

Bioaccessibility of PBDEs present in indoor dust: a novel dialysis membrane method with a Tenax TA® absorption sink

Article

Accepted Version

Creative Commons: Attribution-Noncommercial-No Derivative Works 4.0

Kademoglou, K., Williams, A. C. and Collins, C. D. (2018) Bioaccessibility of PBDEs present in indoor dust: a novel dialysis membrane method with a Tenax TA® absorption sink. *Science of the Total Environment*, 621. pp. 1-8. ISSN 0048-9697 doi: <https://doi.org/10.1016/j.scitotenv.2017.11.097> Available at <https://centaur.reading.ac.uk/74332/>

It is advisable to refer to the publisher's version if you intend to cite from the work. See [Guidance on citing](#).

To link to this article DOI: <http://dx.doi.org/10.1016/j.scitotenv.2017.11.097>

Publisher: Elsevier

All outputs in CentAUR are protected by Intellectual Property Rights law, including copyright law. Copyright and IPR is retained by the creators or other copyright holders. Terms and conditions for use of this material are defined in the [End User Agreement](#).

www.reading.ac.uk/centaur

CentAUR

Central Archive at the University of Reading

Reading's research outputs online

1 Supporting information

2 Bioaccessibility of PBDEs present in indoor dust: A novel dialysis membrane method with a Tenax
3 TA[®] absorption sink

4 Katerina Kademoglou^{a*}, Adrian C. Williams^b, Chris D. Collins^{a*}

5 ^aSoil Research Centre, Department of Geography and Environmental Science, University of Reading,
6 Whiteknights campus, RG6 6DW, Reading, UK

7 ^bSchool of Pharmacy, University of Reading, Whiteknights campus, RG6 6AD, Reading, UK

8

9 * - Corresponding authors: Katerina Kademoglou: a.kademoglou@pgr.reading.ac.uk or
10 Katerina.kademoglou@gmail.com; Chris Collins: c.d.collins@reading.ac.uk

11

12 Number of pages: 8

13 Number of figures: 3

14 Number of tables: 2

15

16

17 **Materials and methods**

18 **Chemicals and reagents**

19 Native standard solutions of BDE 28, 47, 77, 100, 128, 153, 154, and 183 were purchased from
20 Cambridge Isotope laboratories Inc. (UK). Purity of all standards was >98% unless otherwise stated.
21 Standard stock solutions were prepared in toluene for all compounds. Sodium sulphate (anhydrous,
22 granular/powder, 99% pure), high purity grade Silica gel pore size 60 Å, 70-230 mesh, 63-200 µm
23 (product code: #60741, Sigma-Aldrich), Florisil® 100-200 mesh (product code: #10104980, Acros
24 Organics), concentrated Sulfuric acid (H₂SO₄) 96% analytical grade (Fisher Scientific, UK), Tenax®
25 TA Porous Polymer Adsorbent, 60-80 mesh (product code: #11982, Sigma-Aldrich), Standard grade
26 regenerated cellulose (RC) Spectra/Por™ 3 (18mm flat width, 1.1mL/cm dialysis membrane MWCO
27 3.5 kDa) (Spectrum Labs Inc., USA, product code: #11425859; FisherScientific, UK), micro
28 centrifuge filters lined with 0.45µm pore size nylon filter 1.5mL volume capacity (product code #516-
29 0236, VWR) and 19mm Small Silver Binder Clips (product code: #WW-376137, Staples Inc, UK.).
30 Analytical grade inorganic salts were provided from Fisher Scientific (Loughborough, UK). All
31 biological reagents used for media preparation and organic solvents used for extraction and clean-up
32 steps were of HPLC grade and were obtained from Sigma-Aldrich (Gillingham, UK). Empty, pre-
33 fritted polypropylene filtration tubes (6 mL) for silica SPE and Florisil cartridge preparation (2 g, 6
34 mL) were purchased from Sigma-Aldrich (UK). For 5% acidified silica gel preparation, concentrated
35 sulphuric acid (H₂SO₄, >96%) was used and was purchased from Fisher Scientific. Briefly, 1.9 mL of
36 pure sulphuric acid was added drop-wise to 50 g of hexane-washed, oven-dried silica gel under
37 continuous and vigorous stirring. Glass test tubes were cleaned by soaking for at least 12 h in a
38 phosphate-free, alkali solution. After washing, the tubes were rinsed with deionised water, dried at
39 100 °C for at least 12 h and burned at 400°C to remove all traces of organic contamination

40 **Target analytes and analytical characteristics**

41 Table SI 1 – Target analytes and physicochemical properties calculated from EPISuite 4.1™.

Abbreviation	Full name	Molecular formula	MW (Da)	Log K _{ow}	Water solubility (mg/L) 25 °C	Vapour pressure (mm Hg, 25 °C)
BDE-28	2,4,4'-Tribromodiphenyl ether	C ₁₂ H ₇ Br ₃ O ₁	406.895	5.88	0.02642	9.16E-06
BDE-47	2,2',4,4'-Tetrabromodiphenyl ether	C ₁₂ H ₆ Br ₄ O ₁	485.791	6.77	0.001461	1.58E-06

BDE-100	2,2',4,4',6-Pentabromodiphenyl ether	C12 H5 Br5 O1	564.688	6.84	0.000394	3.10E-08
BDE-153	2,2',4,4',5,5'-Hexabromodiphenyl ether	C12 H4 Br6 O1	643.584	8.55	4.15E-06	1.86E-07
BDE-154	2,2',4,4',5,6'-Hexabromodiphenyl ether	C12 H4 Br6 O1	643.584	8.55	4.15E-06	1.41E-07
BDE-183	2,2',3,4,4',5,6'-Heptabromodiphenyl ether	C12 H3 Br7 O1	722.48	9.44	2.16E-07	2.45E-08

42

43 Table SI 2 Concentrations in dust samples and analytical confirmation of dust and SRM 2585
44 concentrations after spiking with PBDEs (200 µL of PBDEs native standard mix 1 ng/µL). All
45 concentration values are in ng/g.

Target analyte	*Concentration in UK dust before spiking	Concentration in UK dust after spiking	Expected concentration after spiking	§Recovery %	
BDE-28	11.4	186.1	211.4	88.0	
BDE-47	9.0	190.8	209.0	91.3	
BDE-100	2.5	188.1	202.5	92.9	
BDE-153	5.2	225.6	205.2	109.9	
BDE-154	2.2	178.4	202.2	88.2	
BDE-183	29.3	179.4	229.3	78.2	
Target analyte	*Concentration in SRM 2585	Concentration in SRM 2585 after spiking	Expected concentration after spiking	§Recovery %	*Ref value
BDE-28	15.3	190.3	215.3	88.4	46.9
BDE-47	446.5	589.2	646.5	91.1	497
BDE-100	35.8	188.1	235.8	79.8	43.8
BDE-153	137.5	363.8	337.5	107.8	119
BDE-154	99	264.7	299.0	88.5	83.5
BDE-183	52.5	204.6	252.5	81.0	43

46 *Taken from (Kademoglou et al., 2017)

47 § Recovery %= (Concentration in dust after PBDE spiking / Expected concentration) x 100

48 Table SI 3 - Composition of 1 litre of media used in the fed CEPBET test. Fed state conditions
49 achieved by addition of dietary components in stomach and colon media. From (Tilston et al., 2011)

Stomach, 1h, pH=2.5	
Reagent	Amount added in 1 L
Sodium malate (maleic acid)	0.5 g
Tri-sodium citrate	0.5 g
Lactic acid 85% w/w	420 µL
Acetic acid (glacial)*	500 µL
Pepsin (porcine)	1.25 g
Small Intestine, 4h, pH=7	
Bile salts	1.78 g
Pancreatine (porcine)	0.5 g
Colon, 16h, pH=6.5	
Mucin type II (porcine stomach)	4.0 g
Sodium chloride	4.5 g
Potassium chloride	4.5 g
Sodium bicarbonate	1.5 g
Magnesium sulphate hexahydrate	1.25 g
L-Cysteine Hydrochloride	800 mg
Potassium phosphate	500 mg
di-potassium phosphate	500 mg
Bile salts	400 mg
Calcium Chloride	189.0 mg
Haemin (>80%, bovine)	500 mg

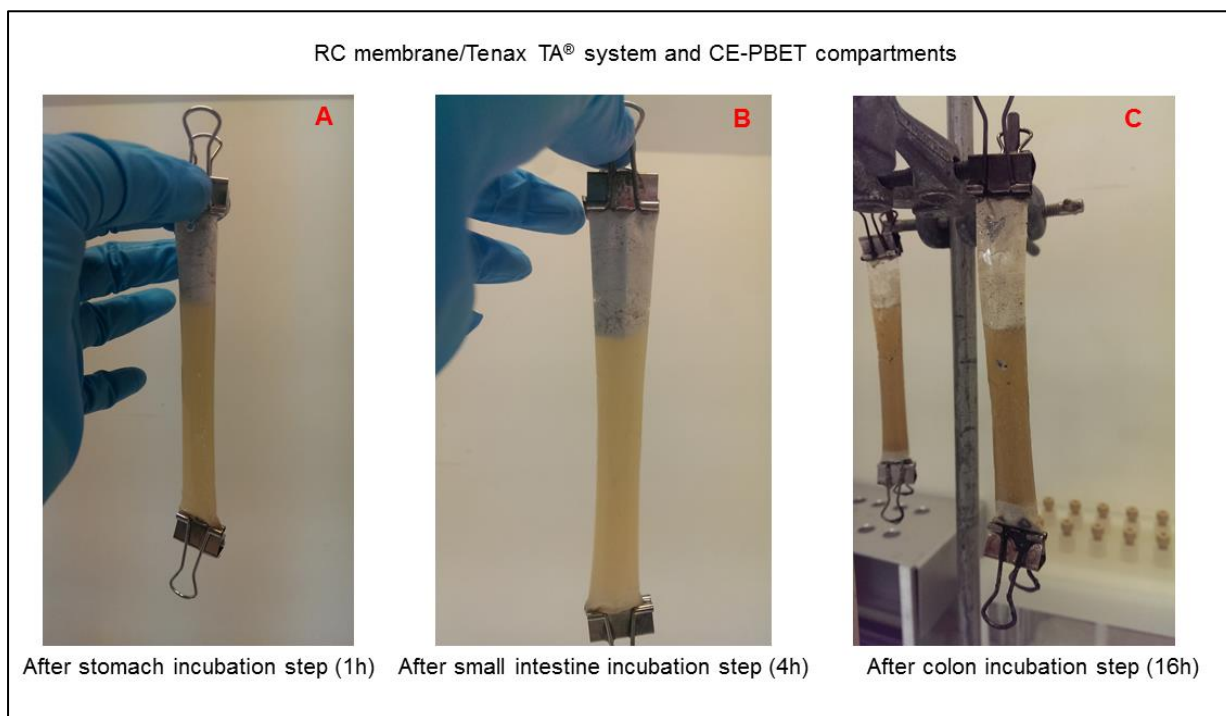
Iron (II) sulphate heptahydrate	5.0 mg
Dietary components	
Starch (potato)	5.0 g
Peptone (casein)	34 g
Tryptone (vegetable)	6.1 g
Yeast extract	4.5 g
Casein	3.0 g
Pectin (citrus)	2.0 g
Xylan (beechwood)	2.0 g
Arabinogalactan (larch)	2.0 g
Guar gum	1.0 g
Inulin (chicory)	1.0 g

50

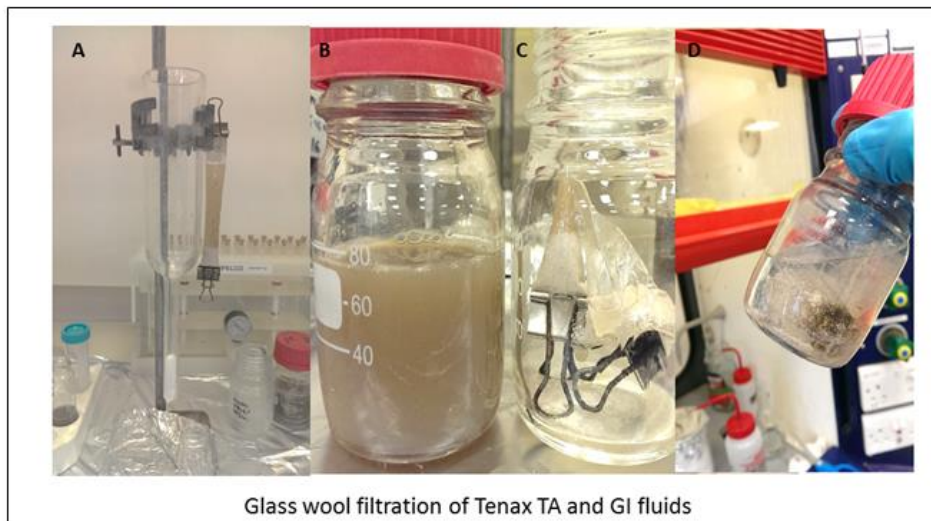
51 **Instrumental analysis**

52 A Thermo Trace GC Ultra system equipped with a Thermo TG-SQC capillary column (15 m x
53 0.25mm x 0.25 μ m) coupled to a Thermo ITQ 1100 mass spectrometer in electron ionisation mode
54 ((EI-MS) was connected through a heated transfer line (300°C). The injection temperature was set at
55 92 °C, hold 0.04 min, ramp 700 °C/min to 295 °C and 5 μ L of cleaned extracts in toluene were
56 injected for GC analysis. Injection was performed under a pressure of 0.19 bar until 1.25 min in
57 pulsed splitless mode 50 mL/min after 1.25 min. The GC temperature program was 90 °C, hold 1.50
58 min, ramp 10°C/min to 300°C, hold 3 min, ramp 40 °C/min to 310 °C, hold 5 min. Helium was used
59 as a carrier gas with a flow rate of 1.0 mL/min.

60 **RC membrane /Tenax TA[®] system**



Sample preparation and Tenax TA[®] recovery



Step 1: SI and colon fluids

- Collect SI and Colon fluids (spin 15 min at 3500rpm)
- Spike 200ng ISTDs
- Add 30mL Hex/EtOAc 1:3 (x2)
- R'n'R shake for 1h
- Subject for LLE (x2)
- Collect extracts + add Na₂SO₄
- Spin 15 min at 3500rpm
- Collect organic phase
- Subject to Florisil[®] fractionation & SPE clean-up (F1 only)

Step 2: Tenax TA[®] recovery

- After SI incubation, filter SI fluids using glass wool
- After colon incubation, filter Tenax TA[®] from RC membrane using glass wool filtration
- Collect glass wool filters from SI and colon fluid filtration in one bottle
- Chop RC membrane in 4 smaller pieces
- Add the 19mm metallic clippers for extraction as well

Step 3: Tenax TA[®] and residual dust

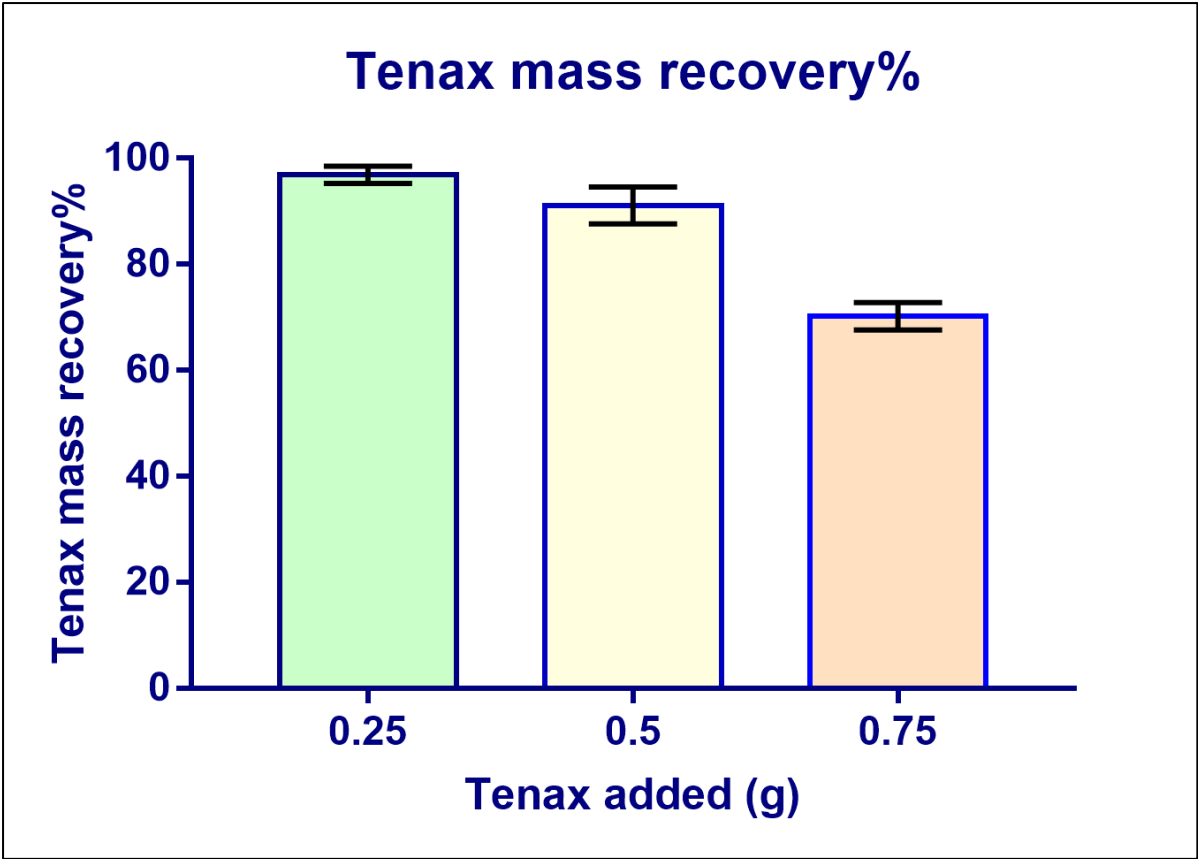
- Spike 200ng ISTDs
- Add 30mL Ace/Hex1:3 (x2)
- R'n'R shake for 1h
- Subject for ultrasonication (x2)
- Collect extracts + add Na₂SO₄
- Spin 15 min at 3500rpm
- Collect organic phase
- Subject to Florisil[®] fractionation & SPE clean-up (F1 only)

Step 4: Before Florisil[®] fractionation

- Collect all extracts (approx 50-60mL each) from SI, colon, Tenax TA[®] and residual dust
- Concentrate to 1mL using a BUCHI Syncore[®] evaporator
- Extracts ready (1mL in hexane) for Florisil[®] fractionation & SPE clean-up (F1 only)

66

67 **Figure SI 2** – Schematic representation of sample preparation of CE-PBET fluids and residual dust, as well as Tenax TA recovery using glass wool filtration



68

69 **Figure SI 3** Bar chart presenting Tenax TA mass recovery% in different amounts of Tenax TA tested

Table SI 4 – Extraction efficiency (%) for small intestine and colon compartment using LLE, Tenax TA[®] and residual dust with ultrasonication assisted extraction. All samples were assessed in triplicates (n=3).

Target analyte	Small Intestine (n=3)			Colon (n=3)			Tenax TA [®] (n=3)			Residual dust (n=3)		
	AVG%	STDEV	RSD%*	AVG%	STDEV	RSD%	AVG%	STDEV	RSD%	AVG%	STDEV	RSD%
BDE-28	74.8	6.0	8.0	76.8	9.2	12.0	66.7	0.1	9.0	71.9	6.5	9.0
BDE-47	87.7	2.9	3.3	82.9	1.9	2.3	77.1	0.1	8.5	68.0	5.7	8.5
BDE-100	69.2	9.4	13.6	77.7	10.5	13.5	54.2	0.1	6.0	52.0	3.1	6.0
BDE-153	58.6	0.03	4.4	77.7	0.1	16.6	89.0	0.1	10.0	92.9	6.0	6.5
BDE-154	96.7	0.0	2.6	79.3	13.2	0.2	103.7	0.1	10.0	86.0	5.8	6.7
BDE-183	92.2	0.1	13.8	66.2	0.1	17.9	90.3	0.00	0.1	65.5	0.0	0.1

*RSD%= (STDEV/AVG)*100

References for SI

- Kademoglou, K., Xu, F., Padilla-Sanchez, J.A., Haug, L.S., Covaci, A., Collins, C.D., 2017. Legacy and alternative flame retardants in Norwegian and UK indoor environment: Implications of human exposure via dust ingestion. *Environ. Int.* 102, 48–56. doi:10.1016/j.envint.2016.12.012
- Tilston, E.L., Gibson, G.R., Collins, C.D., 2011. Colon Extended Physiologically Based Extraction Test (CE-PBET) Increases Bioaccessibility of Soil-Bound PAH. *Environ. Sci. Technol.* 45, 5301–5308. doi:10.1021/es2004705