DATA REPOSITORY ITEM 2006109

METHODS

Coring. A total of seven sediment freeze cores (Wright, 1980) were taken from the lower basin of the Pettaquamscutt River Estuary between 1999 and 2004 (Figs. 1, DR1). In each case, a stainless steel box measuring 165 cm x 20 cm x 8 cm was filled with crushed dry ice and methanol and sealed with a vented lid. This corer was lowered from a pontoon platform or frozen water surface into the sediment and left for 15-20 minutes. During this time, sediment and pore water froze to the outside of the corer box, maintaining the original sediment structure. The corer was raised back to deck and the four side slabs of sediment were removed from the box faces. Each slab was individually wrapped in aluminum foil, kept frozen, and restricted from light exposure during transport, storage, and subsampling. Age Model. The age model for the composite sedimentary record was constructed using varve counts, which were analyzed in thin section after impregnation of the sediment. In preparation for thin section generation, the most intact face of each of the seven cores was cut into chunks approximately 6 cm x 4 cm x 3 cm. These chunks were split perpendicular to the laminae in order to archive material that corresponds to the thin section produced. The working sub-chunks were freeze-dried and imbedded with Spurr resin (Pike and Kemp, 1996; Spurr, 1969). The resulting slab was thin sectioned using standard petrographic technique.

Thin sections were scanned on a flat-bed scanner with transparency capabilities under cross-polarized films to produce tagged image file format (tiff) images with resolutions of 1440 dots per inch (dpi) (De Keyser, 1999). The images were analyzed using Adobe Photoshop® and lamination boundaries were marked with the path tool. Paths were exported and processed using an algorithm that counts and measures the thickness of each lamination (Francus et al., 2002). The seven resulting chronologies were cross-checked with

each other and compiled in order to produce a master varve chronology. Counting errors were determined to be less than 1% on individual sections.

The varve chronology has been validated using radiometric age controls (²¹⁰Pb, ¹³⁷Cs, ¹⁴C) (Lima et al., 2005) (Table DR1) as well as known introduction dates for a number of pollutants (Pb, PCBs, DDT) and pollen (*Ambrosia* and *Rumex*) (Fig. DR2). All samples for radiocarbon analysis were terrestrial macrofossils (leaves) and were analyzed at the National Ocean Sciences AMS Facility, Woods Hole, MA. Radiocarbon ages were converted to calendar years using the CALIB 4.3 program (Stuiver et al., 1998). Although one of the radiocarbon dates does not fit the age model within the errors, the weight of evidence from all other age controls supports the varve age model. Sample NR03-1 92 is anomalously old, however this is most likely due to remobilization of terrestrial macrofossils during European land clearing (*Ambrosia* and *Rumex* horizons are at the same core depth). Despite this radiocarbon sample issue, the terrestrial origin of the samples is preferable due to the lack of a reservoir correction.

Fossil Pigment Analysis. Frozen sediment samples were scrapped off of the archive sediment slabs produced during the thin-sectioning process. This approach enabled us to precisely determine the age of each sample. A total of 495 samples were analyzed over the 980-year record. For each sample, approximately 0.25 grams of wet sediment was weighed into a glass scintillation vial and placed in a water bath sonicator at 4° C. The pigments were extracted by successive sonication (1 minute) in cold acetone until the extracts were colorless. The combined extracts were filtered through a 0.45 um Acrodisc 13 PTFE membrane filter. Care was taken throughout the extraction process to keep the samples and acetone on ice and in the dark as much as possible in order to preserve the pigments from degrading.

Pigments were analyzed by high performance liquid chromatography (HPLC) (Bianchi et al., 1996; Wright et al., 1991). The HPLC system consisted of a Waters 2690 Alliance separation module with a 996-photodiode array detector (PDA) and a 474 scanning fluorescence detector with excitation set at 410 nm and emission at 660 nm. Pigments were identified and quantified by comparing retention times and PDA spectra to authentic standards. Pigment concentrations (μ g/l) were converted to mass accumulation rates (MARs) (μ g/cm²yr) using centimeter-scale dry bulk density measurements and annual varve sedimentation rates.

Spectral Analyses. In order to run a spectral analysis on the Bchle MAR time-series, the data were resampled at 2-years. In order to ensure a normal distribution of the data, a log transformation was applied to this resampled series. Spectral analysis was performed using the multi-taper method with three tapers. Significant peaks were identified with respect to a first order serially autocorrelated process (AR(1)) at the 90%, 95%, and 99% confidence levels (Mann and Lees, 1996).

The wavelet transform was computed with the entire Bchle MAR time-series, resampled at 2 years, using a Morlet wavelet function. The ends of the series padded with zeroes to prevent spurious data at the edges of the transform (Torrence and Compo, 1998).

Cross spectral analysis (Fig. DR3) was performed between the Bchle MAR and WNAO time series (1824-1960) (Jones et al., 1997) using the ARAND Crospec program (Howell). Both series were first resampled at 2-years in Analyseries (Paillard et al., 1996), and then run on the Crospec program with 30 lags. The large coherence at *ca*. 8-year periodicity is significant at >80% confidence.

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Data Repository Figure Captions

Figure DR1. Detailed locus map of the Pettaquamscutt River Estuary, Rhode Island, USA. Note coring location in the lower kettle basin of the upper portion of the estuary.

Figure DR2. Age model for the varved portion of the Pettaquamscutt River lower basin sediment record. Composite depth scale was computed using mean varve thicknesses for each year, and adjusted to a common zero depth at 1999 AD. ²¹⁰Pb data from Lima *et al.* (Lima et al., 2005). Additional age controls include ¹³⁷Cs peaks in 1986 and 1963 (Lima et al., 2005), rise from background concentrations of organic pollutants (PCBs and DDT in the 1930s) and metals (Pb in the 1850s), as well as European settlement and clear-cutting in the region (*Ambrosia* and *Rumex* rises from background around 1700). Radiocarbon data are presented in Table DR1, and the most significant calibrated date for each sample is plotted here with the associated error bars. One radiocarbon sample (*) is anomalously old due to land clearance and remobilization of older macrofossils from watershed during European settlement in the area.

Figure DR3. Cross spectral analysis of Pettaquamscutt River Bchle and WNAO (Jones et al., 1997) time series (1824 - 1960). Note the significant coherence between the series in the ca. 8-year NAO band.

Table DR1. PETTAQUAMSCUTT RIVER RADIOCARBON DATA

Sample	Composite	Material	Lab	¹⁴ C age	2σ calibrated age	Relative area
Name	Depth (cm)		ID	(yr BP)	ranges (yr AD)	under
						distribution
NR03-1	64	Leaf	OS-	225 ± 40	1523 - 1568	0.052
78		pieces	47531		1627 - 1692	0.390
					1727 - 1812	0.460
					1919 - 1949	0.098
NR03-1	78	Leaf	OS-	345 ± 40	1461 - 1640	1.000
92		pieces	47616			
NR04-2	124	Leaf	OS-	435 ± 40	1411 - 1519	0.925
J5		pieces	47532		1593 - 1622	0.075
NR04-2	186	Leaf	OS-	915 ± 110	900 - 920	0.021
T3		pieces	47749		940 - 1290	0.979

All analyses were conducted at the National Ocean Sciences AMS Facility. Calibrations were calculated using the CALIB 4.3 program (Stuiver et al., 1998).

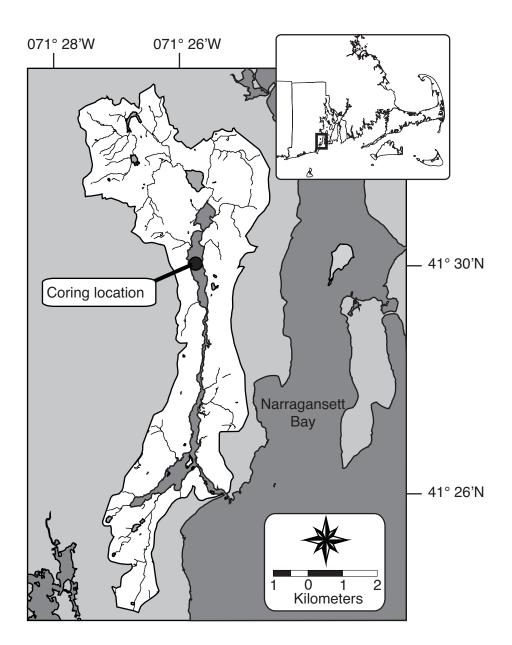


Fig. DR1

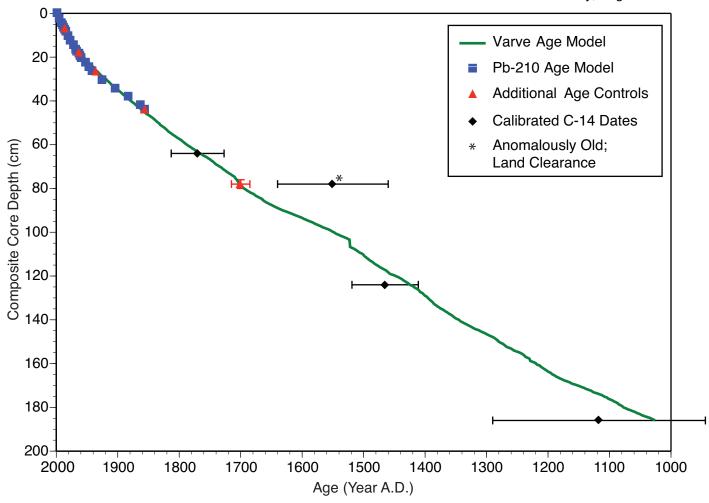


Fig. DR2

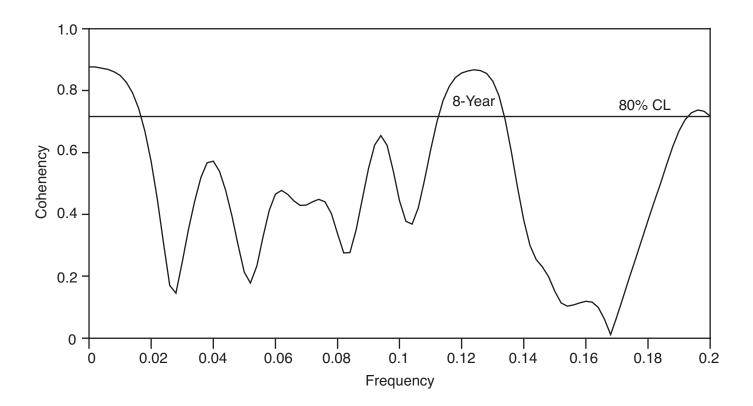


Fig. DR3