Dredged Material Disposal Site Monitoring Around the Coast of England: Results of Sampling (2023-2024)

Tees (Inner and Outer)

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Executive Summary

This report presents the scientific findings of, and implications for subsequent monitoring based on, the results from dredged material disposal site monitoring conducted under a Cefas/Marine Management Organisation (MMO) Service Level Agreement (SLA 1.2) project ('C6794' hereafter) around the coast of England during 2023-2024 (financial year).

The main aims of this report are:

- to aid the dissemination of the survey results;
- to assess whether observed changes resulting from dredged material disposal are in line with predictions;
- to compare the results with those of previous years (where possible);
- to facilitate our improved understanding of the impacts of dredged material disposal at both a site-specific and a national (i.e. non site-specific) level.

Two disposal sites were targeted for assessment during this period: Inner Tees (TY160) and Outer Tees (TY150), both located off the northeast coast of England. A single survey was conducted to sample the two sites on 25th July 2023 aboard the Research Vessel (RV) *Cefas Endeavour*. The survey comprised 20 sediment sampling stations: seven and two within the Inner Tees and Outer Tees sites respectively; and 11 outside the disposal sites. These stations have previously been sampled under this project, allowing the resulting data acquired in 2023 to be compared with historical data. Sampling attempts at three of the planned stations were unsuccessful in 2023 due to coarse sediment preventing effective operation of the grab. Data regarding sediment particle size assessment (PSA), organic carbon (OC), and sediment contaminants (i.e., polycyclic aromatic hydrocarbons (PAHs) and organohalogens (OHs)) for the 17 successfully sampled stations are presented and discussed in the present report.

The sediments within and surrounding the Tees disposal sites were predominantly unimodal sands, muddy sands and some sandy muds, with small but varying amounts of gravel. The highest mud contents were found in sediments within the two disposal sites, while the four stations furthest offshore, to the east of Outer Tees, were somewhat comparable in their sediment granulometric characteristics showing low to moderate mud contents relative to those across the survey area. Organic carbon (OC) values ranged from 0.14 % m/m to 6.09 % m/m in the <2 mm sediment fraction, the highest values generally being observed within the Inner Tees disposal site.

The highest summed PAH concentration found at the Inner Tees site was 83,300 µg kg^{-1} dw (dry weight) on the southern corner of the disposal site, with high concentrations also being observed at the western boundary and in the centre of the disposal site (69,300 µg kg^{-1} dw and 61,700 µg kg^{-1} dw respectively). At Outer Tees, the highest summed PAH concentration was 9,450 µg kg^{-1} dw, northwest of the disposal site boundary. The data are compared with effects range low (ERL) and effects range median (ERM) PAH values within the report. Evaluation of the PAH data indicates that the source in all the sediment samples from Inner and Outer Tees was predominantly petrogenic with >71 % of the PAH content arising from oil rather than combustion sources. Temporally, PAHs across the survey area remain generally comparable to those observed historically (2007 to 2013), with some stations showing slight increases, some showing decreases, with others remaining relatively consistent.

Regarding OHs, polychlorinated biphenyls (PCBs) were detected at all 17 of the stations sampled in 2023 (∑ICES7 PCBs ranged from 0.043 µg kg^{-1} dw to 2.27 µg kg^{-1} dw). The highest concentrations were observed within the Inner Tees disposal site, although one station within this site showed one of the lowest measured concentrations. Polybrominated diphenyl ethers (PBDEs) were detected in all the 17 stations sampled (∑11 PBDEs ranged from 0.078 µg kg^{-1} dw to 2.95 µg kg^{-1} dw), with BDEs 47 and 99 being detected at all stations. Again, the highest concentrations witnessed were within the Inner Tees disposal site boundary. Two congeners, BDE99 and BDE47, representative of the penta BDE (Pentabromodiphenyl ether) technical mix, were responsible for 47 to 62 % of the ∑11 PBDEs concentrations. Concentrations of OHs are compared within the report to Canada's Federal Environmental Quality Guidelines (FEQGs) (which are used by OSPAR) and Cefas Action Levels (ALs). The temporal assessment indicated that no notable change in OH concentrations can be discerned across the Inner and Outer Tees survey area.

The results of sampling conducted in July 2023 under the auspices of C6794 indicate that there has been no evident change in sediment contaminant concentrations within and around the Inner and Outer Tees disposal sites compared to data previously sampled under this project. As these two sites, the Inner site in particular, generally receive large quantities of material on an annual basis, future monitoring is recommended (in three years' time, for example) to help

ensure that any potential changes to the current sediment characteristics in this region are identified as early as practicably possible.

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1 Introduction

1.1 Regulation of disposal activity in England

Disposal of waste at sea is strictly regulated through the licensing requirements of the Marine and Coastal Access Act 2009 (MCAA). The MCAA provides the principal statutory means by which England complies with EU law, such as the Water Framework Directive (WFD, 2000/60/EC), the Habitats and Species Directive (92/43/EEC), the Wild Birds Directive (79/409/EEC), and international obligations such as under the OSPAR Convention and the London Convention and Protocol (LCLP), in relation to disposals at sea. Following the UK's departure from the EU at the end of 2020, the UK legislation transposing these EU Directives was amended to ensure it operated effectively following the UK's departure.

Pursuant to the OSPAR Convention and LCLP, only certain wastes or other matter are permitted for disposal at sea. During the 1980s and 1990s, the UK phased out sea disposal of most types of waste, including industrial waste and sewage sludge. Since then, dredged material from ports and harbours, and a small amount of fish waste, has been the only type of material routinely licensed for disposal at sea.

The Marine Management Organisation (MMO) regulates, and is responsible for, licensing activities in the marine environment around England, including the disposal of dredged material at sea. The MMO assesses the suitability of dredged material for disposal at sea in line with the OSPAR guidelines for the management of dredged material (OSPAR, 2014), and the LCLP. These guidelines provide generic guidance on determining the conditions under which dredged material may (or may not) be deposited at sea and involve the consideration of alternative uses, disposal sites and the suitability of the dredged material for aquatic disposal including the presence and levels of contaminants in the material, along with perceived impacts on any nearby sites of conservation value.

One of the roles of Cefas is to provide scientific advice to the MMO on the suitability of the material for sea disposal at the application stage and, once a licence is granted, to provide technical advice on any monitoring undertaken as a result of licence conditions. Advice on the licensing of dredged material disposal at sea is provided by Cefas' Sustainable Environmental Assessment for Licencing (SEAL) team; work conducted under C6794 helps underpin the scientific rationale for such advice (see Section 1.3).

1.2 Disposal sites around England

There are currently 228 open sites designated for dredged material disposal around the coast of England, not all of which are used in any one year. While the majority of these are located along the coast of the mainland, generally within a few miles of a major port or estuary entrance, a significant number are positioned within estuaries (e.g. the Humber Estuary) or on intertidal mudflats as part of beneficial use schemes (Bolam et al., 2006).

Total quantities annually disposed to coastal sites around England vary year to year, from 10 Mt (wet weight) to 40 Mt (wet weight). Individual quantities licensed may range from a few hundred to several million tonnes, and the physical characteristics of the material may vary

from soft silts to stiff clay, boulders or even crushed rock according to origin, although the majority consists of finer material (Bolam et al., 2006).

1.3 Overview of Cefas / MMO project C6794 'Monitoring of dredged material disposal sites'

The dredged material disposal site monitoring project C6794, funded by the MMO, falls under a service level agreement (or SLA) between the MMO and Cefas. Operationally, this project represents a continuation of the disposal site monitoring programme SLAB5, which was a component of a former SLA between Defra and Cefas; this SLA formerly ceased at the end of March 2015. C6794 was initiated on 1st April 2015, and, thus, while the project and work planned under this project are termed here under C6794, any reference to its predecessor project is inevitable (i.e. to its survey work, reports or other scientific outputs), and will continue to be referenced herein as SLAB5.

In summary, C6794 provides field evaluations ('baseline' monitoring and 'trouble-shooting' surveys) at dredged material disposal sites around the coast of England. A major component of the project is, therefore, the commissioning of sea-going surveys at targeted disposal sites. Such field evaluations under C6794 are designed to ensure that:

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

The outcomes of such surveys contribute, either directly or indirectly, to the licensing process by ensuring that any evidence of unacceptable changes or practices is rapidly communicated and acted upon by the MMO. As such, there are inherently strong links and ongoing discussions between the approaches and findings of this project with the work carried out by Cefas' SEAL team and the licensing team within the MMO. The scientific outcomes of the work undertaken within C6794 are circulated to the Cefas SEAL team and the MMO *via* a number of routes including peer-reviewed publications (including both activity-specific and site-specific findings), reports, direct discussions, and internal and external presentations. The production of this report forms an important element of such scientific communication. The current report, which presents the findings of work undertaken during 2023-24, constitutes the 16th in the series. The previous reports are accessible *via* the following link:

Dredged material disposal site monitoring round the coast of England - GOV.UK (www.gov.uk)

It is not the purpose of this report to present a detailed appraisal of the processes giving rise to impacts (see Section 1.5) but to encapsulate the essence of the impacts associated with this activity at specific sites targeted within year.

1.4 Sites monitored

The C6794 project identifies disposal sites to target for data acquisition based on a transparent prioritisation basis. Sites considered to represent those of greatest ecological interest or risk (e.g., recent or predicted large increases in disposed tonnage, new marine protected areas designated in the vicinity, local stakeholder interests) are ultimately prioritised, and the MMO

liaises closely with Cefas' SEAL team and Cefas scientists as part of this site selection process. Two disposal sites were targeted for Cefas monitoring during 2023-24: Inner Tees (TY160) and Outer Tees (TY150), both located off the northeast coast of England. These sites are referred to interchangeably with various aliases:

- Tees Bay A; Inner Tees; TY160
- Tees Bay C; Outer Tees, TY150

1.5 Aims of this report

This report does not aim to present a critique of the processes leading to observed changes at dredged material disposal sites around the coast of England. Such appraisals are conducted *via* other reporting routes, either *via* discussions with Cefas' SEAL team, presentations and subsequent publications at national and international conferences, and *via* papers in peer-reviewed journals (e.g., Bolam and Whomersley, 2005; Bolam et al., 2006; Birchenough et al., 2006; Bolam, 2014; Bolam et al., 2014a; Rumney et al., 2015; Bolam et al., 2016a; Bolam et al., 2021a). The aims of this report are:

- to present the results of sampling undertaken during 2023-24 under C6794, thereby aiding the dissemination of the findings under this project;
- to indicate whether the results obtained are in line with those expected for each disposal site, or whether subsequent investigations should be conducted;
- where possible, to compare the 2023-24 results with those of previous years to provide a temporal assessment (see Bolam et al., 2009; 2011a; 2012a; 2012b; 2014b; 2015a; 2015b; 2016b; 2017; 2018; 2019; 2020 and 2021b for reports of previous years' monitoring);
- to facilitate our improved understanding of the impacts of dredged material disposal at both a site-specific level and a national level; and,
- to promote the development of scientific (or other) outputs under C6794.

Due to the geographical proximity of the two sites, the approaches and outcomes of the survey for the two sites are presented together in this report.

2 The sites

2.1 Inner Tees and Outer Tees

The two Tees dredged material disposal sites (Inner Tees, TY160; Outer Tees, TY150) are both located offshore of the mouth of the Tees Estuary. The Inner Tees (TY160) dredged material disposal site is located within proximity to the mouth of the Tees and receives large quantities of material dredged from the ports of the Tees Estuary. The Outer site, located in slightly deeper water and just several miles offshore from the Inner site, has traditionally been less used for maintenance material but reserved largely for the receipt of capital dredging. The two sites have been the recipient of monitoring under C6794 (and its predecessor projects, e.g., SLAB5) for a number of years, most recently being in 2020 at the Inner site (for sediment organic

carbon, and organohalogens) and in 2021 at the Outer site (for sediment particle size and macrofaunal assemblages).

The River Tees is associated with many historic and ongoing chemical industries, including brominated flame-retardant producers, which have, in combination with the river's highly mineralised catchment, resulted in elevated contaminants within dredged sediments. Within the Tees Estuary there has also historically been a breach in the half-tide embankment allowing erosion of the enclosed mudflat; sediments of which were contaminated with high levels of lead and zinc. Construction works to repair this breach were subsequently licenced and undertaken. Analysis of dredged material from the Tees has displayed some of the highest levels of PAHs found in UK marine sediments (Bolam et al., 2012b). Various literature also indicates the river to exhibit high concentrations of other persistent organic pollutants relative to rivers of a similar nature in the UK and Europe (Allchin et al., 1999; Boon et al., 2002, Nicolaus et al., 2015). In view of the legacy contamination and the implications of this for the suitability of material for dredging and subsequent sea disposal at the two sites, there is an elevated needed to maintain a 'watching brief' of the levels of certain contaminants in the sediments within and surrounding the two Tees disposal sites. Commensurate with this, sampling under C6794 during 2023 will focus on sampling sediments of the two disposal sites and those of its environs, and their assessment for polycyclic aromatic hydrocarbons (or PAHs) and organohalogens (OHs). Stations previously sampled by Cefas under the auspices of C6794 (and its predecessor projects) will be targeted to allow a temporal assessment of these contaminant types to be conducted.

3 Sampling design and approaches

The seabed grabbing survey for sediment particle size assessment (PSA), organic carbon (OC) and contaminants (i.e., PAHs, OHs) assessment at Inner and Outer Tees was designed principally on the specifications for previous surveys. The two sites have been sampled on a number of occasions under this project and, to allow comparisons to be made between years, each survey has targeted the same stations. Thus, these stations may be regarded to represent a time-series and further sampling at the same stations allows a temporal assessment of the contaminants concentrations. Thus, the 20 stations (seven and two at Inner Tees and Outer Tees, respectively inside, and 11 outside the disposal sites) sampled (Figure 1) are those which have been targeted mostly in previous survey campaigns.

The grab sampling methods and subsequent sample processing adopted those of previous surveys were adopted for 2023 to maximise the robustness of temporal assessments. A Day grab (0.1 m^2) was deployed to sample the sediments and on retrieval, the surface sediments (top 2-3 cm) were carefully extracted using a stainless-steel spatula and placed in pentane-rinsed glass jars (for PAHs and OHs) or plastic bags (PSA, OC). A digital photograph image was taken of the grab sample prior to the removal of the surficial sediments. The grab buckets and sampling equipment (stainless steel spatula) were rinsed with 95% pentane between each sampling station. All samples were immediately frozen (-20 degrees) for storage. The processing of all samples for sediment PSA, OC, PAHs, OHs and metals were conducted in accordance with

Cefas' procedures (see Appendices 1, 2 and 3 further details on methods and assessment procedures for PSA, PAHs and OHs respectively).

The sampling was conducted on board the RV *Cefas Endeavour* on 25th July 2023 as part of a multidisciplinary survey under the Defra-funded Clean Seas Environmental Monitoring Programme (CSEMP). All 20 planned stations were targeted, while the survey failed to successfully acquire grab samples from three stations (OT4, OT7, IT1; Figure 2) and the positions of two stations (OT5, OT6) had to be relocated away from seabed assets which have been installed since the previous survey campaign in 2013. The data from these two stations are not used, therefore, as part of station-specific temporal assessments.

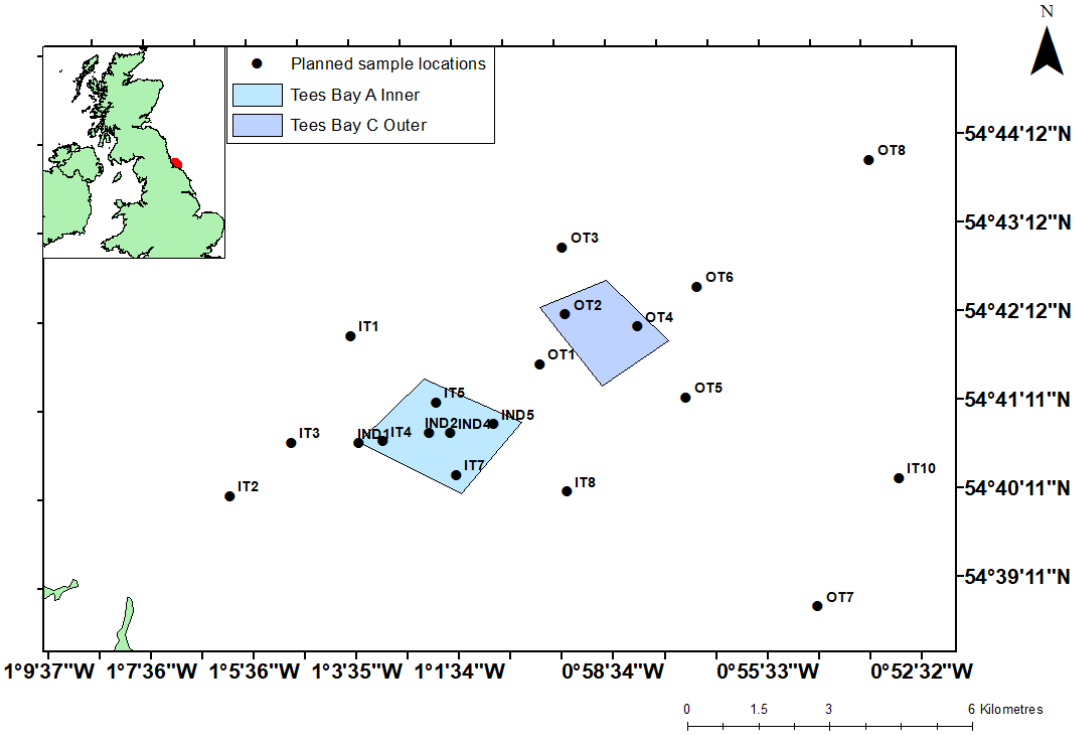

Figure 1. Location of the 20 stations planned for sediment sampling in and around the Inner (left) and Outer (right) Tees dredged material disposal sites, July 2023.

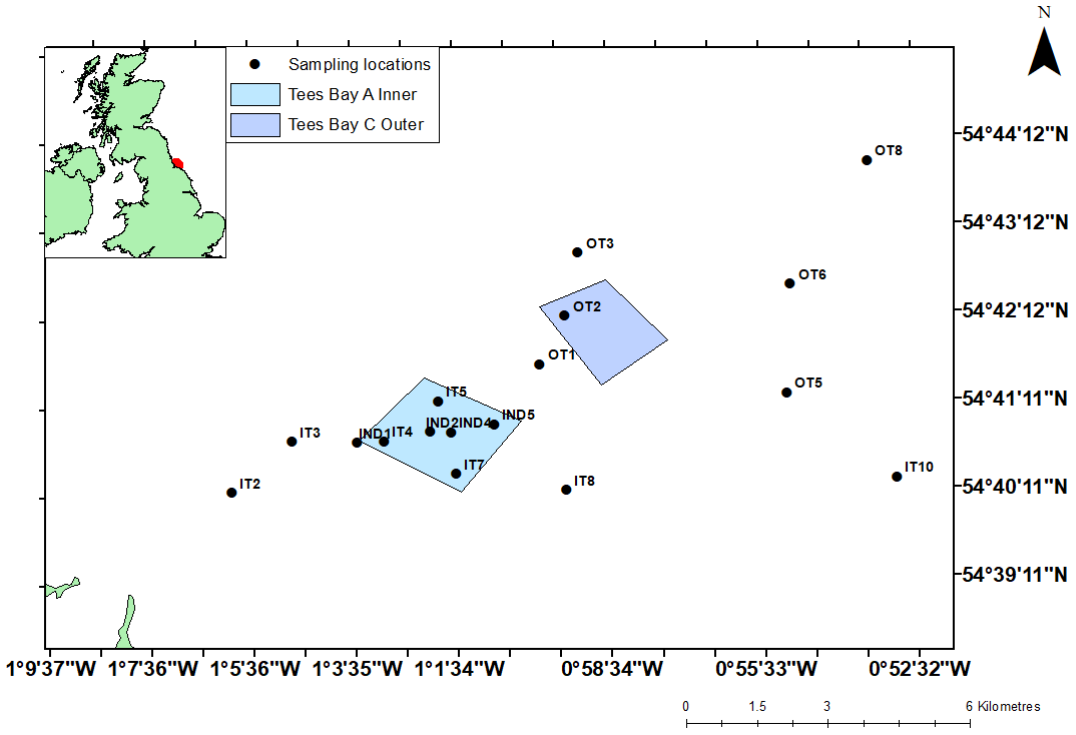

Figure 2. Location of the 17 stations sampled in and around the Inner (left) and Outer (right) Tees dredged material disposal sites, July 2023. Samples were not collected at IT1, OT4 and OT7. OT5 and OT6 were moved to the east due to cable installation now in place.

4 Results

4.1 Sediment particle size

The sediments within and surrounding the Tees disposal sites were predominantly unimodal sands, muddy sands and some sandy muds, with small but varying amounts of gravel. The sediments from the 17 stations sampled in 2023 are classified into five sediment groups (Table 1).

Table 1. Average sediment descriptions (top) and statistics (bottom) for each sediment group at Tees (Inner and Outer) based on samples collected in 2023. Number of samples in the second column (top table) relates to all samples from Tees over preceding years, used to derive the sediment groups.

Sediment group	Number of samples	Sample Type	Sediment description	MODE 1 (µm):	MODE 2 (µm):	MODE 3 (µm):
T1	14	Bimodal, Very Poorly Sorted	Slightly Gravelly Sandy Mud	75.4	38250.0	
T2	63	Unimodal, Poorly Sorted	Slightly Gravelly Muddy Sand	106.7		
T3	24	Polymodal, Very Poorly Sorted	Gravelly Muddy Sand	150.9	603.5	1200.0
T4a	17	Unimodal, Moderately Sorted	Slightly Gravelly Sand	150.9		
T4b	57	Unimodal, Poorly Sorted	Slightly Gravelly Sand	150.9		

Sediment group	Gravel (%)	Sand (%)	Silt/clay (%)	Very coarse sand (%)	Coarse sand (%)	Medium sand (%)	Fine sand (%)	Very fine sand (%)
T1	4.82	34.16	61.03	1.29	2.38	4.54	10.53	15.41
T2	0.59	80.13	19.27	0.80	1.87	4.99	28.30	44.17
T3	16.10	67.15	16.75	13.07	14.19	11.90	16.47	11.52
T4a	0.49	90.15	9.36	0.57	1.89	6.35	56.47	24.86
T4b	2.12	91.17	6.72	2.17	4.40	14.41	53.44	16.75

Temporal changes in sediment groups are shown in Table 2 for each station sampled during 2006 to 2014 and those in 2023. Stations have shown some changes in sediment groups in 2023, with, for example, increasing mud content changing from sediment group T3 to T1 (gravelly muddy sand to slightly gravelly sandy mud) at OT2; from T4b to T2 (unimodal sand to slightly gravelly muddy sand) at IND4 and IND5; and from sediment group T4b to T3 (unimodal sand to gravelly muddy sand) at IT3. However, some stations displayed a decreased mud content in 2023, changing from sediment group T1 to T4b (slightly gravelly sandy mud to unimodal sand) at IND2; IT10, OT1, and OT3 changing from sediment group T3 to T4a/T4b (gravelly muddy sand to unimodal sand); and IND1 and IT4 changing from T2 to T4b gravelly muddy sand to unimodal sand. However, many of these changes at stations have sporadically been observed in previous years, indicating that the 2023 data generally reflect what has been observed previously. Only two stations in 2023, IND5 (T2) and IT10 (T4a), were classed as sediment groups not previously observed for the station.

Table 2. Sediment groups for each station sampled between 2006 to 2014, and in 2023 at Inner and Outer Tees.

	Year									
Station code	2006	2007	2008	2009	2010	2011	2012	2013	2014	2023
IND1	T2	T2	T4b	T2	T2	T2	n	T2	n	T4b
IND2	T4b	T4b	T4b	T1	T4b	T4b	n	T1	T1	T4b
IND4	n	T4b	T2	T2	T4b	T2	T4b	n	n	T2
IND5	n	T4b	T4b	T4b	T4b	T4b	T4b	n	T4b	T2
IT3	T4b	T1	T4b	n	T1	T4b	T3	T4b	T4b	T3
IT4	T2	T2	T2	T2	T2	T2	T2	T4b	T2	T4b
IT5	T4a	T2	T4b	T4b	T2	T4b	T4b	T2	n	T2
IT7	T4a	T4b	T2	T2	T2	T2	T2	T1	T2	T2
IT8	T2	T2	T2	T2	T2	T2	T2	T2	T2	T2
IT10	T3	T2	T3	T4b	T3	T3	n	T3	T3	T4a
OT1	T4b	T4b	T4b	T4b	T4b	T4b	n	T4b	T3	T4b
OT2	T4b	T1	T4b	T3	T3	T3	n	T1	T3	T1
OT3	T4b	T3	T4b	T3	T3	T3	n	T3	T3	T4b
OT8	T4a	T4a	T4a	T4a	T4a	T4a	n	T4a	T4a	T4a

Figure 3 reveals the predominantly sandy nature of the sediment across the Tees survey area in 2023 with some variation in silt/clay (mud) component as shown in Figure 4. The highest mud contents were found in sediments within the two disposal sites, with OT2 inside the Outer Tees site showing the highest mud proportions, followed by IT7 and IND4 all within the Inner Tees site (Figure 4). Apart from IT3, the nearshore stations were generally the sandiest with low gravel and mud contents. Three of the four stations furthest offshore, to the east of Outer Tees (OT5, OT6, IT10), were somewhat comparable in their sediment granulometric characteristics, showing low to moderate mud contents relative to those across the survey area.

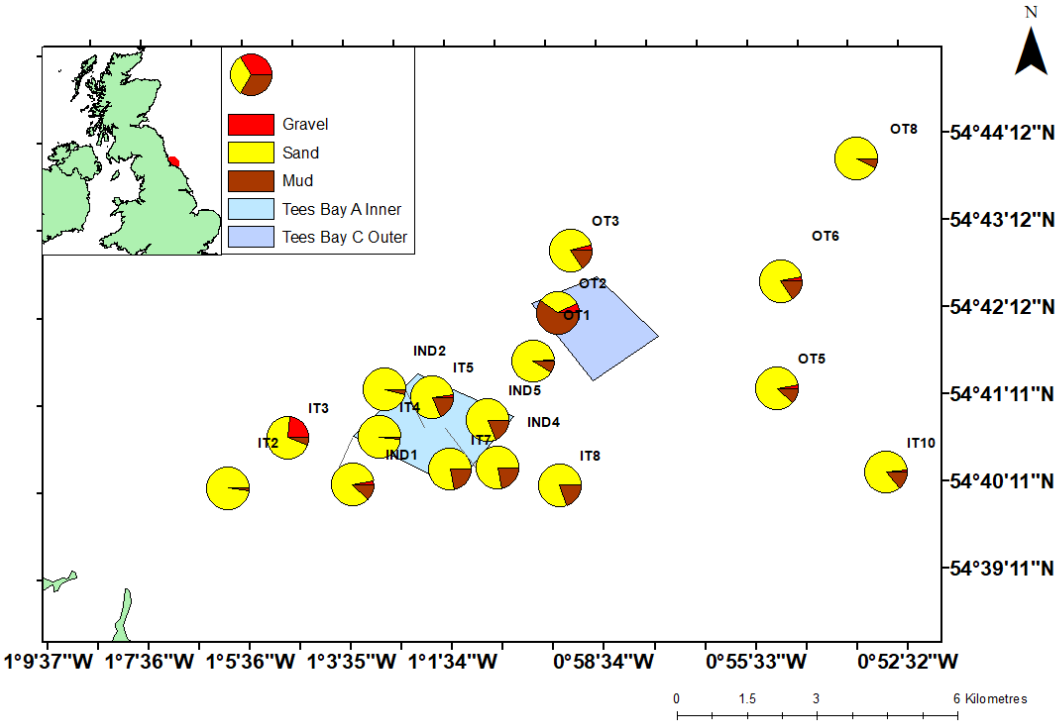

Figure 3. Pie chart of the main sediment types (gravel, sand, mud) comprising the sediments sampled within and in the vicinity of the Inner (left) and Outer (right) Tees dredged material disposal sites, July 2023.

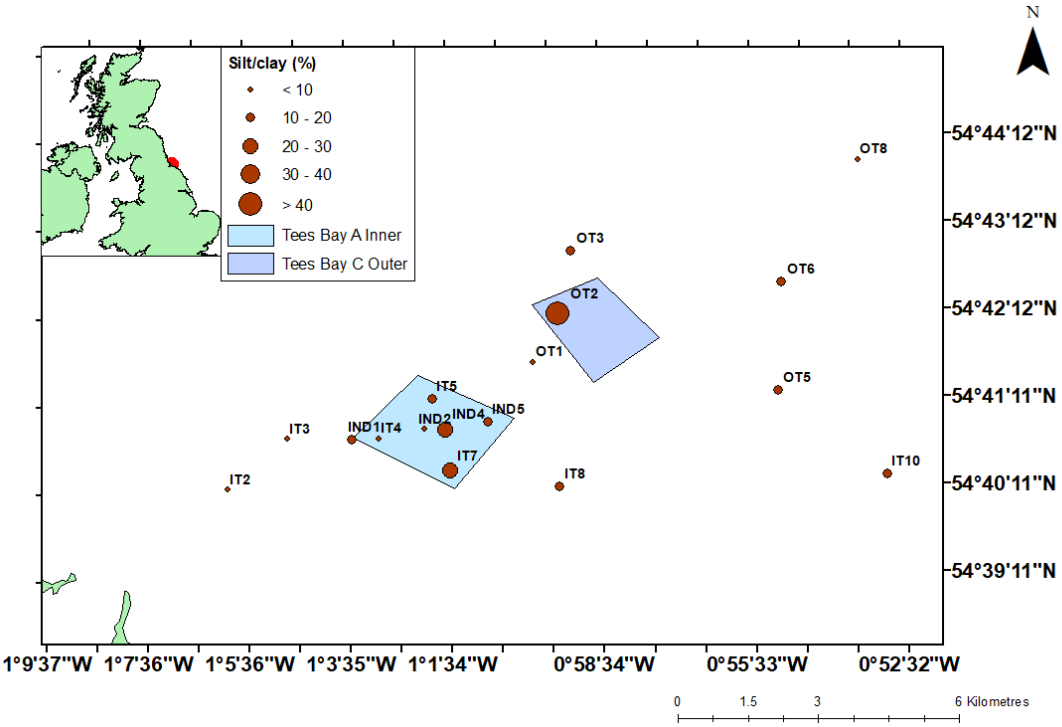

Figure 4. Bubble plot of the silt/clay contents of the sediments sampled within and in the vicinity of the Inner (left) and Outer (right) Tees dredged material disposal sites, July 2023.

4.2 Sediment organic carbon content

Organic carbon (OC) values ranged from 0.14 % m/m to 6.09 % m/m in the <2 mm sediment fraction (Figure 5). These are slightly lower than in previous years (Figure 6) but within the comparable range for the Tees survey area based on data from 2009, 2010, 2011, 2014 and 2023 which has displayed a minimum of 0.16 % m/m and a maximum of 10.29 % m/m OC. However, temporal assessments using an average across all stations sampled might, to a certain extent, be affected by the fact that the number of stations sampled between years varies slightly. In 2023, the highest values observed were within the Inner Tees disposal site, and at IT8 to the southeast of the site (Figure 5).

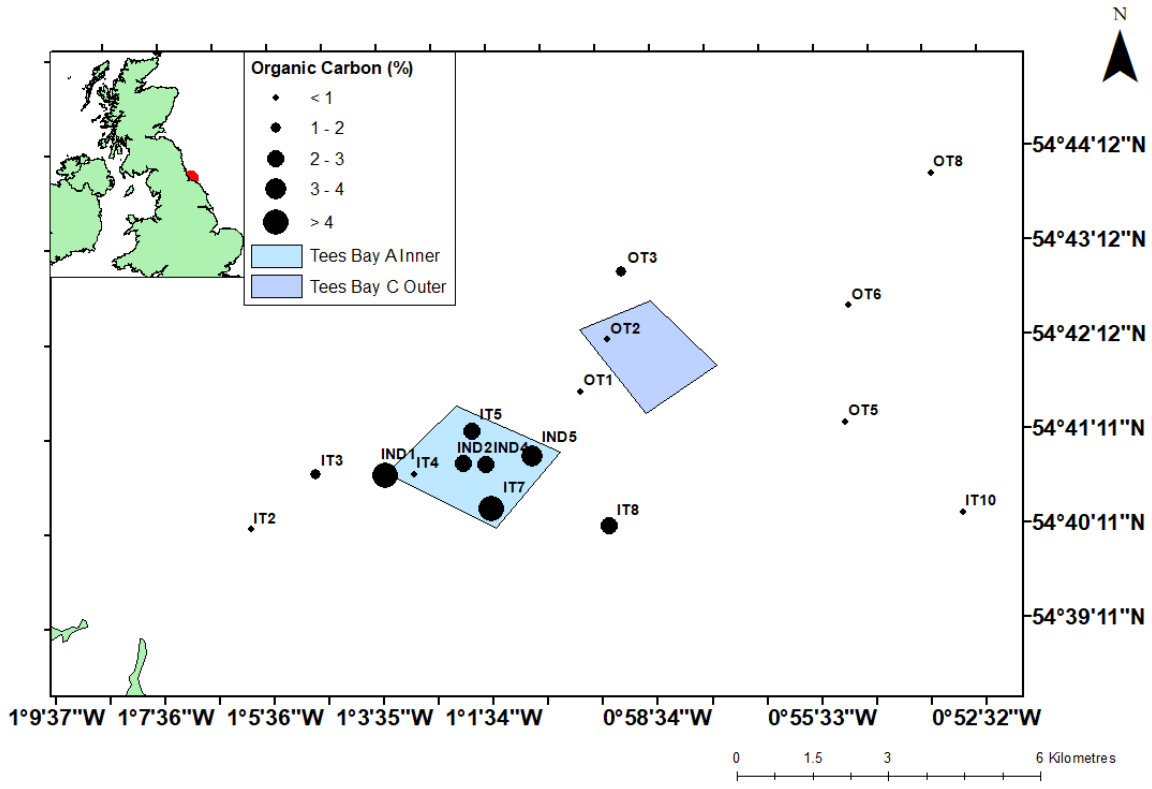

Figure 5. Sediment organic carbon content (%) of the sediments sampled within and in the vicinity of the Inner (left) and Outer (right) Tees dredged material disposal sites, July 2023.

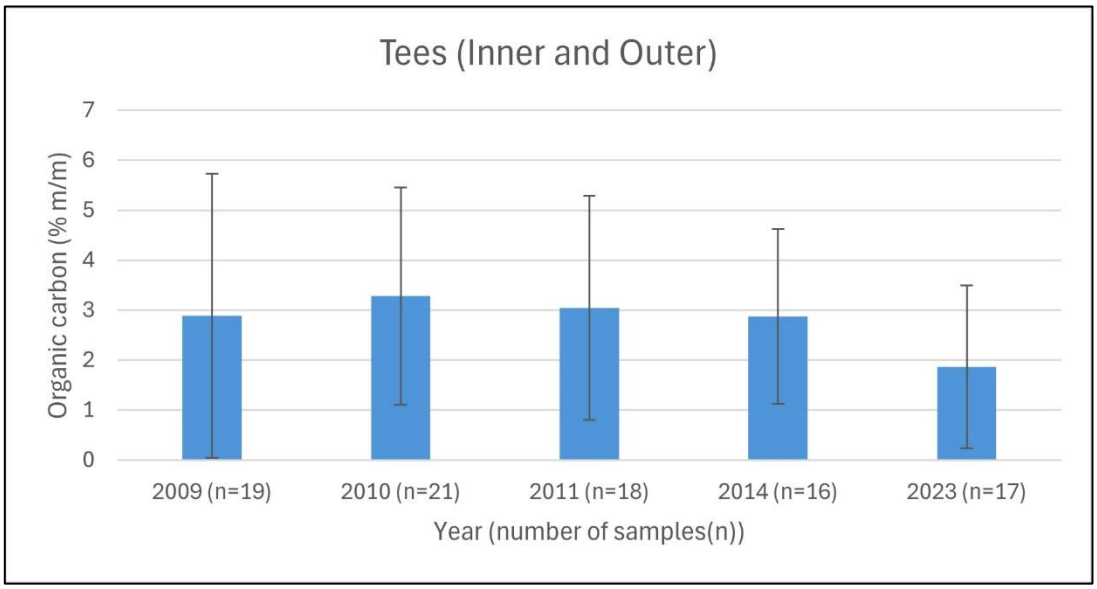

Figure 6. Average sediment organic carbon content (%) of the sediments for 2009, 2010, 2011, 2014 and 2023.

4.3 Sediment contaminants

4.3.1 Polycyclic aromatic hydrocarbons (PAHs)

At Inner Tees the highest summed PAH concentration found in 2023 was 83,300 µg kg^{-1} dw at IT7 on the southern corner of the disposal site (Figure 7). High concentrations were also found at IND1 on the western edge and IND2 in the centre of the disposal site (69,300 µg kg^{-1} dw and 61,700 µg kg^{-1} dw respectively) The lowest summed PAH concentration was 928 µg kg^{-1} dw found at IT2 which is to the west of the disposal site. Inner Tees was last analysed for PAHs in 2013 and the highest summed concentrations that year were similarly found at IT7 and IND1 as well as IT4. The lowest summed concentrations found in 2013 were at IT3.

At Outer Tees the highest summed PAH concentration for 2023 was 9,450 µg kg^{-1} dw found at OT3 which lies northwest of the disposal site boundary. The lowest summed PAH concentration was 1,190 µg kg^{-1} dw at OT8 which lies to the far northeast of the site boundary. In 2013 the highest summed concentration was 24,000 µg kg^{-1} dw at OT5 and the lowest was 3,020 µg kg^{-1} dw at OT8.

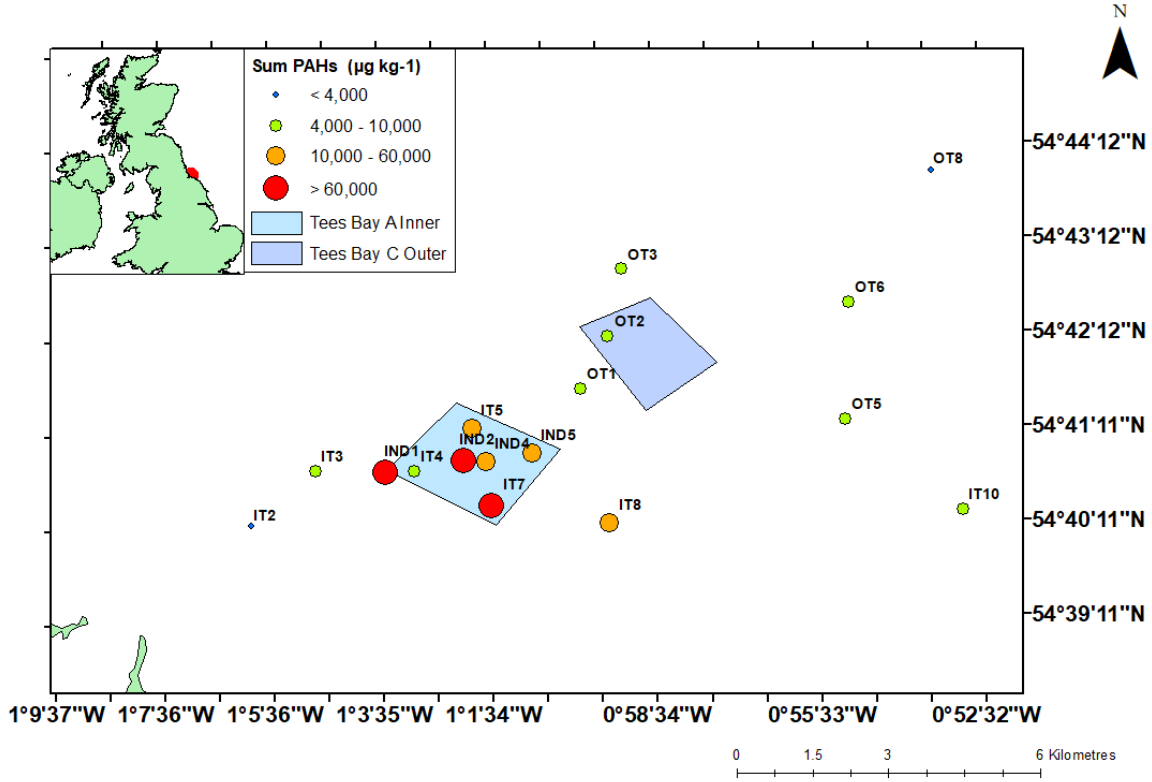

Figure 7. Summed PAH concentrations (µg kg^{-1} dw) of the sediments sampled within and in the vicinity of the Inner (left) and Outer (right) Tees dredged material disposal sites, July 2023.

All Inner Tees stations were found to exceed the effects range low (ERL; Long et al., 1998) for low molecular weight (LMW) PAHs with the exception of IT2. The effects range median (ERM; Long et al., 1998) for LMW PAH was exceeded at seven of the stations associated with Inner Tees and its environs: the stations where the ERM LMW was not breached were IT4, IT3, IT10, and IT2 which are all (except IT4) outside the disposal site boundary. The ERL for the high molecular weight (HMW) PAHs was breached at five stations (IT7, IND1, IND5, IT5, IT8) which are either within the disposal site boundary or, in the case of IT8, to the southeast. None of the stations exceeded the ERM for HMW PAHs.

All seven of the Outer Tees stations were found to exceed the ERL for LMW PAHs with the exception of OT8 which is found furthest offshore to the northeast of the area. No stations exceeded ERM for LMW or ERL and ERM for HMW PAHs.

Evaluation of the PAH data indicates that the source in all the sediment samples from Inner and Outer Tees was predominantly petrogenic with >71 % of the PAH content arising from oil rather than combustion sources (i.e., pyrogenic).

Data are available to analyse temporal trends of PAHs from 2007 to 2023 (Table 3). At Inner Tees, concentrations of PAHs fluctuate year on year at most stations both inside and outside the disposal site boundary. The 2023 data show increased concentrations from 2012/2013 at stations IND2 and IND5, with levels at IND2 being the highest found during the 2007-2023 period for this station.

Decreased concentrations of PAH were found at stations IT10, IT3, IT4 and IT8 and the remaining stations were found to have similar levels to 2012 or 2013.

At Outer Tees concentrations have been generally much lower across all stations than at Inner Tees in the 2007-2023 testing period. In 2023, the concentration at OT1 increased very slightly since last tested in 2013 but all other stations have seen decreases, some quite significant such as at station OT2.

Table 3. Temporal trends (2007-2023) in summed PAH concentrations (µg kg^{-1} dw) for the stations sampled at Inner and Outer Tees in July, 2023.

	2007	2008	2009	2010	2011	2012	2013	2023
IND1	20,500	109,000	156,400	87,500	105,600		77,000	69,300
IND2		14,800	8,620	56,500	46,300		36,900	61,700
IND4	73,000	51,200	58,100	51,000	90,400	33,700		32,600
IND5	99,300	22,400	17,100	7,650	70,900	22,300		52,800
IT2			627	10,200				928
IT3				75,800	8,540	64,700	10,100	7,460
IT4	101,100	57,500	55,700	76,600	91,600	48,700	92,700	9,100
IT5		76,100	98,600	56,500	119,700	58,200	55,300	52,600
IT7	37,300	50,200	47,200	50,900	132,100	67,900	115,700	83,300
IT8	42,500	32,600	59,700	34,200	40,400	42,900	54,600	28,800
IT10		11,200	4,620	18,500	11,800		42,800	6,650
OT1		2,560	9,000	7,970	7,960		4,530	6,550
OT2		16,000	13,000	15,800	14,500		19,500	4,620
OT3	4,020	8,630	5,600	13,600	22,200		13,100	9,450
OT8		2,240	3,000	2,800	2,600		3,020	1,190

4.3.2 Organohalogens (OHs)

At Inner and Outer Tees, polychlorinated biphenyls (PCBs) were detected at all 17 of the stations sampled in 2023 at Tees (∑ICES7 PCBs ranged from 0.043 µg kg^{-1} dry weight (dw) to 2.27 µg kg^{-1} dw (Figure 8). The highest ∑ICES 7 PCBs concentration of 2.27 µg kg^{-1} dw was found at IT7 within the Inner Tees disposal site, with the next highest ∑ICES 7 CB concentrations: 1.97 µg kg^{-1} dw; 1.14 µg kg^{-1} dw; and 1.10 µg kg^{-1} dw, at IND5, IT5 and IND4 respectively, these also are located within the Inner Tees disposal site. Other high ∑ICES 7 PCBs values (1.02 µg kg^{-1} dw, 0.79 µg kg^{-1} dw) were found at IT8 and IND1, to the southeast and west, respectively, of the Inner site. The lowest ∑ICES 7 PCBs concentrations meanwhile were at observed at OT2, IT4 and IT2, with concentrations of 0.043 µg kg^{-1} dw, 0.058 µg kg^{-1} dw and 0.060 µg kg^{-1} dw, respectively. While OT2 is located within the Outer Tees disposal site, interestingly IT4 is located within the Inner site where many of the highest concentrations were witnessed. Thus, even within the Inner Tees disposal site, ∑ICES 7 PCBs concentrations show great spatial variability.

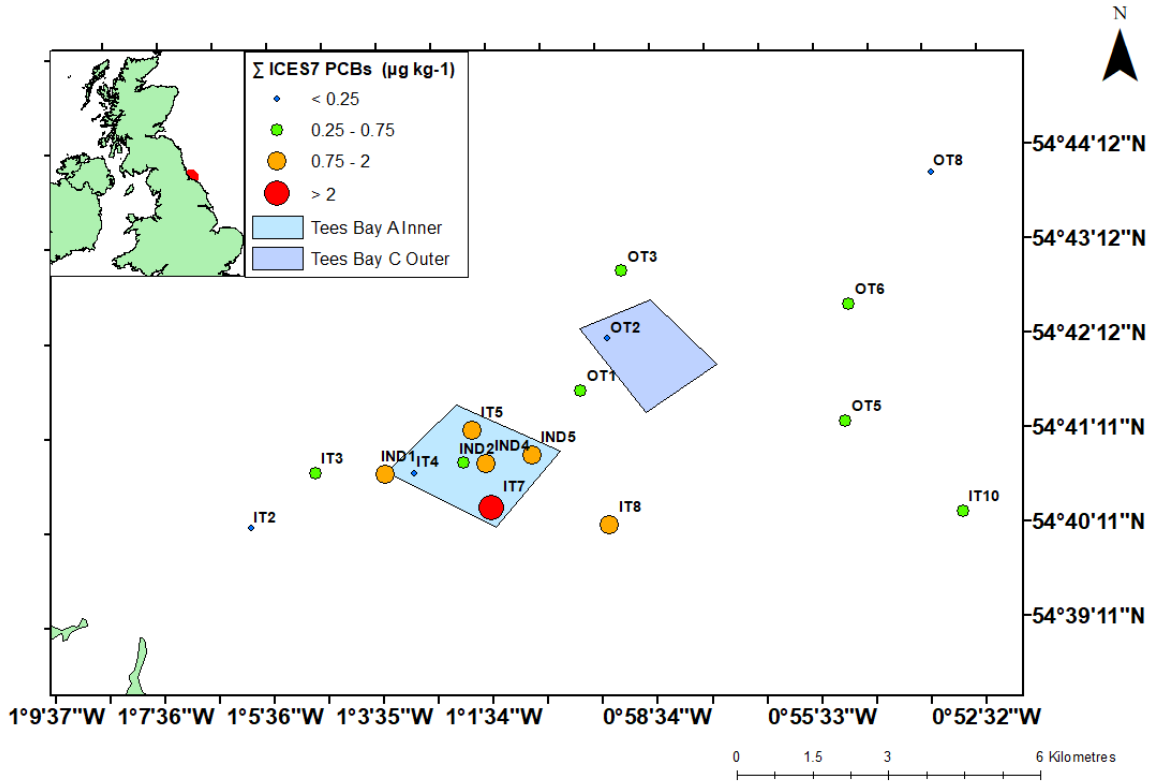

Figure 8. ∑ ICES7 PCBs concentrations (µg kg^{-1} dw) of the sediments sampled within and in the vicinity of the Inner (left) and Outer (right) Tees dredged material disposal sites, July 2023.

Polybrominated diphenyl ethers (PBDEs) were detected in all of the 17 Inner and Outer Tees stations sampled in 2023 (∑11 PBDEs range 0.078 µg kg^{-1} dw to 2.95 µg kg^{-1} dw), with at least BDEs 47 and 99 detected at all stations (Figure 9). The highest ∑11 PBDEs concentrations were in the Inner Tees disposal site at IT7 (2.95 µg kg^{-1} dw) and IND5 (2.09 µg kg^{-1} dw) with the next highest values of 1.18 µg kg^{-1} dw and 1.10 µg kg^{-1} dw (IT5 and IND4 respectively) also within the Inner Tees disposal site. Lowest concentrations were at IT2, OT2 and IT4, with ∑11 PBDEs concentrations of 0.078 µg kg^{-1} dw, 0.090 µg kg^{-1} dw and 0.099 µg kg^{-1} dw, respectively. Two congeners, BDE99 and BDE47, representative of the penta BDE (Pentabromodiphenyl ether) technical mix, were responsible for 47 to 62 % of the ∑11 PBDEs concentrations. BDE183 was detected at 14 of the 17 stations which is indicative of widespread use of the octa- (Octabromodiphenyl ether) or deca BDE (Decabromodiphenyl ether) technical mixes.

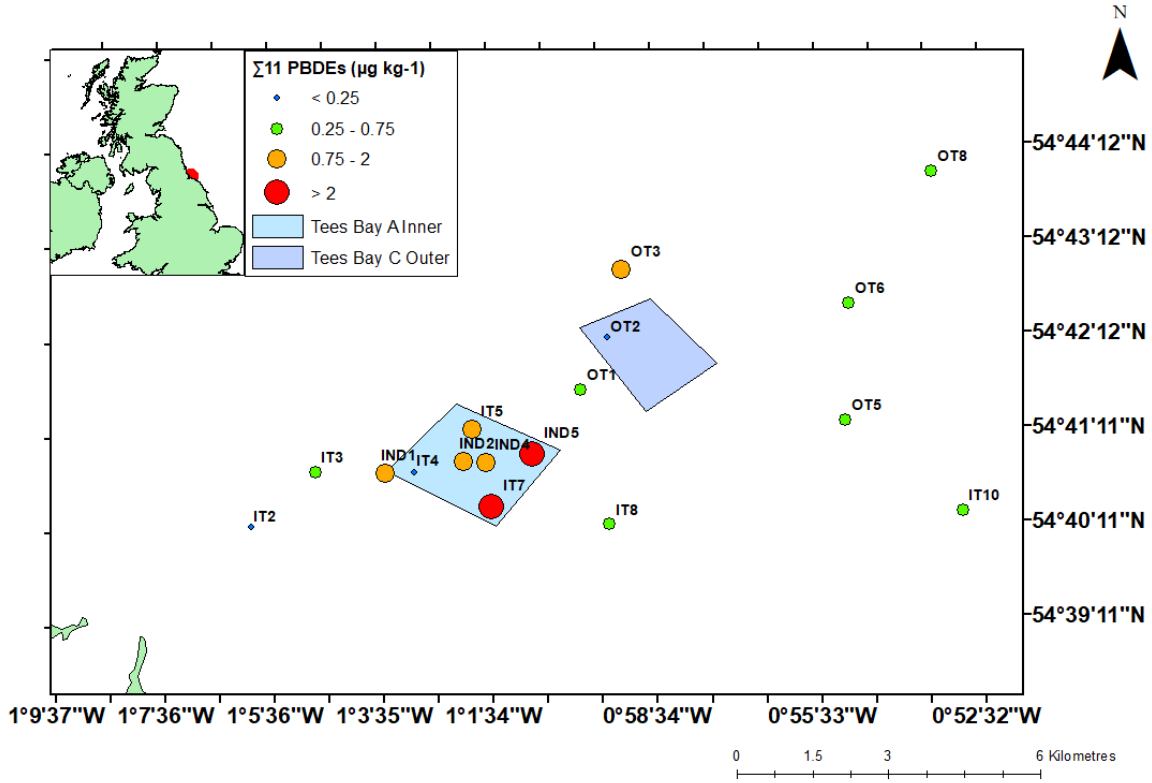

Figure 9. ∑11 PBDEs concentrations (µg kg^{-1} dw) of the sediments sampled within and in the vicinity of the Inner (left) and Outer (right) Tees dredged material disposal sites, July 2023.

BDE209 was detected at all the 17 Inner and Outer Tees stations (Figure 10) and at higher concentrations than the other measured organohalogens (range 0.17 µg kg^{-1} dw to 47.3 µg kg^{-1} dw). The highest concentration of 47.3 µg kg^{-1} dw was detected at IND4, with 45.2 µg kg^{-1} dw at IND5 and 35.4 µg kg^{-1} dw at IND2, all within the Inner Tees disposal site. Other notable values were also within the Inner Tees disposal site, with 21.9 µg kg^{-1} dw at IT7 and 12.7 µg kg^{-1} dw at IT5. Lowest concentrations meanwhile were evidenced at IT4, IT2 and OT2 (0.17 µg kg^{-1} dw, 0.27 µg kg^{-1} dw and 0.30 µg kg^{-1} dw, respectively). When included with the other BDEs, BDE209 constituted 63 to 98 % of the PBDEs present in the Inner and Outer Tees stations. BDE209 is indicative of the decaBDE technical mixture, which had been in use more recently than the other technical mixtures, although its use has been restricted in the EU since 2008.

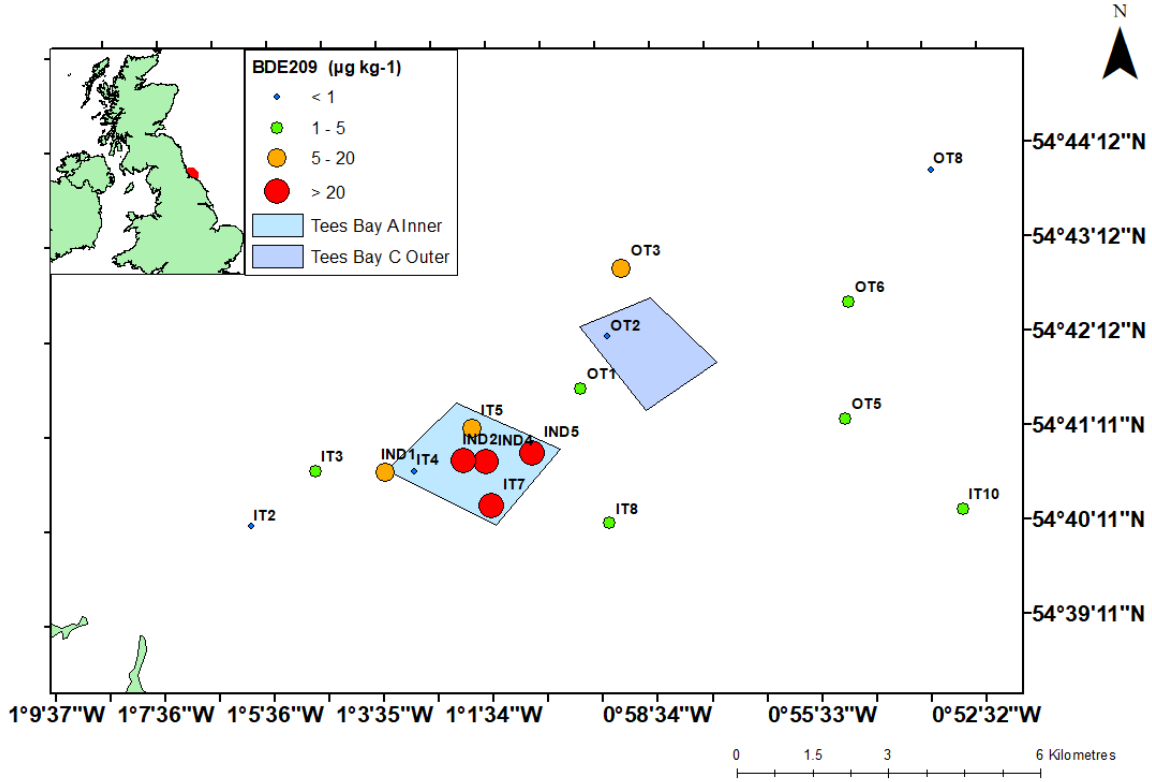

Figure 10. BDE209 concentrations (µg kg^{-1} dw) of the sediments sampled within and in the vicinity of the Inner (left) and Outer (right) Tees dredged material disposal sites, July 2023.

Organochlorinated pesticides (OCPs) were present at low concentrations, always <1 µg kg^{-1} dw, when detected across the Tees survey stations. ∑6 DDTs (dichlorodiphenyltrichloroethane) concentrations ranged from <LOD (limit of detection (i.e., 0.25 µg kg^{-1} dw)) to 2.04 µg kg^{-1} dw, with IND4, IT7 and IND5 having ∑6 DDTs concentrations of 2.04 µg kg^{-1} dw, 1.78 µg kg^{-1} dw, and 1.14 µg kg^{-1} dw, respectively (Figure 11). Hexachlorobenzene (HCB) was detected at 14 out of 17 stations at concentrations and ranged from <0.02 µg kg^{-1} dw (LOD) to 0.55 µg kg^{-1} dw, with the highest value at IT7 within the Inner Tees site. Dieldrin was detected at 16 out of 17 stations sampled at concentrations ranging from <0.02 µg kg^{-1} dw (LOD) to 0.48 µg kg^{-1} dw, and hexachlorocyclohexanes (HCHs) were detected at one of the 17 stations (∑3 HCHs range <LOD to 0.090 µg kg^{-1} dw), both these concentrations are close to their LODs.

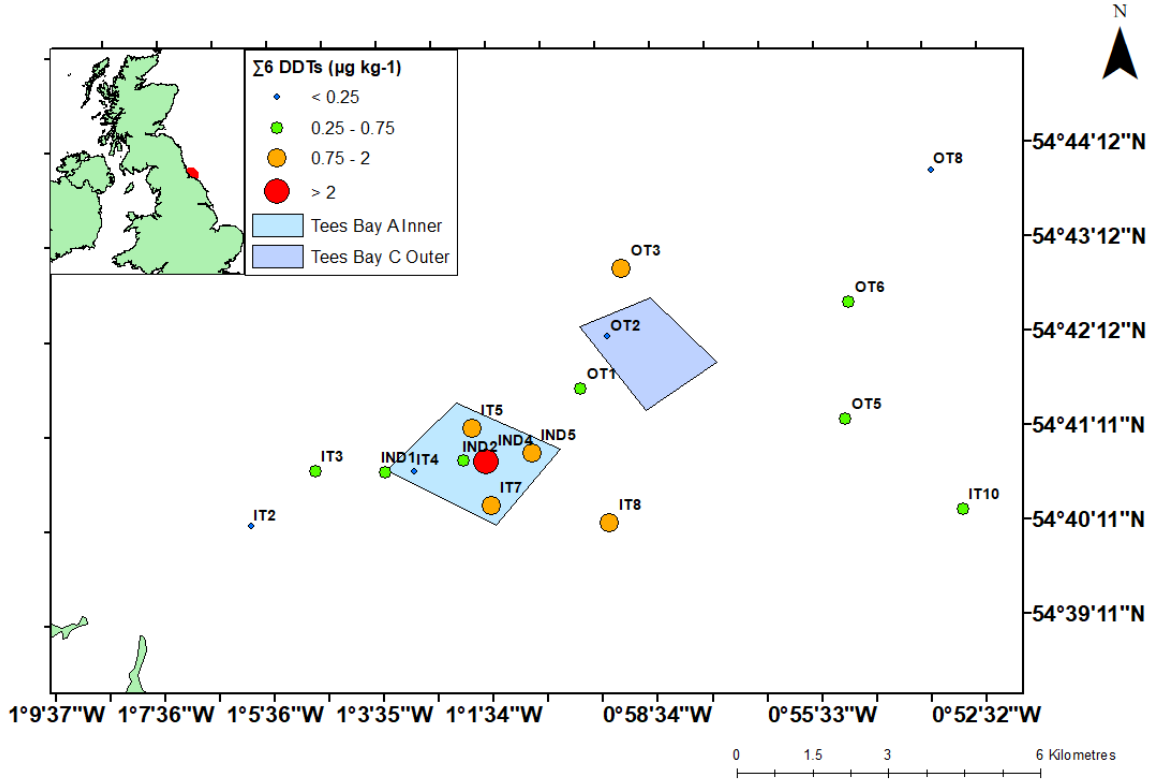

Figure 11. ∑6 DDTs concentrations (µg kg^{-1} dw) of the sediments sampled within and in the vicinity of the Inner (left) and Outer (right) Tees dredged material disposal sites, July 2023.

According to the OSPAR guidelines, all stations had 'good' environmental status for all ICES 7 PCBs and all PBDEs with Canada's Federal Environmental Quality Guidelines (FEQGs), and therefore had 'good' status overall. Concentrations of PCBs and dieldrin were below Cefas AL1 at all stations. ∑6 DDTs concentrations were above Cefas AL1 at three of the 17 stations: IND4, IT7 and IND5. No Cefas AL2 exists for ∑DDTs. Similarly, no Cefas ALs currently exist for PBDEs including BDE209, although some have recently been proposed for consideration by Defra as to whether to be implemented at a statutory level (Mason et al., 2021). These used the OSPAR Environmental Assessment Criteria (EACs) for a proposed AL2 (pAL2) and a value one third of this for a proposed AL1 (pAL1). Using these proposed levels, no stations are above pAL2 for any BDE, but IT2, IT7, OT3, IT10, OT6, OT5 and OT8 would be above pAL1 for BDE99 and IND2, IND4 and IND5 would be above pAL1 for BDE209. All other PBDEs are below pAL1 at all stations. Similarly, Cefas ALs have been proposed for individual PCB congeners, also using the OSPAR EACs for pAL2 and a value one third of this for pAL1. Using these proposed levels, no stations sampled at Tees in 2023 exceeded pAL2 for any PCB, but CB118 at three stations (OT1, OT6 and OT5) would be above pAL1 for CB118. All other PCBs were below pAL1 at all stations.

There are data available to investigate temporal trends of OHs contaminants from 2003 to 2023 (Table 4, Table 5, Table 6, Table 7). At most stations, ∑ICES 7 PCBs concentrations were similar to, or lower

than, what has been measured when last sampled in 2014 or 2021. Exceptions are at IND1 and IND5 where concentrations increased, concentrations at the latter in 2023 were above the range previously observed from 2003 to 2021. Meanwhile, concentrations observed at IT3 and IT7 in 2023, which were elevated in 2021, are once again within the range observed from 2006 to 2014.

For PBDEs, there is temporal trend data available from 2006 to 2023. At most stations, ∑11 PBDEs concentrations are similar to or lower than what has been measured when last sampled in 2014 or 2021. Exceptions are for IND1, IT3, IND2, IND5 and OT3 where concentrations increased, but still within the range previously observed from 2006 to 2021. IT5 and IT7, which had elevated results in 2021, are once again within the range observed from 2006 to 2014.

For BDE209, there is temporal trend data available from 2008 to 2023. At most stations, BDE209 concentrations are lower than what has been measured when last sampled in 2014 or 2021. The exceptions are at IND1, IT3, IND2, IND4, IND5, OT1, OT3 and IT10. For IND2, IND4 and IND5, BDE209 concentrations are above the range previously observed from 2008 to 2021.

There are data available to assess temporal trends of ∑DDTs from 2003 to 2023. Previous years to 2021 only included three chemicals in the total calculation, thus, the same is conducted here for the 2023 data. However, the additional o,p'- chemicals (see Sections 8.1.6 and 8.2) measured in 2023 would contribute less than a third extra to the ∑6DDTs. At most stations, ∑3DDTs concentrations are similar to or lower than what has been measured when last sampled in 2011 or 2021. Exceptions are at IT3, IND2, IND5 and OT1 where concentrations increased slightly. Levels at these stations are in the range previously observed from 2003 to 2021.

Table 4. Temporal trends (2003-2023) of ∑ICES 7 PCBs concentration (in µg kg^{-1} dw) at Inner and Outer Tees in the stations sampled during 2023.

	2003	2006	2007	2008	2009	2010	2011	~	2014	~	2021	2023
IT2	*0.7					*0.7	*0.7					0.06
IT1		0.83	1.54		2.13	2.04			2.71		0.71	
IND1		*0.7	*0.7	*0.7	1.96	*0.7	1.46				0.66	*0.79
IT3	*0.7	*0.7	5.09	*0.7		4.58	*0.7		*0.7		7.12	0.56
IT4	26.4	*0.7	2.8	*0.7	2.75	2.03	1.42		2.04		0.43	0.06
IND2		*0.7		*0.7	*0.7	2.72	*0.7		1.19		0.47	0.39
IND4			4.62	1.76	2.15	*0.7	1.23					1.10
IT5	*0.7	*0.7		0.92	*0.7	1.21	1.27				6.55	1.14
IT7	24.1	*0.7	1.7	*0.7	1.04	1.6	1.6		1.09		4.80	2.27
IND5			0.95	*0.7	*0.7	*0.7	*0.7		*0.7		0.28	1.97
IT8	*0.7	*0.7	1.5	1.64	1.79	1.13	1.23		4.67		2.69	1.02
OT1		*0.7		*0.7	*0.7	*0.7	*0.7		*0.7		0.26	0.43
OT2		*0.7		*0.7	*0.7	0.91	0.86		2.1			0.04
OT3		0.9	*0.7	*0.7	*0.7	1.17	0.84		*0.7			0.59
IT10	*0.7			1.08	0.93	1.85	1.0		1.37		1.33	0.44
OT8		*0.7		*0.7	*0.7	*0.7	*0.7		*0.7			0.11

* Represent concentrations where all ICES 7 congener concentrations were below LODs. In 2021, LODs are 10 times lower than in earlier years, 0.02 µg kg-1 dw for individual congeners instead of 0.2 µg kg-1 dw.

Table 5. Temporal trends (2003-2023) of ∑11 BDEs concentration (in µg kg^{-1} dw) at Inner and Outer Tees in the stations sampled during 2023.

	2006	2007	2008	2009	2010	2011	~	2014	~	2021	2023
IT2				0.30	5.44						0.08
IT1	3.75	2.43		1.75	2.73			3.03		0.44	
IND1	2.85	0.92	0.50	2.10	1.27	1.75				0.36	0.83
IT3	1.08	9.55	0.36		7.76	0.21		0.29		0.33	0.52
IT4	3.17	6.19	1.99	4.13	6.41	2.17		5.76		0.47	0.01
IND2	1.02		0.22	*0.11	29.4	0.43		2.51		0.28	0.76
IND4		3.31	2.99	2.57	1.18	1.27					1.10
IT5	1.04		1.84	1.45	1.87	2.54				6.10	1.18
IT7	1.32	1.20	0.64	1.40	3.04	3.11		2.34		26.8	2.95
IND5		1.19	0.20	0.20	0.19	2.68		0.32		0.19	2.09
IT8	1.22	2.51	0.95	1.66	1.19	1.89		2.20		2.06	0.73
OT1	0.84		0.18	0.23	0.53	0.46		2.05		0.15	0.32
OT2	1.06		0.38	0.43	1.24	1.08		2.84			0.09
OT3	1.71	1.04	0.73	0.26	1.26	1.15		2.69			0.76
IT10			0.60	0.68	2.85	1.42		2.27		1.04	0.69
OT8	0.96		0.79	0.35	0.58	0.60		0.52			0.27

*Represent estimates of concentrations for samples where all 11 PBDE congener concentrations were below limits of detection (LODs). Limits of detection for PBDEs improved between 2007 and 2008 and therefore values assigned to congeners below LOD are lower from 2008 onwards, resulting in a step decrease in ∑11 PBDEs concentration for samples with congeners below LODs.

Table 6. Temporal trends (2008-2023) of BDE209 concentration (in µg kg^{-1} dw) at Inner and Outer Tees in the stations sampled during 2023.

	2008	2009	2010	2011	~	2014	~	2021	2023
IT2		0.87	2.96						0.27
IT1		20.9	9.16			17.3		3.03	
IND1	1.46	9.65	3.29	17.4				0.82	6.44
IT3	1.17		31.0	0.05		0.86		0.51	2.84
IT4	13.3	26.6	12.3	3.11		31.9		0.93	0.17
IND2	*0.05	*0.05	32.4	2.21				1.28	35.4
IND4		9.95	2.65	3.22					47.3
IT5	7.42	2.16	10.0	8.71		8.79		46.6	12.7
IT7	1.76	5.27	10.5	12.71		105		34.3	21.9
IND5		*0.05	*0.05	10.1		0.88		0.74	45.2
IT8		5.89	3.54	7.74		10.1		9.64	4.52
OT1	0.58	0.70	2.35	0.26		7.4		0.50	2.17
OT2	1.27	1.38	2.56	0.56		9.7			0.30
OT3	2.37	0.80	3.57	0.71		6.26			7.91
IT10	2.19	1.97	6.43	1.36		7.45		3.10	4.41
OT8	0.75	*0.05	1.53	0.30		1.86			0.92

*Represent estimates of concentrations for samples where BDE209 concentrations were below limits of detection (LODs).

Table 7. Temporal trends (2003-2023) of ∑3DDTs concentration (in µg kg^{-1} dw) at Inner and Outer Tees in the stations sampled during 2023.

	2003	~	2006	2007	2008	~	2010	2011	~	2021	2023
IT2	0.60						*0.3				0.07
IT1			1.43	2.01			1.01			0.40	
IND1			0.85	0.99	1.12		0.47	0.80		1.12	0.66
IT3	0.41		0.64	3.73	0.63		1.95	0.44		0.31	0.45
IT4	0.55		0.88	1.63	0.88		0.89	0.78		0.15	*0.07
IND2			0.58		0.45		0.95	0.76		0.24	0.44
IND4				2.02	1.17		*0.3	0.93			1.73
IT5	0.41		0.65		1.55		1.15	0.99		2.25	0.72
IT7	3.65		0.60	1.4	0.81		1.58	1.14		2.55	1.45
IND5				1.81	0.41		0.3	0.68		0.15	1.00
IT8	0.45		0.65	1.91	0.71		0.91	1.04		1.44	0.83
OT1			0.58		0.64		1.12	0.67		0.16	0.29
OT2			0.81		0.66		2.08	0.84			*0.07
OT3			0.88	1.4	0.73		2.11	0.85			0.70
IT10	*0.3				0.89		0.84	0.93		0.82	0.49
OT8			0.78		0.65		*0.3	0.62			0.14

*Represent estimates of concentrations for samples where ∑DDTs concentrations were below limits of detection (LODs). ∑DDTs is the sum of three chemicals (p,p'-DDE, p,p'-TDE, p,p'-DDT). Limits of detection for individual DDTs improved between 2011 and 2021 by a factor of 2-10, depending on chemical.

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6 Appendix 1: Sediment particle size assessment methods

Sediment samples were analysed at half phi intervals using a combination of laser diffraction (<2 mm fraction) and dry sieving techniques. Traditionally, dry sieving is completed for all sediment >1 mm fraction based on the National Marine Biological Analytical Quality Control Scheme PSA guidance (Mason, 2022). However, for the Tees 2023 samples, as the <63 µm can be requested for trace metals analyses the PSA methodology has been adapted and the sediment is wet split at 63 µm instead of 1 mm, and then all the sediment >63 µm fraction is dry sieved at half phi intervals. For temporal comparisons, the results were summarised by using half phi intervals to 63 µm using sieve data only, and total <63 µm representing the silt/clay (mud) fraction.

Further work is underway to compare both methods currently measured. Gradistat software (Blott and Pye, 2001) was used to produce sediment statistics. In addition, the sieved full particle size distribution (PSD) data (at 0.5 ϕ intervals) were grouped using the *kmeans* clustering function in R (R Core Team, 2023). This method of clustering is widely used for such datasets, for example, see Cooper and Barry (2020). Five sediment groups were determined as the best group output for the Tees sediment sample data, based on a combination of the highest Calinski–Harabasz (C–H) statistic (Orpin and Kostylev, 2006), alongside expert judgement. Sediment characteristics and profiles for each of these final groups are presented in the results section of this report (Section 4.1).

7 Appendix 2: Polycyclic aromatic hydrocarbons (PAHs) assessment methods

7.1 Sample extraction

Sediment samples, collected in glass jars, were frozen immediately after collection and not defrosted until required for analysis. Each homogenized wet sediment sample was extracted using alkaline saponification followed by liquid/liquid extraction. A sample of sediment was taken for a total solids determination as all results are reported on a dry weight (dw) basis. The sample extract was then passed through an alumina chromatography column in order to remove polar compounds, concentrated to 1 ml and sealed in a vial. A suite of alkylated and parent PAH were then determined using coupled gas chromatography/mass spectrometry (GC/MS). Quantification was by means of deuterated internal standards added prior to digestion, with analytical quality control samples being run within each sample batch. Full details can be found in Kelly et al. (2000).

7.2 Method used for assessment

Cefas currently has action level limits for contaminants such as trace elements and PCBs but none currently exist for PAHs. Reviews of what has been investigated in other countries has indicated that the most promising of the currently available co-occurrence methods is the Effects Range Low/Effects Range Median (ERL/ERM) methodology which is founded on a large database of sediment toxicity and benthic community information (Long et al., 1998).

The ERL/ERM methodology derives SQGs (sediment quality guidelines) representing, respectively, the 10^{th} and 50^{th} percentiles of the effects dataset and can be derived for individual PAH compounds. In a regulatory context, where SQGs are to be used as informal (non-regulatory) benchmarks to aid in the interpretation of sediment chemistry (Long et al., 1998), this becomes complicated where a large number for individual PAH are determined, as is usually the case. This has led to separate ERL/ERM derived SQGs being set for “Low molecular weight PAHs” and “High molecular weight PAHs”. In this context, LMW PAHs include 2- and 3-ring PAH compounds: naphthalene; monomethyl naphthalenes; acenaphthene; acenaphthylene; fluorene; phenanthrene; and anthracene. HMW PAHs include the 4- and 5-ring PAH compounds: fluoranthene; pyrene; benz[*a*]anthracene; chrysene; benzo[*a*]pyrene; and, dibenz[*a,h*]anthracene. Although a wider suite of PAHs is routinely determined for both licensing and monitoring purposes, these can be considered as toxicity markers for the PAH as a whole. The ERL and ERM concentrations applied are given in Table 8.

Table 8. ERL and ERM concentrations for LMW and HMW PAHs in sediments. The limits for LMW PAH are lower than those for HMW PAH as they carry a higher acute toxicity.

PAH compounds	ERL (µg kg^{-1} dw)	ERM (µg kg^{-1} dw)
LMW PAH	552	3,160
HMW PAH	1,700	9,600

8 Appendix 3: Organohalogens (OHs) assessment methods

8.1 Methods

Full details of the analytical methodology are given in Bersuder et al. (2020).

8.1.1 Sample extraction

Sediment samples were air dried and sieved (<2 mm) in a controlled environment. 10 g of dried sediment were mixed with sodium sulphate, transferred to a glass Soxhlet thimble and topped with 1 cm of sodium sulphate. A solution containing $^{13}C_{12}$-labelled ICES7 PCBs ($^{13}C_{12}$-CB28, $^{13}C_{12}$-CB52, $^{13}C_{12}$-CB101, $^{13}C_{12}$-CB118, $^{13}C_{12}$-CB138, $^{13}C_{12}$-CB153 and $^{13}C_{12}$-CB180), labelled OCPs (d_6-alpha-HCH, d_6-gamma-HCH, $^{13}C_6$-HCB and $^{13}C_{12}$-p, p'-DDT), fluorinated-BDEs (F-BDE69 and F-BDE160), and $^{13}C_{12}$-labelled BDE209 was added as recovery standard to all samples prior to the extraction step. Samples were extracted over a 6 h period using 50:50 *iso*-hexane:acetone, with an average of 9 - 10 cycles h^{-1}. Sulphur residues were removed at this stage with copper filings.

8.1.2 Sample extract clean-up

An aliquot of the Soxhlet extract was cleaned up and using alumina (5 % deactivated) columns. The eluate contained polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polybrominated diphenylethers (PBDEs).

8.1.3 Analysis of PCBs and OCPs by GC-MS/MS

After addition of internal standard CB53, CB112 and CB200, PCB and OCP concentrations were determined with an Agilent 7890A GC coupled with 7000 QQQ-MS/MS in positive electron impact mode (ESI+). The separation of analytes was performed using two 25.0 m × 200 µm, 0.33 µm-film-thickness DB-5 capillary columns (J&W) with a backflush system installed. The carrier gas and collision gas were helium (1.4ml min^{-1}) and nitrogen (1.5ml min^{-1}), respectively. The initial oven temperature was 90 °C, held for 2 min, then increased to 165 °C at 15 °C min^{-1}, to 285 °C at 2 °C min^{-1}, to 310 °C at 40 °C min^{-1} and finally held for 10 min, with the column backflush instigated when the oven reached 285 °C (total run time 71.7 mins). The injector temperature, ion source and quadrupole temperatures were 270 °C, 280 °C and 150 °C, respectively. A 1-µl extract was injected in pulsed-splitless mode with a purge time of 2 min.

8.1.4 Analysis of PBDEs by GC-MS/MS

After addition of internal standard CB200, PBDE concentrations were determined with a Shimadzu 2010plus GC with TQ8050 QQQ-MS/MS in positive electron impact mode (ESI+). The separation of analytes was performed on a 15.0 m × 250 µm, 0.15-µm-film-thickness Rtx-1614

capillary column (Restek). The carrier gas was helium (1.28 ml min^{-1}) and the collision gas was argon. The initial oven temperature was 120°C, held for 1.00 min, then increased to 275°C at 15 °C min^{-1}, to 300 °C at 50 °C min^{-1}, and finally held for 5 min. The injector temperature and source temperature were 340 °C and 230 °C, respectively. A 1-µl extract was injected in pulsed-splitless mode with a purge time of 2 min.

8.1.5 Analysis of BDE209 by GC-MS

BDE209 concentrations were determined with an Agilent 6890Plus GC with 5975C MS in NCI mode. The separation of analytes was performed on a 15.0 m x 250 µm, 0.1-µm-film-thickness DB-1 capillary column (J&W). The carrier gas was helium (1.3 ml min^{-1} constant flow, average velocity 59 cm s^{-1}) and the reagent gas was methane (40 psi). The initial oven temperature was 90 °C, held for 1.0 min, then increased to 200 °C at 25°C min^{-1}, to 295 °C at 10 °C min^{-1}, and finally held for 20 min. The injector temperature and detector temperature were 250 °C and 200 °C, respectively. A 1-µl extract was injected in pulsed splitless mode with a 20 psi pulse until 1 min and a purge time of 2 min.

8.1.6 Quantitation methods

The identification of PCBs and OCPs was based on the retention time of individual standards in the calibration mixtures. Quantitation was performed using internal standards and nine calibration levels (range 0.1 to 200 ng ml^{-1}). The combined PCB and OCP standard solutions contained the following 41 compounds in iso-octane: Hexachlorobenzene; hexachlorobutadiene, alpha-HCH, beta-HCH, gamma-HCH, *p,p'*-DDE, *p,p'*-TDE, *p,p'*-DDT, *o,p'*-DDE, *o,p'*-TDE, *o,p'*-DDT, dieldrin, heptachlor, heptachlor epoxide, endosulfan-I, endosulfan-II, endosulfan sulfate; IUPAC CB101; IUPAC CB105; IUPAC CB110; IUPAC CB118; IUPAC CB128; IUPAC CB138; IUPAC CB141; IUPAC CB149; IUPAC CB151; IUPAC CB153; IUPAC CB156; IUPAC CB158; IUPAC CB170; IUPAC CB18; IUPAC CB180; IUPAC CB183; IUPAC CB187; IUPAC CB194; IUPAC CB28; IUPAC CB31; IUPAC CB44; IUPAC CB47; IUPAC CB49; IUPAC CB52; IUPAC CB66. Concentrations were corrected for the recovery of the labelled recovery standards.

Quantitation for PBDEs was performed using internal standards and 10 calibration levels (range 0.05 to 100 ng ml^{-1}). The PBDE standard solutions contained the following 11 compounds in iso-octane: IUPAC BDE17; IUPAC BDE28; IUPAC BDE47; IUPAC BDE66; IUPAC BDE100; IUPAC BDE99; IUPAC BDE85; IUPAC BDE154; IUPAC BDE153; IUPAC BDE138; IUPAC BDE183; plus an additional 13 compounds: IUPAC BDE3; IUPAC BDE7; IUPAC BDE15; IUPAC BDE49; IUPAC BDE71; IUPAC BDE77; IUPAC BDE119; IUPAC BDE126; IUPAC BDE156; IUPAC BDE184; IUPAC BDE191; IUPAC BDE196; IUPAC BDE197; together with the internal standard IUPAC CB200 and recovery standards F-BDE69 and F-BDE-160. Concentrations were corrected for the recovery of the F-BDE recovery standards.

Quantitation of BDE209 was performed using an internal standard and seven calibration levels (range 0.5 to 500 ng ml^{-1}). The BDE209 standard solutions contained IUPAC BDE209 in iso-octane, plus an additional three compounds IUPAC BDE206; IUPAC BDE207; IUPAC BDE208; together with the internal standard $^{13}C_{12}$-labelled IUPAC BDE209.

8.1.7 Quality assurance/ quality control procedures

AQC procedures included reagents purification, method blanks, and use of control charts created from repeated analysis of the NIST-1944 Certified Reference Material (CRM) and Quasimeme CEMP-245 materials.

8.2 Method used for assessment

PCB, OCP and BDE concentrations were determined in the sediments and reported on a dry weight basis. The ∑ICES 7 CBs (CB28, CB52, CB118, CB153, CB138, CB170, CB183), and the sum of all 25 measured CBs (∑CBs) were calculated, together with ∑DDTs (*p,p'*-DDE, *p,p'*-TDE, *p,p'*-DDT, *o,p'*-DDE, *o,p'*-TDE, *o,p'*-DDT). Where individual congener concentrations were below the limit of detection (LOD) of 0.02 µg kg^{-1}, a value of half the LOD was inserted for calculation of summed concentrations. The ∑11 BDEs were calculated. Where individual congener concentrations were below the LOD of 0.02 µg kg^{-1}, a value of half the LOD was inserted for calculation of summed concentrations. The congener patterns were evaluated, with BDE183 a marker constituent of the octa-BDE technical mix, and the other BDEs constituents of the penta-BDE technical mix. Additionally, BDE209 ("Deca BDE") concentrations were calculated. Where BDE209 concentrations were below the LOD of 0.1 µg kg^{-1}, a value of half the LOD was inserted.

The Total Organic Carbon (TOC) content in the <2 mm fraction determined at the sampling stations was used to additionally calculate the contaminant concentration normalised to 2.5 % TOC content.

Concentrations of PCBs and OCPs in the sediment were compared with various action limits, to investigate whether any adverse effects in benthic biota were likely to expected as a consequence of their presence. There are no action limits available to compare PBDE concentrations with at the present, although some were recently proposed. Concentrations are expressed on a dry weight basis unless otherwise stated.

The current Cefas action limits for dredge disposal are: PCBs Action level 1 if ∑ICES7 CBs > 10 µg kg^{-1} or ∑CBs > 20 µg kg^{-1} and action levels 2 if ∑CBs > 200 µg kg^{-1}; OCPs Action level 1 if ∑DDTs > 1 µg kg^{-1}, dieldrin > 1 µg kg^{-1}, no Action level 2 for either ∑DDTs or dieldrin. Concentrations are expressed on a dry weight basis.

OSPAR in Charting Progress2 (CP2) have set criteria for Background Assessment Concentrations (BAC) and Environmental Assessment Concentrations (EAC) for the ICES7 CBs in sediments (see Table 9). Concentrations are expressed in µg kg^{-1} dry weight normalised to 2.5 % organic carbon. Concentrations below BACs would be considered to have high environmental status.

Concentrations significantly below EACs could be considered to have good environmental status and those above, bad environmental status.

Table 9. OSPAR assessment criteria for CBs in sediment from CP2.

Sediment (µg kg^{-1} dry weight, normalised to 2.5 % TOC)		
Compound	**BAC**	**EAC**
CB28	0.22	1.70
CB52	0.12	2.70
CB101	0.14	3.00
CB118	0.17	0.60
CB138	0.15	7.90
CB153	0.19	40.00
CB180	0.10	12.00

OSPAR MIME have recently adopted the Canadian FEQG (Federal Environmental Quality Guidelines) levels as EAC results for PBDEs, and also calculated BAC values. These thresholds are shown in Table 10.

Table 10. OSPAR assessment criteria for BDEs in sediment from Canadian FEQGs.

Sediment (µg kg^{-1} dry weight, normalised to 2.5 % TOC)		
Compound	**BAC**	**EAC**
BDE28	0.05	110.00
BDE47	0.05	97.50
BDE66	0.05	97.50
BDE85	0.05	1.00
BDE99	0.05	1.00
BDE100	0.05	1.00
BDE153	0.05	1100.00
BDE154	0.05	1100.00
BDE183	0.05	14000.00
BDE209	0.05	47.50

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