Passive sampling and analysis of cyclic siloxanes
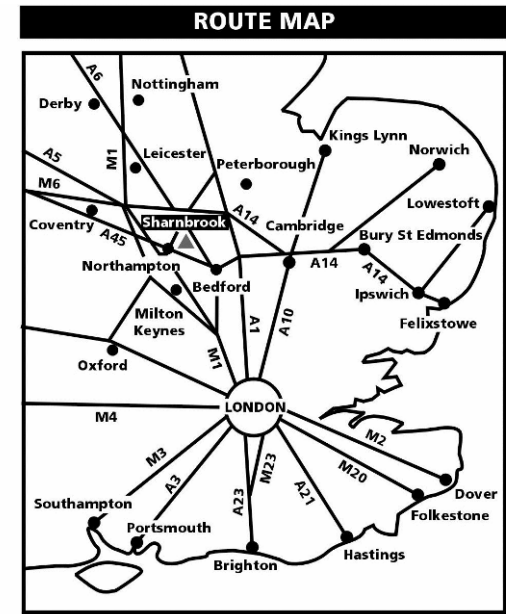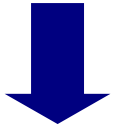
Chris Sparham 27 May 2009

NORMAN expert group meeting

Safety & Environmental Assurance Centre

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Safety & Environmental Assurance Centre

ROUTE MAP

Addresses Consumer, Occupational and Environmental safety and supports Sustainability
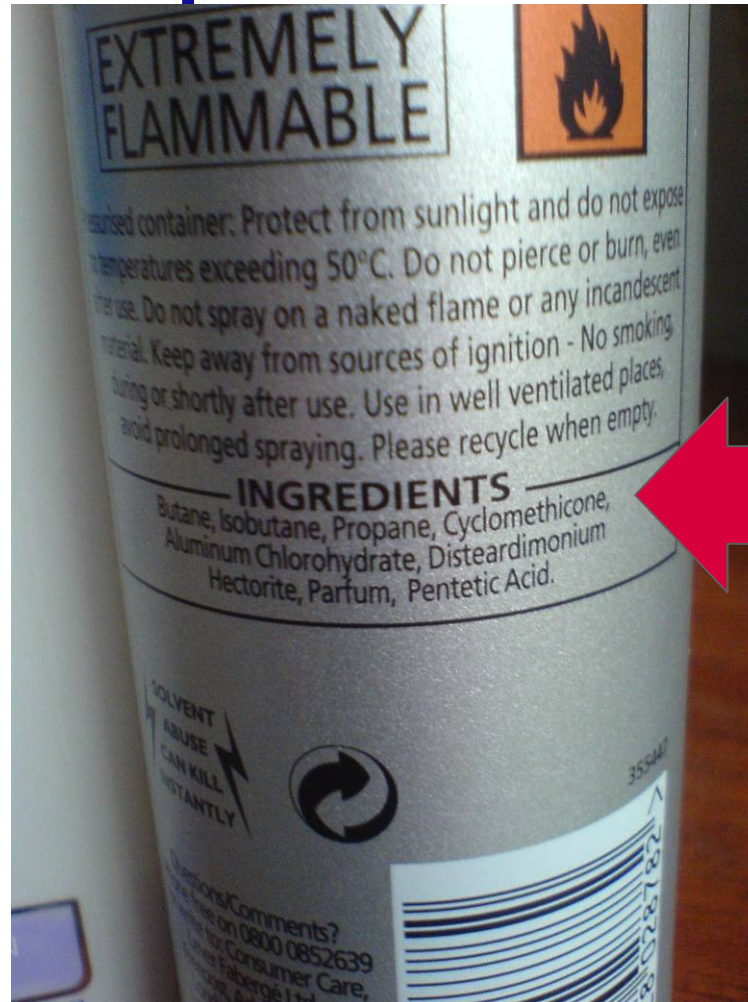
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Aims of presentation

- Properties of siloxanes
  - Why is Unilever interested in these materials?
- Blank issues – quality control
- Water monitoring
- Sediment monitoring
- Why identify passive sampling approach
- Passive sampling
  - Choice limitations
  - Design
  - Initial work

Cyclic Volatile Methylsiloxanes (cVMS)

- Cyclic Siloxanes
  - D4, D5, D6
- Clear, volatile, low molecular weight liquids with very low water solubility
- Used in the manufacture of larger siloxane polymers and as base fluid or fragrance 'carrier' for a range of consumer applications including -
  - Personal care (skin, hair, deodorancy)
  - Household care products
- Beneficial physical and chemical properties
  - very low mammalian toxicity (D5)
  - adequate evaporation rate
  - low surface tension
  - no odour

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Decamethylcyclopentasiloxane (D5) in products

Properties of D5 relevant to analysis

- **Low solubility in water**
  - 17 µg/L at 23 °C
- **High Henry's law constant**
  - Log K_{AW} ~ 3
- **High Log P**
  - Log K_{ow} = 8.0
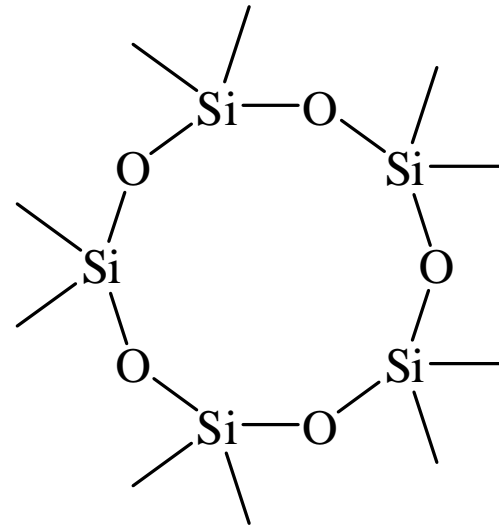
Chemical Formula: $C_{10}H_{30}O_5Si_5$
Exact Mass: 370.09

Monitoring data

- Environmental monitoring data are required to compare with modelling/theoretical predictions about fate of D5

- In particular it's partitioning behaviour between environmental compartments

  - Therefore, analysis in surface water

  - Analysis in sediment

  - Lack of data on the local scale i.e. UK rivers

- Post-doctoral projects

  - Michael McLachlan and colleagues at ITM Stockholm (time trends, spatial distribution and bioaccumulation)

  - Passive sampling (Portsmouth University)

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Blank issues

Source of D5 contamination	Solution
Septum	Low bleed Septa used and injector temperature reduced Also on-column preferred, septumless head or Merlin
GC column	PEG based (non-siloxane) columns used
Lab Air	Use of clean air enclosure Lab air (0.35 µg/m^3 D5) Enclosure air (0.04 µg/m^3 D5) Critical for low level water and sediment analysis
HS Vial Caps	Butyl not silicone
Personal Care Products (Analysts)	Do not wear!

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Last year

This year

GC/MS equipment

Combi/Pal auto sampler/6890 GC/5975 MS

Surface water analysis

Headspace vials placed on Gerstel multi purpose sampler (MPS2)
Agitated and heated at 80 °C for 10 min
1 mL aliquots sampled using a gas tight syringe

Separation: Agilent 6890 GC split/splitless injector (heated to 150 °C) 10:1
Column flow: 1 mL/min with helium carrier gas
Column: 30 m x 0.25 mm J & W DB-Wax column with film thickness 0.5 µm
Oven Conditions: 40 °C for 4 min, heat to 150 °C at 8 °C/min, held for 5 min

Detection: Agilent 5973 MSD operated in electron impact (EI) mode
& single ion monitoring (SIM) with ions m/z 73, 267 and 355
(D5)and m/z 75, 270 and 360 ($^{13}C_5$ - D5 internal standard)

Calibration: Curve constructed (range 0 - 958 ng/L) using internal standards
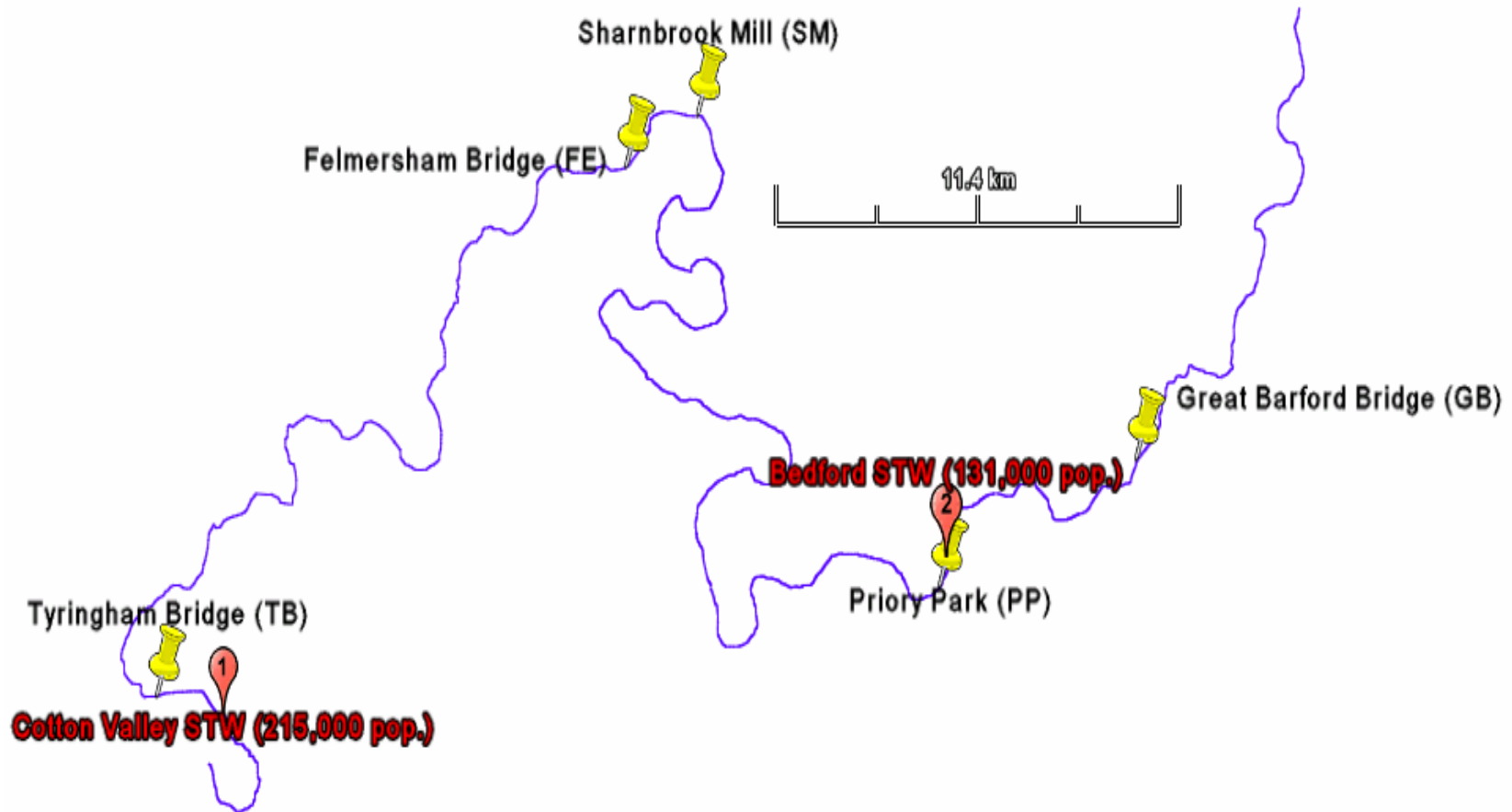
Recovery of mass-labelled spikes: Typically 90 % for all the samples analysed.
Recoveries decreased when levels of DOC and SS were high

LOD: Currently 3 to 6 ng/L based on background levels of D5

River Great Ouse sampling sites

Sampling and Analysis of Water

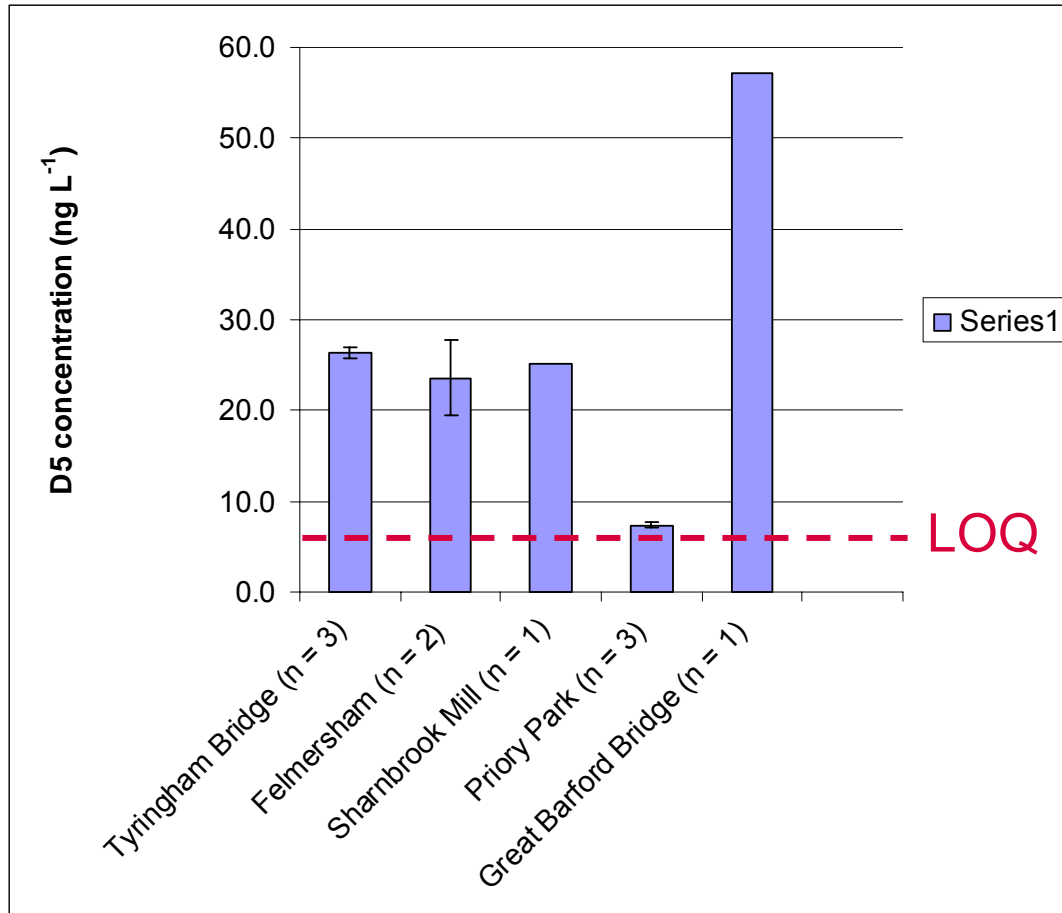Samples taken in the field using a sub-surface sampler using a 1 Litre glass bottle.

Analysis in field

Water samples prepared for analysis in headspace vials out in the field (including addition of internal standard).

Microlitre syringes used for spiking with the needle inserted below liquid surface.

River Great Ouse (water)

Headspace GC/MS

Contents lists available at ScienceDirect

Journal of Chromatography A

Journal homepage: www.elsevier.com/locate/chroma

Determination of decamethylcyclopentasiloxane in river water and final effluent by headspace gas chromatography/mass spectrometry

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ARTICLE INFO

ABSTRACT

A method is described for the analysis of decamethylcyclopentasiloxane (D$_5$) in river water and treated waste water using headspace gas chromatography/mass spectrometry. Internal standard addition to samples and field blanks was carried out in the field to provide both a measure of recovery and to prevent any exposure of samples to laboratory air, which contained background levels of D$_5$. Measured levels of D$_5$ were typically in the range <10–29 ng L^{-1} in the River Great Ouse (UK) with slightly higher levels in the River Nene (UK). The measured concentration of D$_5$ in treated waste water varied between 31 and 400 ng L^{-1}, depending on the type of treatment process employed.

Sediment sampling – old grab

Samples collected using stainless
steel grab sampling device

Sediment sampling- heavier grab

Sampling and analysis of sediment

Surface sediment passed through 2 mm stainless steel sieve into acetone-rinsed 1 L jars (PTFE-lined caps)

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Sampling and analysis of sediment

Transfer to centrifuge tubes in the field

Accelerated solvent extraction (ASE)

Sediment analysis

- Centrifuged and triplicate 2.5 ± 0.02 g aliquots dried with hydromatrix (~ 6 g)

- Spike ASE cell (33 mL) with internal standard ($^{13}C_5$-D5)

- 100 °C, 1500 psi, heat 5 min, static 5 min, flush vol 50 % (33 mL cell), purge time 150 s

- Extract once using ethyl acetate (~ 50 mL)

- On-column (OC) injection (5 µL) onto fused silica pre-column (10 m, 0.53 mm) Zebron ZB –5HT INFERNO 30 m x 0.25 mm (0.25 µm film)

- Calibration 0 to 20 ng/mL (LOQ 0.1 ng/mL)
  - D5 *m/z* 73, 267,355; IS *m/z* 360 (SIM)

Sediment data
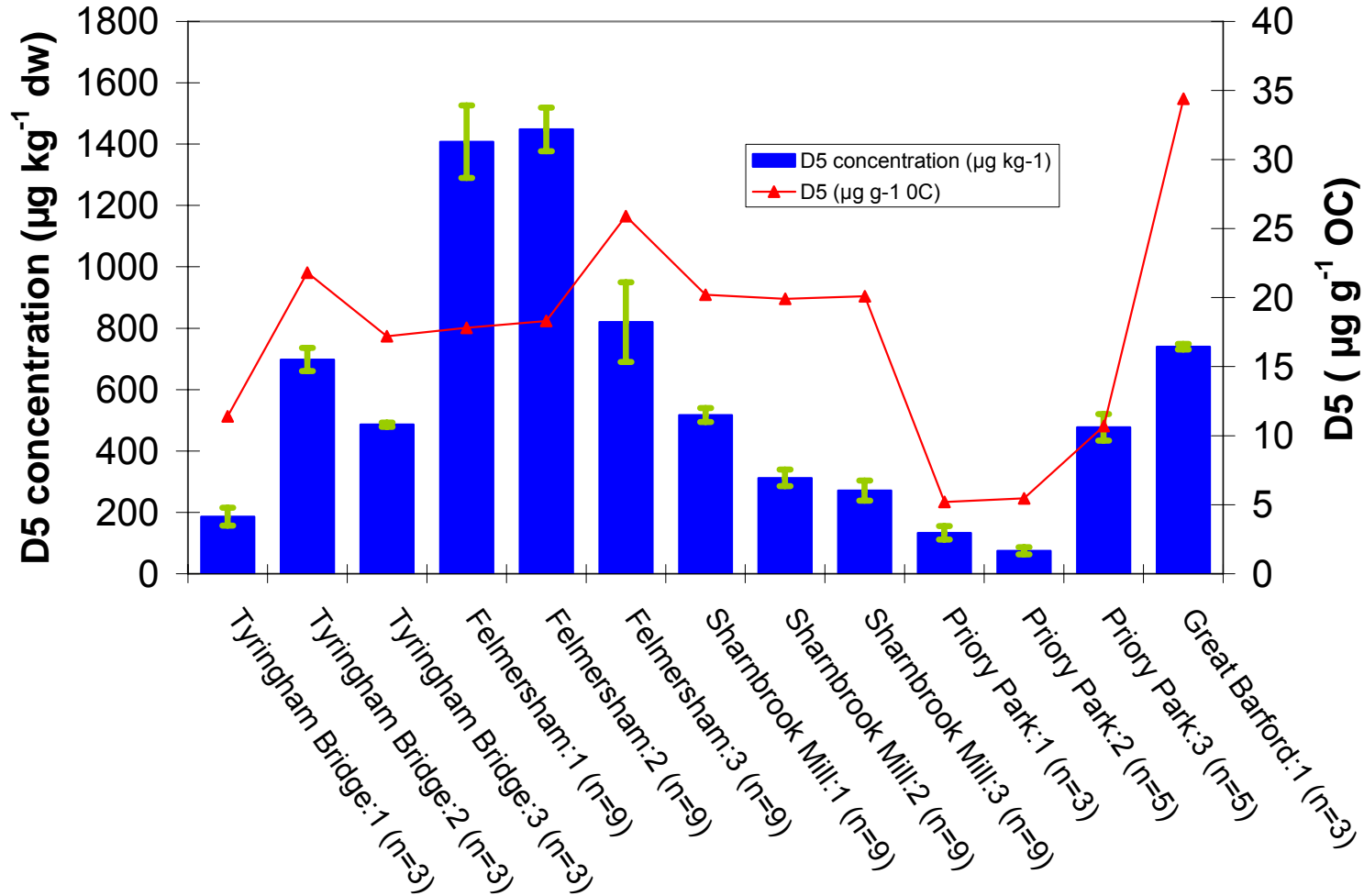
Quality Control

D5 Field Blank (Sanford Lake)	[a]8 – 30 µg/kg, dw (typically < 10 µg/kg, dw)	Full procedural (from sieving on river bank To analysis by GC/MS
IS recovery ($^{13}C_5$-D5)	85 – 124 % (n = 64)	Spiked ASE cell compared to calibration standards (averaged as appropriate)
Typical native D5 recovery (spike 548 µg/kg, dw)	89 ± 7 (n = 3)	Spiked in sediment and left to contact

[a]Data obtained in the range 37 to 114 µg/kg, dw prior to clean air cabinet

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Conclusions River Great Ouse

- All sediment results reported without blank correction
  - Sample concentrations > 3 x field blank (LOQ)
- Range of D5 concentrations in sediment = 75 to 1448 µg/kg
- Range of D5 concentrations in water = 7 to 57 ng/L
- Relationship between D5 present and the amount of OC
- (~ 20 µg g^{-1} OC typical)
- Consider "Total accessible" fraction of D5 in sediment

Practical approaches for estimating bioavailability

- Earliest approach by JJ Pignatello examined the reversible sorption of aliphatic halocarbons in soil

    - Desorption by repetitive batch extraction (water extraction)

    - Desorption with continuous removal of contaminant from the aqueous phase (e.g. Tenax extraction)

- More recent investigators have compared Tenax extraction with pore-water concentrations estimated using SPME

Batch desorption (water)

- Sediment containing D5 886 µg/kg, dw (solids 30%, OC 3.2%)
- 20 g wet weight in centrifuge tube (foil covered cap)
- ~70 ml of 0.01 M $CaCl_2$ (no headspace)
- Place on roller at 20 °C for 24 h
- Centrifuge at 3000 rpm (20 min)
  - Or until supernatant is clear
- Analyse D5 concentration in supernatant using HS GC/MS
  - Remove all supernatant and replace 0.01 M $CaCl_2$
  - Analyse for DOC as required
- Repeat each day

Batch desorption (water) - practical

Batch desorption (water) - plots

D5 desorption from sediment

Cumulative D_5 desorbed from sediment (ng)

- FE1
- FE2
- FE3

Time days
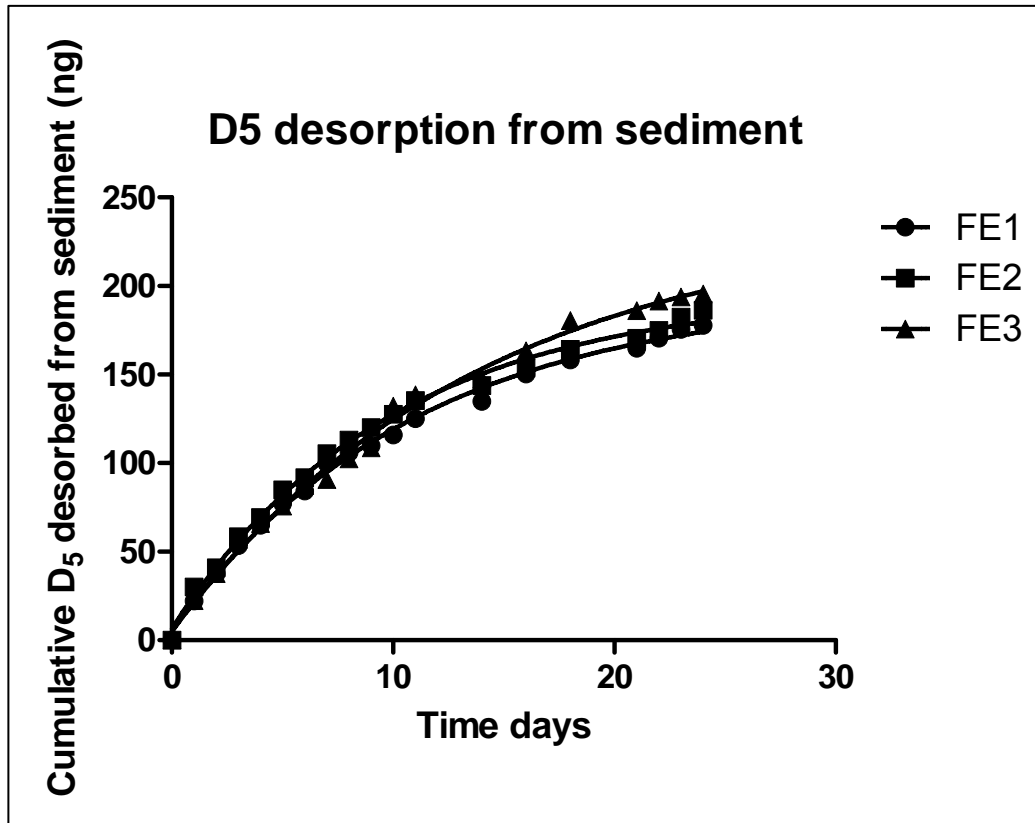
Initially 5351 ng D5, < 4% desorbed (from modelled value, 205 d)

K$_{oc}$ apparent

- After 24 days repeated extraction < 3.5 % of D5 in the sediment was desorbed into the aqueous phase.
- After equilibration (> 9 days) C$_{water}$ (ng/L) was determined (Dissolved Organic Carbon < 1 mg/L)
- At this point D5 measurements were freely dissolved
- In the last 4 days of the test the log Koc values ranged from 5.5 - 5.9.
- Total accessible fraction of D5 very low

K_{oc} apparent calculations

$$K_d(LKg^{-1}) = \frac{C_{solids}(ng/kg)}{C_{water}(ng/L)}$$

$$K_{oc} = \frac{K_d \times 100}{\%OC}$$

Why identify passive sampling?

- Time-weighted average (TWA), freely dissolved concentrations in surface water
  - Lower detection limit possible
    - Lake with no direct effluent input, only atmospheric deposition
    - Urbanised catchment and estuary (sea water)
- Potential use in sediment to establish freely dissolved pore water concentration

Collaboration with Portsmouth University

- Research team led by Graham Mills, Richard Greenwood
  - Post doc Enamul Hoque

Passive Sampling

- Concentrations of dissolved D5 in environmental waters is often low, near or below the detection limit of bottle sampling combined with GC-MS techniques (headspace)

- One way forward is to increase the mass available for analysis by using passive samplers

- A range of passive sampling devices is available, but not all are suitable for this application because of the unusual properties (high $logk_{OW}$, and high volatility) of this compound

Passive Sampling: types

- **SPMDs are not suitable because of the need to extract the analyte from the triolein receiving phase and clean up and concentrate the extract**
  - This would lead to losses
- **Chemcatcher, membrane-enclosed sorptive coating sampler (MESCO) are not suitable because of low uptake rates for compounds as non-polar as D5**
- **Sheet samplers without diffusion limiting membrane**
  - Silicone rubber sheets have high sampling rates but contain D5 monomers, and polymers that break down to produce D5 during handling (particularly at higher temperatures used in cleaning before deployment) and so it is difficult to obtain low blank levels
  - This can limit level of detection

Passive sampling: types

- Polyoxymethylene (POM) is a more crystalline plastic, and whilst having low contamination with D5 has slower uptake rates than are available with the silicone rubber sheets

- Low density polyethylene (LDPE) provides a compromise, and this was selected as a starting point for the development of a passive sampler at Portsmouth

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LDPE Passive Sampler

- LDPE sheet samplers have been used for compounds (e.g. large PCBs and PAHs) of similar polarity, but lower Henry's constant

- This material is available in a range of thicknesses and in large sheets and so can be cut to provide the necessary area for sampling, and shape for convenient handling

- Can be readily extracted in a range of solvents

LDPE Passive Sampler

- LDPE sheets are generally contaminated with D5 from either contact during manufacture or uptake from the air during storage
- Cleaning is necessary prior to use
  - Thermal desorption
  - Solvent extraction steps

LDPE: PRCs

- Potential for loading performance reference compounds (PRCs) onto LDPE prior to deployment to provide an *in situ* calibration, thus overcoming problems associated with the impact of variation in turbulence and temperature during deployment

- Loading using solutions of D5 and PRCs in Methanol : water (50 : 50, v/v)

- Extraction in solvents

  - MeOH – compatible with headspace analysis

  - Hexane – direct injection (large volume)

Overall conclusions

- GC/MS methods described suitable for measuring total D5 concentrations in R Great Ouse (UK) surface water and sediment
  - Good control of blanks (clean air cabinet)
- Total accessible fraction in sediment very low
  - Repetitive batch extraction from water (< 3.5% of D5 desorbed in 24 days)
  - LogK$_{OC}$ determined in the range 5.5 to 5.9
- Passive sampling using LDPE identified
  - LOQ 0.1 to 1 ng/L (target)
  - Enable monitoring below current LOQ

Acknowledgements

- Project leader Roger van Egmond (Environment)
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