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Determination of decamethylcyclopentasiloxane in river and estuarine sediments in the UK

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ABSTRACT

Robust analytical procedures for the measurement of decamethylcyclopentasiloxane (D_5) in river and estuarine sediments and their application in determining environmental concentrations in the UK are presented for the first time in this work. Novel approaches to minimise commonly reported artefacts are utilised, improving the confidence in the concentrations of D_5 reported. Accelerated solvent extraction (ASE) and liquid–solid extraction methods are compared. Both methods use on-column injection gas chromatography/mass spectrometry (GC/MS). Measurements of D_5 concentrations in sediments sampled from the river Great Ouse and from the Humber estuary (UK) are also reported. ASE was suitable to measure concentrations of D_5 in sediments obtained from the river Great Ouse, UK (186–1450 ng g^{-1}, dry weight) and octamethyltetracyclosiloxane (D_4, 12–24 ng g^{-1}, dry weight). C_{12} linear alkybenzene (C_{12} LAB), which can be used as a chemical marker for sewage effluent related emissions, was also measured in this analysis. Liquid–solid extraction was optimised to provide more confidence in the lower D_5 concentrations measured in the Humber estuary, UK (49–256 ng g^{-1}, dry weight). A Limit of quantitation (LOQ) for D_5 of 57–110 and 4 ng g^{-1} dry weight was determined for ASE and liquid–solid extraction, respectively.

1. Introduction

The current understanding of the fate and behaviour of decamethylcyclopentasiloxane (D_5) in the aquatic environment is largely based on laboratory experiments and subsequent modelling of these data. D_5 is pending risk management (minimise releases to the aquatic environment and achieve the lowest level of release that is technically and economically feasible) subject to a board of review decision by the Canadian Environment Agency [1] and is currently under review by the UK Environment Agency [2]. It is therefore important to improve understanding of the environmental fate and behaviour of this material, including concentrations in relevant environmental media.

D_5 enters the environment through a variety of sources but mostly from the use of personal care (PC) products. Due to its volatility, a large proportion of D_5 used in these applications will evaporate and it is thought that less than 10% of the total D_5 that is formulated in PC products is washed off to enter wastewater treatment plants. Here it is removed through both adsorption to suspended solids ($\log K_{OC}$ 5.17–6.12 [2–4]) and volatilisation. A review of the occurrence of siloxanes in wastewater and sludge has been published by Dewil et al. [5].

The D_5 that does reach surface waters via treated effluent continues to be removed via a number of processes including volatilisation, adsorption to dissolved and particulate organic carbon (DOC, POC) and acid and base-catalysed hydrolysis [3,6]. D_5 is likely to partition to sediments because it is hydrophobic. The critical compartment in the aquatic environment is therefore sediment, with highest concentrations expected in those associated with surface waters that receive continuous effluent containing cyclic volatile methyl siloxanes (cVMS). To support the environmental risk assessment and provide accurate measurements of this high volume chemical, recent publications detail the development of robust methods for the analysis in air [7] and surface water [8]. A proposed method for sewage sludge has also recently been validated [9].

There are however very few data in the primary literature regarding concentrations of D_5 in sediment and the methods of analysis that were used. From other literature sources the following methods and results are available: during a Nordic monitoring programme [10], detectable levels of D_5 in marine sediment in urban areas in the range 1.8–130 ng g^{-1} dry weight were obtained, with one much higher concentration of 2000 ng g^{-1} dry weight from Roskilde. The analytical method consisted of a purge and trap procedure. Surface sediments and sediment cores have also been

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analysed from Lake Ontario by Dow Corning (cited by Brookes et al. [2]). In Toronto harbour, which is fairly heavily contaminated, the highest determined value for D_5 was 780 ng g^{-1} dry weight. The analytical method utilised solvent extraction with hexane and acetonitrile followed by GC/MS.

Linear alkylbenzenes (LABs) with C_{10}–C_{14} normal alkyl chains are industrially sulphonated to produce linear alkylbenzene sulphonates (LAS). Approximately 1–3% of LABs escapes sulphonation and therefore they are impurities in commercial products. Thus domestic wastewater contains LABs which are hydrophobic and adsorbed onto particles in the sewage treatment process. LABs have been used to apportion the contribution of sewage derived organic chemicals to the environment from waste water [11]. In addition, Takada and Ishiwatari [12] demonstrated how the concentration ratio of internal to external isomers could be used to estimate the degree of LAB degradation.

The purpose of the present study was to develop suitable methods to measure levels of D_5 in a number of sediments. At the same time, the potential sources of contamination were exhaustively investigated and novel solutions provided. Recently, Varaprath et al. [13] reviewed some of the issues surrounding the analysis of silicones at trace levels, including the potential sources of background contamination. Extreme care must be taken to minimise the sources of artefacts and siloxane contamination, which can originate from vial caps, septa, gas chromatography columns and use of personal care products by laboratory workers leading to elevated ambient air concentrations.

2. Materials and methods

Two sample preparation methods are described with ease of blank control assessed in each case: one utilising accelerated solvent extraction (ASE) and the other utilising a two component solvent liquid–solid extraction. Both methods employed on-column injection gas chromatography/mass spectrometry (GC/MS). A chemical marker of domestic sewage effluent emissions, LAB was analysed to provide a reference for the concentrations (and sources) of D_5 determined.

2.1. Solvents, standards and materials

Decamethylcyclopentasiloxane (D_5) and octamethylcyclotetrasiloxane (D_4) were purchased from Sigma–Aldrich (>98% purity, Gillingham, UK). The internal standards used in the study were $^{13}C_4$-octamethylcyclotetrasiloxane and $^{13}C_5$-decamethylcyclopentasiloxane ($^{13}C_4$–D_4 and $^{13}C_5$–D_5), synthesised by Moravek Biochemicals (>99% pure, Brea, CA, USA). Solvents were high pressure liquid chromatography grade and purchased from Rathburn Chemicals (Walkerburn, UK). Ultrapure water was obtained from a Milli Q Plus® system (Millipore, Watford, UK). A linear alkylbenzene (LAB) commercial mixture was provided by Unilever Port Sunlight, and contained a chain length distribution of 9, 33, 33 and 20% (w/w) of C_{10}–C_{13}, respectively. The distribution of the C_{12} positional isomers 6-C_{12}, 5-C_{12}, 4-C_{12}, 3-C_{12} and 2-C_{12}, is 8.40, 7.95, 5.90, 5.55 and 4.95% (w/w) of the total LAB concentration, respectively. The homologue and positional isomer distribution were determined by GC/FID/MS at the Safety & Environmental Assurance Centre, Unilever. The internal standard used for LAB analysis was dodecyl($^{13}C_6$-benzene) (attached in the 1-position, Sigma–Aldrich).

2.2. Sediment sampling and handling

River sediment samples were taken with a small Van Veen Grab sampler (Duncan & Associates, Grange-over-sands, UK) and sieved (2 mm) using an acetone-cleaned stainless steel sieve and collection tray (Cole-Parmer, Hanwell, UK). Sediments were stored in solvent-cleaned glass straight sided jars (1 L, Teflon lined caps) and sub-sampled by transferring into centrifuge tubes (75 mL, Fleischacker, Schwerte, Germany) as required, in the field. Three separate grab samples were taken approximately 120 m, 150 m and 200 m downstream of Felmersham bridge (river Great Ouse, UK, National Grid Reference SP 990 578, collection date 27/08/08). Three separate grab samples were taken approximately 50, 80 and 100 m upstream of Tyringham bridge (river Great Ouse, UK, SP 857 465, collection date 23/09/08). Intertidal sediment samples (surface, 1–2 cm) from the Humber estuary were obtained by the Institute of Estuarine & Coastal Studies (IECS) using a solvent-cleaned stainless steel scoop and placed in 1 L jars, as described above. Sediments were collected from six sites in the Humber estuary, UK (Grid reference, date of collection): Chowder Ness (TA 004 230, 1/10/09), Paull Holme (TA 171 250, 24/9/09), Stone Creek (TA 234 188, 15/10/09), Welwick (TA 333 181, 29/09/09), Skeffling (TA 369 182, 15/10/09) and Cleethorpes (TA 318 081, 2/10/09). These sites form a transect moving from the middle of the estuary to the outer part and samples were collected at low tide and transferred to glass jars without sieving and stored at 4 °C until transported to Unilever. Tenax-TA® (60-/80 mesh, Buchem bv) and ENV+® (International Sorbent Technology) resins (0.2 g) enclosed in Nylon pouches (heat-sealed) and cleaned using ASE, were exposed in identical jars while sediments were collected to assess any possible significant contamination via the atmosphere.

A Dionex ASE 200 accelerated solvent extractor (Dionex, Camberley, UK) equipped with stainless steel extraction cells (33 mL) was used for the extractions. Diatomaceous earth used for drying the wet sediments was also obtained from Dionex. Zero grade nitrogen (BOC, Surrey, UK) was used on the instrument. ASE solvent collection was carried out in 60 mL vials (24 mm, EPA) with polypropylene screw cap, 12.5 mm centre hole and butyl/PTFE septa (Kinesis, St Neots, UK). Liquid–solid extraction was carried out in 28 mL vials with foil lined caps (VWR International Ltd., Lutterworth, UK). All critical sample preparation was carried out in a clean air cabinet ('OS' carbon filtration system, Bigneat, Waterlooville, UK). A field blank/lab blank sediment was obtained from Sanford Lake (MI, USA) courtesy of Dow Corning. This lake is not subject to effluent discharge and was therefore suitable as a blank sediment.

2.3. ASE extraction (river sediment)

Sediments were centrifuged at 1500 rpm for 10 min and as much overlying water as possible was removed. Triplicate aliquots of approximately 2.5 g were accurately weighed into separate beakers in a clean air enclosure. Diatomaceous earth (pre-extracted on the ASE with ethyl acetate was added to the sediment and then thoroughly mixed before transfer into 33 mL ASE cells with a solvent rinsed cellulose filter in the bottom. These cells were then spiked with 20 μL of an internal standard solution in acetone, at least 3 cm below the surface of the solid mixture ($^{13}C_5$–D_5 was spiked at 38.3 ng g^{-1} wet weight of sediment). Each cell was extracted with ethyl acetate using the following ASE conditions: no preheat cycle, heat (5 min), static (5 min), temperature (100 °C), pressure (1500 psi), flush (150 s), flush volume (50%) and cycles (1). After extraction the Butyl rubber/PTFE collection vial caps were replaced with a freshly solvent rinsed cap and the extracts dried with anhydrous sodium sulphate as required. The extract was then transferred into a 50 mL volumetric flask and made to volume with ethyl acetate. An aliquot of each extract was transferred into a 1.5 mL chromatographic vial for GC/MS analysis.

Table 1
Method validation of accelerated solvent extraction (ASE) in spiked samples of lake, estuarine and river sediment ($n = 3$).

	Analyte	Lake sediment	Estuarine sediment	River sediment
Concentration measured (ng g^{-1}, dw, mean ± sd)	D_5	33 ± 5[a]	135 ± 4[a]	486 ± 37[a]
% Recovery (mean ± sd)		73 ± 18	77 ± 5	89 ± 7
Concentration measured (ng g^{-1}, dw)	D_4			161 ± 28[a]
% Recovery (mean ± sd)				78 ± 14
Concentration measured (ng g^{-1}, dw, mean ± sd)	6-C_{12} LAB	13 ± 1[b]		24 ± 6[a]
% Recovery (mean ± sd)		74 ± 4		103 ± 25
Concentration measured (ng g^{-1}, dw, mean ± sd)	5-C_{12} LAB	14 ± 1[b]		32 ± 3[a]
% Recovery (mean ± sd)		81 ± 4		120 ± 11
Concentration measured (ng g^{-1}, dw, mean ± sd)	4-C_{12} LAB	10 ± 1[b]		26 ± 4[a]
% Recovery (mean ± sd)		80 ± 8		94 ± 14
Concentration measured (ng g^{-1}, dw, mean ± sd)	3-C_{12} LAB	9 ± 1[b]		41 ± 5[a]
% Recovery (mean ± sd)		74 ± 9		110 ± 14
Concentration measured (ng g^{-1}, dw, mean ± sd)	2-C_{12} LAB	10 ± 1[b]		52 ± 2[a]
% Recovery (mean ± sd)		90 ± 7		130 ± 6
Concentration measured (ng g^{-1}, dw, mean ± sd)	Total C_{12} LAB	56 ± 4[b]		177 ± 11[a]
% Recovery (mean ± sd)		80 ± 8		114 ± 7

[a] Wet sediment dried with Diatomaceous Earth and analysed by on-column gas chromatography/mass spectrometry.
[b] Wet sediment spiked, freeze-dried and analysed by splitless gas chromatography/mass spectrometry (decamethylcyclopentasiloxane [D_5]; octamethyltetracyclosiloxane [D_4]; linear alkylbenzene [LAB]; dry weight, dw).

2.4. Liquid–solid extraction rolling method (estuarine sediment)

The triplicate sediments from each sample site were opened in a clean air cabinet and approximately 2 cm of the top layer of sediment was removed from each sample, as a precaution against contamination, before homogenising and centrifuging the wet sample as described earlier. Triplicate aliquots of approximately 1.0 ± 0.2 g of estuarine sediment were accurately weighed from each centrifuged aliquot into separate 28 mL glass screw cap vials. To each of these, 5 mL of acetonitrile followed by 5 mL of hexane were added. These were then spiked with 9.58 ng g^{-1} wet weight $^{13}C_5$–D_5 and rolled for 60 min before being centrifuged at 1000 rpm for 10 min. An aliquot of the hexane layer was transferred into a chromatographic vial for analysis by GC/MS.

In order to measure LAB, estuarine sediments were freeze dried (Severn Science LS40 Freeze Drier) at –40 °C. Once a dried constant weight was achieved, the sediments were ground using a pestle and mortar and stored in glass vials with foil lined caps. LAB were extracted using ASE methodology described previously, 2.5 g of dried sediment was mixed with diatomaceous earth and spiked at 12 ng g^{-1} with dodecyl($^{13}C_6$-benzene). Extracts were concentrated using a nitrogen blow down apparatus to less than 3 mL and quantitatively made to 3 mL with ethyl acetate in a volumetric flask before an aliquot was transferred into a chromatographic vial for GC/MS analysis.

2.5. GC/MS analysis

GC/MS analysis of D_5 in all samples was performed on an Agilent Technologies (Stockport, UK) 6890/5973 or 5975 GC/MS system. Each aliquot of 5 μL was injected at 100 μL/min in pseudo on-column mode using an adapted PTV inlet fitted with a Merlin Microseal® (Phenomenex, Macclesfield, UK). The oven was, held at an initial temperature of 75 °C for 2 min for an injection of ethyl acetate (67 °C for hexane) and was then heated to 250 °C at 10 °C/min and held for 2 min. Helium carrier gas (Technical grade, Air Products, Crewe, UK) was used at a flow of 1 mL/min through a Zebron ZB-5HT column (Phenomenex, 30 m × 0.25 mm i.d. × 0.25 μm d_f). A retention gap (10 m × 0.53 mm) was connected to the front end of the analytical column to facilitate on-column injection. The MS was operated in electron ionisation (EI) mode and single ion monitoring (SIM) with ions m/z 73, 267 and 355 monitored for D_5 and m/z 360 monitored for the $^{13}C_5$–D_5 internal standard and ions m/z 133, 207 and 281 monitored for D4 and m/z 285 monitored for the $^{13}C_4$–D_4 internal standard. These ions were monitored from 4 to 8 min. The LAB ions of m/z 91, 105 and 218, 232, 246, and 260 for C_{10}–C_{13}, respectively were monitored for the remainder of the 21.5 min run. Calibration standards were prepared in ethyl acetate or hexane as required in the range 0–19 ng mL^{-1} for D_4 and D_5 ($n = 8$, $^{13}C_5$–D_5 and $^{13}C_5$–D_4 1.9 ng mL^{-1}) and 0–200 ng mL^{-1} for LAB ($n = 8$, dodecyl($^{13}C_6$-benzene) 2 ng mL^{-1}). Internal standard-corrected calibration plots were made for the D_4, D_5 and C_{12} LAB isomers (only C_{12} LAB isomers were measured in this work with individual calibrations for each isomer calculated from the % w/w distribution stated earlier) and the sediment extracts quantified against these plots. A 25 μL injection volume was also used for LAB injecting at 50 μL/min and only monitoring the LAB ions as required.

LAB analysis in the Humber extracts was carried out by making a 1 μL splitless injection at 250 °C. The oven was held at an initial temperature of 50 °C for 2 min then heated to 280 °C at 20 °C/min and held for 5 min. Helium carrier gas was used at a flow of 1.3 mL/min through a 30 m × 0.25 mm Zebron ZB-5HT column of film thickness 0.25 μm (Phenomenex). The 5975 MSD was operated in EI mode and SIM with ions, m/z 91, 105, 246 monitored for C_{12} LAB isomers and 98, 139 and 252 monitored for the dodecyl($^{13}C_6$-benzene) internal standard. Calibration standards were prepared in ethyl acetate in the range 0–1000 ng mL^{-1} for LAB ($n = 6$, dodecyl($^{13}C_6$-benzene) 10 ng mL^{-1}). Only C_{12} LAB isomers were measured as discussed before.

Table 2
Method validation of liquid–solid extraction and on-column gas chromatography/mass spectrometry for lake and estuarine sediment spiked with decamethylcyclopentasiloxane (D_5) ($n = 3$).

	Analyte	Lake sediment	Estuarine sediment
Concentration measured (ng g^{-1}, dw, mean ± sd)	D_5	26 ± 5	153 ± 10
% Recovery (mean ± sd)		85 ± 18	113 ± 12

dw: dry weight.

2.6. Carbon analysis

Inorganic carbon, total carbon and organic carbon (calculated by subtracting the inorganic carbon content from the total carbon content) were determined on dry samples of sediment, using

Table 3
Concentration of octamethyltetracyclosiloxane (D_4), decamethylpentacyclosiloxane (D_5) and linear alkylbenzene (LAB, C_{12} isomers) in sediment samples taken from the River Great Ouse by accelerated solvent extraction and on-column gas chromatography/mass spectrometry – Felmersham [August 2008].

Sample name	OC[a] (% dw)	D_4 (ng g^{-1} dw, $n=9$)	D_5 (ng g^{-1} dw, $n=9$)	D_5 (μg g^{-1} OC, $n=9$)	6 C_{12}- LAB (ng g^{-1} dw, $n=3$)	5 C_{12}-LAB (ng g^{-1} dw, $n=3$)	4 C_{12}-LAB (ng g^{-1} dw, $n=3$)	3 C_{12}-LAB (ng g^{-1} dw, $n=3$)	2 C_{12}-LAB (ng g^{-1} dw, $n=3$)	Total C_{12}- LAB (ng g^{-1} dw, $n=3$)	Internal (I)/external (E) LAB ratio
Felmersham Grab 1	7.9	20 ± 3	1410 ± 120	18 ± 2	71 ± 1	38 ± 4	13 ± 1	<5	<4	133	>4.7
Felmersham Grab 2	7.9	24 ± 3	1450 ± 71	18 ± 1	61 ± 4	31 ± 2	12 ± 2	<5	<4	114	>4.3
Felmersham Grab 3	3.2	12 ± 2	820 ± 130	26 ± 4	34 ± 1	15 ± 2	<5	<5	<4	60	>4.3
LOD[b]	n/a	7	37	n/a	7	7	5	5	4	27	n/a
LOQ[c]	n/a	22	110	n/a	21	20	15	14	12	82	n/a

[a] Organic carbon is determined using a Shimadzu TOC V solids module.
[b] LOD in sediment (ng g^{-1} dw) = $\frac{\text{blank concentration (ng/mL)} \times \text{final extract volume (mL)}}{\text{sediment dry weight (g)}}$. Sediment dry weight is determined by oven-drying overnight at 105 °C, limit of detection (LOD) = lowest concentration that can be measured in a sediment based on either ASE blanks or field blanks concentration whichever is highest.
[c] Limit of quantification (LOQ) calculated as three times LOD.

Table 4
Concentration of octamethyltetracyclosiloxane (D_4), decamethylpentacyclosiloxane (D_5) and linear alkylbenzene (LAB, C_{12} isomers) in sediment samples taken from the River Great Ouse by accelerated solvent extraction and on-column gas chromatography/mass spectrometry – Tyringham Bridge [September 2008].

Sample name	OC[a] (% dw)	D_4 (ng g^{-1} dw)	D_5 (ng g^{-1} dw)	D_5 (μg g^{-1} OC)	6-C_{12}-LAB (ng g^{-1}dw)	5-C_{12}-LAB (ng g^{-1} dw)	4-C_{12}-LAB (ng g^{-1} dw)	3-C_{12}-LAB (ng g^{-1} dw)	2-C_{12}-LAB (ng g^{-1} dw)	Total C_{12} LAB (ng g^{-1} dw)	Internal (I)/external (E) LAB ratio
Tyringham bridge Grab 1 ($n=3$)	1.6	<19	186 ± 29	11 ± 2	40 ± 10	28 ± 4	16 ± 3	<11	<10	93 ± 17	>2.8
Tyringham bridge Grab 2 ($n=3$)	3.2	<19	695 ± 38	22 ± 1	294 ± 57	214 ± 35	118 ± 27	61 ± 13	21 ± 5	707 ± 132	2.6
Tyringham bridge Grab 3 ($n=3$)	2.8	<19	486 ± 7	17 ± 0.2	191 ± 5	125 ± 17	61 ± 8	17 ± 3	<10	402 ± 32	>3.7
LOD[b]	n/a	19	19	n/a	17	16	12	11	10	65	n/a
LOQ[c]	n/a	57	57	n/a	50	47	35	33	29	195	n/a

[a] Organic carbon is determined using a Shimadzu TOC V solids module.
[b] LOD in sediment (ng g^{-1} dw) = $\frac{\text{blank concentration (ng/mL)} \times \text{final extract volume (mL)}}{\text{sediment dry weight (g)}}$. Sediment dry weight is determined by oven-drying overnight at 105 °C, limit of detection (LOD) = lowest concentration that can be measured in a sediment based on either ASE blanks or field blanks concentration whichever is highest.
[c] Limit of quantification (LOQ) calculated as three times LOD.

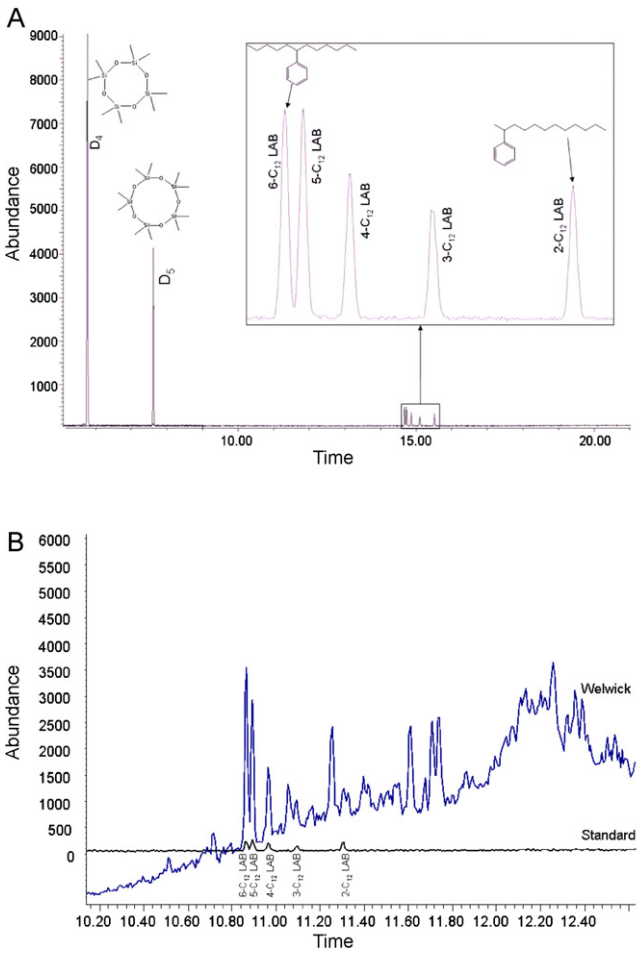

Fig. 1. Typical extracted ion chromatograms obtained on a Zebron ZB-5HT column (Phenomenex, 30 m × 0.25 mm i.d. × 0.25 μm df). (a) A 5 μL injection using on-column gas chromatography/mass spectrometry (GC/MS) via a retention gap (10 m × 0.53 mm) of a standard containing octamethyltetracyclosiloxane (D_4, 4.8 ng mL^{-1}), decamethylpentacyclosiloxane (D_5, 4.8 ng mL^{-1}) and linear alkylbenzene (LAB, 6-C_{12}, 5-C_{12}, 4-C_{12}, 3-C_{12} and 2-C_{12} at 4.2, 4.0, 3.0, 2.8 and 2.5 ng mL^{-1}, respectively). (b) A 1 μL splitless GC/MS injection of a sample from Welwick containing 25 ng g^{-1}, dry weight total C_{12} LAB and a standard containing LAB, 6-C_{12}, 5-C_{12}, 4-C_{12}, 3-C_{12} and 2-C_{12} at 8.4, 8.0, 5.0, 5.6 and 5.0 ng mL^{-1}, respectively.

a Shimadzu TOC V combined with solids module SSM 5000A (Milton Keynes, UK). Total carbon was determined as follows: a known mass of sediment was added to a boat which was then introduced into a furnace at 900 °C in the presence of oxygen. The carbon liberated as CO_2 was then carried to a non-dispersive infrared detector. The amount of carbon detected was calculated in relation to a standard curve generated using glucose. Inorganic carbon present in the sample was determined by the addition of phosphoric acid at 200 °C, with detection of CO_2 as described before. The amount of inorganic carbon was calculated against a calibration curve generated with sodium hydrogen carbonate.

3. Results and discussion

3.1. Method validation

In previous work [8] it was hypothesised that use of a clean air cabinet would reduce the effect of contamination from laboratory air in sample preparation. The propensity of D_5 to sorb to organic carbon (OC) in sediment has been demonstrated in other studies [2,3] and is confirmed in the present study. A lesser degree of field blank contamination was observed when all preparations were carried out in a clean air cabinet where the laboratory air was passed through a carbon-containing filter. D_5 in the field blank was determined in the range 10–42 ng g^{-1} dry weight for clean air cabinet preparation compared to 37–114 ng g^{-1} dry weight for preparation in the laboratory (ASE). In another experiment D_5 in the field blank was measured in the range 0.5–1 ng g^{-1} dry weight when stored for 24 h in a clean air cabinet compared to 2–6 ng g^{-1} dry weight when stored on the laboratory bench for 24 h (liquid–solid extraction). The air concentration of D_5 in the clean air cabinet was measured in the range 2–40 ng m^{-3} using a method adapted from Kierkegaard and McLachlan [7]. These concentrations were typically 10–100-fold lower than the surrounding laboratory air where D_5 was measured at the same time in the range 200–350 ng m^{-3}. In other areas of the building concentrations up to 11000 ng m^{-3} were measured. The use of on-column injection (lower temperature, 75 °C) with either a septumless head or Merlin microseal offered significant improvement over a hot splitless injection (typically 150 °C). It was also found that control of the injection procedure was more critical than choice of column phase with satisfactory instrumental blanks obtained on a high temperature stable siloxane column (typical instrument detection limits for on-column and splitless were 0.5 and 3.7 pg D_5 injected, respectively). The use of personal care products during sampling and analysis was avoided by analytical staff.

In the ASE sample preparation the method necessitated the chemical drying of wet sediment with diatomaceous earth. It was found to be essential to pre-extract the diatomaceous earth with ethyl acetate and only remove it from the ASE cell when ready to mix with sediment (mixing being carried out in a clean air cabinet). Even using the above precautions, a technique that further minimised exposure of sediment to ambient air was necessary to provide more reliable data for sediments containing lower D_5 levels. For this type of sample, transferring sediment directly into a vial before extracting with a two solvent system proved more successful. In addition, to avoid repeated contact of solvent with ambient air or further processing to break emulsions, a gentle rolling procedure (1 h) with only one aliquot of solvent provided good recovery of analyte. This was shown to be efficient by examining a second extract of the same sediment, which was shown to contribute less than five percent of the initial recovery.

3.2. Quality control data

The instrument detection limit was determined as the amount of analyte injected giving a response three times the zero calibration standard (typically 0.5 pg injected for D_4 and D_5). The apparent concentration of D_5 in field blanks (Sanford lake sediment) was determined in the range 8–30 ng g^{-1} dry weight for ASE extracted samples using a clean air cabinet. A much greater degree of control over background contamination was obtained with the liquid–solid rolling method where the majority of field blanks were determined at ~1 ng g^{-1} dry weight. This field blank data was used to determine the limit of detection (LOD) of each method. A limit of quantification (LOQ) was obtained by applying a factor of 3 to the LOD. The recoveries obtained from both extraction procedures were found to be satisfactory, as shown in Tables 1 and 2. The most efficient method of spiking cVMS into sediment was to add into water overlying wet sediment and then to roll overnight, before removal of water and centrifugation as described earlier. This process limited volatile losses associated with spiking directly into wet sediment. An estuarine sediment was also compared by the two extraction methods giving results of 208 ± 20 (rolling) and 230 ± 9 (ASE), ng g^{-1} dry

Table 5
Concentration of decamethylpentacyclosiloxane (D_5) and linear alkylbenzene (LAB, C_{12} isomers)in sediment samples taken from the Humber estuary measured by liquid–solid rolling extraction and ASE, respectively, followed by gas chromatography/mass spectrometry.

Sample name	OC[a] (% dw)	D_5 (ng g^{-1} dw, $n=9$)[b]	D_5 (μg g^{-1} OC)	6-C_{12}-LAB (ng g^{-1} dw)	5-C_{12}-LAB (ng g^{-1} dw)	4-C_{12}-LAB (ng g^{-1} dw)	3-C_{12}-LAB (ng g^{-1} dw)	2-C_{12}-LAB (ng g^{-1} dw)	Total C_{12} LAB (ng g^{-1} dw, $n=3$)[c]	Internal (I)/external (E) LAB ratio
Chowder Ness	1.7	256 ± 44	15	26 ± 2	17 ± 2	10 ± 1	3 ± 0.1	4 ± 1	60 ± 5	2.5
Paull Holme	1.3	103 ± 18	8	16 ± 2	10 ± 1	7 ± 1	4 ± 0.4	4 ± 1	41 ± 4	1.7
Stone creek	1.3	66 ± 5	5	10 ± 2	7 ± 1	5 ± 1	2 ± 1	1 ± 0.3	26 ± 5	2.0
Welwick	1.1	66 ± 13	6	9 ± 1	7 ± 1	5 ± 1	2 ± 1	2 ± 0.3	25 ± 4[d]	2.0
Cleethorpes	1.0	49 ± 7	5	8 ± 1	6 ± 1	5 ± 1	2 ± 1	2 ± 1	23 ± 3[e]	1.6
Skeffling	1.6	65 ± 8	4	12 ± 1	9 ± 1	6 ± 2	2 ± 0.3	3 ± 2	32 ± 5	1.8
LOD[f]	n/a	1	n/a	2	2	1	1	2	7	n/a
LOQ[g]	n/a	4	n/a	5	7	2	2	5	21	n/a

[a] Organic carbon (OC) determined using a Shimadzu TOC V solids module.
[b] Triplicate measurements on 3 replicates.
[c] Aliquot pooled from each replicate, freeze dried and analysed in triplicate.
[d] Re-analysed as stability sample, after 6 weeks storage (25 ± 3.4, I/E = 2.0).
[e] Re-analysed as stability sample, after 6 weeks storage (21 ± 0.3, I/E = 1.9).
[f] LOD in sediment (ng g^{-1} dw) = $\frac{\text{blank concentration (ng/mL)} \times \text{final extract volume (mL)}}{\text{sediment dry weight (g)}}$. Sediment dry weight is determined by oven-drying overnight at 105 °C, limit of detection (LOD) = lowest concentration that can be measured in a sediment based on either ASE blanks or field blanks concentration whichever is highest.
[g] Limit of quantification (LOQ) calculated as three times LOD.

weight ($n=3$), respectively. Generally the data indicated greater precision was obtained with the ASE method, which also provided a combined extraction for LAB. However liquid–solid extraction provided a better LOQ, as a result of better blank control and a lower dilution of sediment into final volume of solvent used. Recovery of LAB using both chemical drying and freeze drying with ASE was also considered to be fit for purpose, allowing application of these methods to real samples to provide relative concentrations of this chemical marker (Table 1). The recoveries of LABs greater than 100% in Table 1 can be explained due to a matrix effect in the on-column method for river sediment which suppressed the dodecyl($^{13}C_6$-benzene) internal standard response greater than that of the measured LAB isomers, thus increasing measured recovery. The alkyl chain in dodecyl($^{13}C_6$-benzene) was attached in the 1-position and eluted after 2-C_{12} LAB. A typical chromatogram showing the separation of D_4, D_5 and LAB is shown in Fig. 1(a).

3.3. Field work

The results of samples taken from Felmersham on the river Great Ouse (Bedfordshire, UK) are shown in Table 3. D_5 was determined in the range 820–1450 ng g^{-1} dry weight and D_4 was measured at a much lower concentration in the range 12–24 ng g^{-1} dry weight (results for D_4 lie between the LOD and LOQ, however are still reported due to a lower risk of ambient contamination with this analyte). Despite the control measures employed, a relatively high LOQ of 110 ng g^{-1} dry weight for D_5 was obtained for this batch of samples. The concentrations measured were however significantly higher than this LOQ and results are quoted without blank correction. The LOQ was determined on each sampling occasion, from data obtained in the analysis of a sample field blank (including exposure and sieving as for real samples in the field and processing through all the analysis steps). When expressing the Felmersham concentrations of D_5 normalised to the organic carbon (OC) content, a much narrower range of 18–26 μg g^{-1} OC was determined, demonstrating the affinity of D_5 with organic material in sediment. The concentration of D_5 in sediment stored in the laboratory was found to be very stable, shown by repeat analysis of the same sediment (stored in 1 L glass jars under refrigerated storage, over a period of 6 months). The concentration of C_{12} LAB in the Felmersham samples was determined in the range 60–133 ng g^{-1} dry weight (where C_{12} LAB is approximately one third of total LAB). Takada and Ishiwatari [12] proposed the internal/external ratio for the C_{12} positional isomers (I/E ratio; a ratio of the sum of 6- and 5-C_{12} LAB to the sum of 4-, 3- and 2-C_{12} LAB) to quantitatively evaluate the degree of LAB degradation. Where the LAB isomers are not detected the LOD value has been included in the totals and used in I/E calculations, resulting in a greater than value for the ratio (Table 3). The data clearly show that the external isomers have been more rapidly biodegraded, giving an elevated I/E ratio (>4.3) with respect to the I/E ratio present in commercial C_{12} LAB (0.6–1.1) [12].

The results of samples taken from Tyringham bridge on the river Great Ouse are shown in Table 4. D_5 was determined in the range 186–695 ng g^{-1} dry weight and D_4 was not detectable <19 ng g^{-1} dry weight. An LOQ of 57 ng g^{-1} dry weight for D_5 was obtained for this batch of samples. The concentrations measured were again quoted without blank correction. The concentration of D_5 normalised to the organic carbon (OC) content was in the range 11–22 μg g^{-1} OC, again confirming the affinity of D_5 to OC in sediments. A higher concentration of C_{12} LAB was determined for these sediments, in the range 93–707 ng g^{-1} dry weight. An I/E ratio in the range 2.6–3.7 was obtained, which is again a much higher ratio than present in commercial LAB.

Results from the Humber estuary (UK) are shown in Table 5. A field blank sediment (Sanford lake) was again processed with all sediments in the laboratory, which has been shown to be the most critical location for contamination with D_5. As a surrogate for control sediment, Tenax containing pouches were exposed in open jars in the field at the time of collection of sediment. Although concentrations of D_5 above blank pouches could be measured after desorption into hexane, these were not considered significant. D_5 concentrations at the six sites were determined in the range 49–256 ng g^{-1} dry weight. This data clearly shows an improved LOQ of 4 ng g^{-1} dry weight for D_5 and concentrations measured were again quoted without blank correction. The concentration of D_5 normalised to the organic carbon (OC) content was in the range 4–15 μg g^{-1} OC. The concentration of C_{12} LAB was determined for these sediments, in the range 23–60 ng g^{-1} dry weight. An I/E ratio in the range 1.6–2.5 was obtained. As the results in Table 5 indicate, some of the reported 2-C_{12} LAB values were close to the LOD of the method. The concentration decrease of D_5 in sediments from inner to outer estuary was mirrored by the C_{12} LAB concentration. The LAB concentrations are consistent with those measured by Raymundo and Preston [14], where 2.5–85 ng g^{-1} dry weight (total LAB) were measured in coastal sediments offshore of the Humber estuary. Typical chromatograms of the LAB analysis are shown in Fig. 1(b).

4. Conclusions

Two solvent extraction methods for the analysis of D_5 in sediment are described, including the critical precautions that are required to minimise introduction of D_5 from the ambient environment. ASE using ethyl acetate could simultaneously extract D_4, D_5 and C_{12} LAB from chemically dried sediment. The additional determination of C_{12} LAB was found to be useful in linking the presence of the siloxanes with sewage inputs. It could potentially be used as a quality control check, as samples containing D_5 but not LAB may have been contaminated by D_5 from the sampling or analytical procedures. The ASE method gave good precision and is currently the preferred method for sediment samples containing higher siloxane levels, but the increased manipulation in sample preparation made blanks more difficult to control. An alternative procedure utilising liquid–solid extraction provided a simple technique, validated for D_5 only. This method was preferred for samples containing low levels of D_5 where LOQs of around 4 ng g^{-1} dry weight are achievable. Both methods used on-column gas chromatography/mass spectrometry which effectively reduced instrumental artefacts for D_5. The most difficult area to control with respect to background contamination is the ambient air, but this problem was effectively eliminated by the use of clean air cabinets. The present study also provides valuable information on the concentrations of D_5 in some UK river and estuarine sediments.

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