1,3-tris-(2-methyl-4-hydroxy-5-tert butylphenyl) butane (synonym Topanol) was identified and confirmed in the cores by GC/MS but was not reliably quantified by capillary chromatography. Topanol (CAS # 1843-03-4) is insoluble in water, has a log K_{ow} of 11.07 and a melting point of ~185 °C according to the SPARC chemical modeling system (Karikhoff, McDaniel, Melton, Vellino, Nute & Carreira, 1991). To accurately measure this compound, an alternate analytical method was developed using high performance liquid chromatography (HPLC). This compound was extracted from the sediments with three sequential extractions of acetonitrile and sonication followed by centrifugation. Extracts were combined and volume reduced under nitrogen. The extracts were analyzed by UV fluorescence with a Waters model 2690 HPLC fitted with a 4.6 x 150 mm C18 column (Waters, Milford, MA). Extraction method development and validation was performed by spiking known quantities of this compound into clean local sediment, homogenizing and storing for 90 days at 4°C in the dark. Recovery was assessed using these spiked sediments as a surrogate reference material with a mean recovery of 91% (n=3). A method detection limit (MDL) study was conducted with a MDL of 7.0 ng/g calculated for Topanol based on a 2-g sediment sample.

Sediment Chronology In this study sediment cores were dated using several techniques. Cores from the MC and SJ sites were analyzed radiometrically using gamma spectrometry to measure ^{210}Pb, and ^{137}Cs as described in Appleby

(1986). Briefly, dried sediment samples were analyzed using direct

gamma assay with Ortec HPGe GWL series well type coaxial low background intrinsic germanium detectors (Ortec, Oak Ridge, TN). ^{210}Pb was determined via its gamma emission at 46.5 keV, and ^{226}Ra by the 295 keV and 352 keV ?-rays emitted by its daughter isotope ^{214}Pb following three weeks storage to allow radioactive equilibration. ^{137}Cs was measured by its emissions at 662 keV. Detector efficiencies were determined using calibrated sources and corrections were made for the effect of self-absorption of low energy ?-rays within the sample. Radiometric dates were calculated using the constant rate of supply (CRS) ^{210}Pb dating model (Appleby, 1978) and corrected where appropriate using the 1963 depth determined from the ^{137}Cs stratigraphic record as a reference level (Appleby, 2001). Persistent organic chemicals such as PCBs, PAHs and pesticides (i.e., anthro-markers) with known dates of introduction to the environment were employed as dating proxies in all three cores using data compiled by the US Public Health Service (ATSDR, 2000). Other contaminants present in the sediment cores such as Topanol and Hg were used in manufacturing processes locally and were also employed based on information available from public records (Menzie-Cura, 2003). Storm layers (sand) present in the cores were compared with the dates of several 20th century hurricanes to provide further validation of the dating process.

Results and Discussion

Dating profiles At MC, radiometric dating of the core was problematic due to uncertainties in the nature and quality of the fallout records (Table 2, Figure 2). Unsupported ^{210}Pb concentrations decline irregularly with depth, suggesting significant irregularities in the

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process of sedimentation at this core site. Further, although the ^{137}Cs concentration has a relatively well defined peak at a depth of 9 ± 1 cm, it is not certain that this feature records the 1963 fallout maximum. The abrupt decline of both ^{210}Pb and ^{137}Cs immediately below this peak raises the possibility that the records have been strongly influenced by factors other than the rate of supply from the atmosphere, for example a hiatus in the supply of sediment, or more likely a sediment supply depleted in these fallout radionuclides. The ^{210}Pb inventory of the core (1900 Bq m^{-2}) corresponds to a mean ^{210}Pb supply rate of 59 Bq m^{-2} y^{-1}, well below the estimated atmospheric flux in this region of ~150 Bq m^{-2} y^{-1}. Using other dating proxies present to determine sedimentation rates, MC has an average rate of 0.56 cm yr^{-1} dating from the 1970s back to the 1880s (Table 3, Figure 3). Sedimentation rates derived from the locally occurring proxies (e.g., Topanol, Hg) are in good agreement with the others which were determined using U.S. national dates of introduction to the environment (ATSDR, 2000). In this core, distinct sand layers are present at 29 and 39 cm depth which indicate periods where high energy events may have resuspended surface sediment. Using the chronology developed with the anthro-markers, these sand layers correspond to 1938 and 1954, dates in which major hurricanes struck this area, providing further evidence for the accuracy of the anthro-marker derived rates. Overall, sedimentation rates at MC were very consistent over time (Table 3) (Figure 4). This is attributed to several factors such as the sheltered location of MC, which minimizes resuspension, and the absence of bioturbating organisms in the sediment core and in surficial sediment. Grain size distribution throughout the core at this location remained relatively uniform, with only small shifts in the proportions of sand and silt (Figure 5). Sediment porosity showed little change downcore, with only a

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slight decline below 42 cm indicating minimal core compaction. Based on the anthro-marker and storm layer data presented, a sedimentation rate of 0.56 cm yr^{-1} was used to determine the chronology of this core.

At the SJ site, unsupported ^{210}Pb concentrations decline a little irregularly with depth, though the overall trend (down to a depth of 33 cm) closely resembles that of an exponential relation (Table 2, Figure 6). The ^{210}Pb inventory of the core (7100 Bq m^{-2}) corresponds to a mean ^{210}Pb supply rate of 220 Bq m^{-2} y^{-1}, significantly above the estimated atmospheric flux in this region of ~150 Bq m^{-2} y^{-1}. This suggests the core is from a site with a good depositional record. ^{137}Cs data was well resolved downcore with concentrations peaking at 33 cm, which based on atmospheric maximums, date this depth as 1963. 1963 is also the start of production of the local anthro-marker Topanol in Dighton (ENSR, 1997) which first appears at 33 cm at this site providing validation of the dating accuracy of the ^{137}Cs (Figure 3). The mean post-1963 sedimentation rate is thus reliably estimated to be 0.80 cm yr^{-1} (Table 3). CRS model ^{210}Pb dates calculated using the 1963 depth as a reference point suggest the sedimentation rates were a little higher in the 1960s. This is supported by the pre-1963 anthro-markers (Table 3) which indicate mean sedimentation rates during the first half of the 20th century of between 0.89 and 1.1 cm yr^{-1}. In this core hurricane sand layers were found at 45 and 73 cm depth with calculated sedimentation rates of 0.89 and 1.1 cm yr^{-1}, respectively, agreeing well with the other markers used to date this core (Table 3). Using selected dating markers, a sedimentation rate of 0.94 cm yr^{-1} was used to determine the chronology of this core (Table 3).

Radiometric dating was not performed on the SR core due to the mixed results

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obtained from the other two coring locations. The sediment at this site is primarily sand, with

some shifting in the distribution between sand and silt apparent (Figure 5). Porosity data for

this core is very consistent, indicating little compaction has taken place at this location

(Figure 5). Calculated sedimentation rates at this site ranged from 0.36-0.73 cm yr^{-1}, the

most variable of all three sites (Table 3). Some of this observed variability might be due to

sediment mixing or resuspension at this location. Storm layers from the 1938 and 1954

hurricanes were also present in this core at 22 cm and 33 cm depth, agreeing well with the

sedimentation rates from the anthro-markers (Figure 3). The anthro-marker data suggest

lower rates of sedimentation in recent years than at the beginning of the 20th century. To

account for this, an age model was developed by applying a second order polynomial fit to

the data which resulted in a r^2 of 0.98 (Figure 4). The resulting equation (y = -2E-06x^2 +

0.0047x + 0.3296) was used to determine chronology.

Spatial and temporal trends of PCBs PCBs were present in each core with maximum

concentrations of 21.4, 3.02, and 1.47 µg/g for MC, SR and SJ, respectively. PCBs were

first introduced to the environment in approximately 1929 (USDOC, 1972), with

concentrations at each location increasing subsequently upcore. Common to all core sites

is the rapid rise in PCB levels during the late 1940s (Figure 7). With the highest

concentrations of PCBs measured at MC, it is likely that they were released to the river from

the industrial facility in Dighton. Based on the core data, it is apparent that much of the PCB

was transported downriver to SJ, yet tidal action was sufficient to transport significant

amounts upriver to SR. PCB levels at MC increase from the 1960s to their highest measured

levels around 1991 despite termination of PCB production and unregulated use in the U.S.

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by the late 1970s (Erickson, 1992). At SJ, a slow decline in PCB levels was noted from the 1950s peak, yet the plot clearly shows PCBs are still being deposited at this site, indicating downriver transport of contaminated sediments ostensibly from MC. PCB trends at MC from the 1960s onward are not reflected at SR, potentially indicating changes in the form in which they are being discharged to MC (Figure 7). The increase in PCB levels at MC following the 1977 ban is likely to be due to erosion of contaminated soils and sediments at locations upstream in Muddy Cove Brook rather than industrial process related releases. This would explain why the peak concentrations at MC around 1991 are not reflected at either the SR or SJ sites.

Spatial and temporal trends of PAHs In North America, most releases of anthropogenic PAHs to the environment began in the early 1880s, coinciding with the emerging use of petroleum products. SPAH values maximize at 14 and 34 µg/g at SR and SJ respectively, to more than 356 µg/g at the MC site (Figure 8). Each of the cores exhibit temporal PAH trends that indicate discrete sources, distinguishing them from the other sites. Located upriver, the SR site has the lowest overall concentrations, increasing sharply during the 1930s with values peaking in the 1950s (Figure 8). The area surrounding the site and the Segregansett River is undeveloped, raising questions on the source of the PAHs. Based on the location and levels of PAHs, it is likely that a combination of road runoff and inputs from locomotive traffic on the adjacent railway bridge were contributors, as were discharges upriver from industry in Taunton.

At SJ, the temporal trend of PAHs does not follow the other sites with elevated levels of PAHs present in the core to a depth of 200 cm. This is prior to widespread use of

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petroleum products and implies either large-scale sediment disturbance at the site or contamination. An historical review of activities in and around Somerset provides an explanation for the presence of PAHs in the sediment prior to the 1880s. Large quantities of coal were mined nearby in Portsmouth, Rhode Island to fuel a copper smelter located adjacent to the mine on the East Passage of Narragansett Bay (Garman, 1978). The copper smelter operated from the mid-1860s to the early 1880s (Garman, 1978). Within Somerset, the jetty adjacent to the coring site is the remnant of a railroad bridge that once spanned the Taunton River. Construction of this bridge was completed in 1866 and was a major rail link for coal transport (Hart, 1946). Simultaneously, the Nation's first creosote production facility was being built in Somerset, for the purpose of treating railroad crossties (Webb, 1991). During bridge construction, significant sediment disruption occurred with PAHs emanating from the creosote facility likely contaminating the sediment. Consequently, PAH data below depths corresponding to the 1870s and its use as a dating proxy at this site is of little utility. PAHs at this location reached 30 ug/g by 1880, reflecting creosote production, combustion of coal by nearby industry and the operation of coal powered locomotives in the immediate area. In the 1920s levels peak again with a subsequent, sustained decline reflecting diminishing use of the railway bridge and its dismantling in 1944 (Hart, 1946). Inputs from the 1960s to present remain relatively constant, suggesting atmospheric contributions from the two active coal fired power plants on the river and road runoff.

At MC, PAHs are present at a depth corresponding to the 1880s, increasing over-time until late into the 20th century (Figure 8). The influence of anthracene on the ΣPAH signal is remarkable because this trend is absent at SR and SJ (Figure 8). Anthracene,

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elevated relative to the other measured PAHs, starts in the late 1940s, peaking in the 1960s

with >90% of the SPAH present as anthracene compared to mean values of 2.1% and 3.6%

for SR and SJ, respectively. The source of anthracene at MC is attributed to manufacture of

textile dyes which were produced in Dighton (Menzie-Cura, 2003). Anthracene is commonly

used as a feedstock to synthesize anthraquinone based textile dyes. Based on the levels of

anthracene at MC and the sustained duration of release, either anthracene or its degradation

products would be expected at SR or SJ at elevated levels. Degradation of anthracene by

biotic and abiotic processes yields anthraquinone, with only minor degradation occurring

once anthracene has been sequestered in the sediment (McKinney, Pruell & Burgess, 1999).

 GC/MS analysis of sediments at MC indicate significant levels of anthraquinone present

while the SJ site has only trace amounts (<1 ng/g) (data not shown). It appears that once in

the river, anthracene was rapidly degraded in the water column by microbial, chemical or

photo-oxidation processes (McKinney, Pruell & Burgess, 1999) and never reached the

sediments at SJ or SR. Aside from the high levels of anthracene present in MC, the other

PAHs remained relatively proportional throughout each of the cores and between sites.

In an attempt to identify the primary source of measured PAHs, source ratios were

calculated for selected PAHs and compared to values compiled by Yunker

) (Table 4). Source ratios have been

used previously to distinguish between petrogenic and pyrogenic sources of PAHs in

sediments. Three ratios, fluoranthene to fluoranthene plus pyrene Fl/(Fl+Py),

benz[a]anthracene to sum molecular weight 228 (BaA/228) and indeno[1,2,3-*cd*]pyrene to

indeno[1,2,3-*cd*]pyrene plus benzo[*ghi*]perylene IP/(IP+Bghi) were used to assess source

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origin. For Fl/(Fl+Py) and (BaA/228), ratios below 0.5 indicate petrogenic origins while

ratios at 0.5 and above have been attributed to pyrogenic sources (Yunker et al., 2002). In

the case of IP/(IP+Bghi), ratios below 0.2 suggest petrogenic inputs while ratios of 0.2 and

above indicate pyrogenic sources with ratios near 0.5 implying wood and coal combustion

(Yunker et al., 2002). For all sites, mean source ratios calculated downcore agree with

literature values listed for combustion (Table 4). In particular, our values closely match those

for wood and coal combustion. Coal was used extensively as an energy source locally for

mills and smelters in the past and since 1923, coal burning power plants have operated

within a 10 km radius of the study area. The presence of the power plants and the low

temporal variability (e.g., SD) observed throughout the cores implies that the long-term

source of PAHs to the study area is largely atmospheric in origin and has not changed

appreciably in the last 125 years. Source ratios calculated for SJ prior to 1880 exhibit a shift,

especially for the FL/(Fl+Pyr) ratio which may be due to the creosote plant established in

1865.

Metals Trends Temporal trends downcore at SR and SJ indicate that effluents discharged

into Muddy Cove Brook, and subsequently into MC, were a major source of the study metals

to the river during the 20th century. Prior to this date, there is strong evidence that large scale

metal discharges occurred in and around SJ. In Somerset, the metal foundries and pottery

mills located along the shoreline were probably major contributors of many of these metals

present in the sediments (Hart, 1946). Another potential source of Pb and Cu between the

1860s to 1880s at this location may be the copper smelter in Portsmouth which released

considerable quantities of Cu and Pb to the water and atmosphere (Garman, 1978; Nixon,

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1995).

Pb concentrations increase sharply at the turn of the century at MC exceeding 1600 μg/g at one point (Figure 9). The high levels of Pb is due primarily to the production of lead oxide in Dighton and its apparent discharge through MC. The Pb trends observed at MC agree with those at SR and SJ, indicating that it is the primary source of Pb to the Taunton River during the 20th century (Figure 6). At all three sites however, some part of the total Pb measured although not definable in this study, is likely to be atmospheric in origin. The use of lead as an additive in gasoline started in the 1920s increasing over time to the mid 1970s when leaded automotive fuels were starting to be phased out (Nriagu, 1989). At SJ, Pb levels are elevated prior to MC releases with peak levels present in the early 1870s. This early Pb signal is due primarily from the use of lead-based glazes in pottery mills in the Somerset vicinity (Hart, 1946), with some contribution from the copper smelter in Portsmouth possible (Garman, 1978). For all sites however, Pb levels present a declining trend from the 1950s to present indicating that releases to the river have been significantly reduced.

At MC, Cr levels increase at the beginning of the 20th century peaking late in the 1980s (Figure 10). Temporal trends of Cr at MC agree reasonably well with those at SJ and SR, identifying it as a major source of Cr to the Taunton River during the 20th century. One phenomenon observed with Cr is the small decline in concentrations at SJ following 1950 relative to MC when compared to the other metals. This relates to the estuarine behavior of Cr and its speciation at the time of discharge. Depending on the oxidation state of the Cr when discharged, it may not have been conducive to adsorption to particles

), extending its transport distance before sorption processes removed it from

Flegal, 1995

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the water column. This observation is reflected at SR as well, with Cr being the contaminant

with the highest measured levels at this site. Finally at SJ, Cr levels remain consistently high

back into the 19th century, reflecting sustained releases to the river during this period from

local pottery production and its use as a dye in local textile operations (Nixon, 1995).

Cu increases from background at MC early in the 20th century with levels building over

time and peaking in the 1980s (Figure 11). Temporal trends of Cu at SJ track well with MC

during this time, with co-occurring peaks in the 1980s. The SR trend exhibits a general

similarity with MC over time, whereas peak values increasing in the 1940s and declining in

the late 1960s do not correlate with those of MC (Figure 11). Upriver in the city of Taunton,

numerous companies sited on the river produced copper goods, which likely contributed to

the contamination at SR. At SJ, Cu levels are elevated back to the 1870s, indicating early

sources of Cu at this location, prior to releases to MC at Dighton. At SJ, both Pb and Cu have

concentrations which peak at approximately 1880 (Figures 9, 11), suggesting that these two

metals may have a common source, the smelter at Portsmouth. During its operation the

smelter was estimated to have annually emitted up to 2.3 and 3.2 tons of Pb and Cu

respectively, to the atmosphere (Nixon, 1995). This source and the use of Cu in pottery

glazes locally in Somerset account for the elevated levels observed at SJ.

The use of Hg in textile processes (e.g., felt finishing) during the 1800s was common,

with use and discharge of Hg early on in the Taunton area apparent (Figure 12). More

recently, textile dyes using Hg were produced at the Dighton facility, with Hg effluent

discharged to Muddy Cove Brook and subsequently entering MC (Menzie-Cura, 2003).

During synthesis of some anthraquinone dyes, Hg is used as a sulfonation catalyst. This was

probably the case at Dighton as the anthracene peak noted at MC coincides with the Hg peak (Figures 8, 12). Hg release is estimated to have started around the mid-1950s based on core data from MC. Use of Hg at the chemical facility was terminated in 1971 according to publicly available documents (Menzie-Cura, 2003), with steep declines in concentration visible at MC and the other sites. Hg levels remain highly elevated twenty years after discharge was halted, evidence that continued release of contaminants into MC has occurred, likely due to erosion of contaminated soils and sediments from Muddy Cove Brook. For Hg, recent temporal trends at SR and SJ agree well with MC. Hg however, remains elevated downcore at SJ at relatively constant concentrations, reflecting early releases in the Somerset vicinity likely from textile and metalworking activities as well as the combustion of coal.

Contaminant Transport With the dates of discharge for many of the contaminants released into MC established, it is possible to better understand their subsequent transport in the Taunton River. One compound discharged into the Taunton River via MC, Topanol, was used to evaluate contaminant transport in the study area. Topanol is well suited for this purpose as it is a unique compound with production and discharge occurring only at the Dighton chemical plant within the watershed, and has been found to be stable in sediment. Confirmed dates of Topanol discharge exist (Table 3), with production starting in 1963 (ENSR, 1997). It appears in the MC and SJ cores at this time, but not at SR (Figure 13). High levels of Topanol were noted at MC in the early 1980s, continuing into the 1990s with peak levels exceeding 3900 µg/g. Downstream at SJ, peak concentrations reached 37 µg/g with a clearly resolved temporal trend matching MC's. At SR levels are much lower at 1 µg/g,

reflecting less efficient upriver transport of this compound. This data provides confirmation for transport of contaminants from the discharge point at MC to locations up and down the Taunton River. Furthermore, the general transport response of Topanol, that is higher concentrations of contaminants downriver at SJ compared to SR, is reproduced with most of the contaminants reported as originating from MC.

Another tracer application of Topanol is to assess the vertical distribution of contaminants in the sediments. At SR and SJ, elevated concentrations of Topanol are still present at the sediment surface even though production ended in 1993. Calculated sedimentation rates for SR and SJ estimate that 4 cm and 10.5 cm of sediment would have been deposited at each site respectively since the end of production. Topanol's high Log K_{ow} of 11.07 makes significant advection by porewater diffusion highly unlikely. On the other hand bioturbation is an effective mode of transport for hydrophobic organic contaminants. However, no bioturbating organisms were present in the cores sampled or at the sampling sites. The levels of Topanol at the surface at these sites indicate that active transport of this compound is still occurring in the river. This also explains the elevated levels of PCBs and Hg at the sediment surface of SJ and SR, long after their discharge to MC ceased (Figures 7, 12).

The ability of particle-bound contaminants to migrate and maintain their presence at the sediment surface has broad implications with respect to a sediment's toxicity. From the core data presented, we have seen that daily tidal movements and riverine flow, can transport large quantities of contaminants over time, potentially impacting uncontaminated areas. Of obvious concern but not discussed here are contaminants released during

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resuspension along with the inevitable changes in bioavailability when sediment bound contaminants are deposited at the sediment-water interface. In small estuaries such as the Taunton River where discharges of contaminants have generally ceased, periodic sediment resuspension is responsible for maintaining relic contaminants at the sediment surface long after their discharge has been terminated.

Summary and Conclusions

Three sediment cores were collected along a transect in the Taunton River estuary and examined to determine the spatial and temporal trends of PCBs, PAHs and heavy metals, as well as ascertaining their sources to the river. Age models and sedimentation rates were developed for each site using a combination of radiometric dating, contaminant markers, and changes in sediment lithology resulting from major storm events. PCBs were found to have originated to a large extent from a single source near the Muddy Cove coring site and were transported downriver. At all locations, PAHs appear to be mainly pyrogenic in origin with source ratios suggesting that coal and wood were the primary combustion sources. One notable exception was Muddy Cove, where very high levels of anthracene were present. At the other sites however, elevated levels of anthracene were absent, suggesting degradation in the water column by biotic or abiotic processes. Metal trends varied greatly over time, with high levels of Cr, Cu and Pb accumulating in the sediments in the Somerset vicinity during the late 1800s. During the 20th century, Dighton was the primary source of metals including Hg to the river with temporal trends showing large scale downriver transport to Somerset Jetty. The use of Topanol as a particle tracer provided further evidence of the magnitude of

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contaminated sediment transport occurring between sites. Finally, the application of different dating proxies to accurately determine sediment chronologies at each of the sites confirms their utility in reconstructing contaminant histories in estuaries.

Table 1. Sediment core information.

Location	River location (km)*	Average Salinity	Core Collection Date	Coring Location
Somerset Jetty	8.6	25	6/10/2004	N 41° 45.960 W 71° 07.105
Muddy Cove	13.5	15	5/21/2003	N 41° 48.688 W 71° 07.245
Segregansett	15.2	5	6/10/2004	N 41° 49.502 W 71° 07.138

* Measured from mouth of Mt Hope Bay

Table 2. Fallout radionuclide concentrations in the Muddy Cove and Somerset Jetty cores Unsupported Pb 210 (^{210}Pb$_{xs}$) and Cesium 137 (^{137}Cs) in Becquerels kg^{-1}.

Muddy Cove			Somerset Jetty		
Depth (cm)	^{210}Pb$_{xs}$ Bq kg^{-1}($\pm$)	^{137}Cs Bq kg^{-1} ($\pm$)	Depth(cm)	^{210}Pb$_{xs}$ Bq kg^{-1}($\pm$)	^{137}Cs Bq kg^{-1} ($\pm$)
0.5	74.3 (7.5)	4.1 (1.2)	2.5	74.4 (1.1)	5.0 (1.4)
1.5	72.2 (8.0)	5.8 (1.2)	5.5	77.2 (2.5)	5.4 (1.5)
3.5	52.8 (8.9)	5.8 (1.2)	8.5	59.0 (4.0)	6.4 (1.9)
4.5	20.8 (6.4)	4.8 (1.0)	12.5	37.2 (6.1)	6.6 (1.6)
6.5	22.3 (8.9)	6.4 (1.1)	16.5	42.1 (8.1)	6.0 (1.4)
8.5	18.6 (5.6)	10.6 (1.0)	20.5	31.1 (10.0)	6.1 (1.5)
9.5	22.7 (6.5)	11.2 (1.2)	24.5	22.2 (12.1)	8.1 (2.0)
12.5	-10.0 (7.7)	1.0 (1.1)	28.5	25.2 (14.2)	9.6 (1.8)
14.5	8.4 (4.8)	0.0 (0.0)	32.5	16.2 (16.3)	13.0 (1.8)
16.5	-1.2 (3.3)	0.7 (0.7)	36.5	-4.5 (18.5)	5.9 (1.9)
18.5	-2.0 (5.2)	0.0 (0.0)	39.5	3.4 (20.3)	5.3 (1.5)
19.5	0.5 (5.4)	0.0 (0.0)	42.5	1.0 (22.1)	0.0 (2.4)
22.5	-14.2 (6.2)	0.0 (0.0)	46.5	-2.4 (24.5)	0.0 (1.4)
26.5	-1.6 (7.6)	0.0 (0.0)	48.5	-7.3 (25.7)	0.0 (1.4)
29.5	4.8 (4.3)	0.0 (0.0)			

Table 3. Dating proxies used to establish sediment chronologies and sedimentation rates at each of the study sites.

Dating Proxy	Date of introduction to environment	Date of Termination	Sedimentation rate (cm yr^{-1})		
			SR	MC	SJ
^{210}Pb	NA	NA			0.80
Hg	unknown	1971	0.36	0.57	
Topanol	1963	1991		0.57	0.81
^{137}Cs	1963-maxima	NA			0.81
Hurricane Carol	1954	1954	0.44	0.57	0.89
Aldrin	1948	1989	0.41	0.59	0.96
DDT as p'p DDE	1939	1973	0.45	0.55	0.88
Hurricane of 1938	1938	1938	0.50	0.57	1.1
PCB	1929	1977	0.47	0.54	0.99
PAH	~1880	NA	0.73	0.55	

Average sedimentation rates (** Equation applied to determine rate)	**	0.56	0.94

Note: The introduction date of all chemical dating proxies were used to calculate sedimentation rates except for Hg, where the date of termination of use was used. Only one marker from each date was used to calculate sedimentation rates at SJ and the ^{210}Pb was not used.

Table 4. Calculated source ratios of select PAHs at coring locations: fluoranthene /fluoranthene+pyrene Fl/(Fl+Py), indeno[1,2,3-*cd*]pyrene /indeno[1,2,3-*cd*]pyrene+benzo[ghi]perylene Ip/(Ip+Bghi) and benz[a]anthracene/sum of PAHs present as molecular weight 228 BaA/228. * From Yunker et al., (2002)

Location	Fl/(Fl+Py) (SD)	BaA/228 (SD)	IP/(IP+Bghi) (SD)
MC	0.52 (0.03)	0.51 (0.03)	0.49 (0.04)
SR	0.51 (0.03)	0.51 (0.06)	0.52 (0.01)
SJ (2004-1880)	0.43 (0.04)	0.49 (0.02)	0.48 (0.04)
SJ (prior to 1880)	0.50 (0.03)	0.48 (0.022)	0.47 (0.004)
Coal tar SRM (1597)*	0.58	0.54	0.53

| Wood soot* | 0.50 | 0.43-0.49 | 0.55 |
| Hard coal briquettes* | 0.57 (0.03) | 0.43 (0.04) | 0.52 (0.04) |

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Figure 13. Downcore Topanol plots at SR, SJ and MC.

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