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Baseline

Organic pollutants, heavy metals and toxicity in oil spill impacted salt marsh sediment cores, Staten Island, New York City, USA

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ABSTRACT

Sediment cores from Staten Island's salt marsh contain multiple historical oil spill events that impact ecological health. Microtox solid phase bioassay indicated moderate to high toxicity. Multiple spikes of TPH (6524 to 9586 mg/kg) and Σ16 PAH (15.5 to 18.9 mg/kg) were co-incident with known oil spills. A high TPH background of 400–700 mg/kg was attributed to diffuse sources. Depth-profiled metals Cu (1243 mg/kg), Zn (1814 mg/kg), Pb (1140 mg/kg), Ni (109 mg/kg), Hg (7 mg/kg), Cd 15 (mg/kg) exceeded sediment quality guidelines confirming adverse biological effects. Changes in Pb^{206/207} suggested three metal contaminant sources and diatom assemblages responded to two contamination events. Organic and metal contamination in Saw Mill Creek Marsh may harm sensitive biota, we recommend caution in the management of the 20–50 cm sediment interval because disturbance could lead to remobilisation of pre-existing legacy contamination into the waterway.

The Arthur Kill strait separates Staten Island, New York from New Jersey and is one of the worlds' most important navigable estuarine channels, forming a key commercial connection between New York City and ports in New Jersey (e.g., Newark) and the Atlantic Ocean (Fig. 1). Compilation of historical petroleum and chemical spills reported to the US coast guard from 1987 to 1991 in the New York–New Jersey Harbor Estuary report that the Arthur Kill experienced 427 spill events ranging from 13,698 to 12,612,596 US gallons per-year and average of 2,541,939 US gallons (Gunster et al., 1993). Taken together, this data confirmed that the Arthur Kill suffered the largest spills and that they occurred more frequently than the other waterways of the New York–New Jersey Harbor Estuary. Consequently, the salt marshes of Staten Island constitute an important refuge for wildlife within the urban-industrial mosaic of the New York–New Jersey Harbor Estuary (NOAA, 2001). However, few studies have evaluated the longer term fate or toxicity of these historical pollution events.

The purpose of the current research was to assess pollution in urban, fuel spill impacted salt marsh sediments using multiple lines of evidence down two separate 90 cm cores to compare (1) vertical changes in persistent organic and heavy metal contamination; (2) compare

organic and metal concentrations to appropriate non-statutory sediment quality guidelines; (3) to assess the impact of the pollutants by laboratory toxicity tests and on in-situ diatom community structure.

Sediment cores were collected at 40 36 27.87912 N, 74 11 27.50687 W (± 5 m) from Saw Mill Creek Marsh, Staten Island, New York, USA on June 10th 2013 (Fig. 1). Replicate cores (A and B) were collected 10 m apart. In the laboratory each core was sectioned at 2 cm intervals, freeze-dried, sieved and the < 2 mm fraction ground to a fine powder in an agate ball mill (Beriro et al., 2014).

Sediment toxicity was evaluated on 7 g using the Microtox® Solid Phase Test (SPT) with *Vibrio Fischeri* (strain NRRL B-1117) and luminescence measured on a M500 Toxicity Analyser.

Total concentrations of all organic compounds and grouped compound classes as well as heavy metals are reported on a dry weight basis (e.g. mg/kg, dry weight). Total petroleum hydrocarbons were extracted with dichloromethane (DCM)/ acetone (1:1 v/v) (ASE 200, Dionex), fractionated by TLC and measured by Iatroscan Mk6 with a LOD 3 mg/kg (Vane et al., 2019). Polyaromatic hydrocarbons (PAH) samples were prepared and analysed by Gas Chromatography – Mass Spectrometry (GC/MS) (Vane et al., 2013). The marine/Harbor reference material

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Fig. 1. Study area and core locations on Saw Mill Creek, Staten Island, New York, USA.

(NIST 1941b) was used to ensure PAH concentrations were within expected limits (Wise et al., 2004). Comparison to certified PAH values and confirm a good match with regression coefficients ranging from 0.98 to 0.99 for 14 of the 15 PAH (Supplementary 1).

Heavy metals were determined by digestion of 0.25 g sediment with HF/HClO₄/HNO₃ and concentration and isotope ratios measured using a quadrupole ICP-MS instrument (Agilent 7500c). Details of accuracy, precision compared to reference materials and post data collection processing methodology have been reported previously (Kemp et al., 2012; Vane et al., 2011). The limits of detection (mg/kg) for metals discussed herein for sediment quality assessments were Cr, 0.05, < 0.3, Ni, < 0.9 Cu, Zn < 0.4, As < 0.03 and Cd < 0.04. The dataset was log transformed and subject to a factor analysis to elucidate elemental associations with “latent variables” performed as principal components analysis and Varimax rotation.

Eleven samples were prepared using remaining available material from Core A (40–90 cm) at 5 cm intervals. At least 300 valves per samples were counted in parallel transects using phase-contrast light microscopy at ×1000 magnification. A variety of general and specialist coastal floras were consulted, and valves identified to species level. Data from each core were divided into assemblage zones using optimal sum of squares partitioning. Ordination analysis was completed using CANOCO 4. With an axis 1 gradient of < 1.5, a Principal Components Analysis (PCA) was the preferred ordination technique. A PCA was applied to square root-transformed percentage abundance data and allowed the exploration of major trends within the diatom data.

Comparison of the Saw Mill Marsh Creek microtox EC₅₀ values to published environmental criteria confirm that the studied marsh sediments (0–90 cm) have elevated toxicity and that this varies with depth (Fig. 2). A substantial portion of core A by number of samples (72%) and core B (63%) were categorised as toxic which suggested a more detailed investigation of organic and metal contaminants was required (Fig. 2). Total petroleum hydrocarbon concentrations for core A ranged from 492 to 6524 mg/kg with a mean of 1567 mg/kg ($n = 48$) and for Core B ranged from 470 to 9586 mg/kg with a mean 2333 mg/kg ($n = 47$) (Fig. 3). Core A exhibits multiple petroleum hydrocarbon spikes, starting from base of the core, the first occurs at 80 cm (1775 mg/kg), a second at 48 cm (6524 mg/kg) and a third multi-lobed event spanning 40 to 15 cm (~4000 mg/kg) (Fig. 4). Core B shows elevated TPH at 88 cm (4565 mg/kg), 62 cm (9586 mg/kg) and 49 cm (6082 mg/kg) and a broad peak spanning 40 to 11 cm (~4000 mg/kg) (Fig. 3). Although individual TPH peaks are of primary interest, it is recognised that both TPH profiles show a high baseline background of 400–700 mg/kg (Fig. 3). These values contrast with marsh and creek sediments of the Delmarva Peninsula (Virginia) and the Barnegat Bay-Little Egg Harbor back barrier marshes (New Jersey) which yield TPH

of just 86–100 mg; where the origin of TPH is attributed to related compounds in the cord grasses (*S. patens* and *S. alterniflora*) (Kim et al., 2018; Vane et al., 2008). Therefore, in this current study, the high background TPH concentrations (400–700 mg/kg) is attributed to minor input (~100 mg/kg) from in-situ marsh grasses augmented by an even higher (300–600 mg) diffuse background of TPH possibly originating from New York's aerial urban dusts and or deposition of contaminated sediment from the creek, Arthur Kill waterway (Fig. 1).

Comparison of saturate, aromatic and combined resin/asphaltene concentrations show that the resins are the main component in the lower intervals (50–90 cm) whereas the two peaks in the upper intervals (0–50 cm) are dominated by lower molecular weight saturate hydrocarbons. The switch from resin to saturate dominated compound classes maybe due to the original hydrocarbon composition (crude oil) or the type of refining processes applied or both. Alternatively, these differences could be caused by natural weathering processes (Stout and Wang, 2007). The near surface rise in total resin-asphaltene concentrations observed in both cores is possibly attributable to the unintentional release of diesel and biodiesel (550,000 US gallons) due to rupturing of storage tanks during Hurricane Sandy, 2012.

Examination of the $\Sigma 16$ PAH concentration-depth profiles (Fig. 4) shows a background of low PAH concentrations at 90 to 55 cm ranging from 1.42 to 3.72 mg/kg (core A) and 2.85 to 4.57 (core B) punctuated by higher concentrations of 5.19 mg/kg at 67 cm (core A) and 9.61 mg/kg 62 cm (core B). The rise in $\Sigma 16$ PAH and parallel increase in TPH probably corresponds to past contamination events including possible fuel spills (Fig. 4). Both $\Sigma 16$ PAH profiles show a return to low background PAH values of about 3 mg/kg before an abrupt rise to the highest $\Sigma 16$ PAH of 18.89 and 15.34 mg/kg at 51 to 47 cm which corresponds to the visually observed black bitumen layer. The upper portions of both cores from above 45 to 20 cm show elevated $\Sigma 16$ PAH ranging from 5.40 to 12.46 mg/kg before returning to low values of 3–4 mg/kg at 11 cm and finally increasing near surface at 5 cm (Fig. 4). The PAH concentrations of bed, foreshore and marsh sediments of the Arthur Kill have been previously measured using GC/MS analysis (Crawford et al., 1995; Dimou et al., 2006; Huntley et al., 1995; Iannuzzi et al., 1995; Rustic, 2011). A comprehensive study of sedimentary PAH in non-shipping channel bed-sediments captured in 58 vibrocores within the Newark Bay Estuary showed that the Arthur Kill (mean $\Sigma 17$ PAH of 37 ± 81.7 mg/kg (dry wt), median PAH of 17 mg/kg) had higher concentrations than Kill van Krull (mean 15 ± 11.9 mg/kg, median 7.9 mg/kg (Huntley et al., 1995). The depth profiled PAH concentrations presented here for Saw Mill Creek marsh fall within these earlier published PAH concentration ranges suggesting that the bed channel sediments and marsh sediments are contaminated to a similar degree.

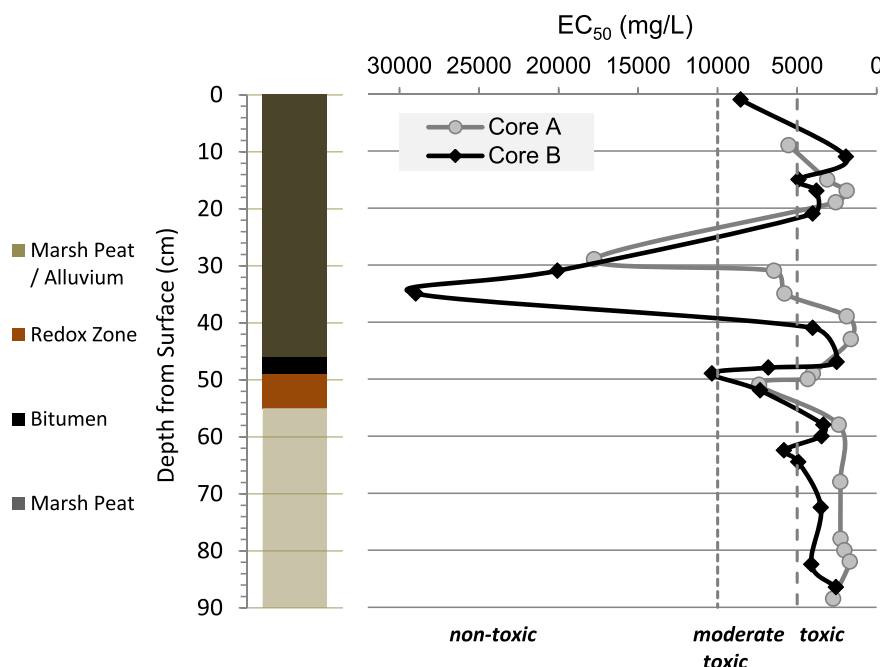


Fig. 2. Downcore toxicity determined by Microtox solid phase extraction test for two shallow sediment cores from Saw Mill Creek Marsh, Staten Island, New York City.

Benzo[a]pyrene (B[a]P) is used as a key indicator of persistent organic pollution because it is the second-most toxic of the parent PAH, is ubiquitous in most urban soils (Kim et al., 2019; Vane et al., 2014) and is widely utilised to infer PAH risk to human health via ingestion (oral), respiratory (lung) and dermal pathways (Cave et al., 2010; Cave et al., 2015; Cave et al., 2018). The B[a]P concentration profiles presented in Fig. 4 show that this consistently tracked the rise (1 to 1.5 mg/kg) and fall (0.2–0.5 mg/kg) of the Σ 16 PAH where it constituted 8–12% of the total USEPA16 PAH. In this current study B[a]P was present at a mean of 1.4 mg/kg \pm 2.19 and median 0.80 mg/kg which falls in the range expected of highly polluted marshes but ten times higher than that reported in similarly vegetated but less urbanised coastal-wetland sediments of the eastern USA (e.g. Barnegat Bay-Little Egg Harbor, New Jersey (mean B[a]P of 0.04 mg/kg)) (Vane et al., 2008).

Cluster analysis of the PAH concentrations suggests that Saw Marsh Creek has received PAH pollution from at least three different sources and that these are present in both cores (Supplementary 2). However,

the lack of original (end-member) fuel samples from known historic spill events such as Hurricane Sandy tank rupture (2012), underground pipe rupture Moses Creek (1990) and or Cibro Savannah explosion (1990) limits further attempts at an environmental forensic based provenance. Nevertheless, identification of multiple sources down-core at Saw Marsh Creek marsh is in itself useful in reconstructing the contaminant history of the site and possibly to aiding legal cases where retrospective implementation of the polluter pays principle maybe sought.

Comparison of B[a]P concentrations with sediment quality guidelines shows that only the maxima at 48 cm corresponding to the bitumen interval exceeded the effect range median (ERM, 1.6 mg/kg) (Fig. 4). In contrast, the smaller PAH events at 67 and 61 cm and 5 cm fell between the effects range low (ERL, 0.4 mg/kg) and ERM criteria and the remaining intervals fell below ERL (Fig. 4). Therefore, only the main contamination spike at 48 cm is likely to cause harm to sensitive sediment dwelling biota. Conversely, those spikes containing lower B

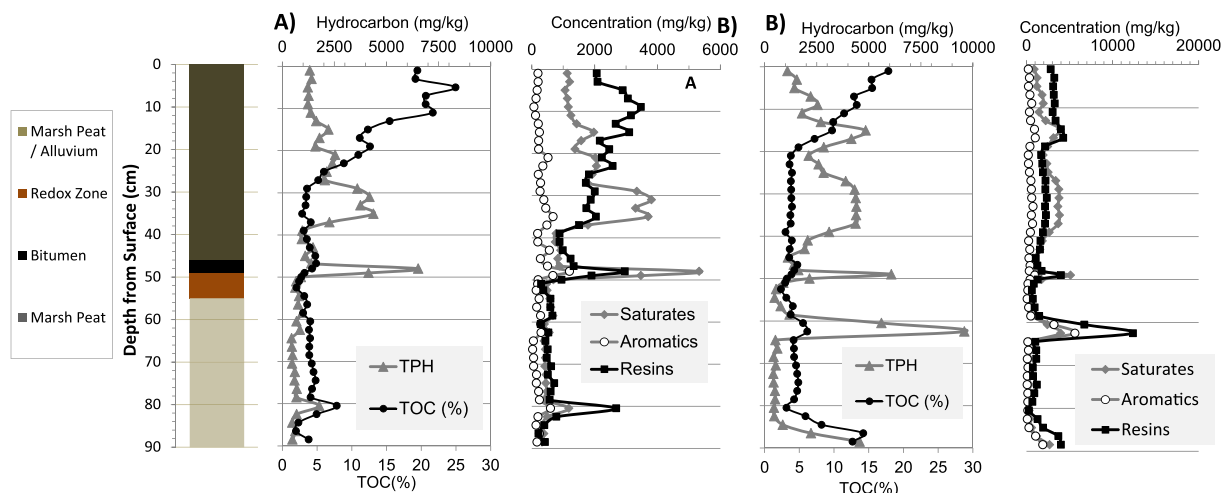


Fig. 3. Downcore petroleum hydrocarbon (TPH) concentrations expressed on a dry weight basis in sediments from Saw Mill Creek Marsh, Staten Island, New York City.

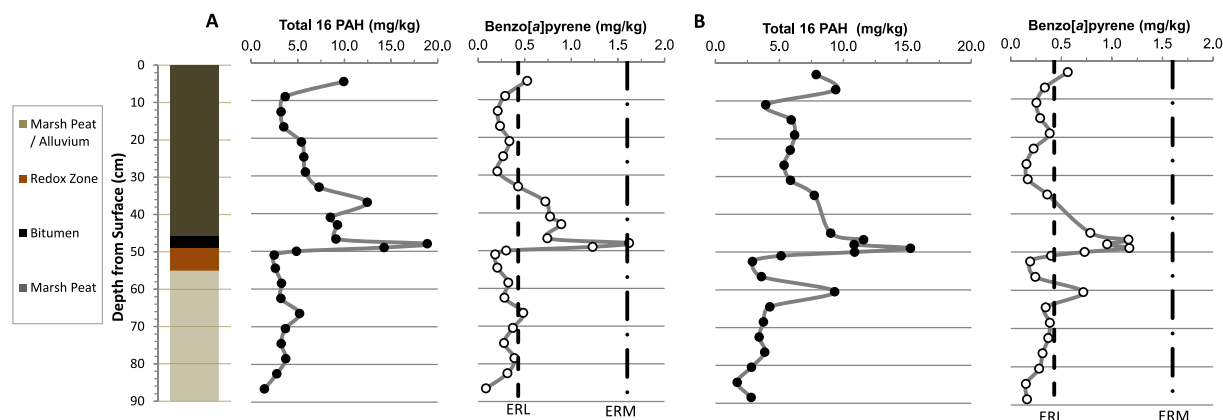


Fig. 4. Polyaromatic hydrocarbons ($\Sigma 16$ PAH) and benzo[a]pyrene B[a]P concentrations expressed on a dry weight basis in sediments from Saw Mill Creek Marsh, Staten Island, New York City.

[a]P concentrations that fall between ERL-ERM criteria may cause harm and those below ERL will not have adverse effect on sediment dwelling biota.

A common approach to characterising PAH source (e.g. petrogenic vs. pyrolytic) in river and coastal sediments is to use PAH isomeric ratios. Inspection of the Phen/Anth to Fanth/Pyr isomeric plot reveals a rather ambiguous outcome with neither pyrolytic (combustion) nor petrogenic (petroleum) criteria being fully satisfied (Fig. 5). Overall, the isomeric and non-isomeric bi-plots suggests that the PAH contained in Saw Mill Creek Marsh are not sourced from crude oil but are in fact sourced from a variety refined products that have undergone either distillation processing or were subject to heating (combustion). In addition, the possibility of a contribution from atmospherically transported pyrogenic PAH cannot be ruled out.

The vertical distribution of heavy metals Cu, Zn, Pb, Cr, As, Ni, Cd

and Hg exhibit multiple peaks in the upper 0 to 50 cm and fewer peaks in the lower 50–90 cm (Fig. 6). Some of the highest heavy metal concentrations were coincident with the visually observable bitumen interval at 50 to 48 (Fig. 6). The concentration ranges of selected metals of cores A and B are presented together with the appropriate sediment quality guideline value in Table 1. Inspection of the aggregated data reveals that many of the sediment intervals fall between ERL and ERM or above the ERM value and with the exception of Cd very few intervals fall within effects range low (ERL) (Long et al., 1995).

Of the trace metals evaluated Hg exceeded the ERM benchmark most frequently with > 54% (core A) and 60% (core B) above ERM (Table 1, Fig. 6). This finding supports earlier studies which concluded that sediment hosted Hg was one the main environmental variables of concern to benthic macrofaunal assemblages in Neck Creek, Main Creek, Richmond Creek and Saw Mill Creek sites (Staten Island) (Goto

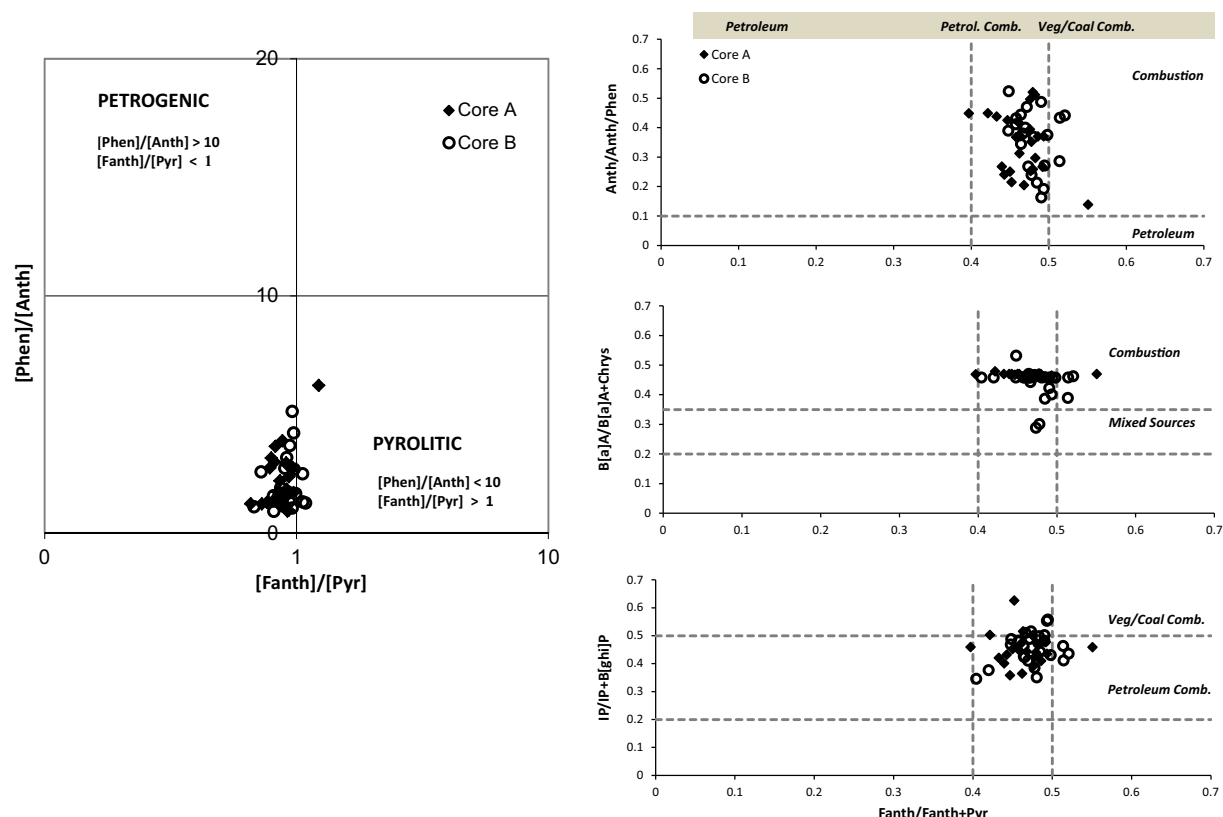


Fig. 5. PAH isomeric ratio plot for source assignment based on thermodynamic stabilities and associated anthropogenic processes.

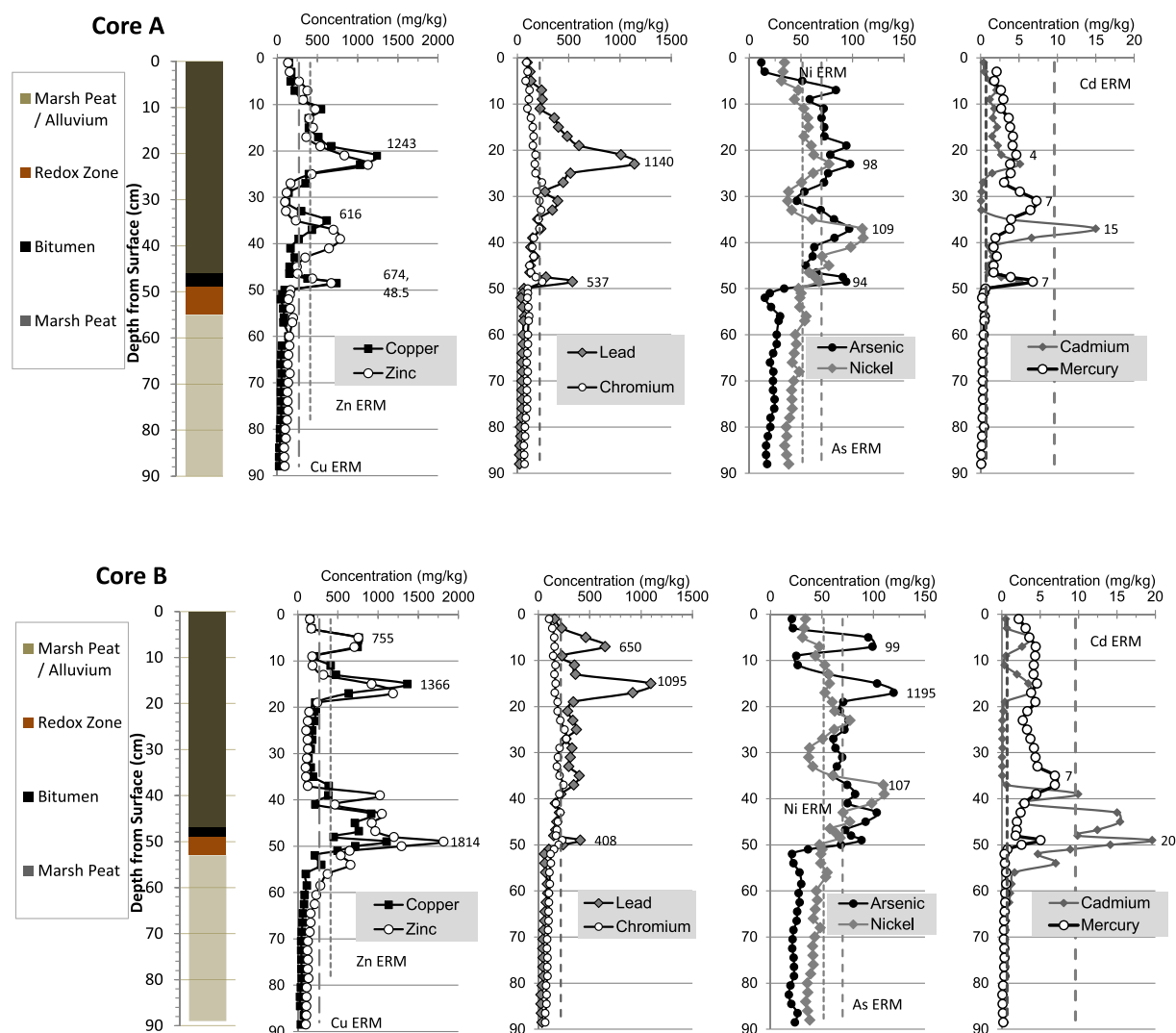


Fig. 6. Down-core changes in heavy metal concentration on a dry weight basis, Saw Mill Creek Marsh, Staten Island, New York City.

and Wallace, 2010). A similar picture of partial exceedance for some heavy metals is obtained by comparison with other alternative and relevant values such as those for New York State sediments (Table 1).

Recent studies of New York marshes have matched metal concentrations (Pb, Cu, Va, As, Cd, Se, Sn, Ni) to regional emissions and waste-incineration discharge trends enabling construction of a ~200 yr diffuse event chronology (Kemp et al., 2017; Peteet et al., 2018). However, such an approach is challenging in marshes receiving chronic event spills because the magnitude of shift from pre-anthropogenic baseline to peak input to return is overprinted by metals content of local pollution (e.g. sewage sludge, industrial effluent, crude and fuel oils). For example, the Pelham Bay chronology was based in part on a Cu baseline ~10 mg/kg to peak at 122 mg/kg and Cd 0.22 mg/kg to 1.66 mg/kg whereas in this current study the Cu baseline ~56 mg/kg to peak 1243 mg/kg and Cd 0.42 mg/kg to 15.0 mg/kg; a similar situation was found for all other metals.

$^{206/207}\text{Pb}$ can be used to identify different sources of pollution in marsh and estuarine sediments. Both cores exhibited clear changes in Pb concentrations and $^{206/207}\text{Pb}$ with the main concentration spikes from both cores demonstrated a very significant drop in isotope ratio to 1.173–1.174 before recovering to c. 1.195 at the tops of the cores (Fig. 7). These patterns suggest that the early concentration spike was of different isotopic source to the main concentration spike. The decrease in $^{206/207}\text{Pb}$ ratio in core B at ~60 cm depth is not observed in

core A but aligns with the proposed oil spill event suggested from the rise in TPH and PAH concentrations which supports possible localised event only affecting Core B at that 62 cm (Figs. 3 & 4). To de-construct the relationship between isotopic sources and concentrations of Pb in sediments we plotted the reciprocal of the Pb concentration versus the isotope ratio (Fig. 8, Table 2). In the simplest situation, of a background uncontaminated source of one isotopic ratio composition being contaminated with increasing amounts of a lead source with a different isotopic composition, the data will form a simple linear array with the background isotopic source being at the extreme right hand side of the graph and its y-axis value indicating its isotopic value. Then, extrapolating the array until the x-axis equals zero indicates the isotopic composition of the contaminant. In the event of two or more contaminant lead sources with different isotopic signatures, mixing with the background Pb, the data will fall within one or more mixing triangles. Where the sides of these triangles meet x-axis = 0, indicates the likely source isotopic compositions (Fig. 8). The plot suggests that the background isotopic lead ($^{206/207}\text{Pb}$) composition S-1 is 1.206; but as this is unlikely to be the true background concentration, potentially this value maybe higher. As lead concentrations in the core increase, this is associated with the addition of lead from two isotopic sources S-2 (1.198) and S-3 (1.180); although the possibility of additional sources between these values must be considered. Finally, the main concentration spike in concentration is dominated by source S-4 with an

Table 1
Comparison of summary metal concentrations expressed on a dry weight basis in Saw Mill Creek Marsh sediments to reported guidelines.

Summary core A (mg kg ⁻¹)				Sediment quality guidelines*			Sediment screening criteria for New York State	
Metal	Range	Mean	Median	< ERL	ERL-ERM	> ERM	Lowest effect	Severe effect
As	11.5–97.8	48	46	8.2 (0)	(39)	70 (8)	6.0	33.0
Cd	0.05–15.0	1.5	0.6	1.2 (31)	(15)	9.6 (1)	0.6	9.0
Cr	62.4–242.8	129.3	110.5	81 (6)	(41)	370 (0)	26	110.0
Cu	25.0–1243.1	243.5	145.6	34 (3)	(29)	270 (15)	16	110.0
Pb	21.1–1140	210.5	123.4	46.7 (0)	(36)	218 (11)	31	110.0
Hg	0.06–7.3	2.1	1.6	0.15 (3)	(18)	0.71 (25)	0.15	1.3
Ni	31.2–110.3	52.5	48.4	20.9 (0)	(28)	51.6 (19)	16.0	50.0
Zn	86.9–1128.9	288.5	165.4	150 (17)	(19)	410 (11)	120	270.0

Summary core B (mg kg ⁻¹)				Sediment quality guidelines*			Sediment screening criteria for New York State	
Metal	Range	Mean	Median	< ERL	ERL-ERM	> ERM	Lowest effect	Severe effect
As	17.9–119.6	50.9	36.4	8.2 (0)	(32)	70 (15)	6.0	33.0
Cd	0.1–19.6.0	3.2	0.6	1.2 (29)	(11)	9.6 (7)	0.6	9.0
Cr	67.3–272	148	154	81 (5)	(42)	370 (0)	26	110.0
Cu	30.0–1366	304.0	181.9	34 (2)	(29)	270 (16)	16	110.0
Pb	25.7–1095	225	168.6	46.7 (9)	(17)	218 (21)	31	110.0
Hg	0.1–6.9	2.3	2.2	0.15 (2)	(17)	0.71 (28)	0.15	1.3
Ni	33.9–95.4	54.8	46.0	20.9 (0)	(27)	51.6 (20)	16.0	50.0
Zn	101–1814	409.3	169.49	150 (19)	(13)	410 (15)	120	270.0

Values in parentheses are the number of core intervals within each guide range. *(Long et al., 1995).

isotopic composition c. 1.170–1.175 (Fig. 8). These isotopic sources are difficult to attribute to particular origins as the total range within the data set 1.173–1.206 is much narrower than classic extremes of Broken Hill type (1.040) or Joplin Picher, Mississippi Valley type (1.370) but are consistent with stable Pb ratios reported from marshes in New Jersey (Kemp et al., 2012) and Connecticut (Kemp et al., 2015; Vane et al., 2011). However, the Pb isotope data do suggest at least 3 different contaminant sources, none of which are Mississippi Valley type lead. The down-core comparison between Pb concentration and isotope ratio indicates the S-4 lead is associated with the event with the highest Pb contamination, whereas smaller events and the general increase in Pb concentration at depths shallower than 50 cm in both cores is

associated with a mixture of the local Pb S-1 with different amounts of contaminant Pb S-2 and S-3.

The results of the diatom and PCA analyses are shown in Figs. 9 and 10. The diatom stratigraphy is that of a typical coastal environment, and is dominated by *Paralia sulcata*; a marine species with a high tolerance for a range of environments (McQuoid and Nordburg, 2003). The diatom stratigraphy can be split into three significant zones. Diatom zone ST-D1 (80–90 cm). Alongside the facultatively planktonic *Paralia sulcata* (c. 30% of the assemblage data), this zone comprises of a number of diatom species (occurring at abundances of c. 5%) that have a preference for epiphytic habitats (*Planothidium delicatulum*, *Navicula cryptonella*, *Tryblionella hungarica*, *Tabularia fasciculata*). The salinity

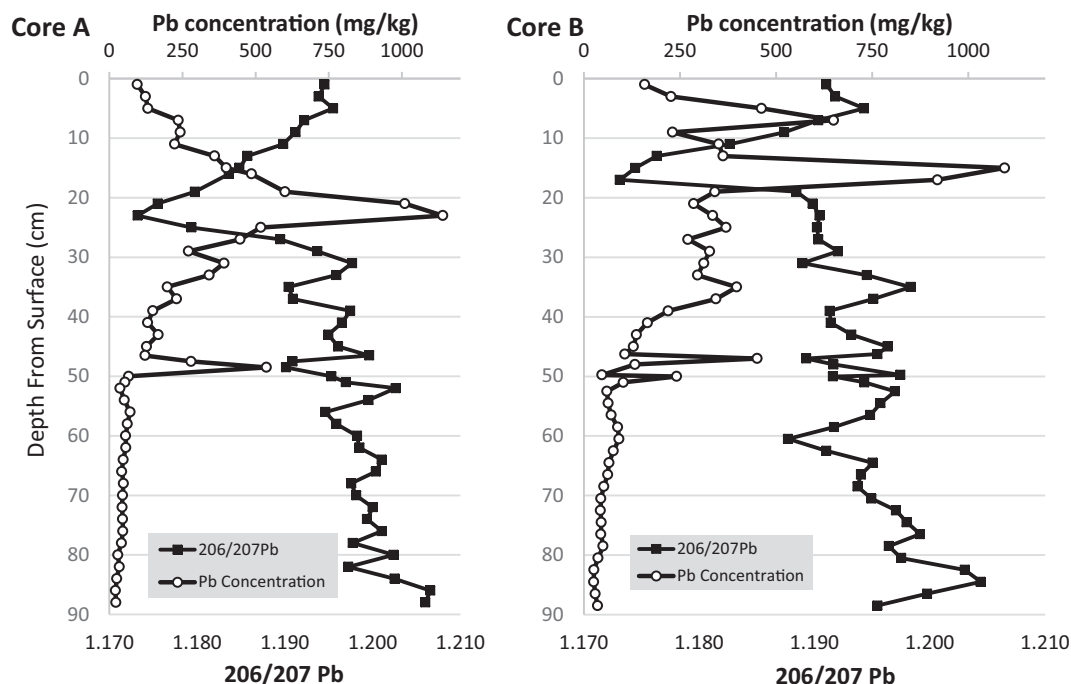


Fig. 7. Lead (Pb) concentrations expressed on a dry weight basis and ^{206/207}Pb isotope ratios of Saw Mill Creek Marsh, Staten Island, New York City.

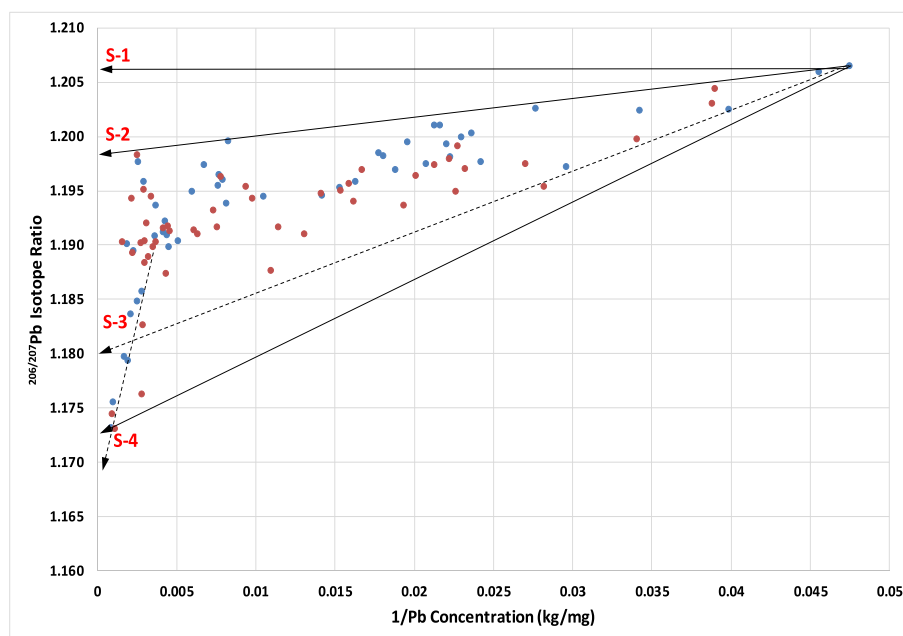


Fig. 8. Identification of multiple lead (Pb) sources in Saw Mill Creek Marsh, Staten Island, New York City.

tolerance of these species ranges from freshwater to brackish. PCA sample scores are at their highest values in this zone, and steadily decline throughout (reaching a minimum after the ST-D1/ST-D2 boundary [80 cm]), suggesting a shift in the overall composition of the diatom assemblage. The drop in PCA values is coincident with a rise in the total organic carbon, and the early increase (and subsequent peak) in values of total petroleum hydrocarbons (TPH; Fig. 3) and corresponding spikes in the proportion of hydrocarbon saturates, aromatics, and resins. At this time, there is no change in the heavy metal concentrations, and the sediments are highly toxic throughout (EC₅₀; Fig. 3).

Diatom zone ST-D2 (50–80 cm). The ST-D1/ST-D2 boundary [80 cm] sees a decline in the diatom species that represent epiphytic habitats. In the absence of further biological data that represent higher plant species (e.g. pollen, macrofossils), it is suggested the influx of organic pollutants and high toxicity caused a demise in vegetation in the marsh and subsequently caused a decline in diatom species representative of these habitats. The removal of this vegetation allowed planktonic marine/brackish species, such as *Paralia sulcata*, *Thalassiosira eccentrica*, *Tryblionella compressa*, and *Diploneis smithii* and benthic (epipelagic) species (*Luticola mutica*, *Achnanthes brevipes*) to become relatively more important. The diatom assemblage remains relatively stable throughout this period (PCA sample scores; Fig. 10), and this coincides with relatively stable concentration of total petroleum hydrocarbons (TPH; Fig. 3), and low concentrations of heavy metals (Fig. 7).

Diatom zone ST-D3 (40–50 cm). The ST-D2/ST-D3 boundary [50 cm] marks another shift in the diatom assemblage. PCA sample scores increase marginally, and the majority of benthic and epiphytic species have all but disappeared from the stratigraphy. The marine/brackish species *Paralia sulcata*, *Diploneis smithii*, *Tryblionella compressa* and *Thalassiosira eccentrica* persist and dominate the diatom

assemblage. The change in diatom assemblage coincides with a rapid increase in heavy metal contaminants (Fig. 6), and a spike in the values of total petroleum hydrocarbons (TPH; Fig. 3). Again, the mechanism of cause and effect cannot be elucidated with the information, but it is likely that the influx of pollutants was toxic to plant life (e.g., Hester et al., 2016), and may have played a role in disruption of a biofilm on the salt marsh surface; hence preventing the colonisation of the surface sediments by benthic species.

A tiered approach to pollution delivered via chemical concentrations, laboratory bioassay and diatom community structure of sediments from Saw Mill Marsh Creek revealed multiple legacy pollution episodes including oiling events over and above a more diffuse urban background. These findings imply that legacy pollution events captured within marsh cores remain a potent environmental threat that needs to be considered by government regulators and wetland managers particularly when considering natural erosion, dredging or other forms anthropogenic disturbance. Sediment quality was assessed by benchmarking PAH and metal concentrations against published sediment quality guidelines (SQG). For the organic pollutants measured herein these comparisons revealed that benzo[a]pyrene exceeded ERM and is therefore potentially a cause for concern. Comparison of metal concentrations to consensus-based SQG showed multiple exceedances for Cu, Zn, Pb, As, Ni and Hg, particularly in the upper 50 cm of the cores. We therefore conclude that the hydrocarbon pollution and metals contained within the near surface sediment (0–50 cm) from this area of Saw Mill Creek Marsh are of potential environmental concern. It is important to note that we do not assert that this is necessarily true for the entire Saw Mill Creek Marsh area or other marshes of the Arthur Kill Staten Island (although it is a possibility) as this would require a more extensive coring and analytical program than that presented in this baseline study.

Supplementary data to this article can be found online at <https://>

Table 2
Significant factor loadings for multi-element geochemical profiling.

	Factor-1	Factor-2	Factor-3	Factor-4	Factor-5	Factor-6
Variance accounted for (%)	32.5	26.4	14.0	9.2	8.6	4.3
Positive Loading	Sn, Pb, Sb, As, Cr, Cu	Al, La, Ce, Tl	Cd, Zn, Ni	S, Fe	Mn	^{206/207} Pb
Negative Loading	^{206/207} Pb, Mn	TOC, Mo			U, P, Mo	V

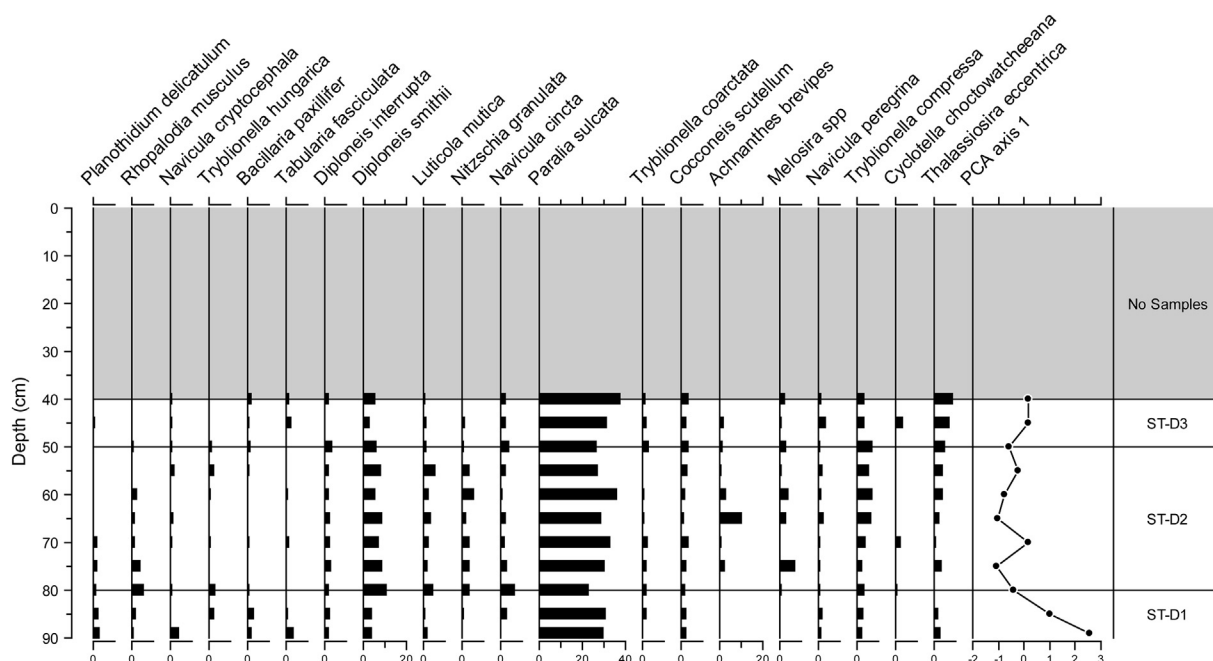


Fig. 9. Diatom analysis of Staten Island Core A (40–90 cm), showing all species > 3% abundance. Diatom species are ordered according to their weighted-average abundance (descending). The output of the PCA analysis (axis 1 sample scores) are also shown. The three significant diatom zones (ST-D1, ST-D2, ST-D3) are marked.

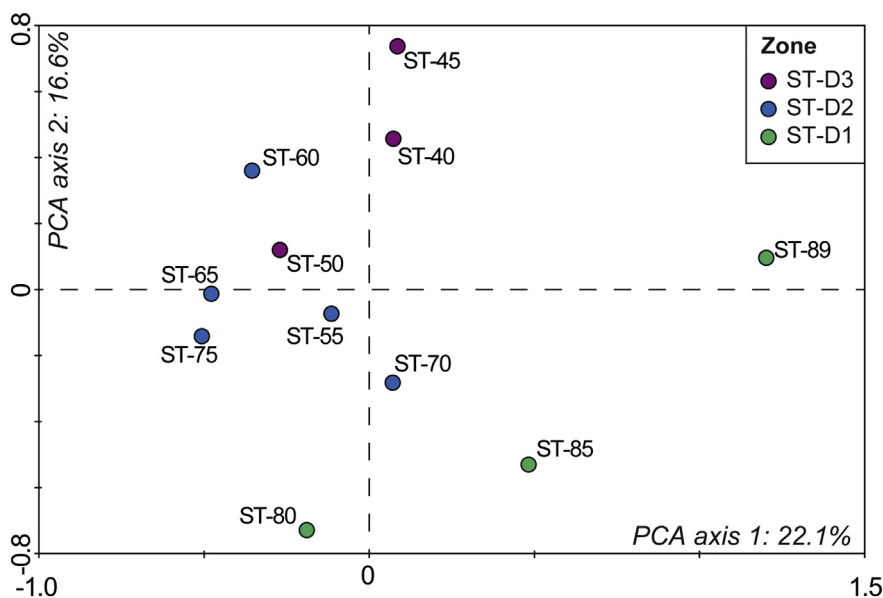


Fig. 10. Output of the principal components analysis (PCA), showing both axis 1 and axis 2, which represent the two main gradients in the diatom data. The samples are colour coded according to the stratigraphic zone in which they sit (see Fig. 10). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Beriro, D.J., Vane, C.H., Cave, M.R., Nathanail, C.P., 2014. Effects of drying and

comminution type on the quantification of Polycyclic Aromatic Hydrocarbons (PAH) in a homogenised gasworks soil and the implications for human health risk assessment. *Chemosphere* 111 (0), 396–404.
 Cave, M.A., Wragg, J., Harrison, I., Vane, C.H., Van de Wiele, T., Nathanail, P., Ashmore, M.A., Thomas, R., Robinson, J., Daly, P., 2010. Comparison of a batch mode and dynamic bioaccessibility tests for PAHs in soil samples. *Environ. Sci. Technol.* 44, 2654–2660.
 Cave, M.R., Vane, C.H., Kim, A., Moss-Hayes, V.L., Wragg, J., Richardson, C.L., Harrison, H., Paul Nathanail, C., Thomas, R. and Wills, G., 2015. Measurement and modelling of the ingestion bioaccessibility of polyaromatic hydrocarbons in soils. *Environmental Technology & Innovation*, 3(0): 35–45.
 Cave, M.R., Wragg, J., Beriro, D.J., Vane, C., Thomas, R., Riding, M., Taylor, C., 2018. An overview of research and development themes in the measurement and occurrences of polyaromatic hydrocarbons in dusts and particulates. *J. Hazard. Mater.* 360, 373–390.
 Crawford, D.W., Bonnevie, N.L., Wenning, R.J., 1995. Sources of pollution and sediment contamination in Newark Bay, New Jersey. *Ecotoxicol. Environ. Saf.* 30 (1), 85–100.
 Dimou, N.K., Su, T.-S., Hires, R.I., Miskewitz, R., 2006. Distribution of polychlorinated biphenyls in the Newark Bay Estuary. *J. Hazard. Mater.* 136, 103–110.
 Goto, D., Wallace, W.G., 2010. Relative Importance of Multiple Environmental Variables

- in Structuring Benthic Macrofaunal Assemblages in Chronically Metal-Polluted Salt Marshes. 60. pp. 363–375.
- Gunster, D.G., Gillis, C.A., Bonnevie, N.L., Abel, T.B., Wenning, R.J., 1993. Petroleum and hazardous chemical spills in Newark Bay, New Jersey, USA from 1982 to 1991. *Environ. Pollut.* 82 (3), 245–253.
- Hester, M.W., Willis, J.M., Rouhani, S., Steinhoff, M.A., Baker, M.C., 2016. Impacts of the Deepwater Horizon oil spill on the salt marsh vegetation of Louisiana. *Environ. Pollut.* 216, 361–370.
- Huntley, S.L., Bonnevie, N.L., Wenning, R.J., 1995. Polycyclic aromatic hydrocarbon and petroleum hydrocarbon contamination in sediment from the Newark Bay Estuary, New-Jersey. *Arch. Environ. Contam. Toxicol.* 28 (1), 93–107.
- Iannuzzi, T.J., Huntley, S.L., Bonnevie, N.L., Finley, B.L., Wenning, R.J., 1995. Distribution and possible sources of polychlorinated-biphenyls in dated sediments from the Newark Bay Estuary, New-Jersey. *Arch. Environ. Contam. Toxicol.* 28 (1), 108–117.
- Kemp, A.C., Sommerfield, C.K., Vane, C.H., Horton, B.P., Chenery, S., Anisfeld, S., Nikitina, D., 2012. Use of lead isotopes for developing chronologies in recent salt-marsh sediments. *Quat. Geochronol.* 12, 40–49.
- Kemp, A.C., Hawkes, A.D., Donnelly, J.P., Vane, C.H., Horton, B.P., Hill, T.D., Anisfeld, S.C., Parnell, A.C., Cahill, N., 2015. Relative sea-level change in Connecticut (USA) during the last 2200 yrs. *Earth Planet. Sci. Lett.* 428, 217–229.
- Kemp, A.C., Hill, T.D., Vane, C.H., Cahill, N., Orton, P.M., Talke, S.A., Parnell, A.C., Sanborn, K.S., Hartig, E.K., 2017. Relative sea-level trends in New York City during the past 1500 years. *The Holocene* 27 (8), 1169–1186.
- Kim, A.W., Vane, C.H., Moss-Hayes, V., Engelhart, S.E., Kemp, A.C., 2018. PAH, PCB, TPH and mercury in surface sediments of the Delaware River Estuary and Delmarva Peninsula, USA. *Mar. Pollut. Bull.* 129 (2), 835–845.
- Kim, A., Vane, C., Moss-Hayes, V., Beriro, D., Nathanail, C., Fordyce, F., Everett, P., 2019. Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in urban soils of Glasgow. *Earth and Environmental Science Transactions of the Royal Society of Edinburgh* 108 (2–3), 231–248.
- Long, E.R., MacDonald, D.D., Smith, S.L., Calder, F.D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine estuarine sediments. *Environ. Manag.* 19 (1), 81–97.
- McQuoid, M.R., Nordburg, K., 2003. Environmental Influence on the Diatom Silicoflagellate Assemblages in Koljo Fjord (Sweden) over the Last Two Centuries. 26(4). pp. 927–937.
- NOAA, 2001. Assessment and Characterisation of Salt Marshes in the Arthur Kill (New York and New Jersey) Replanted after a Severe Oil Spill. U.S. Department of Commerce.
- Peteet, D.M., Nichols, J., Kenna, T., Chang, C., Browne, J., Rezaa, M., Louisa Libermanb, K., Stern-Protza, S., 2018. Sediment starvation destroys New York City marshes' resistance to sea level rise. *Proceedings of the Natural Academy of Sciences* 115 (41), 10281–10286.
- Rustic, G.T., 2011. Polycyclic Hydrocarbon Contamination in and Around the Arthur Kill, Staten Island, New York. MSc thesis Thesis. Rutgers University, New Jersey, New Jersey (65 pp).
- Stout, S.A., Wang, Z., 2007. Oil Spill Environmental Forensics: Finger Printing and Source Identification. Elsevier, Amsterdam (537 pp).
- Vane, C.H., Harrison, I., Kim, A.W., Moss-Hayes, V., Vickers, B.P., Horton, B.P., 2008. Status of organic pollutants in surface sediments of Barnegat Bay-Little Egg Harbor Estuary, New Jersey, USA. *Mar. Pollut. Bull.* 56 (10), 1802–1808.
- Vane, C.H., Chenery, S.R., Harrison, I., Kim, A.W., Moss-Hayes, V.M., Jones, D.G., 2011. Chemical signatures of the Anthropocene in the Clyde estuary, UK: sediment-hosted Pb, ^{207/206}Pb, total petroleum hydrocarbons, polyaromatic hydrocarbon and polychlorinated biphenyl pollution records. *Phil. Trans. R. Soc. A* 369, 1085–1111.
- Vane, C.H., Rawlins, B.G., Kim, A.W., Moss-Hayes, V., Kendrick, C.P., Leng, M.J., 2013. Sedimentary transport and fate of polycyclic aromatic hydrocarbons (PAH) from managed burning of moorland vegetation on a blanket peat, South Yorkshire, UK. *Sci. Total Environ.* 449, 81–94.
- Vane, C.H., Kim, A.W., Beriro, D.J., Cave, M.R., Knights, K., Moss-Hayes, V. and Nathanail, P.C., 2014. Polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) in urban soils of Greater London, UK. *Appl. Geochem.*, 51(0): 303–314.
- Vane, C.H., Lopes, dS, Kim, R.A., W, A., Moss-Hayes, V., Fordyce, F.M., Bearcock, J.M., 2019. Persistent organic pollutants (PAH, PCB, TPH) in freshwater, urban tributary and estuarine surface sediments of the River Clyde, Scotland, UK. *Earth and Environmental Science Transactions of the Royal Society of Edinburgh* 108 (2–3), 299–314.
- Wise, S.A., Poster, D.L., Schantz, M.M., Kucklick, J.R., Sander, L.C., Lopez de Alda, M., Schubert, P., Parris, R.M., Porter, B.L., 2004. Two new marine sediment standard reference materials (SRMs) for the determination of organic contaminants. *Anal. Bioanal. Chem.* 378 (5), 1251–1264.