

Dredged Material Disposal Site Monitoring Round the Coast of England: Results of Sampling (2020-2021)

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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 Service Level Agreement (SLA 1.2) project (C6794 hereafter) round the coast of England during 2020-2021 (financial year).

The main aims of this report are:

- o to aid the dissemination of the monitoring results;
- to assess whether observed changes resulting from dredged material disposal are in line with predictions;
- o 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.

One disposal site was targeted for assessment during this period*: Inner Tees (TY160). Seabed sampling at 11 stations within and in the vicinity of TY160 in April 2021 revealed that chlorobenzenes (CBs) (Σ ICES 7 CBs range 0.26-7.1 µg kg⁻¹ dw) and the brominated diphenyl ethers (BDEs) BDE47 and BDE99 (Σ 11 BDEs range 0.2-26.8 µg kg⁻¹ dw) were detectable within the sediments at all the sampled stations. While organochlorines (OCs) were not detected at some stations, they were present at low concentrations (generally <1.0 µg kg⁻¹ dw) at others, except for p,p'-TDE which displayed a concentration of 1.4 µg kg⁻¹ dw at one station within the disposal site.

According to OSPAR guidelines, most stations had 'good' environmental status for all ICES 7 CBs and 'good' status overall. One station inshore of the disposal site was classed as 'bad' environmental status for CB118 but 'good' status overall, while a further station inside the site was categorised as 'bad' environmental status for BDE99 but 'good' status overall. No station was classed as 'bad' status overall.

Concentrations of CBs and dieldrin were below Cefas action level 1 (AL1) at all stations. ∑6 DDTs concentrations were above Cefas AL1 at four (i.e., IT7, IT5, IT8 and IND1) of the 11 stations.

As the Inner Tees disposal site has been the subject of seabed sampling for sediment contaminants over a number of years (as far back as 2003), comprehensive data exist from which a temporal assessment can be undertaken. The data reveal that OH concentrations have remained more-or-less comparable, although some stations, both within and outside the disposal site, displayed increased levels of certain OH compounds (e.g., CBs and BDEs) in 2021.

The data acquired through the sampling conducted in 2021 have allowed an important assessment of the current levels of OHs in the sediments within and in the vicinity of the Inner Tees dredged material disposal site. The site continues to represent an important recipient of significant amounts of material dredged from the Tees and, given the industrial nature of the estuary and its legacy sediment contamination, subsequent assessments of the site would be regarded as necessary. Unless significant changes to the disposal regime of the site are anticipated, we propose that sampling for sediment contaminants at Inner Tees, which should potentially also include polycyclic aromatic hydrocarbons (or PAHs), be conducted *circa* every three years.

* The delayed survey, planned for the 2020-2021 financial year period, was conducted during April 2021.

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 the UK 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 Protocol, 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 the London Protocol, 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). 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' Science for Sustainable Marine Management (SSMM) 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 approximately 110 open sites (numerous sites are opened and closed every year) designated for dredged material disposal round 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. Humber) or on intertidal mudflats as part of beneficial use schemes (Bolam et al., 2006).

Although total quantities vary year to year, approximately 40 Mt (wet weight) are annually disposed to coastal sites around England. Individual quantities licensed may range from a few hundred to several million tonnes, and the nature 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' SSMM team and the licensing team within the MMO. The scientific outcomes of the work undertaken within C6794 are circulated to the Cefas SSMM 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, within which a summary of the findings is presented (Section 2), forms an important element of such scientific communication. The current report, which presents the findings of work undertaken during 2020-21, constitutes the 13th in the series. The previous reports are accessible *via* the Defra website:

https://www.gov.uk/government/publications?departments%5B%5D=centre-for-environment-fisheriesand-aquaculture-science

It is not the purpose of this report to present a detailed appraisal of the processes giving rise to impacts at a site (see Section 1.5) but to encapsulate the essence of the impacts associated with this activity in its entirety around the coast of England.

1.4 Sites monitored

To aid with determining which disposal sites should be selected for sampling in any one 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 disposal site, and where these lie within the tiering system (i.e. their perceived environmental risk) depict where that site lies within the tiered system. This ultimately determines whether that site is considered for sampling during a particular year. It is intended that this approach increases the transparency of the decision-making process regarding disposal site selection for C6794 monitoring, i.e. it establishes a model for site-specific decisions regarding sampling.

A tiered survey design and site assessment system, therefore, facilitates the prioritisation of dredged material disposal sites in terms of the need for, and the scale of, monitoring required at each site. In practice, this method provides a scientifically valid rationale for the assessment of risks associated with relinquished, current and proposed disposal sites to the surrounding environment and amenities.

One disposal site was targeted for Cefas monitoring during 2020-21: Inner Tees (TY160). This site was identified following consultation between Cefas' SSMM team, Cefas scientists in a number of key disciplines (e.g. benthic ecology, sediment contaminants), together with a significant involvement from the MMO. A further site was assessed under this project during this reporting period, Nab Tower (off the Isle of Wight). The outcomes of the desk-based, modelling study for that site are presented in a separate report.

1.5 Aims and structure 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' SSMM 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). The aims of this report are:

- to present the results of sampling undertaken during 2020-21 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 2020-21 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; and 2019 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.

In accordance with the format first established for Bolam et al. (2011a), and that used within subsequent reports (Bolam et al., 2012a; 2012b; 2014b; 2015a; 2015b; 2016b; 2017; 2018; 2019; 2020), the main findings and conclusions regarding Inner Tees are presented within Section 2 (below). More detailed scientific data for the site, together with their interpretation, are described in Section 5. For background information regarding the Inner Tees disposal site, the reader is directed towards Sections 5 and 6.

2 Conclusions and implications for further monitoring

The main findings of the monitoring undertaken during 2020-21 are presented within this section, together with their implications regarding the need for subsequent monitoring under C6794. However, it should be noted that these data, and the conclusions based on them, do not represent the sole basis of such final decisions regarding monitoring; up-to-date intelligence regarding potential changes to the disposal regime and/or stakeholder concerns are all embraced within, and have a direct bearing on, the selection process for disposal site monitoring under this project. Thus, the recommendations for monitoring presented here, although representing an important component of the decision-making process, may or may not be altered by other factors.

2.1 Inner Tees

The Inner Tees 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 site has been the recipient of monitoring under SLAB5 for several years (Bolam et al., 2009; 2011a; 2012; 2014b). The disposal site has been shown to have a very homogeneous substrate of muddy sand with occasional small lumps of black mud and black flecks indicative of coal particles (Bolam et al., 2009; 2011). The site receives most of the 2.7 Mt of maintenance dredged material per year from the Tees Estuary, the Seaton Channel and Hartlepool.

Seabed sampling at 11 stations in 2021 revealed that sediment organic carbon concentrations ranged between 0.25 and 5.83 % m/m in the <2 mm sediment fraction: these are slightly lower than in previous years.

Assessment of the sediments for organohalogens (OHs) revealed that both chlorobenzenes (CBs) (\sum ICES 7 CBs range 0.26-7.1 µg kg⁻¹ dw) and the brominated diphenyl ethers (BDEs) BDE47 and BDE99 (\sum 11 BDEs range 0.2-26.8 µg kg⁻¹ dw) were detectable at all the sampled stations. While organochlorines (OCs) were not detected at some stations, they were present at low concentrations (generally <1.0 µg kg⁻¹ dw) at others, except for p,p'-TDE which displayed a concentration of 1.4 µg kg⁻¹ dw at one station within the disposal site.

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Concentrations of CBs and dieldrin were below Cefas action level 1 (AL1) at all stations. ∑6 DDTs concentrations were above Cefas AL1 at four (i.e., IT7, IT5, IT8 and IND1) of the 11 stations.

As the Inner Tees disposal site has been the subject of seabed sampling for sediment contaminants over a number of years (as far back as 2003), comprehensive data exist from which a temporal assessment can be undertaken. The data reveal that OH concentrations have remained more-or-less comparable, although some stations, both within and outside the disposal site, displayed increased levels of certain OH compounds (e.g., CBs and BDEs) in 2021.

The data acquired through the sampling conducted in 2021 have allowed an important assessment of the current levels of OHs in the sediments within and in the vicinity of the Inner Tees dredged material disposal site. The site continues to represent an important recipient of significant amounts of material dredged from the Tees and, given the industrial nature of the estuary and its legacy sediment contamination, subsequent assessments of the site would be regarded as necessary. Unless significant changes to the disposal regime of the site are anticipated, we propose that sampling for sediment contaminants at Inner Tees, which should potentially also include polycyclic aromatic hydrocarbons (or PAHs), be conducted *circa* every three years.

3 Acknowledgements

Many Cefas staff have helped contribute to the work which has been conducted to produce this report. Such staff have been involved in all aspects of the work from an early stage, e.g. during discussions of the specific issues regarding dredged material disposal sites around the coast of England (e.g. Cefas' SSMM team), through to the field sampling and the laboratory processing of the various components. Staff within the Cefas Sedimentology and Chemistry teams are gratefully thanked for processing the samples which form the core of this report. Finally, staff on the RV *Cefas Endeavour* CSEMP survey are to be thanked for their role in acquiring the samples which form the basis of the present report.

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5 Results (Appendix 1)

5.1 Inner Tees Background

The Inner Tees 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 site has been the recipient of monitoring under SLAB5 for several years (Bolam et al., 2009; 2011a; 2012; 2014b). The Inner Tees disposal site has been shown to have a very homogeneous substrate of muddy sand with

occasional small lumps of black mud and black flecks indicative of coal particles (Bolam et al., 2009; 2011). The site receives most of the 2.7 Mt of maintenance dredged material per year from the Tees Estuary, the Seaton Channel and Hartlepool.

Many chemical industries, including brominated flame-retardant producers, are located along the Tees 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).

Under C6794, sediments of the Inner Tees disposal site, and those of its environs, were assessed for sediment organic carbon and organohalogens (OHs hereafter) concentrations during the reporting period 2020-21 (the delayed survey was conducted during April 2021). In consequence to its historical legacy, brominated flame retardants continue to be an issue regarding dredging and marine disposal of sediments. Stations previously sampled by Cefas under the auspices of SLAB5 were targeted to allow a temporal assessment to be conducted.

5.2 Survey design

The survey at Inner Tees comprised of 11 seabed stations; five (IT4, IT5, IT7, IND2, IND5) within the disposal site and six (IT1, IT3, IT8, IT10, OT1, IND1) positioned at various distances outside, and different directions from, the disposal site boundary (Figure A1.1). These stations have been previously sampled under the auspices of C6794/SLAB5 and thus their targeting in 2021 was heavily weighted by the opportunity to afford a temporal assessment of seabed variables. The principle of this historic design is that while the stations inside the site provide an assessment of sediments characteristics that are likely to be directly affected by dredged material disposal, those (IT1, IT8) in the immediate vicinity and along the main sediment transport pathway which runs along a SSE-NNW trajectory are likely to reflect indirect changes resulting from the disposal (i.e., following sediment dispersal from either the plume or subsequent remobilisation and deposition). Stations located away from the main transport pathway (IT3, IT10, OT1) are intended to reflect the unimpacted scenario. The samples were acquired using a Shipek grab during 27th April 2021 aboard the RV Cefas Endeavour.

5.3 Inner Tees Results

5.3.1 Sediment organic carbon

The organic carbon concentrations of the sediments sampled at Inner Tees range from 0.25 to 5.83 % m/m in the <2 mm sediment fraction (Figure A1.1). These are slightly lower than in previous years (Figure A1.2) but within a comparable range (based on Inner Tees data from 2009, 2010, 2011, 2014 and 2021).



Figure A1.1. Organic carbon (% m/m) in the <2 mm fraction at Inner Tees, 2021.





5.3.2 Sediment organohalogens (OHs)

The sediment samples were processed and analysed, and the data assessed, in accordance with current OSPAR guidelines (OSPAR, 2018). Chlorinated biphenyls (CBs) were detected at all the 11 stations sampled at Inner Tees in 2021 (Σ ICES 7 CBs range 0.26-7.1 µg kg⁻¹ dw). Three of the five highest Σ ICES 7 CB concentrations (7.1, 2.7 and 1.3 µg kg⁻¹ dw) were found outside of the disposal site at IT3, IT8 and IT10 respectively (Figure A1.3). Other high values of 6.5 and 4.8 µg kg⁻¹ dw (at IT5 and IT7 respectively) were located within the disposal site (Figure A1.3). Lowest concentrations, with Σ ICES 7 CB concentrations of 0.3 µg kg⁻¹ dw, were observed at OT1 and IND5.



Figure A1.3. \sum ICES 7 CB concentrations sampled at Inner Tees, 2021.

Brominated diphenyl ethers (BDEs), specifically BDE47 and BDE99, were detected at all the sampled stations ($\sum 11$ BDEs range 0.2-26.8 µg kg⁻¹ dw). The highest $\sum 11$ BDEs concentrations were located within the disposal site at IT7 (26.8 µg kg⁻¹ dw) and IT5 (6.1 µg kg⁻¹ dw) (Figure A1.4); the next highest values of 2.1 and 1.0 µg kg⁻¹ dw being found to the east of the disposal site at IT8 and IT10, respectively. Lowest concentrations were at OT1 and IND5 (Figure A1.4), with $\sum 11$ BDEs concentrations of 0.2 µg kg⁻¹ dw. Two congeners, BDEs 99 and 47, were responsible for 54-65 % of the $\sum 11$ BDEs concentrations. BDE183 was detected at nine of the 11 stations which is indicative of the widespread use of the octa- or deca-BDE technical mixes.



Figure A1.4. ∑11 BDEs concentrations sampled at Inner Tees, 2021.

BDE209 was also detected at all stations and at higher concentrations than the other measured organohalogens (range 0.5-46.6 μ g kg⁻¹ dw). The highest BDE209 concentration of 46.6 μ g⁻¹ kg dw was detected at IT5, with 34.7 μ g kg⁻¹ dw at IT7, both within the disposal site (Figure A1.5). Other notable values were to the east of the disposal site at IT8 (9.6 μ g kg⁻¹ dw) and IT10 (3.1 μ g kg⁻¹ dw), and to the northwest of the site at IT1 (3.0 μ g kg⁻¹ dw). Lowest BDE209 concentrations were at OT1 (northeast of the disposal site) and IT3 (west of the site), with concentrations of 0.50 and 0.5 μ g kg⁻¹ dw respectively (Figure A1.5). When included with the other BDEs, BDE209 constituted 56-88 % of the BDEs present across the Inner Tees stations. This BDE209 proportion is lower than what was observed in 2014 at Inner Tees, when BDE209 made up 73-98 % of the BDEs present. BDE209 is indicative of the deca-BDE technical mixture which has been in use more recently than the other technical mixtures, although it's use too has been restricted in the EU since 2008.



Figure A1.5. BDE209 concentrations for the Inner Tees, 2021.

While organochlorine pesticides (OCs) were not detected at some stations, they were present at low concentrations (generally <1.0 μ g kg⁻¹ dw) when detected, except for p,p'-TDE (1.4 μ g kg⁻¹ dw at IT7 within the disposal site). The $\sum 6$ DDT (dichlorodiphenyltrichloroethane) concentrations were in the range 0.2-3.0 μ g kg⁻¹ dw, with IT7, IT5, IT8 and IND1 displaying \sum DDT concentrations of 3.0, 2.6, 1.7 and 1.4 μ g kg⁻¹ dw respectively (Figure A1.6). The majority of the \sum DDT concentrations were DDT metabolites p,p'-TDE and p,p'-DDE. Hexachlorobenzene (HCB) was detected at all 11 stations at concentrations ranging from 0.1-3.6 μ g kg⁻¹ dw; the highest concentration being observed at IT7 in the southern region of the disposal site. Dieldrin (concentrations ranging from <0.1-0.4 μ g kg⁻¹ dw) and HCHs (hexachlorohexanes) (\sum HCHs concentrations range <LOD-0.3 μ g kg⁻¹ dw) were both detected at 10 out of 11 stations. However, these concentrations were close to the limit of detection (LOD) for both compounds.



Figure A1.6. 56 DDTs concentrations for the Inner Tees, 2021.

According to OSPAR guidelines, most stations had 'good' environmental status for all ICES 7 CBs and 'good' status overall. IT3 (inshore of the disposal site) had 'bad' environmental status for CB118 but 'good' status overall, while IT7 had 'bad' environmental status for BDE99 but 'good' status overall. Notably, no station was classed as 'bad' status overall.

Concentrations of CBs and dieldrin were below Cefas action level 1 (AL1) at all stations. Σ 6 DDTs concentrations were above Cefas AL1 at four (i.e., IT7, IT5, IT8 and IND1) of the 11 stations. No Cefas AL2 exists for Σ DDTs.

Currently, no Cefas ALs exist for BDEs including BDE209, but some have recently been proposed. These proposed ALs used the OSPAR EACs for AL2 and a value 1/3 of this AL1. Based on these proposed levels, BDE99 concentrations at IT5, IT10, IT8 and OT1 exceeded Cefas AL1, and that at IT7 in the southern part of the disposal site was above Cefas AL2. Meanwhile, measured BDE209 concentrations at IT7 and IT5 were higher than Cefas AL1 for BDE209. All other BDEs were below Cefas AL1 at all stations. Similarly, using the OSPAR EACs for AL2 and a value 1/3 of this for AL1, Cefas ALs have been proposed for individual CB congeners. Using these proposed levels, one station (IT3) exceeded Cefas AL2 for CB118 and five stations (IT10, IT5, IT7, OT1 and IT8) were above Cefas AL1 for CB118. All other CBs were below AL1 at all stations.

There are data available to assess temporal trends of OH contaminants from 2003 to 2021 (see Table A1.1. to Table A1.4). At most stations, CB concentrations were similar to, or lower than, those measured in 2014. Exceptions were at IT3 (inshore of the disposal site), IT5 and IT7 (both inside the disposal site) where concentrations increased in 2021 (Table A1.1.). Indeed, concentrations at IT3 and IT5 in 2021 were above the range previously observed from 2003-14.

Table A1.1. Temporal trends (2003-2021) of ∑ICES 7 CBs concentrations (µg kg⁻¹ dw) at Inner Tees, 2021.

	2003	2006	2007	2008	2009	2010	2011	~	2014 ~	2021
IT1		0.83	1.5		2.1	2.0			2.7	0.7
IND1		*0.7	*0.7	*0.7	2.0	*0.7	1.5			0.7
IT3	*0.7	*0.7	5.1	*0.7		4.6	*0.7		*0.7	7.1
IT4	26.4	*0.7	2.8	*0.7	2.8	2.0	1.4		2.0	0.4
IND2		*0.7		*0.7	*0.7	2.7	*0.7		1.2	0.5
IT5	*0.7	*0.7		0.9	*0.7	1.2	1.3			6.6
IT7	24.1	*0.7	1.7	*0.7	1.0	1.6	1.6		1.1	4.8
IND 5			1.0	*0.7	0.7	*0.7	*0.7		*0.7	0.3
IT8	*0.7	*0.7	1.5	1.6	1.8	1.1	1.2		4.7	2.7
OT1		*0.7		*0.7	*0.7	*0.7	*0.7		*0.7	0.3
IT10	*0.7			1.1	0.9	1.9	1.0		1.4	1.3

\sum ICES 7 CBs concentration (µg kg ⁻¹)	dw)
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* Concentrations represent estimates for samples 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.

For BDEs, temporal data are available from 2006-2021. At most stations, BDE concentrations were similar to, or lower than, that measured in 2014 (Table A1.2). Exceptions were evident within the disposal site at IT5 and IT7 where concentrations increased. Levels at these two stations were above the range previously observed from 2006-14.

Table A1.2. Temporal trends (2006-2021) of Σ 11 BDEs concentrations (µg kg⁻¹ dw) at Inner Tees, 2021.

				2110	r BBEs series inalish (µg kg 'aw)						
	<u>2006</u>	2007	2008	2009	2010	2011	~	2014	~	2021	
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	
IT3	1.08	9.55	0.36		7.76	0.21		0.29		0.33	
IT4	3.17	6.19	1.99	4.13	6.41	2.17		5.76		0.47	
IND2	1.02		0.22	*0.11	29.4	0.43		2.51		0.28	
IT5	1.04		1.84	1.45	1.87	2.54				6.10	
IT7	1.32	1.20	0.64	1.40	3.04	3.11		2.34		26.8	
IND 5		1.19	0.20	0.20	0.19	2.68		0.32		0.19	
IT8	1.22	2.51	0.95	1.66	1.19	1.89		2.20		2.06	
OT1	0.84		0.18	0.23	0.53	0.46		2.05		0.15	
IT10			0.60	0.68	2.85	1.42		2.27		1.04	

 \sum 11 BDEs concentration (µg kg⁻¹ dw)

*Concentrations represent estimates for samples where all 11 BDE congener concentrations were below LODs. Limits of detection for BDEs 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 BDEs concentration for samples with congeners below LODs.

For BDE209, temporal data are available from 2008-2021. At most stations, BDE209 concentrations in 2021 were mostly lower, often substantially, than that measured in 2014. The exception was at IT5 inside the disposal site where BDE209 concentration increased and was above the range previously observed between 2008 and 2014 (Table A1.3).

Table A1.3. Temporal trends (2008-2021) of BDE209 concentrations (µg kg⁻¹ dw) at Inner Tees, 2021.

	<u>2008</u>	2009	2010	2011	~	2014 ~	2021
IT1		20.90	9.16			17.3	3.03
IND1	1.46	9.65	3.29	17.40			0.82
IT3	1.17		31.00	0.05		0.86	0.51
IT4	13.30	26.60	12.3	3.11		31.90	0.93
IND2	0.05	0.05	32.40	2.21			1.28
IT5	7.42	2.16	10.00	8.71		8.79	46.60
IT7	1.76	5.27	10.50	12.71		105.00	34.30
IND 5		0.05	0.05	10.10		0.88	0.74
IT8		5.89	3.54	7.74		10.10	9.64
OT1	0.58	0.70	2.35	0.26		7.40	0.50
IT10	2.19	1.97	6.43	1.36		7.45	3.10

BDE209 concentration (µg kg⁻¹ dw)

Cefas hold temporal data for Σ DDTs from 2003 to 2021. However, data for previous years only included three DDT chemicals in the total calculation: the same is conducted here for continuity (to note, the additional o,p'-chemicals measured in 2021 would contribute less than a third extra to the Σ 6DDTs). At most stations, Σ 3DDTs concentrations were similar to, or lower than, those observed in 2011 (Table A1.4). Exceptions were at IT5 and IT7 (both inside the disposal site) where Σ 3DDTs concentrations doubled, and at IND1 and IT8 where concentrations slightly increased. Levels at these latter two stations were generally in the range previously observed from 2003-11.

Table A1.4. Temporal trends (2003-2021) of Σ 3DDTs concentrations (in µg kg⁻¹ dw) at Inner Tees, 2021.

	2003	~	2006	2007	2008	~	2010	2011 ~	2021
IT1			1.43	2.01			1.01		0.40
IND1			0.85	0.99	1.12		0.47	0.80	1.12
IT3	0.41		0.64	3.73	0.63		1.95	0.44	0.31
IT4	0.55		0.88	1.63	0.88		0.89	0.78	0.15
IND2			0.58		0.45		0.95	0.76	0.24
IT5	0.41		0.65		1.55		1.15	0.99	2.25
IT7	3.65		0.60	1.40	0.81		1.58	1.14	2.55
IND5				1.81	0.41		0.30	0.68	0.15
IT8	0.45		0.65	1.91	0.71		0.91	1.04	1.44
OT1			0.58		0.64		1.12	0.67	0.16
IT10	0.30				0.89		0.84	0.93	0.82

*∑3DDTs concentration (µg kg⁻¹ dw)

* DDTs is the sum of 3 chemicals (p,p'-DDE, p,p'-TDE, p,p'-DDT). Note, limits of detection for individual DDTs improved between 2011 and 2021 by a factor of 2-10, depending on chemical

6 Assessment methods of contaminants (Appendix 2)

6.1 Organohalogens

6.1.2 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. ¹³C₁₂-labelled BDE209, HCB, alpha-HCH, gamma-HCH, *p*,*p*'-DDT, CB28, CB52, CB101, CB118, CB138, CB153 and CB180 was added as internal 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.

6.1.2 Sample extract clean-up

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

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

After addition of internal standard CB53 and CB112, 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 (1.4 ml min⁻¹) and nitrogen (1.5 ml min⁻¹), respectively. The initial oven temperature was 90°C, held for 2.00 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.

6.1.4 Analysis of PBDEs by GC-MS/MS

After addition of internal standard CB200, PBDE concentrations were determined with a Shimadzu 2010plus GC with TQ8030 QQQ-MS/MS in positive electron impact mode (ESI+). The separation of analytes was performed on a 15.0 m × 250 μ m, 0.15- μ m-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 2 μ l extract was injected in pulsed splitless mode with a purge time of 2 min.

6.1.5 Analysis of BDE209 by GC-MS

BDE209 concentrations were determined with an Agilent 6890 GC with 5973 MS in NCI mode. The separation of analytes was performed on a 15.0 m x 250 μ m, 0.1 μ m 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 1.00 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 2 µl extract was injected in pulsed splitless mode with a 20 psi pulse until 1 min and a purge time of 2 min.

6.1.6 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 9 calibration levels (range 0.1 – 200.0 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'*-DDE, *p,p'*-DDE, *o,p'*-DDT, *o,p'*-DDE, *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 ¹³C₁₂ labelled recovery standards.

Quantitation for PBDEs was performed using internal standards and 10 calibration levels (range 0.05 – 100.00 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 7 calibration levels (range 0.5 - 500.0 ng ml⁻¹). The BDE209 standard solutions contained IUPAC BDE209 in iso-octane, plus an additional 3 compounds IUPAC BDE206; IUPAC BDE207; IUPAC BDE208; together with the internal standard ¹³C₁₂-labelled IUPAC BDE209.

6.1.7 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.

6.1.8 Method used for assessment

PCB, OC and BDE concentrations were determined in the sediments and reported on a dry weight basis. The Σ ICES 7 CBs (CB28, CB52, CB118, CB153, CB138, CB170, CB183), and the sum of all 25 measured CBs (Σ CBs) were calculated. 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 Σ DDTs (*p*,*p*'-DDE, *p*,*p*'-DDT, *o*,*p*'-DDE, *o*,*p*'-DDT) were calculated. The Σ 11 BDEs were calculated. Where individual congener concentrations. The Σ DDTs (*p*,*p*'-DDE, *p*,*p*'-DDT, *o*,*p*'-DDE, *o*,*p*'-DDT) were calculated. The Σ 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. For samples analysed prior to 2008, a different LOD of 0.125 µg kg⁻¹ applied, resulting in higher values substituted for congeners below LODs. 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 μ g kg⁻¹, a value of half the LOD was inserted.

The Total Organic Carbon (TOC) content in the <2 mm fraction determined at a number of representative sampling stations was used to additionally calculate the contaminant concentration normalised to 2.5 % TOC content. The TOC data from the representative stations was used to estimate the TOC content at adjacent stations for which this value was lacking.

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. Concentrations are expressed on a dry weight (dw) basis unless otherwise stated.

The current Cefas action limits for dredge disposal are: Action level 1 if $\sum ICES7 CBs > 10 \ \mu g \ kg^{-1}$, $\sum 25CBs > 20 \ \mu g \ kg^{-1}$, $\sum DDT > 1 \ \mu g \ kg^{-1}$, dieldrin > 1 $\ \mu g \ kg^{-1}$, and action level 2 if $\sum 25CBs > 200 \ \mu g \ kg^{-1}$. Concentrations are expressed on a dry weight (dw) basis.

OSPAR in Charting Progress 2 (CP2) have set criteria for Background Assessment Concentrations (BAC) and Environmental Assessment Concentrations (EAC) for the ICES7 CBs in sediments (see Table A2. 1.). 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 would be classed as bad environmental status. The station is deemed to have 'bad' environmental status if 'bad' status occurs for more than one ICES7 CB congener.

Table A2. 1. OSPAR assessment criteria for CBs in sediment from CP2.

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

Sediment (µg kg⁻¹ dry weight, normalised to 2.5 % TOC)

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 A2.2.

Table A2.2. Canadian FEQG (Federal Environmental Quality Guidelines) levels adopted by OSPAR MIME as EACs thresholds for PBDEs, together with calculated BAC values.

Compound	BAC	EAC
BDE28	0.04	110.00
BDE47	0.04	97.50
BDE66	0.04	97.50
BDE85	0.04	1.00
BDE99	0.04	1.00
BDE100	0.04	1.00
BDE153	0.04	1100.00
BDE154	0.04	1100.00
BDE183	0.04	14000.00
BDE209	0.04	47.50

Sediment (µg kg-1 dry weight, normalised to 2.5 % TOC)

Concentrations in the samples collected for this report were compared with those collected on previous sampling campaigns to investigate temporal trends in sediments at the sampling stations.





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