Environmental risk of trace metals and metalloids in estuarine sediments: an example from Southampton Water, U.K.

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Highlights

- Trace metals and metalloids were examined in sediments from Southampton Water, U.K.
- Geochemical data highlight enrichments in Cu, Zn and Pb in subtidal sediments

- Metal distribution is controlled by sediment composition and anthropogenic activity
- Pollution indices indicate the estuary is moderately impacted by industrial activity
- Further work is needed to assess the current impact of trace metals on local ecology

Abstract

Industrial and commercial port activities are widely recognized worldwide as an important source of pollution to proximal estuaries. In this study we analysed geochemical parameters including major and trace elements, organic matter and sediment texture. Using multivariate statistical tools [correlation, factor and cluster analysis and pollution indices such as Enrichment Factor (EF), Pollution Load Index (PLI) and the Adverse Effect Index (AEI)], we evaluated trace metal and metalloid contamination in surface sediments (and their potential biological impact) from the estuarine environment of Southampton Water, U.K. Geochemical data, multivariate statistical analysis and pollution indices indicate that the spatial distribution of trace metals and metalloids is influenced by both sediment composition (and mixing) and anthropogenic activities. Most trace metal and metalloid concentrations are close to local geological background levels, except for Cu, Zn and Pb. The spatial distribution of these elements indicates that the Exxon oil refinery, Southampton port, local marinas and runoff from domestic and industrial activities act effectively as point sources of these elements. Pollution indices calculations highlight a degraded environment as a result of these pollutants, and further work is needed to assess the current impact of trace metals and metalloids on local ecology.

Capsule abstract: Sub-tidal sediments show enrichment of some trace element concentrations interpreted as the influence of an oil refinery and port activities within Southampton Water.

Keywords: Trace elements, sediment, port activities, oil industry, estuaries, Southampton Water

Introduction

Estuaries are important ecosystems that are defined as semi-enclosed coastal bodies of water with a free connection with the open sea, within which sea water is measurably diluted by fresh water derived from land drainage (Pritchard, 1969). They are ecologically, societally and economically important environments as they supply a range of ecosystem services, act as an important food source (including providing nursery and breeding habitats to many species of birds and fish (NOAA, 2018)) and are frequently major centres for industrial, urban and recreational developments. The main characteristic of estuarine environments is that they are influenced by varying river flows, tidal motions, precipitation and evapotranspiration; all of which generate strong gradients in physico-chemical parameters such as salinity, pH, dissolved oxygen (DO) and nutrients that can significantly modify pollutant behaviour in the environment.

Estuaries, like many other ecosystems, are strongly affected by anthropogenic activities that export trace metals and metalloids. Anthropogenic sources of these pollutants include landfill leachate, agricultural and urban runoff, and industrial and domestic effluents (Chakravarty and Patgiri 2009; Abdelhady et al., 2019). Trace metals and metalloids pose a serious threat to human health and to ecosystems due to their persistence, potential for bio-accumulation, and toxicity (Naser, 2013; Yu et al., 2014; Bing et al., 2016; Singh and Kumar 2017). From a food resource and ecosystem perspective, Kerambrun et al., (2013), for example, based on Fulton´s K condition index, propose that fish from European estuaries with a low anthropogenic impact are healthier than fish from estuaries with a strong anthropogenic influence and which are chronically polluted by trace metals. Park et al., (2019) have shown that the total bio-concentration of trace metals in crabs (*Macrophthalmus japonicus*) affected the expression of chitinase genes and resulted in changes in exoskeleton surface roughness. High concentrations of trace metals in water affected the reproduction process of the fish *Prochilodus argenteus* in the Paraopeva River, Brazil (Paschoalini et al., 2019); while the green mussel (*Perna viridis*) from Jakarta Bay was declared unsafe to eat because of shell malformations caused by trace metals (Riani et al., 2018).

Southampton Water has been relatively well studied historically to assess the effects of trace metals on organisms (Romeril et al. 1979; Matharu 1975; Armannsson et al 1985; Savary et al. 1989; Sharifi et al. 1991), and more recently to examine trace metal sources and distribution (Croudace and Cundy, 1995; Cundy et al., 1997 and Cundy and Croudace, 2017). The second group of papers noted (based on cored sediment profiles) significant historical inputs of hydrocarbons and copper from the Exxon oil refinery at Fawley, on the western shore of Southampton Water, with Pb and Zn inputs derived from mixed urban and industrial sources (in particular, ^{206}Pb/^{207}Pb ratios indicated a complex, mixed marine/ atmospheric input of Pb from regional (automobile emissions) and local (urban/industrial) sources). Despite this historical work, there is a lack of published literature on sedimentary concentrations of trace elements and metalloids, and their spatial variability, with which to assess the current potential impact of trace metals and metalloids on local ecosystems. This is important locally due to recent urban expansion and industrial changes in the Southampton area (including commissioning of a major waste incinerator on the western shore, changes in port volumes and traffic, and expansion in marina activity), and more widely as Southampton Water can be considered as a reference for other estuaries along developed coasts worldwide with similar anthropogenic influences.

This article aims to determine the factors that control the current spatial distribution of trace metal and metalloid contaminants in Southampton Water, UK, which hosts the largest oil refinery and the second largest port in the U.K. We use geochemical analysis of surface (subtidal) sediment, multivariate statistical analysis and various pollution indices to assess contaminant sources, distribution and potential biological impact in this large, urbanised and heavily-industrialised estuarine system.

Study area

The study area is located in the coastal plain estuary of Southampton Water, southern England (Figure 1). The estuary covers an area of approximately 20 km^2 and receives discharges from the Test, Itchen, Hamble, and Meon Rivers (Dyer, 1997). Around the estuary there are various biologically-important coastal ecosystems such as saline lagoons, salt marshes and mudflats that support a range of breeding and migratory birds, crabs and other organisms (JNCC, 2017). To give legal protection to these ecosystems that are located inside and around the estuary the UK government has declared the Lee-on-the Solent to Itchen estuary and the upper Hamble estuary as Sites of Special Scientific Interest (SSSI), while areas such as the Solent and Southampton and the Solent maritime are classed as special areas of conservation (SCA) (GOV.UK, 2019).

The main urban area in the estuary catchment is the city of Southampton with a population of 254,300 habitants and a total area of about 51.8 km^2 (GOV.UK, 2019). The main industries within the estuary are port activities and a major petrochemical refinery and ancillary industries. Southampton Port is the second largest container terminal in the UK and handles around 14 million tonnes of cargo each year (ABP, 2017), while the port hosts 2 million cruise ship passengers annually across four cruise terminals. In addition to the deep water port, there are 11 smaller marinas and boatyards within Southampton Water, including ones located on the Rivers Itchen, Hamble and Test. In order to maintain shipping access and also for capital building projects, dredging activities have been regularly undertaken across the whole area at least for the last 200 years (ABP, 2014). The Exxon oil refinery, based on the western shore around Fawley, is the largest in the United Kingdom and one of the most complex in Europe. It has a mile-long marine terminal that handles around 2000 ships and 22 million tonnes of crude oil and other products every year. The refinery processes around 270 000 barrels of crude oil a day and provides 20 percent of the UK's refinery capacity (Exxon Mobil, 2017).

Material and Methods

Twenty-three sediment samples were collected from Southampton Water in June 2017. Samples were collected using a McIntyre dredge deployed from the University of Southampton's research vessel *RV Callista*, and were kept in plastic bags and stored at 4°C (in darkness) until analysis. Samples were only retained if they visually showed an intact sediment surface, and therefore limited loss of fines during sampling. In order to obtain the most recently deposited sediment, we collected samples in the first centimetre. Each sediment sample was divided in two halves. One half was used for geochemical analysis and loss on ignition (LOI), the other was analysed for granulometry.

Sediment samples were dried at 55°C for 48 hrs and homogenized in an agate mortar by hand. All concentrations in this work were expressed with reference to dry weight. Major and trace elements concentrations were determined using a well-established Wavelength Dispersive X-Ray Fluorescence (WDXRF) method (Croudace and Williams-Thorpe, 1988; Croudace and Gilligan 1990; Croudace et al., 2012; Croudace et al., 2015). A Philips Magix-Pro sequential X-ray fluorescence spectrometer system, calibrated using international geochemical reference samples, was used to analyse pressed powder briquettes. Precision and accuracy were evaluated using the certified reference material MAG-1 and the values for the major elements were from 106.9 to 98.3% except for Na_2O (76.9%) and P_2O_5 (83.5%); while trace elements were from 106.2 to 92.5% except for Cr (110.5%) and Cu (77.8%).

Particle size distribution within the sediment was determined using a Malvern Mastersizer 2000 laser particle size analyser. One gram of homogenized sediment was mixed with 10 mL of dispersant solution of sodium hexametaphosphate. The mixture was stirred for 5 min in order to deflocculate clay particles, after that time a small portion was taken for analysis. Organic matter was estimated using the loss on ignition method; 2 g of dried sediment samples were weighed before and after incineration in a muffle furnace at 600°C for 24 hrs, in order to eliminate organic matter (Ahmed et al., 2018). Total Organic Matter values are reported as a percentage of dry weight.

Multivariate statistical tools, specifically correlation analysis, cluster analysis and factor analysis, were used to interpret the geochemical data. To infer the trace metal and metalloid origin and evaluate any possible adverse effects on benthic biota we employed the geochemical indices of Enrichment Factor (EF), Pollution Load Index (PLI), Adverse Effect Index (AEI) and Sediment Quality Guidelines (SQG). All geochemical indices were calculated using the following equations:

The Enrichment Factor is calculated using the following eq. (1)

$$\mathrm{EF}=\frac{\left(\frac{\mathrm{X_{sample}}}{\mathrm{Y_{sample}}}\right)}{\left(\frac{\mathrm{X_{background}}}{\mathrm{Y_{background}}}\right)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

Where X_{sample} and $X_{background}$ are the concentrations of any trace metal and metalloid analysed in the sample and Y_{sample} and $Y_{background}$ are the concentrations of a conservative element that is used to normalize the data. In this work we used Al_2O_3 as a conservative element because it is not affected by local anthropogenic sources or geochemical changes such as redox processes and represents the clay fraction in these sediments (Cundy and Croudace, 1995; Celis et al., 2013). Also, we used unpublished data from the bottom of a sediment core taken in the relatively pristine adjacent Beaulieu estuary as background (Table S2); as it represents the general lithology of the area and limits any overestimation of background concentrations. This background level was calculated as the average of the last three centimetres of this core. To simplify interpretation, the Enrichment Factor has been divided into ranges that allow levels of trace metal and metalloid enrichments to be set and compared (Birth et al., 2003). A no enrichment level is considered between values from 0 to 1, a minor enrichment from 1 to 3, a moderate enrichment from 3 to 5, while a moderately severe enrichment is from 5 to 10, and finally a severe enrichment is considered when values from 10 to 25 are found.

The Pollution Load Index is calculated from the following equations (Tomlinson et al., 1980).

$$\mathrm{CF}=\left[\frac{\mathrm{C_{mS}}}{\mathrm{C_{mB}}}\right]\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

$$\mathrm{PLI_{sample}}=\sqrt[n]{\mathrm{CF_{metal\ 1}}*\mathrm{CF_{metal\ 2}}*\ldots\mathrm{CF_{metal\ n}}}\ldots\ldots\ldots\ldots\ldots\ldots.(3)$$

Where “CF” is the contamination factor, “C_{mS}” is the trace metal and metalloid concentration in the sample, “C_{mB}” is the trace metal and metalloid concentration in background samples and “n” represents the number of samples. Background was derived using the same method as for the calculation of enrichment factor. According to Tomlinson et al., 1980, PLI values of zero suggest the absence of pollutants, while PLI values of one or greater denotes the presence of pollutants or progressive deterioration of sediment quality.

The Adverse Effect Index is calculated using equation (4)

$$\mathrm{AEI}=\frac{[\mathrm{MC}]}{[\mathrm{SQG_s}]}\ldots\ldots\ldots.\ (4)$$

The adverse effect index (AEI) is applied to evaluate the ratio between the metal concentration in a sediment and the Threshold Effect Level (TEL) values reported and developed by Long et al., 1995, NOAA, 2016; besides inferring whether trace metal and metalloid concentrations in sediment could produce adverse effects on benthic biota (Muñoz et al., 2012; Hamdoun et al., 2015; Baptista et al., 2017). An AEI lower than 1 means that the trace metal and metalloid concentration in the samples is not high enough to produce adverse effects in biota; but if AEI ≥ 1 the metal concentration in the sample could produce adverse effects (Muñoz et al., 2012). Although, TEL information has not been generated for all trace metals and metalloids the AEI remains an important proxy tool with which to assess potential adverse effects of sediment contamination on organisms when there are no corresponding local toxicity studies.

Results

Textural analysis

The sand content in the samples varied from 5.6 to 88.4 %; while clay and silt varied from 0.3 to 5.5% and 11.6 to 94.4% respectively (Table 1). Textural analysis using Shepard (1954)'s classification showed that the predominant sediment texture in the estuary was silt and sandy-silt (Figure 2), except for station 21 where the main texture was sand.

Geochemical composition

The median organic matter (OM) content in the study area was 5.80% and varied from 0.9 to 16.5%. Concentrations higher than the median value were found at stations 1, 2, 3, 4, 9, 12, 22 and 23 and these were located in the same places where there were higher amounts of fine sediment. Major element concentrations varied within the following ranges: 35.1 - 73.8% for SiO_2, 2.34 - 19.6% for CaO, 2.62 - 14.4% for Al_2O_3 and 0.07 - 6.21% for Fe_2O_3 (Table 1). Trace element ranges and their medians are presented in Table 1. Station 3, located close to scrap metal handling and storage facilities exhibited the highest values of Pb (162 $mgkg^{-1}$) and Zn (657 $mgkg^{-1}$) (Figure 1). Station 22, situated close to the main port of Southampton recorded the highest values of V (152 $mgkg^{-1}$) and Rb (118 $mgkg^{-1}$) (Figure 1); while stations 2, 8, 11, 13 and 14 that are distributed in the middle of the estuary and close to the Exxon oil refinery showed the highest concentrations of Ba (349 $mgkg^{-1}$), Sr (537 $mgkg^{-1}$), As (18 $mgkg^{-1}$), Cu (205 $mgkg^{-1}$) and Ni (38 $mgkg^{-1}$) respectively (Figure 1). Pb, Zn and Cu had the highest coefficient of variation (84, 122.8 and 128.8 % respectively) with the greatest concentrations recorded at stations 1, 2, 3 and 13 (Figure 1).

Pollution indices

Enrichment Factor

The enrichment factor values of all the trace metals and metalloids exhibited variations in the degree of enrichment (Figure 3). V and Rb showed levels from no enrichment to minor enrichment; Ni and Ba from minor enrichment to moderate enrichment; Cu and Zn from no enrichment to severe enrichment; Cr and Zr from minor enrichment to moderately severe enrichment; Pb from no enrichment to moderately severe enrichment and As from no enrichment to moderate enrichment; while Sr showed results from minor enrichment to severe enrichment. Cu showed EFs greater than 5 at stations 1 (6.6), 2 (7.9), 3 (14.9), 13 (19.2) and 21 (5.5); Pb at station 3 (9) and Zn also at station 3 (15.8).

Pollution Load Index

The median PLI calculated for the area was 1.1. and varied from 0.5 to 1.6. The stations 1, 2, 3, 4, 6, 7, 9, 11, 13, 14, 15, 19, 22 and 23 exhibited values greater than 1 (Figure 4) and were located in places where high trace element concentrations were found.

Adverse Effect Index

The average AEI values calculated for the estuary show that V, Ni, Cu, Pb, As, Cr and Ba could be associated with adverse effects on organisms, because they exhibited average values higher than 1 (Figure 5). Zn was the only element that showed values lower than 1 in all the stations except 1, 2, 3 and 13 where the AEI values were 1.3, 1.5, 5.3 and 1.1 respectively.

Factor and cluster analysis of sediment samples

A factor analysis was performed to identify the causes of variation in the geochemical and textural datasets from the estuary. Three factors were identified that explained 72% of the system variance. All factors were associated with sediment composition, anthropogenic activities and carbonates from biogenic origin (Table 2). The first factor explained 44% of the total variance and was related to sediment composition (texture and mineralogy) due to its strong controls on major and trace element compositions. The second factor explained 18% of the total variance and was related to anthropogenic activities; this factor grouped Cu, Pb and Zn, contaminant elements supplied to the Southampton Water estuarine system by the Exxon oil refinery and other urban and industrial sources (Croudace and Cundy, 1995; Cundy and

Croudace, 2017), with OM and P_2O_5. Finally, the third factor explained 10% of the total variance and was linked to the biogenic fraction due to its relationship with CaO and Sr.

In order to identify associations between the 23 sediment samples, a cluster analysis was also performed. The cluster diagram showed two main groups (A and B) (Figure 6). Group A (stations 3, 13, 2 and 1) was characterized by a higher content of V, Ni, Cu, Zn, Cr, Ba, Al_2O_3, Fe_2O_3, CaO, O.M, clay and silt, also this group exhibited higher EF of Cu, Pb, Zn and higher PLI values. Group B (the rest of the stations) was constituted by higher concentrations of As, Rb, Sr, Zr, SiO_2 and sand.

Discussion

Major and trace element sources

The geochemical composition and the ternary diagram (Figure S1) showed that the estuarine sediments are rich in SiO_2 (silicates) rather than CaO (carbonates) and Al_2O_3 (aluminosilicates) and highlights a relatively homogenous bulk chemical composition. The negative correlations between CaO with Al_2O_3 (-0.74, $p < 0.05$), K_2O (-0.70, $p < 0.05$), SiO_2 (-0.82, $p < 0.05$), TiO_2 (-0.62, $p < 0.05$) indicated that carbonates are supplied to the system by shell fragments of organisms that live in the sediment such as oysters and bivalves rather than lithogenic sources. OM exhibited a low positive correlation with silt (0.45, $p < 0.05$) and a low negative correlation with sand (-0.45, $p < 0.05$); this suggests that organic matter distribution is at least partly controlled by fine sediment distribution. The positive correlation between Al_2O_3 and K_2O (0.99, $p < 0.05$), MgO (0.93, $p < 0.05$), highlighted the presence of clay minerals such as plagioclases and feldspars.

The trace elements correlations between major elements noted positive correlations of V (0.98, -0.63, $p < 0.05$), Ni (0.69, -0.71, $p < 0.05$), As (0.83, -0.51, $p < 0.05$), Cr (0.84, -0.48, $p < 0.05$), Ba (0.71, -0.77, $p < 0.05$) and Rb (0.98, -0.71, $p < 0.05$) with Al_2O_3 suggesting that these elements are supplied by lithogenic sources through the erosion processes of the catchments of the rivers

Test, Itchen, Hamble and Meon. The negative correlations with CaO indicate that carbonates have diluted their concentrations in the sediment and modified their spatial distribution. Sr exhibited a positive correlation with CaO (0.88, $p < 0.05$), this suggests a marine origin due to this element is a natural component of seawater and it is well known that Sr can substitute Ca from biogenic carbonates. On other hand, the lack of (or lower) positive correlations of Cu, Pb and Zn with almost all the studied geochemical parameters suggests anthropogenic sources supplied these elements (Table S1).

Anthropogenic footprint of Cu, Pb and Zn.

Historically, the anthropogenic footprint in the estuary has been identified through saltmarsh and other sediment cores taken from Southampton, Fawley, Hythe and Humble areas. Croudace and Cundy (1995) reported clear Cu, Pb and Zn profiles in the Fawley area caused by anthropogenic inputs. They noted that anthropogenic Cu was introduced to the estuarine system from the Exxon oil refinery at Fawley, Southampton Water, peaking around 1970 and had exhibited significantly reduced levels since 1971. This profile showed a rapid increase from background levels of 15 to 1022 mg kg^{-1}, which was the maximum value registered in the area. After this peak they observed a Cu concentration decrease to 286 mg kg^{-1}. This element was attributed to the Exxon oil refinery as Copper is used in several processes within the refinery; for example, it is used as catalyst to convert mercaptans to disulphides and cuprous ammonium acetate has been used to remove acetylene gas (Knap, 1979). The lead profile showed an increase in concentration from 24 mg kg^{-1} to a maximum value of 109 mg kg^{-1}, followed by a slight decrease toward the surface (67 mg kg^{-1}). However, to infer the origin Croudace and Cundy (1995) used stable isotope ratios of lead to reveal anthropogenic sources of this element. Their data exposed different Pb sources such as automobile emissions, industrial inputs and fly ash from coal burning.The Zn profile showed a similar distribution to lead, an increase from background levels of 75 to a maximum concentration of 169 mg kg^{-1}, after this there was a small decline in concentration to 161 mg kg^{-1}. Although, they reported an uncertain source of this element, they could deduce the Zn anthropogenic signal when they compared with sediments from the unpolluted Newtown estuary. They noted similar levels to background concentrations found in sediments adjacent to Fawley.

In the present study, the correlation and factor analysis identified that Cu, Pb and Zn reflect the anthropogenic signal of the area. Also, they indicate that V, Cr, Ni, As, Ba and Rb are from lithogenic sources rather than urban and industrial activities and revealed that Sr is likely to be of a marine origin.

The enrichment value distribution of these elements and the cluster analysis results highlight three main sources of the contaminants: the Exxon Oil refinery (sub-area A), the main Southampton harbour (sub-area B) and the scrap metal handling and storage facilities located in the sub-area (C) (Figure 1). Cu was found at stations 11 and 13 (sub-area A) with enrichments values of 2 and 19.2 respectively, in stations 4, 5, 6, 22 and 23 (sub-area B) enrichments of 2.1, 2, 3.4, 2.3 and 2.8, and in stations 1, 2 and 3 (sub-area C) enrichments of 6.6, 7.9 and 14.9. In the case of Pb, we found that the Exxon oil refinery and the scrap metal handling and storage facilities are the principal sources of this element. While for Zn, the main sources are the scrap metal handling and storage facilities. Finally, with all these evidences, it is clear that the spatial distributions observed for Pb, Cu and Zn concentrations provide evidence for continued point source inputs and resulting contamination “hot-spots”.

Risk of adverse effects in organisms.

Data from Southampton Water and the Hamble estuary concerning the impact of trace metals and metalloids on local ecological diversity and functioning are largely historic, but this older literature does highlight a range of adverse biological effects in Southampton Water over the late 20th Century. For example, Romeril (1979) studied the occurrence of Cu, Fe and Zn in the hard-shell clam *Mercenaria mercenaria* and sediments of Southampton Water, and found that all metal concentrations in clam tissue were lower at the seaward end of the estuary and higher in the north part of the estuary. This tendency was attributed to the operation of the

Marchwood Power station in the north of the estuary. Savari (1989) found that the mollusc *Cerastoderma edule* in Southampton Water was affected by Cd, Cu, Fe, Pb, Ni and Zn concentrations in areas in the proximity of pollution sources such as Fawley (i.e. the Exxon oil refinery), Tucker Pile, Bird Pile and Marchwood, reporting that this mollusc was ten times more prevalent in areas distant from pollution input such as Dibden Bay, Netley and Woolston than those located near to Fawley (Exxon oil refinery). Sharifi et al., (1991) noted a change in foraminiferid distribution and an increase in test deformities in relation to heavy metal discharges (such as those from the Exxon oil refinery), and works such as those of Matharu (1975), Armannsson et al., (1985) and Fang (1995) also noted that locations in Southampton Water where mysid populations were formerly abundant were now barren due to pollution by Cd, Cu, Zn, Ni and Fe. This information shows that estuarine organisms have clearly been historically affected by anthropogenic sources such as the Exxon oil Refinery, the Marchwood Power Station and urban discharges.

Using the PLI index values, we can infer that the sediment quality of the estuary is reduced by the presence of pollutants; because we registered PLI values higher than 1 in the 60.8 % of the samples analysed in this work (Figure 4), which means these places had a slight deterioration of sediment quality due to trace metal and metalloid concentrations. Also, using the AEI index, we could deduce that Cu, Pb and Zn results cause adverse effects to benthic organisms because it has been their anthropogenic origin is noted. Other elements such as V, Ni, As, Cr and Ba would need a sequential extraction analysis to infer if a small fraction is bioavailable to benthic organisms. These data highlight that further work is needed to assess the contemporary impact of trace metals and metalloids on local ecological diversity and functioning, to fully assess current ecological status in the Southampton estuary.

Dredge activity evidence and its environmental risk.

As an important economic area, some technical reports for the estuary have stated that the volume of material dredged between 2005 and 2013 was 467, 664 m^3 (ABP, 2014). Croudace and Cundy 1995 using dating of sediment cores noted a reduction in the sedimentation rate from 20 mm yr^{-1} to 5 mm yr^{-1} between 1981 and 1989. This reduction was attributed to dredge activities in the Fawley area prior to the expansion from the oil refinery. Our data identified these dredge activities due to the different sediment textures in the study area. We registered a sandy-silt texture sediment in the main navigation channel that corresponds to stations 5, 8, 11, 14, 15, 16, 18, 19, 20 and 23 (Figure 1); while stations 1, 2, 3, 4, 6, 7, 9, 10, 12, 13, 17, 19 and 22 that do not fall within the navigation channel consisted of predominantly fine sediment (silt) (Figure 1).

In general, the information collected here shows that the estuary and its subtidal sediments are heavily disturbed by dredging activities and if contaminated sediments are not properly handled, they could be a serious threat to locations where these sediments are deposited. A recent work conducted by Cundy and Croudace (2017) indicated that for Pb and Cu (and by inference other sediment-associated trace metal contaminants) continued input through local reworking of extant (i.e. within-estuary) trace metal-labelled sediments has meant that trace metal concentrations in some recent intertidal near-surface sediments remain elevated significantly above background. For subtidal sediments, this reworking of older more contaminated sediments is also likely to exacerbate sediment contamination problems in some areas.

Comparison of pollution levels in Southampton with other estuaries worldwide

Positioning our data in an international context. We identified that Southampton is affected by Cu, Pb and Zn as in other estuaries worldwide (Munksgaard et al., 2013; Liu et al., 2015; Campos et al., 2019). We found median enrichment factors of 3.4 (Cu), 1.6 (Pb) and 1.7 (Zn). Birch et al. 2020 identified that estuaries from Australia, Ireland, China and Brazil exhibited average enrichment factors from 0.9 to 5.1 by Cu, from 1.4 to 5.4 by Pb and from 1 to 4.6 by Zn (Chen et al., 2013; Baptista et al., 2016). Comparing this information, we identify that our data are between these ranges. Although if we rank these values, we observe that Southampton is the second least polluted estuary for these three elements (Table 3). This evidence highlights that although Southampton has and anthropogenic impact from trace elements and metalloids there are other places where the anthropogenic influence is considerably worse such as estuaries from China, Ireland and Brazil (Cordeiro, et al., 2015; Brooks et al, 2016; Chan et al., 2016).

Conclusion

Geochemical data presented for subtidal sediments from Southampton Water show that almost all trace metal and metalloid concentrations recorded are close to local geological background levels; except for Cu, Zn and Pb. The spatial distribution of these elements indicates that the Exxon oil refinery, Southampton port, local marinas and runoff from domestic and industrial activities act effectively as point sources of these elements. The distribution of trace metals and metalloids in the estuary is driven by natural and anthropogenic factors such as the sediment composition, biogenic sediments, sediment reworking, and anthropogenic activities (including dredging). Based on calculated pollution indices, the estuary can be considered moderately impacted by the urban and industrial activities that take place within it. Some of the trace metals present have caused adverse effects in benthic or other organisms in the past, and despite reductions in trace metal inputs the data presented here indicate current sedimentary enrichment of trace metal and metalloids to levels where they are likely to cause adverse effects to benthic organisms. Further work is needed to assess the contemporary impact of trace metals and metalloids on the local ecology, to fully assess current ecological status in the Southampton Water area.

Acknowledgements

OCH is grateful to the Consejo Nacional de Ciencia y Tecnología (CONACYT), Mexico for funding through their scholarship program (No. 209683). This research was supported by internal resources of the Universities of Brighton and Southampton, U.K. Thanks are due to the crew of

RV Callista. We are grateful to L.G. Peter Lyons and Dr. Magda Grove for their technical assistance with the sampling. AC also acknowledges support from the Hong Kong Branch of Southern Marine Science and Engineering Guangdong Laboratory (Guangzhou) in his contribution to this paper.

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