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Polycyclic aromatic hydrocarbons in sediments at dredged material disposal sites around England: Concentrations in 2013 and time trend information at selected sites 2008–2013

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ABSTRACT

The maintenance of navigation channels to ports and the development of their facilities present a need to conduct dredging operations, and the subsequent disposal of dredged material at sea. Contaminant concentrations in candidate dredged material are determined and their possible impacts considered during the licensing process, which can result in the exclusion of some material from sea disposal. Monitoring of disposal sites is conducted in order to ensure that no undesirable impacts are occurring. In this study we consider the levels of polycyclic aromatic hydrocarbons (PAHs) in sediments at a number of disposal sites monitored in 2013 and variations in concentrations over time at three sites during the period 2008–2013. These were assessed using established sediment quality guidelines. Elevated PAH concentrations were generally observed only within the boundaries of the disposal sites studied.

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1. Introduction

As an island nation, much of the UK import and export traffic is by sea, and the development of port facilities and the maintenance of navigation channels are of paramount importance to trade. The disposal of dredged material, whether from capital projects or maintenance dredging activities, is controlled by a system of licences issued under the Marine and Coastal Access Act 2009 which came into force on 1st April 2011. In licensing the disposal of dredged material to disposal sites at sea, numerous conditions associated with the relevant national and international agreements (e.g. the London Protocol 1996, the OSPAR Convention, the Habitats and Species Directive (92/43/EEC), and the Water Framework Directive (2000/60/EC)) must be considered to determine whether likely impacts arising from the dredging and disposal activities are acceptable (MEMG, 2003). Criteria considered under the various conventions and directives include the presence and levels of contaminants in the material to be disposed of, along with perceived impacts on any sites of conservation value in the vicinity of disposal. In addition, any potential for beneficial use of the material (e.g., in beach recharge or managed retreat schemes) must be considered before a disposal consent is issued. One of the roles of Cefas is to provide scientific advice to the licensing authority (the Marine

Management Organisation (MMO)) on the suitability of the material for sea disposal at the application stage and, once a licence is granted, to check that any disposal licence conditions are being met and that no unexpected effects occur. There are approximately 150 sites designated for dredging disposal around the coast of England, not all of which are used in any one year. While the majority of these are located near to the coast of the mainland, generally within a few miles of a major port or estuary entrance, a significant number are located within estuaries (e.g., in the Humber estuary) or on intertidal mudflats as part of beneficial use schemes (Bolam et al., 2006). In total, around 40 million wet tonnes of dredged material are annually disposed of at sea, although this can vary from 28 to 57 million tonnes (for the period between 1986 and 2010). Individual licences may consent the disposal of a few hundred or several million tonnes, and the nature of the material may vary from soft silts to boulders or even crushed rock, although the majority comprises finer material (Bolam et al., 2006).

On behalf of the MMO, Cefas conducts an annual monitoring programme targeting a number of disposal sites. These field evaluations are designed to ensure that:

- environmental conditions at newly designated sites are suitable for the commencement of disposal activities;
- predictions for established sites concerning limitation of effects continue to be met; and
- disposal operations conform with licence conditions.

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In order to assist with the determination of the disposal sites to be sampled during any given year, Cefas has derived a tier-based approach that classifies a number of possible issues or environmental concerns that may be associated with dredged material disposal into a risk-based framework (Bolam et al., 2009; Birchenough et al., 2010). The issues that pertain to a particular disposal site, and the perceived environmental risk, determine where that site lies within the tiered system. This determines whether that site is considered for sampling during a particular year. Disposal sites sampled during 2008–2013 are summarised in Table 1.

During the licensing procedure, contaminant concentrations in candidate dredged material for sea disposal are considered as one of the topics for consideration in the decision to licence sea disposal or not. For many (metals and PCBs, for example) there are defined actions levels – concentrations below action level 1 are considered acceptable; those above action level 2 are not, and some material may be excluded (for example, that from particularly contaminated areas). For PAHs these have not been defined, largely because of the complications resulting from the presence of black carbon (soot, essentially) which reduces bioavailability and so also reduces potential toxic impacts. Studies of contaminants at disposal sites allow an assessment as to whether concentrations within or surrounding the disposal sites are or are not at levels at which biological impacts might occur, and can also indicate any temporal trends. In a recent instance, disposal site monitoring demonstrated the effectiveness of the International Maritime Organisation's worldwide ban on the use of tributyltin in antifouling paints for large vessels, implemented during 2003–2008 (Bolam et al., 2014). In this case, we are examining PAH concentrations in and around dredged material disposal sites and their possible significance; this has not been undertaken previously for disposal sites around England.

Table 1
Dredged material disposal sites sampled during 2008–2013.

Sites sampled (year(s))	Geographical location around coast of England
North Tyne (2008, 2009, 2010, 2011, 2013)	Northeast
Souter Point (2008 to 2012)	Northeast
Inner Tees (2008 to 2013)	Northeast
Outer Tees (2008, 2009, 2010, 2011, 2013)	Northeast
Scarborough (2008)	East
Bridlington (2009)	East
Goole Reach (2008, 2010, 2011, 2012)	East
Eastbourne (2010)	South
Swanage (2010)	South
Rame Head (2008, 2009)	Southwest
Falmouth (2008)	Southwest
Site Z (in Liverpool Bay) (2010, 2013)	Northwest

Table 2
Ranges of concentrations of summed PAH in dredged material disposal site surveys ($\mu\text{g kg}^{-1}$ dry weight). nd: not detected.

Site/year	2008	2009	2010	2011	2012	2013
North Tyne	20,100–227,000	16,600–44,400	14,200–92,500	19,500–45,800		11,300–61,600
Souter Point	20,100–105,000	7740–67,200	2970–54,800	11,400–49,400	48,300–109,000	
Inner Tees	21,900–360,000	627–156,000	7650–87,500	8540–132,000	22,300–92,200	10,100–116,000
Outer Tees	4540–270,000	3000–17,200	2800–66,900	2600–34,800		3020–24,000
Scarborough	1990–58,600					
Bridlington		283–20,900				
Goole Reach	3240–42,400		1110–96,300	341–26,090	1590–107,000	
Eastbourne			nd–212			
Swanage			53–378			
Rame Head	304–19,100	47–5940				
Falmouth	1250–16,300					
Site Z			13–7000			23–4100

2. Materials and methods

Surface sediment samples for PAH assessment were generally collected using grab samplers (0.1 m² modified Day grab, Shipek grab) but sometimes using coring devices (NIOZ corer, vibrocorer). Regardless of sampling device, the top 2 cm of undisturbed sediment was taken for analysis. Samples were transferred to 500 ml glass Beatson jars with solvent-rinsed aluminium foil covering the jar beneath the lid and frozen at $-20\text{ }^{\circ}\text{C}$ until required for analysis. After thawing, each homogenised wet sediment sample was extracted using alkaline saponification and filtered after cooling, followed by liquid–liquid extraction into pentane. The sample extract was reduced in volume to 1 ml using a rotary film evaporator and passed through an alumina chromatography column to remove residual polar compounds (primarily pigments, as lipids are destroyed during the saponification process), reconcentrated to 1 ml and sealed in a glass autosampler vial. A suite of alkylated and parent PAH, including compounds with both petrogenic and combustion sources, were then determined using coupled gas chromatography–mass spectrometry in the electron impact ionisation mode. This suite comprised naphthalene and the C₁–C₃ alkylnaphthalenes, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, C₁ and C₂ phenanthrenes, dibenzothiophene and C₁–C₃ dibenzothiophenes, fluoranthene, pyrene, C₁ pyrenes, benz[a]anthracene, chrysene, C₁ chrysenes, 1,2-benzodiphenylene sulphide, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene and dibenz[a,h]anthracene (Rumney et al., 2014). Quantification was by means of deuterated internal standards added prior to the saponification step, with analytical quality control samples (procedural blanks and either a certified or laboratory reference material) included within each sample batch). Laboratory reference materials are prepared in-house and characterised by multiple replicate analyses. Control charts are then constructed, with warning and control limits plotted at ± 2 and ± 3 standard deviations of the mean value, respectively. Data for the reference material within each batch are then plotted on the control charts in order to allow the day-to-day performance of the method to be monitored, and to determine whether the data for each individual batch can be accepted as valid. Any batches which fail are reanalysed. Alongside the PAH analysis, a separate subsample of the homogenised sediment is dried at $105\text{ }^{\circ}\text{C}$ in order that the wet weight data generated can be recalculated on a dry weight basis. Full details of the method are given in Kelly et al. (2000), and the method has been used routinely since the late 1970s.

3. Results and discussion

The ranges of summed PAH concentrations at each site and for each year of sampling are given in Table 2 and Fig. 1 shows the

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