

Environmental assessment of metal exposure to corals living in Castle Harbour, Bermuda



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ABSTRACT

Environmental contamination in Castle Harbour, Bermuda, has been linked to the dissolution and leaching of contaminants from the adjacent marine landfill. This study expands the evidence for environmental impact of leachate from the landfill by quantitatively demonstrating elevated metal uptake over the last 30 years in corals growing in Castle Harbour. Coral Pb/Ca, Zn/Ca and Mn/Ca ratios and total Hg concentrations are elevated relative to an adjacent control site in John Smith's Bay. The temporal variability in the Castle Harbour coral records suggests that while the landfill has increased in size over the last 35 years, the dominant input of metals is through periodic leaching of contaminants from the municipal landfill and surrounding sediment. Elevated contaminants in the surrounding sediment suggest that resuspension is an important transport medium for transferring heavy metals to corals. Increased winds, particularly during the 1990s, were accompanied by higher coral metal composition at Castle Harbour. Coupled with wind-induced resuspension, interannual changes in sea level within the Harbour can lead to increased bioavailability of sediment-bound metals and subsequent coral metal assimilation. At John Smith's Bay, large scale convective mixing may be driving interannual metal variability in the coral record rather than impacts from land-based activities. Results from this study provide important insights into the coupling of natural variability and anthropogenic input of contaminants to the nearshore environment.

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1. Introduction

Bermuda is a crescent shaped chain of islands located on a seamount in the western North Atlantic and supports some of the most northerly reefs in the world (Fig. 1). The islands are densely populated, and in the absence of suitable landfill space, bulk metal waste and municipal solid waste incinerator ash has been dumped in the sea at a 'foreshore reclamation site' in an inshore basin, Castle Harbour (CH). The marine landfill (or seafill) has grown to encompass an area of 35 acres in the last 25 years (Jones, 2010). Dominated by metal-bearing fine-grain sediment, resuspension in CH can liberate legacy contaminants. Recent surveys have shown that widespread leaching of different contaminant classes (especially metals) has occurred from the landfill resulting in a pronounced halo of contamination in the surrounding sediment (Jones, 2010). Within the halo there is a small patch containing

numerous large brain corals (*Diploria labyrinthiformis*). Some of these corals are large enough to have established themselves before the marine land filling began and have provided a unique opportunity to investigate the geochemistry of the coral skeletons and provide a high-resolution proxy record of environmental contamination associated with the seafill.

Flood et al. (2005) and Jones (2010) provide a detailed historical analysis of widespread anthropogenic influences that have occurred in CH in the last 100 years, including extensive dredging and the commencement of the landfilling processes. Briefly, the dumping started sometime in the early 1970s (although exact dates are uncertain), which included the disposal of cars, buses, and mopeds. Prior to the landfill, extensive dredging occurred in CH to create land for an air station during World War II (Tucker, 1983). According to coral surveys in the 1970s, the dredging caused mass mortality of large, old corals in CH (Dodge and Vaisnys, 1977). More recently bulk waste, such as scrap metal, domestic appliances, construction waste (soils, rubble, and plasterboard), electrical goods, PVC plastics, and used tires were added to the waste stream (Fig. 1C). Since the mid 1990s municipal solid waste incinerator ash, generated from combustion of household garbage, was disposed off at the reclamation site, generally after being cement-stabilized into 1 m³ blocks (Hjelmar, 1996; Jones, 2010). No

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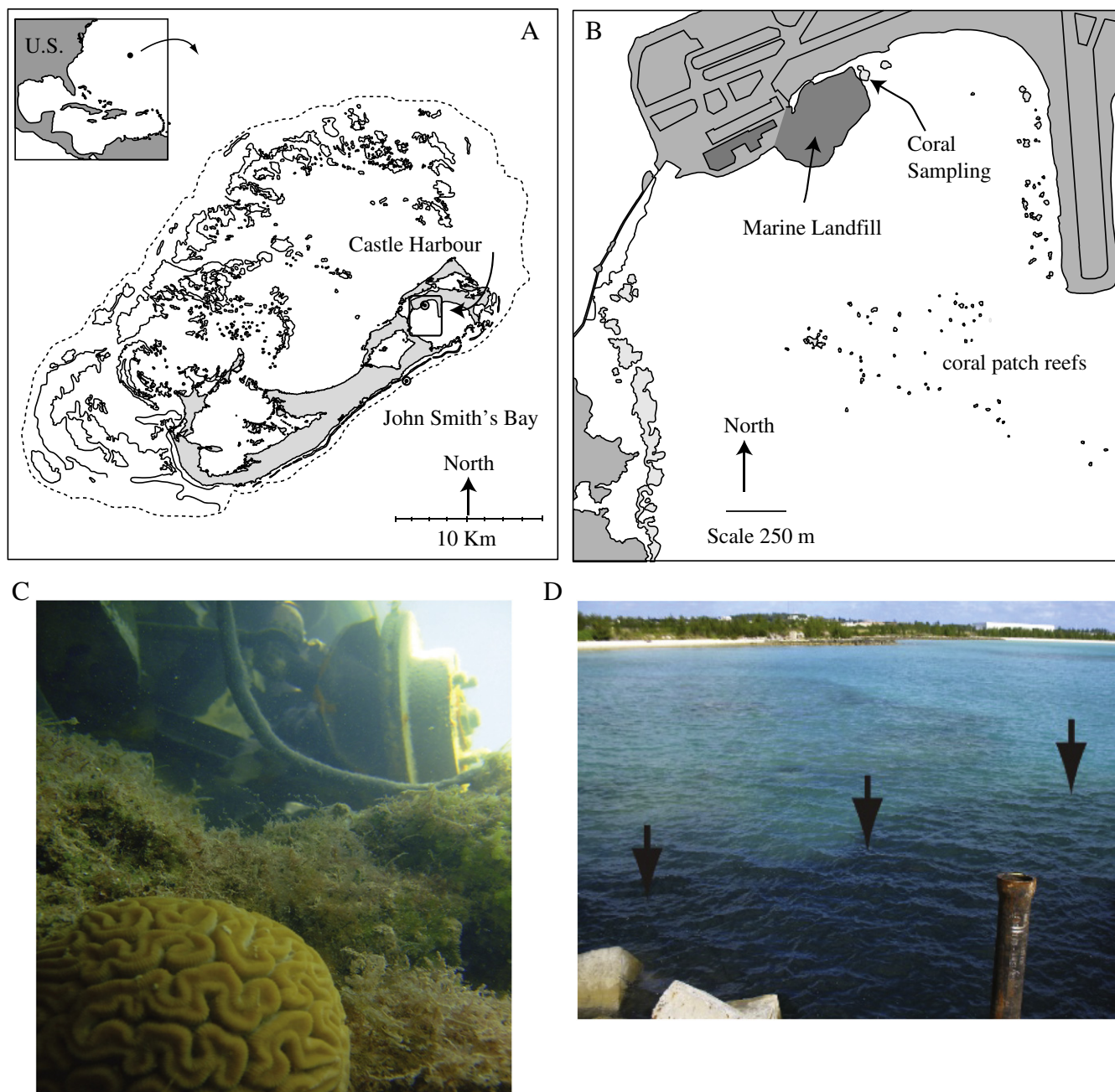


Fig. 1. (A) Map of Bermuda and locality in reference to the eastern United States with coral drilling sites at Castle Harbour and John Smith's Bay indicated by bullets and reef zone delineated by dashed line. (B) Enlarged map of Castle Harbour and location of marine landfill, coral collection sites, and coral patch reefs within the Harbour. (C) Photograph of approximately 20–30 cm *Diploria labyrinthiformis* head from Castle Harbour with marine landfill debris in the background. (D) Black water emanating from the landfill in Castle Harbour at low tide when anoxic material drains out of the landfill.

attempt is made to control the movement of seawater through the landfill and seawater levels rise and fall in synchrony with the external tide.

The geochemistry of coral skeletons has been widely used to study environmental variability, since corals precipitate their CaCO_3 (aragonite) skeleton directly from seawater. High-resolution proxy records extracted from coral skeletons can provide detailed information on environmental change by accurately recording changes in physical and chemical parameters such as SST, river input, salinity, and pollution. Predominantly, this work has focused on stable isotopic ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) and major and minor elemental (Sr/Ca, U/Ca) analyses. The increased environmental threat of toxic contamination to coral reef ecosystems, however, has motivated scientists to employ corals as biomonitors of pollution through the examination of trace metal concentrations.

Many studies have shown uptake of metals by scleractinian corals (Howard and Brown, 1984; Fallon et al., 2002; David, 2003; Reichelt-Brushett and Harrison, 2005; Ramos et al., 2009). Abundances of trace metals in corals have been explored to monitor environmental change and to reconstruct temporal and spatial patterns of contaminant input to the coral reef environment (e.g., Scott, 1990; Guzman and Jimenez, 1992; Bastidas and Garcia, 1999; Fallon et al., 2002; David, 2003; Runnalls and Coleman, 2003; Al-Rousan et al., 2007; Edinger et al., 2008; Prouty et al., 2008; Chen et al., 2010; Wang et al., 2011). Metals are incorporated into coral skeletons through substitution of dissolved metal species via Ca substitution, trapping of particulate matter within the skeletal matrix, and uptake of organic matter from either the coral tissue or directly from the water (see reviews by

Howard and Brown, 1984; Hanna and Muir, 1990; Brown et al., 1991). Biological parameters can also control metal deposition in the skeletal structure, with symbiotic zooxanthellae playing an important role in the accumulation and regulation of trace metals (e.g., Reichelt-Brushett and McOrist, 2003).

Contaminants are bioavailable to corals from ingestion with food (particulate phase), tissue-facilitated transport, and/or passive diffusion through dissolved phase. Uptake of metals can also be a function of the bioavailability in terms of its complexation and binding capacity. For example, Calmano et al. (1993) found that weakly adsorbed contaminants are more bioavailable to aquatic biota relative to complex-mineral bound contaminants. Bioavailability of contaminants can also be increased through resuspension of contaminant sediment (Eggleton and Thomas, 2004). With coral reefs being particularly vulnerable to the amount of sediment provided by anthropogenic activities (Smith and Buddemeier, 1992), resuspension of metal-bearing fine-grained sediment represents a recurring ecological threat. Although there is still debate as to the specifics of metal incorporation (Cohen and McConnaughey, 2003), the relationship between metal exposure and accumulation in coral skeletons is proving a valuable tool for reconstructing natural and anthropogenic change in reef environments.

2. Material and methods

2.1. Field collection

A single colony of *D. labyrinthiformis* (grooved brain coral) was collected (May 2000) from 16 m depth approximately 1 km from the shore of John Smith's Bay (JSB) on the southeastern edge (64°W, 32°N) of the Bermuda platform (Fig. 1A). Because the coral was collected from the edge of the most southern portion of the reef, the site is exposed to open-ocean conditions and represents a pristine environment – an oligotrophic, subtropical gyre. Within 4–5 km of the coral site, water depths reach 1000 m. There are no rivers on Bermuda due to the porous nature of the limestone bedrock, so JSB does not receive terrigenous runoff from riverine input. In contrast to JSB, corals collected in CH were collected approximately 30 m from the edge of the seafill and living at water depth of 3–4 m with restricted water flow (Fig. 1B). The southern edge of the landfill is semi-submerged in the waters of CH, with dumping of bulk waste and cement stabilized ash from the island's incinerator serving as a potential source of contamination to CH (Knap et al., 1991; Flood et al., 2005; Jones, 2010). Sediment near the coral collection site, in the north of the Harbour, is dominated by fine, silt-sized particles (<62 μm) (Knap et al., 1991; Jones, 2010). As a result of high turbidity, visibility is low and light levels are below 50% of incident illumination (Morris et al., 1977; Flood et al., 2005). Within CH, coral cover and species distribution are greatest with increasing distance from the landfill (Flood et al., 2005), with the sediment tolerant *D. labyrinthiformis* serving as the dominant species (Smith et al., 1998).

For trace metal composition, the CH corals were sampled annually, where average growth rates were 5.4 mm yr⁻¹ according to annual density banding revealed in X-radiographs. Samples for Hg analysis were taken from two additional corals from CH, and Hg values are reported for 4-yr increments. Average growth rates based on annual extension rates from JSB yield approximately 3.8 mm yr⁻¹ (Goodkin et al., 2005). Based on this age model, the JSB core was sampled biennially using a diamond blade band saw. In all the coral samples, the septotheca, the area of highest density calcification, was separated from the calyx using a Dremel hand-held tool. Sampling from solid thecal wall helps to minimize the potential for diagenetic alteration or secondary aragonite precipitation due to the isolation of the center of the wall from skeletal pore spaces filled with seawater (Cohen et al., 2004). Further discussion of materials and sampling has been previously published (Cohen et al., 2004; Goodkin et al., 2005).

2.2. Sample treatment and major and minor metal analyses

Standard trace element cleaning of Teflon labware and preparing samples for analysis were conducted in a class-100 clean room environment at the Woods Hole Oceanographic Institution (WHOI). To remove surface contamination associated with handling and to minimize the presence of non-lattice bound phases from the aragonite lattice (e.g., accessory organic and oxide phases associated with adsorbed metals, occlusion and trapping of discrete detrital particles), isolated bulk coral samples were chemically cleaned using previously established methods modified from Shen and Boyle (1988), Guzman and Jarvis (1996), and Bastidas and Garcia (1999) and dried overnight. This process involved a sequence of oxidizing, reducing and leaching steps, with multiple rinses and ultrasonication in Milli-Q water. This protocol did not include a hydrazine step that is typically included to remove oxide coatings, therefore both lattice bound and non-lattice bound elements are reported here. The bulk coral samples were homogenized by crushing with an agate mortar and pestle and passed through polypropylene sieves to an optimal size fraction (200–700 μm) (Shen and Boyle, 1987). The samples were then leached in 0.015 N HNO₃ for 20 min to isolate compound trabeculae.

Approximately 2 mg of the homogenized coral powder (CaCO₃) was weighed out to yield a dissolved Ca concentration of 100 ppm to minimize matrix-induced mass discrimination (Rosenthal et al., 1999). Coral powders were dissolved and diluted with ultra-pure concentrated HNO₃ and 0.1 ppb of an indium (In) was added which served as an internal standard to correct for instrument drift and sample matrix effect. A detailed discussion of relevant methods can be found in Prouty et al. (2008). In brief, major and minor element analyses were carried out on a high-resolution double focusing magnetic sector-field inductively coupled plasma mass spectrometer (HR-SF-ICP-MS) (Finnigan Element2). The samples were analyzed using a self-aspirating 20 μL min⁻¹ nebulizer attached to a quartz cyclonic spray chamber, using argon as a carrier gas. A washout time of 1 min was applied to unknowns and standards and 90 s to blanks. Both low and medium resolution analytical modes were used with a 10% and 80% mass window, respectively, in order to maximize instrument sensitivity. The signal intensity was obtained by integration of the counting signal of the scanning mass over a 4 min acquisition period.

For Hg analysis, approximately 200 mg of the cleaned powder was used without dissolution or further preparation (Lamborg et al., 2013). To investigate signal replication, Hg concentrations were analyzed from two adjacent corals collected from CH. Determination of low-level Hg by calcination–isotope dilution ICP-MS is discussed in Lamborg et al. (2013). In brief, the coral powder was heated to 850 °C while in-line with the ICP and an enriched ²⁰⁰Hg⁰ vapor standard, and the ²⁰²Hg/²⁰⁰Hg ratio integrated in the resulting chromatograph. Primary signal calibration for Hg was achieved using gas injections from a natural isotope abundance saturated vapor standard. The absolute instrument detection limit was approximately 200 amol (10⁻¹⁸ mol), with a practical limit of detection of 2000 amol (Lamborg et al., 2013).

2.3. Numerical time-series analysis

Several statistical techniques were employed that are commonly used with climate data when the time-series are short and noisy, as well as datasets that are non-evenly sampled or with missing values (e.g., Ghil et al., 2002). Spectrum Analysis-Multitaper Method (MTM) (Vautard et al., 1992) was used to perform detailed spectral analysis on the coral metal and meteorological records. Wavelet analysis was also employed to determine both the dominant modes of variability (as detected using singular spectrum analysis) and their variability in time where the time-series is decomposed into time–frequency space (Torrence and Compo, 1998). For identifying common patterns of

variability in the multivariate metal records, Empirical Orthogonal Function (EOF) analysis was used (Preisendorfer, 1988). In a similar manner to principal component analysis, there is decomposition of the dataset to a new coordinate system. The advantage of EOF analysis is that both temporal and spatial patterns can be evaluated (e.g., Fisher, 2002). Meteorological data (e.g., wind) were obtained from National Climatic Data Center (NCDC) and total observations per year were calculated from hourly observations for winds originating from the southeastern quadrant (80–190°) at 10, 15, and 20 m/s. Winds from these directions were selected as they would be blowing over the greatest fetch and thus would be most capable of developing the largest waves and strongest currents that could, in turn, resuspend seabed sediment either at the site of the corals or in adjacent shallower waters and advect it past the corals. Cumulative annual precipitation was computed from hourly precipitation records from the Bermuda Weather Service.

3. Results

3.1. Site comparison

In order to investigate whether corals living in CH have been exposed to contaminants from the adjacent landfill, coral metal ratios from CH and the control site at JSB were compared using a Student's *t*-test over a 19-year period (1975–1994) when the two records overlap. The Student's *t*-test reveals a statistical difference ($p \leq 0.05$) between metals at the two sites (except for Cd/Ca, Cu/Ca, and Fe/Ca ratios) (Table 1). This difference is captured in the concentration whisker-box plots (Fig. 2). Within the group of elements, CH was characterized by greater Ba, Mn, Pb, Zn, and Hg concentrations relative to JSB concentrations. The only elemental ratio elevated at JSB relative to CH was Sr/Ca, which is often driven by changes in sea-surface temperature SST (e.g., Goodkin et al., 2007). The greatest enrichment in the CH coral samples was in the Zn, Mn, and Hg concentrations (Fig. 2). Average CH coral Hg concentrations were 7 to 9 times greater than those measured from JSB. There was no statistical difference (Student *t*-test, $p \leq 0.05$) between coral Hg concentrations measured from the 2 corals in collected in CH. Average Zn concentrations were two orders of magnitude greater at CH than at JSB and Mn concentrations were 4 times greater.

3.2. Castle Harbour

CH coral trace metal concentrations were also compared to sediment and water concentrations from CH (Jones, 2010). Except for Ba and Sr where water concentrations were not available, trace metal sediment concentrations were enriched relative to the water concentrations (Fig. 2). Likewise, CH coral concentrations were also elevated relative to the water concentrations (Student *t*-test, $p \leq 0.05$).

Table 1

The table shows average metal/Ca ratios and their respective standard deviation (\pm SD) for the period of overlap between 1975 and 1994. Student's *t*-test reveals statistical difference ($p \leq 0.05$) between Castle Harbour and John Smith's Bay except for Cd/Ca, Cu/Ca, and Fe/Ca, as indicated by gray text. ^a*n* = 10; ^b*n* = 3.

| Site | Castle Harbour | | John Smith's Bay | |
|----------------|-----------------------|----------|-----------------------|----------|
| | Mean (<i>n</i> = 20) | \pm SD | Mean (<i>n</i> = 10) | \pm SD |
| Cd/Ca mmol/mol | 0.32 | 0.18 | 0.33 | 0.06 |
| Ba/Ca mmol/mol | 4.7 | 0.17 | 4.58 | 0.11 |
| Cu/Ca mmol/mol | 17.43 | 10.16 | 32.2 | 20.2 |
| Pb/Ca mmol/mol | 0.21 | 0.09 | 0.140 | 0.06 |
| Mn/Ca mmol/mol | 2.60 | 1.91 | 0.74 | 0.43 |
| Fe/Ca mmol/mol | 16.12 | 10.24 | 13.74 | 12 |
| Zn/Ca mmol/mol | 1.01 | 1.64 | 3.60E-02 | 2.01E-02 |
| Sr/Ca mmol/mol | 8.98 | 9.94E-02 | 9.05 | 3.69E-02 |
| Hg pmol/mol | 229.73 ^a | 108.70 | 29.42 ^b | 16.10 |

Sediment trace metal concentrations were enriched relative to CH coral concentrations, with the exception of Sr, Fe, and Zn, which displayed distribution coefficients (K_d = concentration in sediment:concentration in coral) of less than 1. Zinc was the only element that did not show a statistical difference (Student *t*-test, $p \leq 0.05$) between coral and sediment concentrations. Relative to CH coral concentrations, the greatest enrichment in sediment trace metal concentrations was observed for Hg and Pb, with K_d values of 1010 and 150, respectively.

The CH core was sampled annually for metal variability from 1975 to 2005. There was a distinct interannual signal in the metals:Ca ratios (Cd/Ca, Pb/Ca, Mn/Ca, Fe/Ca, and Zn/Ca) but no apparent long-term trend except for Sr/Ca and Ba/Ca (Fig. 3). The EOF analysis revealed a dominant first EOF, accounting for 54% of the total variance with little contribution from Sr/Ca and Ba/Ca (Table 2). The first EOF was dominated by individual loadings from Zn/Ca and Mn/Ca at 80%, with equal contribution from Cd/Ca, Pb/Ca, and Fe/Ca at 60%. In comparison, Sr/Ca variability was captured in the second EOF and Ba/Ca variability was captured in the third EOF, suggesting that these two elements were controlled by different processes. The first EOF also captured the interannual periodicity (Fig. 3) with a broad MTM spectrum centered at approximately 4 yrs and passing the 95% confidence interval (Fig. 4A). Morlet wavelet analysis confirmed these results with power spectrum centered between 4 and 6 yrs, as well as a time-dependent component to the periodicity (Fig. 4B–D).

3.3. JSB

The JSB coral was sampled and analyzed biennially for the period 1776 to 1994 (Fig. 5). In order to identify common variance between the biennial metal records, EOF analysis was applied. The first EOF explained 35% of the total metal variance and was characterized by all elements except Sr/Ca and Ba/Ca, with enhanced loadings of Cd/Ca and Zn/Ca ratios (Table 3). In contrast to the first EOF, Sr/Ca and Ba/Ca equally dominated the second EOF. The dominance of high-frequency variability over the long-term trend was captured in the spectral analysis, which showed interannual variability centered on spectral bands of 6 and 9 yrs with additional periodicities at the interdecadal scale of 12 and 18 yrs (Fig. 6A). These results were confirmed by wavelet analysis (Torrence and Compo, 1998) (Fig. 6B–D), which also revealed a time-dependent variability associated with these periodicities. The scale-averaged wavelet power over the 6- to 10-yr band was strongest in the early record (Fig. 6C). In contrast to previous Pb concentration and isotope records from JSB documenting a rise in anthropogenic Pb emissions (Kelly et al., 2009), bulk Pb/Ca values from this study did not capture this rise, most likely resulting from the incorporation of non-lattice bound Pb associated with detrital particles or suspended material (e.g., Neil et al., 1994; Mertz-Kraus et al., 2009).

3.4. Meteorological data

Spectral analysis was conducted on cumulative annual precipitation from 1949 to 2012 and wind speeds > 10 m/s from 1942 to 2012 from the SE (80–190°). The latter was chosen given the highest density of observations relative to wind speeds at 15 and 20 m/s. At the 99% confidence interval, a 3-yr period accounted for 30% of the wind speed variance for winds coming from the SE. For cumulative annual precipitation, a 3-yr period was detected at the 90% confidence interval, accounting for 23% of the variance. Both records also exhibited decadal and multi-decadal periods. For the period of overlap (1975–2005), the wind data and the CH first EOF were statistically correlated (Pearson's product-moment correlation coefficient, $r = 0.59$; $p = 0.05$), with increased winds corresponding to elevated trace metal:Ca ratios as captured in the first EOF (Fig. 7). For the 30-yr period, the 1990s exhibited the greatest number of observations for winds greater than 10 and 15 m/s (Fig. 7A–B). Wind speed greater than 15 m/s was also statistically correlated to the first EOF ($r = 0.52$; $p = 0.05$). This

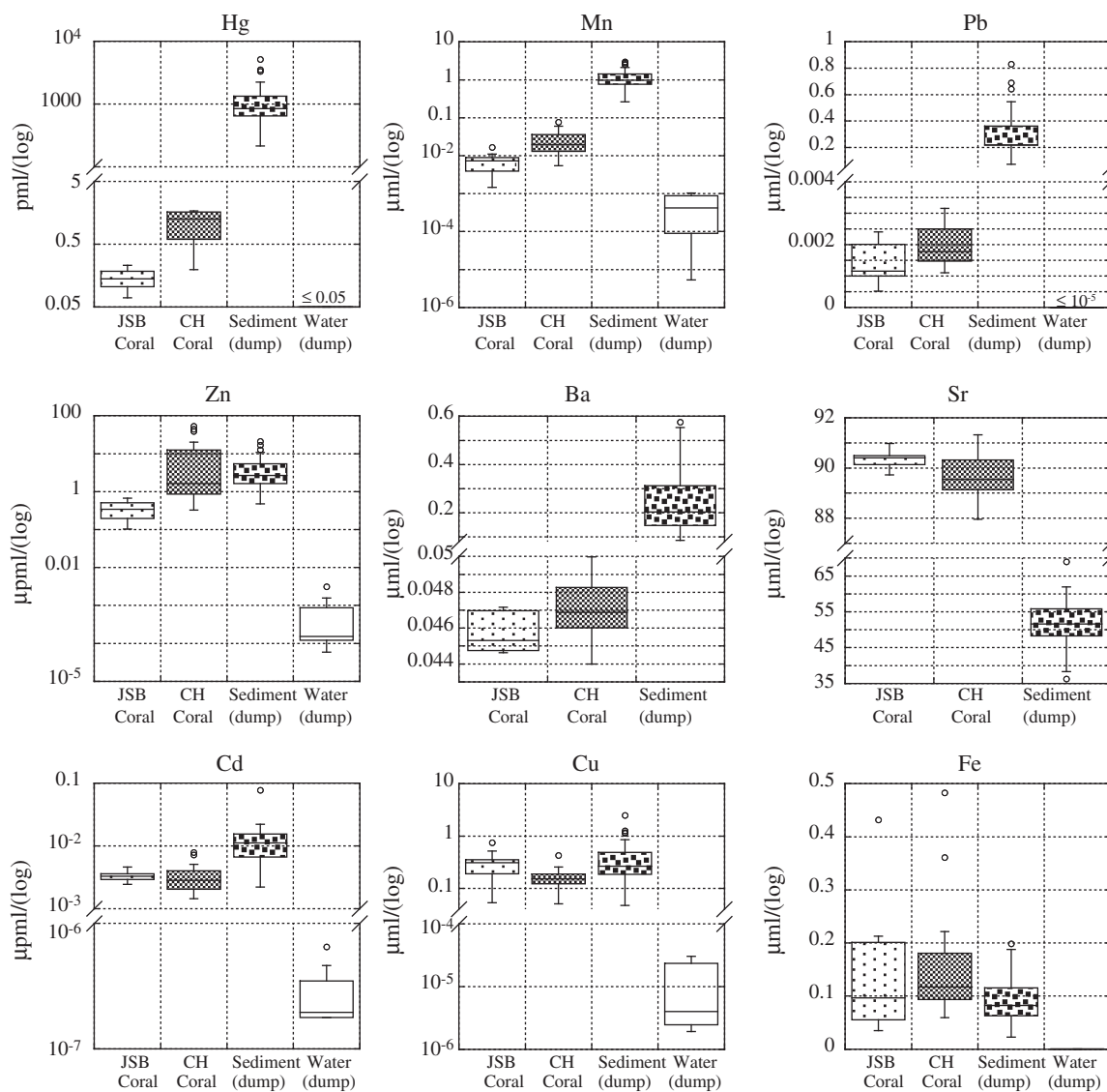


Fig. 2. Whisker-box plots for coral trace metal concentration ($\mu\text{mol/g}$ and pmol/g) from John Smiths' Bay and Castle Harbour, as well as from sediment and water samples collected near the dump (Jones, 2010). Except for Cd, Cu, and Fe, the Student *t*-test reveals a statistical difference ($p \leq 0.05$) between the two coral sites. Boxes show the lower, median, and upper quartiles of the site and outliers, indicated as circles, were defined as either less or greater than 1.5 times the lower or upper quartile range, respectively.

decade was characterized by elevated values in the CH record (first EOF). There was no statistical relationship between cumulative annual precipitation and CH record (first EOF). Monthly mean sea level data were acquired from NOAA stations 2695535 and 2695540 located at the Bermuda Institute of Ocean Sciences and a 12-point running mean was applied to the monthly data. While the monthly sea level data captures a strong interannual signal, there was no statistical relationship between SL and the CH first EOF.

4. Discussion

4.1. Castle Harbour

The dissolution and leaching of contaminants from the CH marine landfill have led to elevated levels of trace metals in the water, sediment, and mussel tissue samples from CH (Jickells and Knap, 1984; Burns et al., 1990; Knap et al., 1991; Smith et al., 1998; Flood et al., 2005; Jones, 2010). Elevated metal:Ca ratios in the proximal CH corals relative to those measured from distal JSB appear to reflect input from land-based activities, specifically leaching of contaminants from the municipal landfill and surrounding sediment. For example, emissions

inventory showed that municipal solid waste incineration is the most significant source of Hg emissions in Bermuda, with an estimated emission of 17 kg/yr and the dump is likely a source of Hg (3.3 kg/yr) for CH (Peters et al., 2008). Results from this study support the hypothesis that there is higher bioaccumulation of metals in corals from CH relative to other areas of Bermuda's nearshore environment (e.g., JSB) that are exposed to open water. While the landfill has increased to encompass an area of 0.10 km² over the last 35 yrs (Jones, 2010), the CH record does not reveal a long-term trend. Instead, coral metal variability appears to be dominated by export of contaminants triggered by periodic input.

Elevated trace metal concentrations in the sediment of CH relative to the water samples suggest that the suspended, metal-bearing fine sediment is a greater source of biologically available metals relative to the dissolved fraction. Given that fine-grained suspended sediment accumulates and concentrates metals (Forstner and Salomons, 1980; Reichelt-Brushett and Jones, 1994), the silt-size sediment in CH may provide an important transport medium for transferring heavy metals to corals. Biogeochemical processes can also play a role, for example elevated coral Zn and Fe levels at CH relative to the sediment may reflect trophic transfer of nutrients through feeding, where zooplankton uptake may be a significant source of metal enrichment (Marshall,

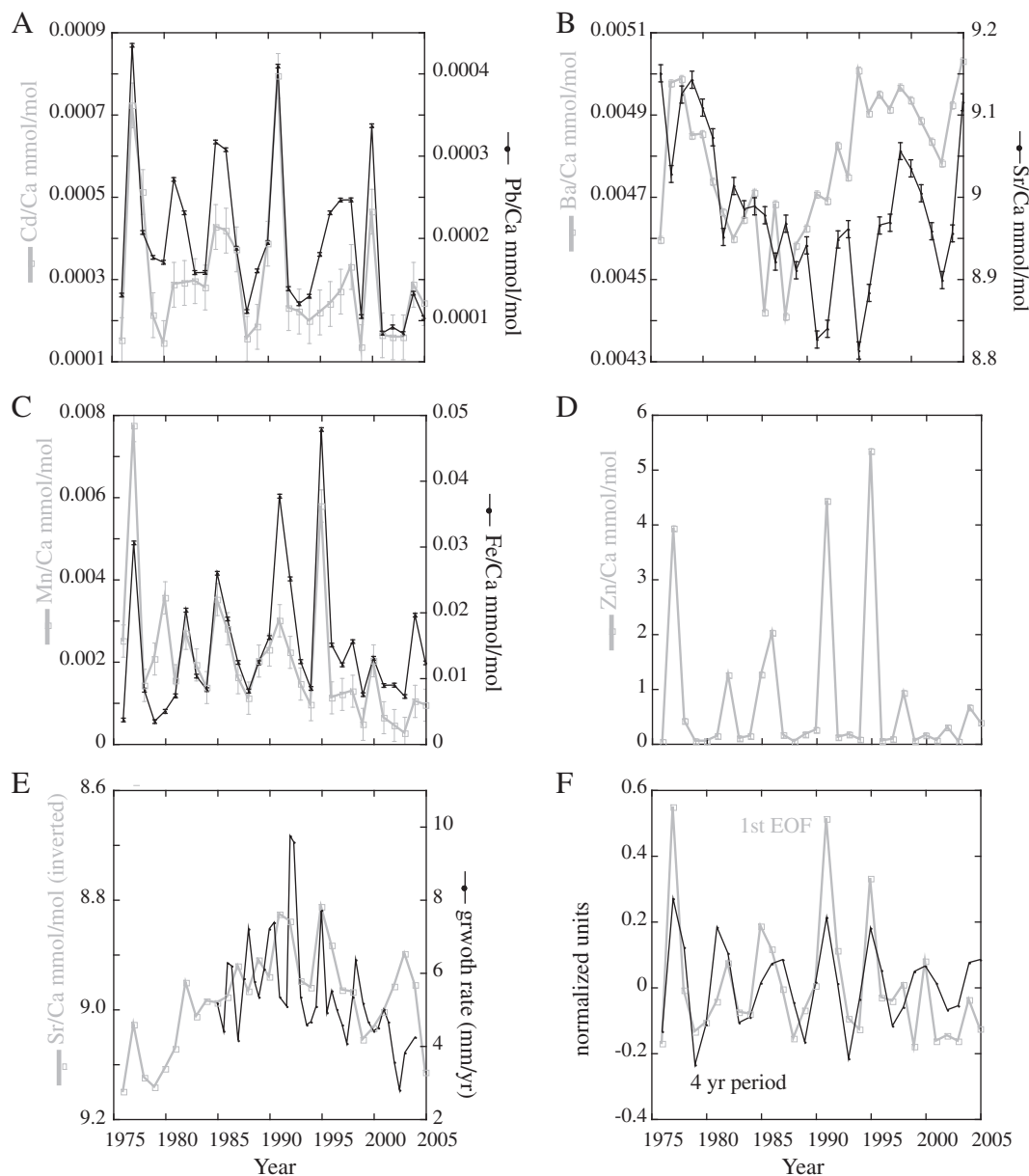


Fig. 3. (A)–(D) Annual metal ratios (mmol/mol) at Castle Harbour from 1975 to 2005. The time-series show distinct interannual variability. (E) Growth rate (black) compared to the annual Sr/Ca time-series (gray; inverted) showing similar behavior for the first 20 yrs. (F) The first EOF (gray) calculated from the annual Castle Harbour (CH) metal record and the spectral results from Spectrum Analysis-Multitaper Method (MTM) displaying statistically significant (95% confidence interval) period at 4.5 yrs (black).

2002). This is particularly true for Zn, which is an essential macronutrient, where reduced tissue-regulation permits greater Zn accumulation in the skeleton (Esslemont, 2000).

Table 2

Percent of variance associated with the first three EOF modes, which accounted for 87% of the annual Castle Harbour metal variance. The first EOF was dominated by the majority of the elements except Ba/Ca and Sr/Ca, where Sr/Ca was characterized by negative eigenmode (as indicated by gray) but was dominant in the second EOF and Ba/Ca dominated the third EOF.

| Metal/Ca | First EOF 54% | Second EOF 18% | Third EOF 15% |
|----------|------------------|-------------------|------------------|
| Cd/Ca | 63.0 | 10.1 | −8.0 |
| Ba/Ca | 1.2 | 19.9 | 73.7 |
| Pb/Ca | 64.6 | 12.5 | −10.6 |
| Mn/Ca | 80.6 | −10.4 | 5.0 |
| Fe/Ca | 66.1 | 3.1 | −0.01 |
| Zn/Ca | 84.3 | −1.1 | 2.9 |
| Sr/Ca | −16.8 | 71.4 | −1.1 |

The coupling of tides and winds can cause resuspension and transport, where metals can change their desorption and binding forms during long-term resuspension events, transforming them into more bioavailable forms (Eggleton and Thomas, 2004). As described in a study conducted on the Great Barrier Reef, periodic turbidity can resuspend fine-grain sediment, depositing and adhering trace metals to mucosal coral surface (Esslemont, 2000). While resuspension events may be short lived, according to extrapolated results from a laboratory-based erosion chamber, metals with strong peaks in release are an important contributor to the calculated annual sediment metal load, releasing dissolved species to the overlying oxic water (Kalnejais et al., 2010). The ecological effect of resuspended contaminated sediment in marine environments is complex (Roberts, 2012); however, the liberation of sediment-bound contaminants is an important problem in mine waste management where resuspension and entrainment of sediment particles by wind-induced motions (e.g., waves and currents) occur (see review by Eggleton and Thomas, 2004).

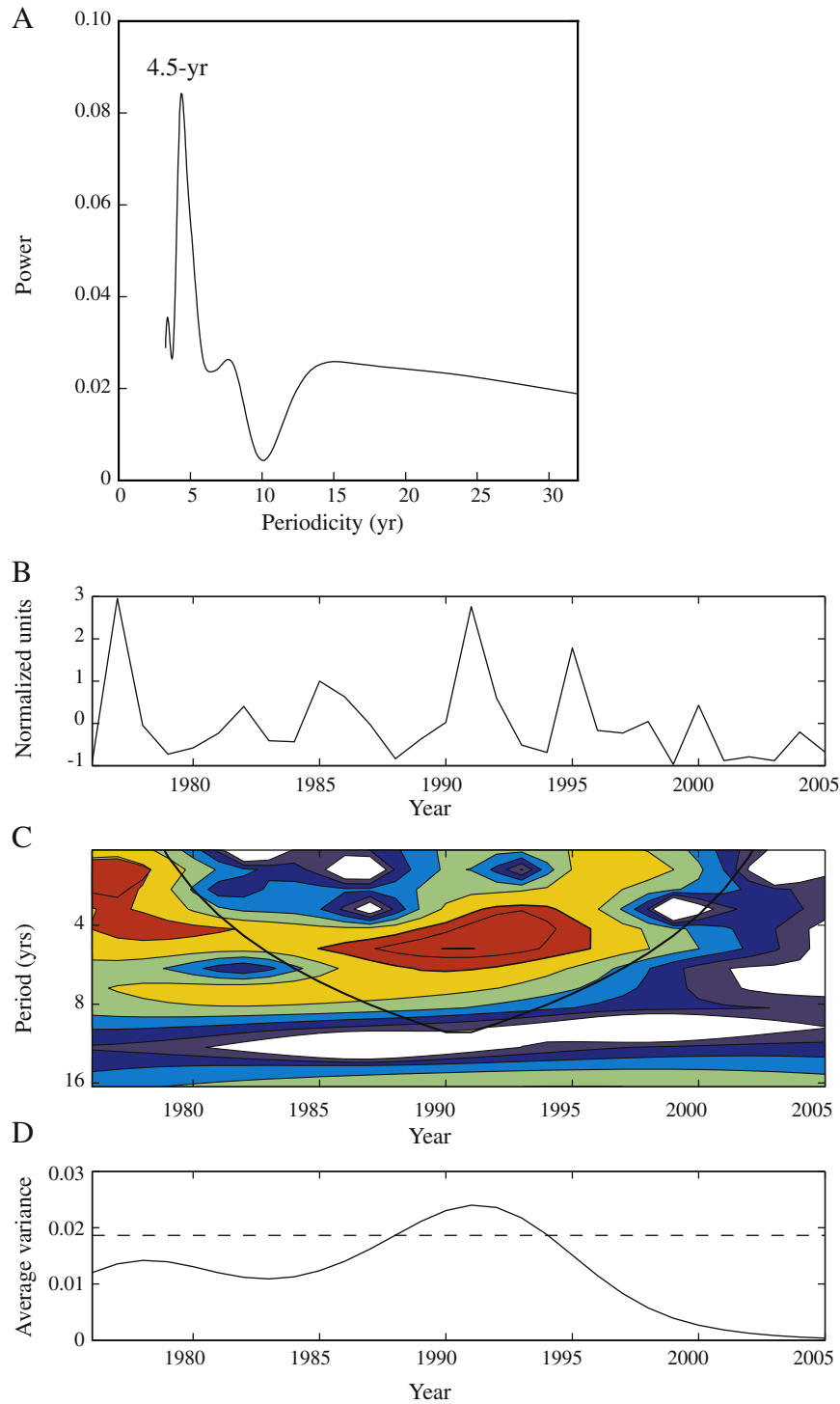


Fig. 4. Results from spectral and wavelet analysis of the first EOF, which accounts for 54% of the Castle Harbour metal variance. (A) Spectral results from Spectrum Analysis-Multitaper Method (MTM) displaying statistically significant (95% confidence interval) period at 4.5 yrs (2 windows). (B) Normalized eigenmode of the first EOF time-series from 1975 to 2005. (C) The wavelet power spectrum with warmer colors indicating greater variance. The x-axis is the wavelet location in time and the y-axis is the wavelet period in years. The contour levels are relative to global wavelet spectrum. Black contour is the 95% confidence level using a red-noise background spectrum. (D) Scale-averaged wavelet power over the 4- to 6-yr band. Thin dashed line is the 95% confidence level.

In shallow coastal waters, like CH, resuspension events can occur frequently due to wind- and wave-induced bottom stresses. In contrast to some studies linking rain to coral metal uptake (e.g., Ramos et al., 2009), CH trace metal variability was not related to cumulative annual precipitation, presumably given the lack of runoff on Bermuda. In contrast, the statistically significant relationship between southeasterly

wind speed (number of observations) and the first EOF at CH (Fig. 7) supports the notion that wind-induced resuspension can lead to increased availability of sediment-bound metals and subsequent coral metal assimilation. According to theoretical bed shear stress calculations (assuming silt-sized carbonate sediment, Nielsen, 1992) and only 5 km of fetch, winds in excess of 30 m/s are needed to exceed the critical

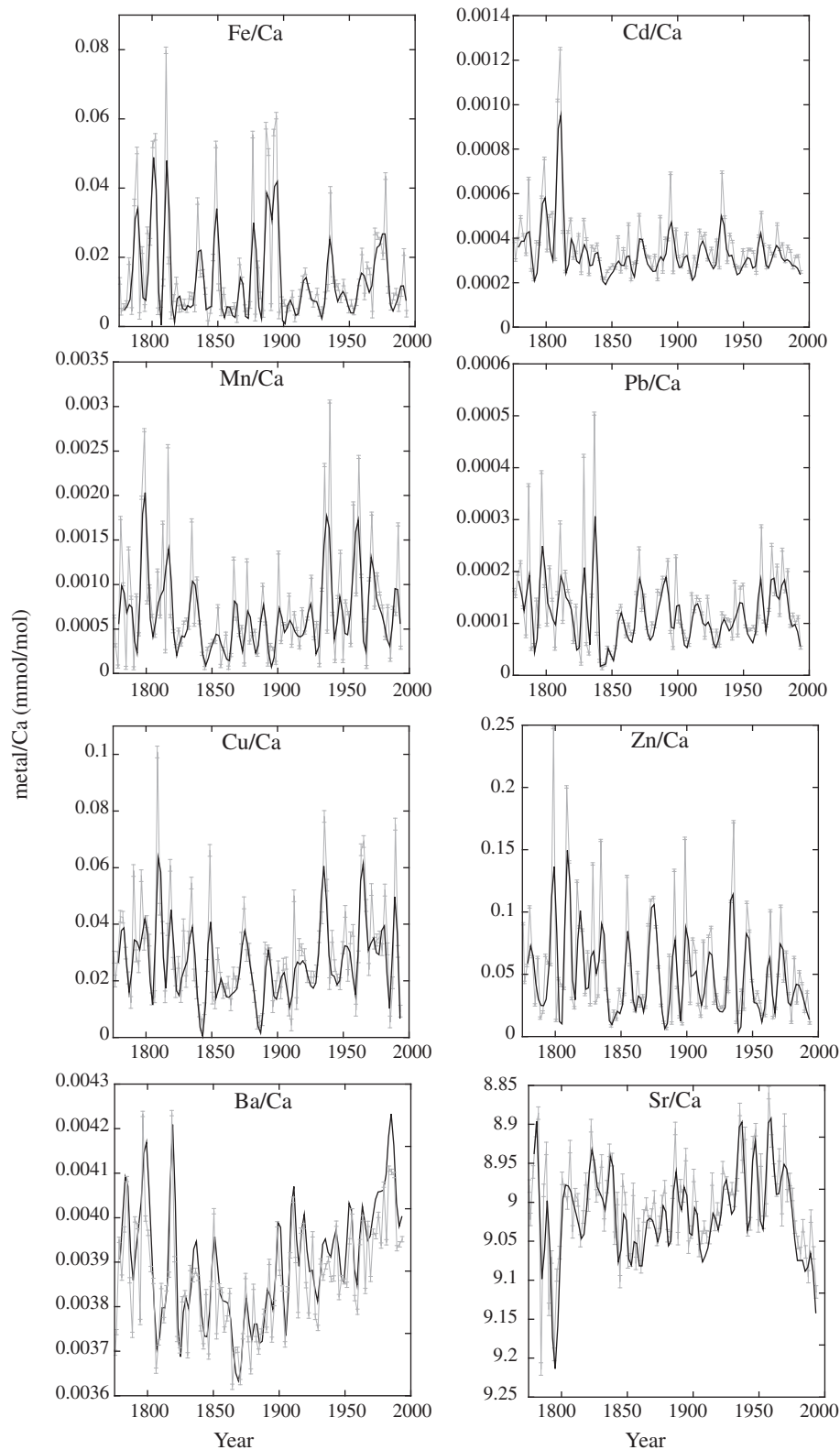


Fig. 5. Biennial record (gray) of metal ratios from John Smith's Bay (JSB) from 1776 to 1995. Error bars represent standard error calculated from analyzing replicates on 76 of the 110 unknowns. Superimposed on the biennial record is the decadal to interdecadal record (black).

shear stress to cause resuspension in CH at a depth of 4 m (Walton, 2002), suggesting that resuspension from the adjacent seabed is likely not a significant contributor to metals in the corals. Although the observed winds were not sufficient to resuspend seabed material at a

depth of 4 m, the winds were sufficient to resuspend material at much shallower depths closer to shore near the dump, and in conjunction with wind-driven currents, advect the resuspended sediment to CH due to the slow settling velocity of the fine-grained material. Additional

Table 3

Percent of variance associated with the first three EOF modes, which accounted for 63% of the total John Smith's Bay metal variance. The first EOF was dominated by the majority of the elements except Ba/Ca and Sr/Ca, where both elements were characterized by negative eigenmodes (as indicated by gray) but were dominant in the second EOF.

| Metal/Ca | First EOF 35% | Second EOF 17% | Third EOF 11% |
|----------|------------------|-------------------|------------------|
| Cd/Ca | 64.7 | -0.04 | -10.49 |
| Ba/Ca | -6.6 | 55.13 | 28.86 |
| Pb/Ca | 37.3 | 3.38 | -0.11 |
| Mn/Ca | 37.1 | -3.71 | 14.72 |
| Fe/Ca | 27.0 | -11.88 | 8.50 |
| Cu/Ca | 40.8 | 6.87 | 0.11 |
| Zn/Ca | 55.8 | 0.79 | -20.50 |
| Sr/Ca | -8.7 | 57.75 | -6.47 |

factors, such as storms and changes in sea level may also need to be considered. The number of days when sea level barometric pressure (an indicator of storms) dropped below 990 mb between 1975 and 2005 was 16, according to NCDC meteorological data. However, these episodic storm events have the potential to mobilize contaminants bound to sediments from the dump when waves several meters high hit the outer wall of the dump, composed of rubble, scrap metal, and ash blocks starting in the mid 1990s.

Previous work suggests that landfill seawater levels rise and fall in synchrony with the external tide (Chapman, 2008), such that the corals are periodically bathed in black water coming from the landfill

(Fig. 1D) versus more pristine Atlantic Gyre seawater. Because the southern edge of the landfill is semi-submerged in the waters of CH, periodic leaching by changes in sea level may contribute to elevated trace metal concentrations in CH. Mean sea level range measured at the Bermuda Biological Station, was 76 cm (NOAA station 2695540). This range is superimposed on interannual variability. Changes in sea level due to tides may also be modulated by interannual oscillation patterns in relative sea level height (RSLH). For example, interannual variability displaying periods of 3 to 8 yrs has been detected in the Atlantic RSLH data (Unal and Ghil, 1995). This interannual signal is consistent with the spectral behavior observed in the CH data with the first EOF displaying a broad MTM spectrum centered at approximately 4 yrs. Export and percolation of contaminants emanating from the landfill may therefore be enhanced during interannual sea level changes. Therefore, the interannual CH coral record may reflect interannual changes in local sea level. The lack of chronic, as opposed to periodic, exposure helps explain the observation that growth rates at CH are elevated relative to those measured in the open ocean at JSB, with little indication that coral growth in CH is impeded despite nearby contamination.

4.2. John Smith's Bay

Trace metal composition of suspended particles in the water column near Bermuda has been linked to both natural and anthropogenic sources including eolian fluxes and advected lithogenic sources (Sherrell and Boyle, 1992; Prospero et al., 1996; Huang and Conte, 2009; Kelly et al., 2009). For example, elevated JSB Fe concentrations

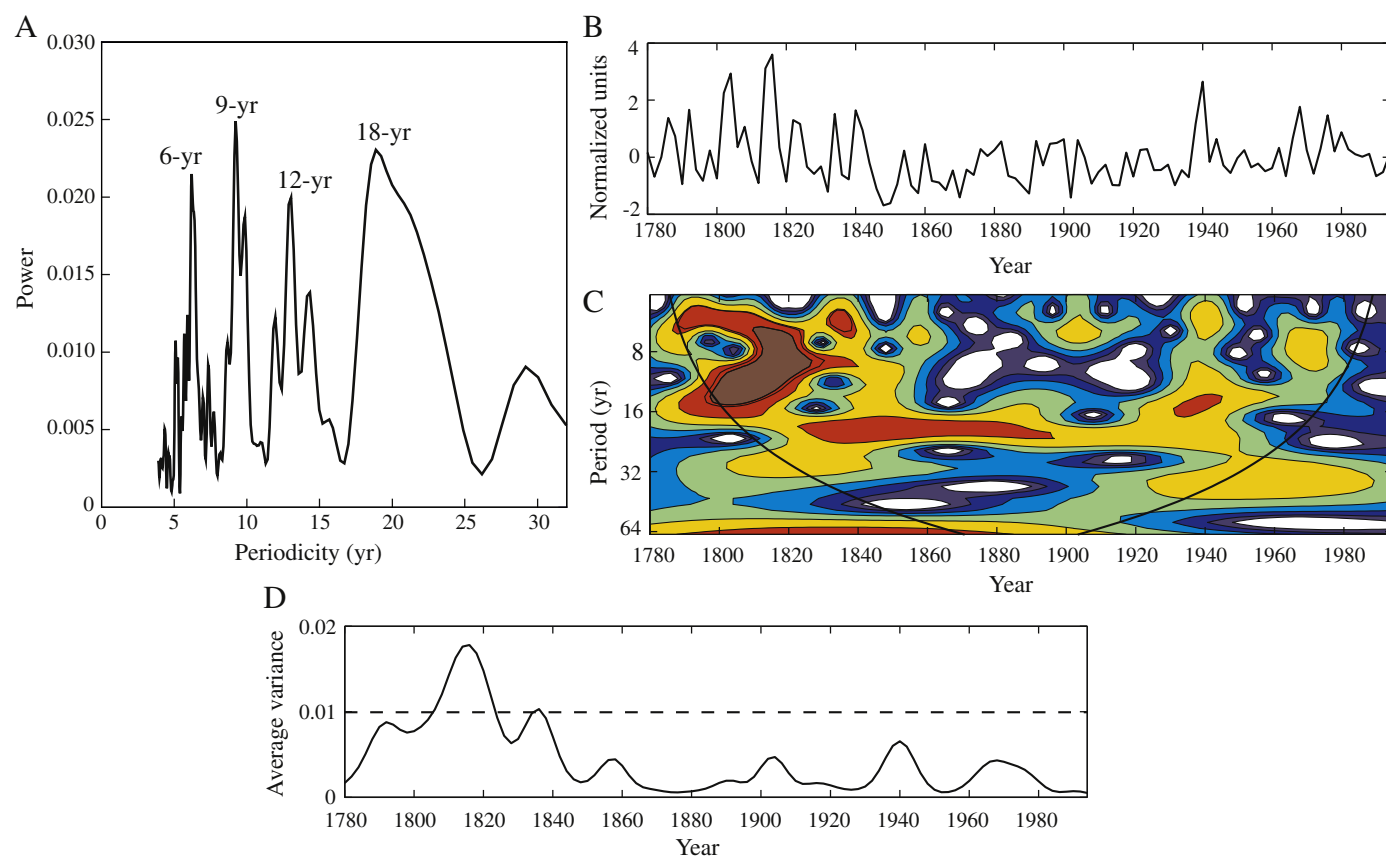


Fig. 6. Results from spectral and wavelet analysis of the first EOF, which accounts for 35% of the John Smith's Bay metal variance. (A) Spectral results from Spectrum Analysis-Multitaper Method (MTM) displaying statistically significant (95% confidence interval) periods at 6-, 9-, 12-, and 18-yr (2 windows). (B) Normalized eigenmode of the first EOF time-series from 1780 to 1985. (C) The wavelet power spectrum with warmer colors indicating greater variance. The x-axis is the wavelet location in time and the y-axis is the wavelet period in yrs. The contour levels are relative to global wavelet spectrum. Black contour is the 95% confidence level using a red-noise background spectrum. (D) Scale-averaged wavelet power over the 4- to 10-yr band. Thin dashed line is the 95% confidence level.

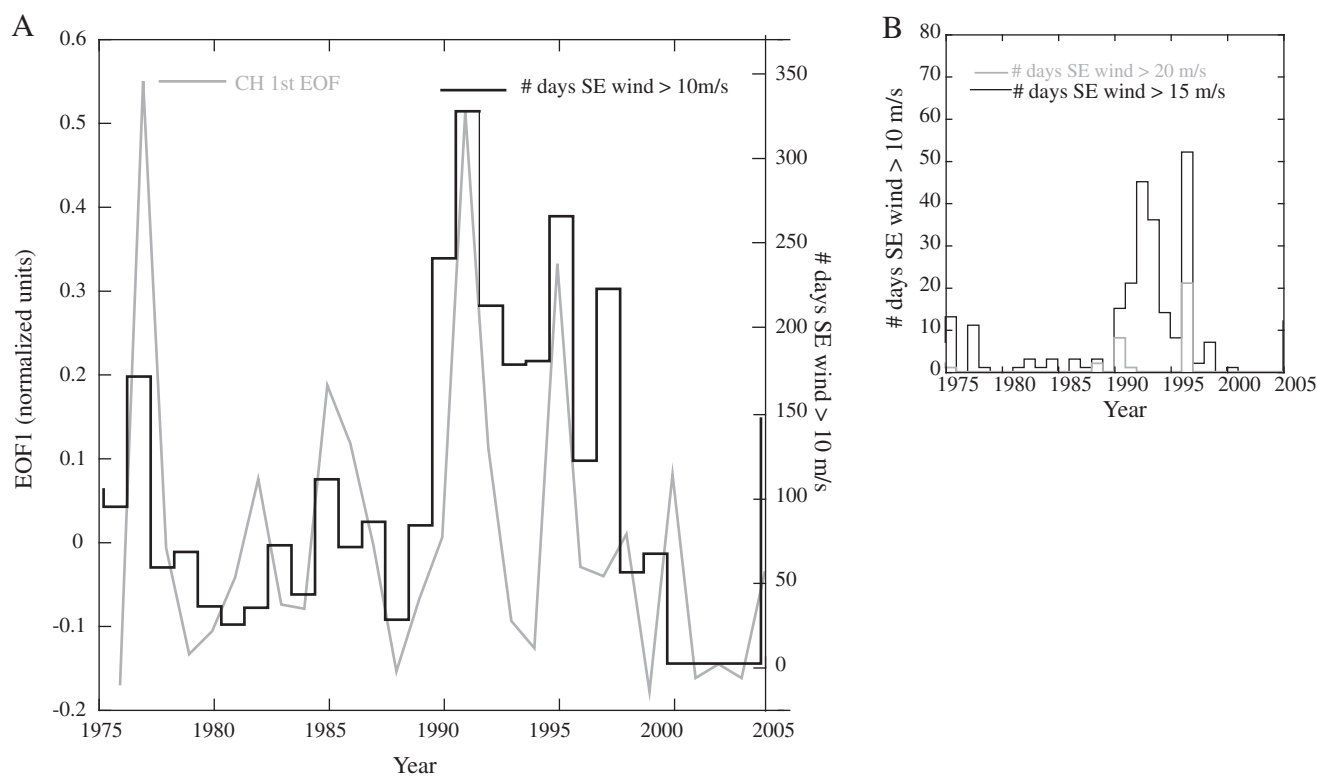


Fig. 7. (A) First EOF from Castle Harbour (CH) geochemical record, representing 54% of the total variance versus annual wind speed (> 10 m/s) observations from the SE quadrant (80–190°) generated from hourly observations. Pearson's product-moment correlation coefficient indicates a statistically significant relationship ($r = 0.59$; $p = 0.05$) between annual wind observations and the CH geochemical time-series. (B) Increased observations of winds at 15 m/s were also observed during the 1990s, with a statistically significant relationship with the CH first EOF ($r = 0.52$; $p = 0.05$).

may reflect aerosol deposition, which has been shown to contribute a biologically important constituent of seawater Fe near Bermuda (Mackey et al., 2012). However, the overall lower trace metal concentrations compared to both CH coral and sediment values suggest that JSB is not exposed to contaminants associated with land-based activities. Instead, large scale convective mixing may be driving interannual metal variability in the JSB record. Though thermocline mixing was not evident in a record of radiocarbon variability from the JSB coral (Goodkin et al., 2012), seasonal overturning and convective mixing, when the mixed-layer depth (MLD) reaches 160–200 m, can cause the nutricline to breach and entrain nutrients into the euphotic zone in the western Sargasso Sea (e.g., Copin-Montégut and Avril, 1993; Hansell and Carlson, 2001; Michaels and Knap, 1996). The effects of deep mixing during the winter are reflected in elevated nitrate concentrations in the surface layer (Goericke and Welschmeyer, 1998).

In most years in the Sargasso Sea near Bermuda, cold, dry winter air that forces convective cooling of surface water is sufficient to induce mixing into nutrient-rich waters at 100 m depth (Lipschultz et al., 2002). In particular, during a negative NAO phase when winter storms are more severe and storm tracks are further to the south, mixing is enhanced and responsible for delivery of cold, nutrient-rich waters to the oligotrophic surface waters in the subtropical gyre, potentially enhancing metal concentrations to the coral reefs. As a result, NAO-related variability plays a role in modulating interannual biogeochemical variability in the surface ocean surrounding Bermuda (Bates, 2001; Oschlies, 2001). The interdecadal frequency observed in the JSB record (Fig. 6A) is also consistent with NAO behavior and can help explain the inverse relationship ($r = -0.35$; $p \leq 0.05$) between the NAO and the first EOF from JSB record after 1900. Likewise, during positive phases of the NAO, the water column is well stratified and surface waters are nutrient depleted, thus reducing the delivery of trace metals to the surface waters surrounding the JSB coral site.

5. Conclusions

Among coastal systems, coral reefs are thought to be especially susceptible to the amount of sediment provided by anthropogenic activities (Smith and Buddemeier, 1992). In Bermuda, Castle Harbour's history of dredging and landfilling has been linked to increase leaching of contaminants into water, sediment, and marine tissue samples. Results from this study expand the environmental assessment of impacts from landfill leaching on the marine environment by quantitatively demonstrating elevated metal uptake in corals growing in CH. Relative to the JSB coral, CH coral Pb, Zn, Mn and Hg concentrations were elevated, in concert with previous studies reporting elevated trace metals in sediment and water samples near the landfill. The CH record does not reveal a long-term trend. Instead, coral metal variability appears to be dominated by export of contaminants triggered by periodic input. Elevated contaminants in the surrounding sediment suggest that resuspension is an important transport medium for transferring heavy metals to corals, with increased winds accompanied by higher coral variability at CH. Coupled with wind-induced resuspension, changes in sea level can enhance export and percolation of contaminants emanating from the landfill. The interplay of natural processes with land-based human activities is critical to evaluating the potential environmental impact of near shore contamination. The temporal and spatial comparisons between the CH and JSB coral records highlight the need to understand these combined effects and their impacts on coral record interpretation and ultimately coral health.

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