

Polybrominated diphenyl ethers and “novel” brominated flame retardants in floor and elevated surface house dust from Iraq

Al-Omran, Layla Salih; Harrad, Stuart

DOI:

[10.1016/j.emcon.2015.10.001](https://doi.org/10.1016/j.emcon.2015.10.001)

License:

Creative Commons: Attribution-NonCommercial-NoDerivs (CC BY-NC-ND)

Document Version

Publisher's PDF, also known as Version of record

Citation for published version (Harvard):

Al-Omran, LS & Harrad, S 2016, 'Polybrominated diphenyl ethers and “novel” brominated flame retardants in floor and elevated surface house dust from Iraq: Implications for human exposure assessment', *Emerging Contaminants*, vol. 2, no. 1, pp. 7-13. <https://doi.org/10.1016/j.emcon.2015.10.001>

[Link to publication on Research at Birmingham portal](#)

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.



Research article

Polybrominated diphenyl ethers and “novel” brominated flame retardants in floor and elevated surface house dust from Iraq: Implications for human exposure assessment

Layla Salih Al-Omran ^{a, b}, Stuart Harrad ^{a, *}^a School of Geography, Earth, and Environmental Sciences, University of Birmingham, Birmingham, B15 2TT, UK^b Division of Food Science, College of Agriculture, University of Basrah, Basrah, Iraq

ARTICLE INFO

Article history:

Received 3 June 2015

Received in revised form

8 September 2015

Accepted 9 October 2015

Available online 29 November 2015

Keywords:

PBDEs

NBFRs

Floor dust

Elevated surface dust

Iraq

Human exposure

ABSTRACT

Concentrations of polybrominated diphenyl ethers (PBDEs) and selected novel brominated flame retardants (NBFRs) were measured in indoor dust from the living areas of 18 homes in Basrah, Iraq. This is the first report of contamination of the Iraqi environment with these chemicals. To evaluate the implications for human exposure, samples were collected from both the floor and from elevated surfaces like tables, shelves and chairs. When normalised for the organic carbon content of the dust sample, concentrations in elevated surface dust of BDE-99, BDE-209, pentabromoethylbenzene (PBEB), bis (2-ethylhexyl) 3,4,5,6-tetrabromophthalate (BEH-TEBP), and decabromodiphenylethane (DBDPE) exceeded significantly ($p < 0.05$) those in floor dust from the same rooms. This suggests that previous studies that base estimates of adult exposure via dust ingestion on floor dust, may underestimate exposure. Such underestimation is less likely for toddlers who are far more likely to ingest floor dust. Concentrations of PBDEs and NBFRs in indoor dust from Basrah, Iraq are at the lower end of levels reported elsewhere. The PBDE contamination pattern in our samples suggests that use in Iraq of the Deca-BDE formulation, exceeds substantially that of Penta-BDE, but that use of the Octa-BDE formulation has been higher in Iraq than in some other regions. Reassuringly, our estimates of exposure to our target BFRs via dust ingestion for the Iraqi population fall well below the relevant health-based limit values.

Copyright © 2015, The Authors. Production and hosting by Elsevier B.V. on behalf of KeAi Communications Co., Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Polybrominated diphenyl ethers (PBDEs) and “novel” brominated flame retardants (NBFRs) are chemicals added to a wide range of consumer products (electrical and electronic equipment, textiles, polyurethane and polystyrene foams) to meet flame retardancy standards set by various jurisdictions worldwide [1–6]. Since in most applications these chemicals are used additively - i.e. they are not covalently linked to the products in which

they are incorporated - they can transfer from such products into the environment. An extensive body of studies have reported the presence of PBDEs in indoor air [7–9], indoor dust [10–21], sediments [22–24] and biota samples [25,26]. Evidence of their persistence and capacity for bioaccumulation, coupled with concerns about their adverse health effects [27–32], have led to widespread bans and restrictions on the manufacture and use of both the Penta- and Octa-BDE mixtures and their listing under the Stockholm Convention on Persistent Organic Pollutants (POPs) [33]. Moreover, manufacture and use of Deca-BDE has been progressively restricted and is currently under consideration for listing under the Stockholm Convention [34]. Such bans and restrictions on the use of PBDEs without concomitant relaxation of flammability standards, has likely resulted in increased production and use of alternatives referred to collectively as novel BFRs (NBFRs). Prime examples of such NBFRs include: pentabromoethylbenzene (PBEB), 2-ethylhexyl-2,3,4,5-

* Corresponding author.

E-mail address: S.J.Harrad@bham.ac.uk (S. Harrad).

Peer review under responsibility of KeAi Communications Co., Ltd.



Production and Hosting by Elsevier on behalf of KeAi

tetrabromobenzoate (EH-TBB), bis (2-ethylhexyl) 3,4,5,6-tetrabromophthalate (BEH-TEBP), 2-bis (2,4,6-tribromophenoxy) ethane (BTBPE), and decabromodiphenylethane (DBDPE) [30]. The exact global production volume of NBRFs is unclear, although one estimate placed production in the mid-2000s at about 18,000 tons per annum, with a projected growth of around 5% per year [35]. Recently, NBRFs have received increasing attention due to their detection in sediments [23,36,37], indoor dust [19,20,38–41], and birds [23]. Recent studies suggest NBRFs may be endocrine disruptors [42], but overall, insufficient information is currently available regarding their fate and toxicological effects [31,43].

The similarity in physicochemical properties and applications between PBDEs and NBRFs leads to the hypothesis that human exposure to NBRFs will occur via similar pathways [35]. Specifically, human exposure to PBDEs occurs via the diet, and via inhalation of (primarily indoor) air, as well as ingestion of indoor dust. The relative significance of each pathway varies considerably according to factors such as: geographical location (dust ingestion appears more important in North America than elsewhere), age (dust ingestion is considered of greater magnitude for young children than adults), and the physicochemical properties of a given PBDE congener (exposure to decabromodiphenyl ether (BDE-209) is dominated by dust ingestion owing to its very low vapour pressure and comparative low capacity for bioaccumulation).

Thus, although the contribution of indoor dust ingestion to overall human exposure is variable, the weight of evidence suggests it likely warrants evaluation for NBRFs. Moreover, the vast majority of exposure assessments conducted to date for both PBDEs and NBRFs, have been conducted in East Asia (China, Korea, and Japan), Europe, and North America [44]. While data is emerging for other regions (including Egypt [20] and Kuwait [40,45]), to our knowledge no information exists concerning the presence of PBDEs and NBRFs in indoor dust in Iraq.

Moreover, no universally accepted standard method exists for the sampling of indoor dust for assessment of human exposure to organic contaminants [46]. To date, the majority of studies collect floor dust. However, a few studies suggested sampling dust from elevated surfaces at least 1 m above the floor in order to exclude dirt, sand and gravel [7,47,48,49,50], and in a study comparing PBDE concentrations in indoor dust collected by different methods, Bjorklund et al. (2012) [50] found that PBDE concentrations in floor dust from vacuum cleaner bags were exceeded by those in researcher-collected dust from elevated surfaces [50]. Similarly, by following the same researcher-collected method for both surfaces, Cequier et al. (2014) [51] found that the median concentration of BDE-209 and non-PBDEs in ESD ($n = 12$) are slightly higher than in FD ($n = 48$), but the difference was not significant. In contrast, concentrations of PBDEs in dust from elevated surfaces in Korean primary schools were lower than those in floor dust [52]. Elucidating whether differences in BFR contamination exist between floor and elevated surface dust is important as the two dust types likely influence human exposure in different ways. While young children are likely more exposed to floor dust, adults likely have greater contact with elevated surface dust. Hence, significant differences between the levels of contamination between floor and elevated surface dust has implications for human exposure assessment.

Against this backdrop, this study tests the hypothesis that concentrations of PBDEs and selected NBRFs in dust from elevated surfaces will exceed significantly those in floor dust from the same rooms. We also aimed to provide the first evaluation of the exposure of the Iraqi population to these contaminants. To test this hypothesis and achieve our aim, we determine concentrations of

PBDEs and NBRFs in samples of elevated surface dust (ESD) and floor dust (FD) from 18 homes in Basrah, Iraq.

2. Materials and methods

2.1. Chemicals and standards

Individual standards of PBDE congeners and internal standards 2,4,4'-TriBDE (BDE-28), 2,2',4,4'-TetraBDE (BDE-47), $^{13}\text{C}_{12}$ -2,2',4,4'-TetraBDE (MBDE-47), 2,2',4,4',5-PentaBDE (BDE-99), $^{13}\text{C}_{12}$ -2,2',4,4',5-PentaBDE (MBDE-99), 2,2',4,4',6-PentaBDE (BDE-100), 2,2',4,4',5,5'-HexaBDE (BDE-153), $^{13}\text{C}_{12}$ -2,2',4,4',5,5'-HexaBDE (MBDE-153), 2,2',4,4',5,6-HexaBDE (BDE-154), 2,2',3,4,4',5,6-HeptaBDE (BDE-183), DecaBDE (BDE-209) 50 ng/ μL and $^{13}\text{C}_{12}$ -DecaBDE (MBDE-209) 25 ng/ μL , BTBPE, EH-TBB, BEH-TEBP, PBEB, and labelled internal standard $^{13}\text{C}_{12}$ -BTBPE (MBTBPE), and $^{13}\text{C}_{12}$ -BEH-TEBP (MBEH-TEBP) 50 ng/ μL , and DBDPE 25 ng/ μL were obtained from Wellington laboratories, Canada (all with purity >98%). Ethyl acetate (EA), Acetone (Ac), n-Hexane, dichloromethane (DCM), iso-octane and concentrated sulfuric acid were purchased from Fisher Scientific, UK. All solvents used during analysis were of analytical grade.

Silica gel (pore size 60 Å, 7–320 mesh) was purchased from Sigma Aldrich, Switzerland; anhydrous sodium sulfate was obtained from Sigma Aldrich, USA, and Florisil (particle size 60–100) was acquired from Fluka, USA. The NIST standard reference material (SRM 2585, "Organic Contaminants in House Dust") from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA), ISOLUTE amino propyl columns, SPE cartridges and frits were purchased from Biotage (Uppsala, Sweden). Acid impregnated silica (44%, w/w) was prepared as described elsewhere [53]. Activated Florisil was prepared by baking at 450 °C for 1 h, cooling and subsequent cleaning with n-hexane (1 cycle extraction by Accelerated Solvent Extraction) and stored until use in a sealed pre-cleaned glass bottle.

2.2. Sample collection

From urban houses in Basrah province, South Iraq (Fig. S1, supporting materials), 2 dust samples were collected from each of 18 houses, between July and August 2013. In each house, one sample was collected from the living area floor (referred to here as floor dust - FD), with a second sample collected that comprised settled dust from elevated surfaces in the same living area such as tables, shelves, bookcases (referred to here as elevated surface dust - ESD). Home-owners were requested to not vacuum floors or elevated surfaces for at least 1 week before sampling. Floor dust samples were collected using a vacuum cleaner (DIRT DEVIL-DDMHH1-1100W), according to a standardised method [10]. Briefly, 1 m² of carpeted floor was vacuumed for 2 min, while for bare floors, 4 m² surface was vacuumed for 4 min. Dust was retained using 25 μm pore size nylon sample socks (Allied Filter Fabric Pty Ltd, Australia) mounted in the furniture attachment tube of the vacuum cleaner. Elevated surfaces (typically between 80 and 150 cm height) were vacuumed for 2–4 min depending on the surface area. After sampling, socks were closed with a twist tie, sealed in a plastic bag and stored at –20 °C. Before sampling, the furniture attachment and the vacuum tubing were cleaned thoroughly using an isopropanol-impregnated disposable wipe. At the time of sample collection, information on potential influences on BFR contamination such as: the number and type of putative sources like electronic devices, foam-filled furniture and floor material, ventilation system, house cleaning method, occupants and time spent in the living area was recorded. Samples were subsequently transferred to Birmingham, UK, for sieving and

analysis. Prior to analysis, all dust samples were passed through a pre-cleaned, n-hexane rinsed 250 μm mesh testing sieve (UKGE Limited, UK), covered with the lid and shaken for 2–4 min. Sieved samples were stored in clean, n-hexane rinsed glass jars and stored at 4 °C until analysis. While our previous work has used a 500 μm mesh sieve, this study employed a 250 μm mesh sieve for two reasons: (1) evidence that concentrations of chemicals like BFRs varies according to particle size [54,55,56] and (2) studies that suggest strongly that particle adherence to human skin falls off markedly at diameters >250 μm [57,58,59].

2.3. Sample extraction

Sample extraction was performed according to Ali et al. (2011b) [60] and van den Eede et al. (2012) [61] with minor modifications. Briefly, in a 12 mL glass centrifuge tube, an accurately weighed (80–120 mg) aliquot of dust was spiked with a mixture of surrogate standards (20 ng of MBDE47, 99, 153, MBTPE, MBEH-TEBP and 40 ng of MBDE-209) in isooctane. The samples were extracted with 2 mL n-hexane: acetone (3:1 v/v), 2x (vortexed for 2 min, sonicated for 5 min) and centrifuged at 3500 rev/min for 5 min. The extraction process was repeated three times and for each extraction process, the supernatant was separated and pooled. This combined extract was evaporated to incipient dryness under a gentle nitrogen stream, resolubilized in 1 mL of n-hexane and vortexed for 1 min.

2.4. Extract purification

The concentrated extract was quantitatively transferred onto a SPE column packed with 2 g Florisil that had been pre-washed and conditioned with ~15 mL of hexane. Analytes were eluted in two fractions: fraction 1 (F1) (PBDEs, DBDPE and PBEB) was eluted with 12 mL of n-hexane, with fraction 2 (F2) (containing BTBPE, EH-TBB, and BEH-TEBP) was eluted with 15 mL of EA. F1 was evaporated to 1 mL under a gentle nitrogen stream and transferred onto a 2 g 44% acidified silica cartridge, pre-conditioned with 15 mL hexane, prior to elution with 15 mL hex: DCM (1:1 v/v). F2 was evaporated to incipient dryness under a gentle nitrogen stream, resolubilised in 2–3 mL hexane, before reduction in volume to 1 mL, and transfer onto an aminopropyl functionalised silica column (0.5 g, pre-washed with 6 mL hexane), eluted with 12 mL hex:DCM (1:1 v/v). F1 and F2 were combined and evaporated under nitrogen flow using a Turbovap (Biotage Turbo Vap® II) to incipient dryness, before resolubilisation in 100 μL of iso-octane containing PCB-129 at 250 pg/ μL ready for GC-MS analysis.

2.5. Instrumental analysis

Aliquots of sample extracts (2 μL) were injected into a gas chromatograph (GC) (Trace 1310 Gas Chromatograph) coupled to a mass spectrometer (MS) (ISQ Quadrupole MS); both (Thermo Fisher Scientific, USA). The GC was equipped with a programmable temperature vaporizer (PTV) injector and fitted with a capillary fused silica column (RESTEK, USA, 15 m X 0.25 mm inner diameter, 0.1 μm film thickness). The MS was operated in ECNI mode for determination of BDE-209 and all target NBFrs (except PBEB), and in EI mode for determination of other PBDEs and PBEB. Helium was used at a flow rate of 1.5 mL/min as a carrier gas, with methane used as standard reagent gas for ECNI-MS. Detailed information about GC/MS analysis parameters are provided as supporting material (Tables S1, S2 and S3). MBDE-47 was used as a surrogate standard for quantification of BDE-28, BDE-47 and PBEB, MBDE-99 was used to quantify BDE-99 and BDE-100, MBDE-153 was used for BDE-153, BDE-154 and BDE-183, MBTPE for BTBPE and EH-TBB,

MBEH-TEBP for BEH-TEBP, while MBDE-209 was used for BDE-209 and DBDPE.

2.6. QA/QC and method validation

All glassware were cleaned by soaking in an alkali solution overnight, before rinsing with tap water, followed by deionised water, baking at 450 °C for 4.5 h, cooling, washing with acetone, and covering with aluminum foil until use. Sodium sulfate was washed with hexane, prior to baking at 400 °C for 4.5 h before use. For GC-MS calibration, a five point calibration was conducted. Good linearity was achieved with a correlation coefficient exceeding 0.99. Three laboratory solvent blanks and one quality control sample (NIST SRM 2585, organics in indoor dust) were processed in parallel with every 18 real dust samples. Limits of detection (LOD) were estimated based on a signal to noise ratio 3:1 and limits of quantification (LOQ) were estimated based on signal to noise ratio of 10:1, Table S4 (Supporting Material).

The efficacy of our analytical method was initially assessed via a matrix spike experiment that measured recoveries of surrogate compounds using our same extraction and clean-up method. Internal standard recoveries ($n = 7$) were assessed using 100 mg of Na_2SO_4 as a surrogate matrix spiked with standard solution. The spiking levels were 200 ng/g for M-BDE-47, M-BDE-99, M-BDE-153, M-BTPE and M-BEH-TEBP, and 400 ng/g for M-BDE-209. PCB-129 was used as recovery determination standard. The results are summarised in Table S5 (supporting material) with average recoveries ranging between 76 and 117% with a standard deviation ranging between 6.4 and 16.8%. Table S5 also shows satisfactory IS recoveries (average 70–101%) determined subsequently for dust samples. No target compounds were detected in reagent blanks. Method accuracy was assessed through replicate analysis ($n = 3$) of SRM 2585, with the PBDE concentrations found in this study comparing satisfactorily to the certified values. For NBFrs, no certified or indicative values were available for SRM2585. Therefore, we compared our detected concentrations with those reported in other studies S6 (supporting material). This comparison suggested our method produced satisfactory results for our target NBFrs.

2.7. Determination of organic carbon content in dust

To test the hypothesis that any differences in FR concentrations between ESD and FD were attributable to differences in organic carbon content of the dust, we measured the OC content of our samples. In 12 homes, sufficient dust was available after BFR analysis to permit determination of organic carbon in both ESD and FD. To achieve this, approximately 20 mg of dust were weighed into 8 by 5 mm tin capsules using a Sartorius (Model MC5, Sartorius AG, Germany) microbalance. These samples were run through a 2000 Elemental Analyser (ThermoFisher Scientific, Netherlands), using EDTA as a standard. Additional standards were run every 15 dust samples to check for machine drift.

2.8. Statistical analysis

Statistical analysis of our data was performed using IBM SPSS statistics software (V. 20) and Microsoft Excel 2013. For the purposes of statistical evaluation, all concentrations below LOD were assigned a value of 0.5 LOQ. The distribution of our concentration data for PBDEs and NBFrs in both FD and ESD were tested using the Shapiro–Wilk test. This - combined with visual inspection - indicated that the data was log-normally skewed ($P < 0.05$), therefore all data were log-transformed prior to comparison of means via a paired t-test. Potential correlations between various parameters

were investigated using Pearson Correlation, with $p < 0.05$ used as the level indicating statistical significance.

3. Results and discussion

3.1. Concentrations of PBDEs and NBRFs in Iraqi house dust

Since to the authors' knowledge PBDEs and NBRFs are not produced in Iraq, we assumed the sources of these chemicals are imported consumer products. Table 1 summarises the concentrations of eight PBDE congeners (BDE-28, 47, 99, 100, 153, 154, 183, and 209) and five NBRFs (PBEB, EH-TBB, BTBPE, BEH-TEBP, and DBDPE) in samples of both ESD and FD from Iraqi homes. Detection frequencies for individual PBDE congeners and NBRFs were 44–100% in both ESD and FD. BDE-209 was the predominant congener with a maximum concentration of 3847 ng/g (ESD) and 2758 ng/g (FD) and a median of 865 ng/g and 612 ng/g for ESD and FD respectively. This is about 35–40 times higher than the median concentration of Penta-BDE congeners (represented by Σ tri-hexa-BDE = BDE-28, 47, 99, 100, 153 and 154) and ~100 times higher than the median concentration of BDE-183 (an indicator of Octa-BDE). This may reflect ongoing use of Deca-BDE despite bans on Penta-BDE and Octa-BDE. The second most abundant compound was DBDPE with a median concentration of 183 ng/g (ESD) and 125 ng/g (FD) followed by BEH-TEBP with median concentrations in ESD and FD of 82.7 ng/g and 64.2 ng/g respectively. Median concentrations of other contaminants ranged from <0.1 ng/g for PBEB and BDE-28 in FD and 15.2 ng/g for BTBPE in ESD.

Table 2 places our data for PBDEs in dust from Iraqi homes sampled in 2013 with those from selected related studies elsewhere in the world. Although our concentrations for Basrah, Iraq exceed generally those for Egypt, Pakistan, and Vietnam, they are at the lower end of those reported globally, and in keeping with

previous studies are substantially lower than those reported for North America. In terms of the congener pattern, the comparatively low abundance of BDEs 47 and 99 observed in this study suggests limited use of the Penta-BDE formulation in Iraq. In contrast, the dominance of BDE-209 implies extensive application of the Deca-BDE product. Of note is the comparatively elevated abundance of BDE-183, which suggests relatively high application of the Octa-BDE formulation in Iraq. No relationships between BFR concentrations in dust and room contents, ventilation type etc. were apparent.

Table 3 places our data for Iraqi homes in context with the more limited international database available for NBRFs. As with the PBDEs, concentrations of our target NBRFs in this study are at the lower end of those reported previously, but lying more towards the mid-range, particularly for BTBPE and DBDPE. Moreover, in line with several previous studies, the ratio of EH-TBB:BEH-TEBP differs from the ratio observed in the commercial FM550 product (4:1) which suggests FM-550 is not the only source of these compounds.

3.2. Comparison of BFR concentrations in floor and elevated surface dust

Following log transformation of concentrations expressed on a dry dust weight basis, a paired t-test was applied to test the hypothesis that concentrations of our target BFRs in ESD would exceed significantly those in FD. This revealed concentrations of BDE-28, BDE-99, BDE-209, PBEB, BEH-TEBP, and DBDPE in ESD to exceed significantly those in FD, with ($P < 0.05$) 0.047, 0.014, 0.002, 0.003, 0.036, 0.031 respectively. These findings were consistent with those of Björklund et al. (2012) [50] who reported concentrations of PBDEs in elevated surface dust to exceed significantly those in vacuum cleaner dust, and with those of Cequier et al. (2014) [51] who reported concentrations of BDE-209 and non-

Table 1
Statistical summary of concentrations (ng/g) of target PBDEs and NBRFs in elevated surface dust (ESD) and floor dust (FD) from Iraqi homes.

Compound	Sample type	Detection %	Mean	Minimum	Maximum	Median	5th %ile	95th %ile
BDE-28	ESD	61	0.57	<0.1	1.82	0.43	<0.1	1.55
BDE-28	FD	44	0.31	<0.1	1.2	<0.1	<0.1	1.11
BDE-47	ESD	94	13.1	<0.1	84.8	6.32	2.58	49.8
BDE-47	FD	83	7.66	<0.1	37.6	3.6	<0.1	28.2
BDE-99	ESD	94	18.5	<0.1	73.8	13	<0.2	71.7
BDE-99	FD	78	11	<0.1	49.2	6.67	<0.2	36.1
BDE-100	ESD	67	2.8	<0.2	12.8	1.14	<0.2	8.72
BDE-100	FD	50	1.64	<0.2	7.43	0.6	<0.2	5.48
BDE-153	ESD	61	6.09	<0.01	25.1	0.73	<0.01	20.7
BDE-153	FD	72	4.32	<0.01	16.9	0.54	<0.01	14.3
BDE-154	ESD	67	1.67	<0.1	8.89	0.74	<0.1	6.22
BDE-154	FD	61	1.94	<0.1	11.3	0.61	<0.1	6.56
BDE-183	ESD	94	7.85	<0.2	18.6	6.9	0.88	15.2
BDE-183	FD	94	11.1	<0.2	46.5	7.5	1.88	37.6
BDE-209	ESD	100	1160	277	3850	865	360	3270
BDE-209	FD	100	762	193	2760	612	306	1590
PBEB	ESD	72	0.41	<0.1	1.52	0.25	<0.1	1.42
PBEB	FD	44	0.14	<0.1	0.55	<0.1	<0.1	0.45
EH-TBB	ESD	78	7.49	<1.3	20.6	6.15	<1.3	19.9
EH-TBB	FD	61	6.8	<1.3	28	5.28	<1.3	16.6
BTBPE	ESD	72	17.5	<9	43.7	15.2	<9	43.1
BTBPE	FD	78	17.1	<9	50.7	14.1	<9	32.2
BEH-TEBP	ESD	100	125	33.9	412	82.7	47.8	368
BEH-TEBP	FD	89	99.5	<6.8	294	64.2	<6.8	248
DBDPE	ESD	100	173	58.1	351	183	64.9	295
DBDPE	FD	100	129	33	269	125	33	214
Σ tri-hexa BDE ^a	ESD	100	42.7	0.33	200	24.8	5.42	162
Σ tri-hexa BDE ^a	FD	100	26.9	1.31	108	15.8	2.3	91.4
Σ BDE ^b	ESD	100	1210	294	3910	924	382	3300
Σ BDE ^b	FD	100	800	217	2810	635	333	1610

^a Sum of PBDEs 28, 47, 99, 100, 153 and 154.

^b Sum of PBDEs 28, 47, 99, 100, 153, 154, 183 and 209.

Table 2

Comparison of median concentrations (ng/g) of PBDEs detected in floor (FD) and elevated surface dust (ESD) in this study with previous reports.

Sampling year-Country (Reference)	Sample type	n	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 183	BDE 209
2013-Iraq (this study)	FD	18	<0.1	3.6	6.67	0.6	0.54	0.61	7.5	612
2013-Egypt [20]	FD	17	0.34	1.7	2.7	0.37	6.62	0.38	1.1	40.2
2011-Kuwait [40]	FD	15	n.a.	9.5	12	2.3	2.4	1.3	1.9	310
2011-Pakistan [40]	FD	15	n.a.	1.3	1.7	0.3	0.6	0.4	1.5	138
n.a.-Hong Kong [66]	FD	23	37.6	102	75.4	84.9	10.9	8.36	77.7	975
2010-China [67]	FD	14	1.45	5.28	3.44	0.52	1.59	0.48	3.73	1610
2006-UK [11]	FD	20	0.53	13	23	4.2	5.2	3.3	13	2800
n.a.-Germany [19]	FD	20	0.1	5.7	9.2	1.6	2.1	1.1	9.3	950
2008-Sweden [50]	FD	19	0.19	15	13	2.7	2.2	1.5	1.5	280
2012-Norway [51]	FD	48	0.68	126	171	33.1	26	12.7	3.22	326
2006-USA [11]	FD	28	14	410	820	160	110	89	16	1300
2006-Canada [11]	FD	10	4.1	140	330	65	43	39	9	560
2007–2008-Canada [41]	FD	116	4.5	280	350	67	42	25	14	1300
2006-New Zealand [11]	FD	20	0.65	24	51	8.9	5.4	5.1	n.a.	n.a.
n.a.-Australia [68]	FD	10	n.a.	60	100	18	13	9	14	730
2013-Iraq (this study)	ESD	18	0.43	6.32	13.0	1.14	0.73	0.74	6.9	865
2008-Sweden [50]	ESD	18	0.78	38	25	5.5	6	2.9	3	520
n.a.-Seweden [48]	ESD	10	1.3	42	52	n.a.	6.6	n.a.	12	320
2008-Vietnam [69]	ESD	6	n.a.	4.1	3.6	n.a.	1.4	n.a.	2.6	160

n.a. = not available.

Table 3

Comparison of median concentrations (ng/g) of NBFRs studied in floor dust (FD) and elevated surface dust (ESD) in this study with previous reports.

Sampling year-Country (Reference)	Sample type	n	PBEB	EH-TBB	BEH-TEBP	BTBPE	DBDPE
2013-Iraq (this study)	FD	18	<0.1	5.3	64.2	14.1	125
2013-Egypt [20]	FD	17	n.a.	0.81	0.12	0.24	n.a.
2011-Pakistan [39]	FD	31	n.a.	0.03	3.5	3.15	14
2008-Belgium [38]	FD	39	n.a.	1	13	2	153
n.a.-Germany [19]	FD	20	n.a.	<3.0	343	<10	146
2012-Norway [51]	FD	48	<0.13	2.54	78.5	3.76	147
2006-USA [70]	FD	19	n.a.	133	142	30	201
2007–2008-Canada [41]	FD	116	n.a.	120	99	30	n.a.
2013-Iraq (this study)	ESD	18	0.25	6.15	82.6	15.23	183
2008-Vietnam [69]	ESD	6	n.a.	n.a.	n.a.	7.1	40
2008-China [15]	ESD + FD	27	0.15	n.a.	n.a.	6.47	2730

n.a. = not available.

PBDEs in elevated surface dust to exceed (albeit not significantly) those in floor dust.

Although paired t-test comparison of the organic carbon (OC) content of paired ESD and FD samples revealed no significant ($p > 0.05$) difference between the two dust categories, we tested the hypothesis that higher concentrations of OC content in ESD lead to significantly higher concentrations of BFRs in such samples. To do so, we conducted a paired t-test comparison using log-transformed concentrations of BFRs normalised to the OC content of both ESD and FD. Although based on a slightly smaller data set ($n = 12$ homes for which the OC content of paired ESD and FD samples were available), this revealed concentrations of BDE-99, BDE-209, PBEB, BEH-TEBP, and DBDPE in ESD to exceed significantly those in FD, with ($P < 0.05$) 0.028, 0.001, 0.015, 0.049, 0.003 respectively. This suggests that differences in organic carbon content between ESD and FD in our study did not exert a substantial influence on the observed differences in BFR concentrations.

We next examined the hypothesis that differences in the particle size distribution found in ESD and FD in our study may explain the elevated concentrations of some BFRs in ESD. Prior to determination of BFR concentrations, we measured (via manual sieving and subsequent gravimetry) the mass of dust in each samples that fell into the following particle size distributions: $<125 \mu\text{m}$ and $125\text{--}250 \mu\text{m}$. Results showed significantly ($p < 0.05$) higher proportions of particles $<125 \mu\text{m}$ in samples of ESD and of particles between $125 \mu\text{m}$ and $250 \mu\text{m}$ in FD. While we combined these size fractions into a single sample for determination of BFRs, over 80% of

Σ BDEs determined in a small number of US indoor dust samples have been reported to be present in particles $<150 \mu\text{m}$ [55], and we suggest that this is one plausible reason for the higher concentrations of some BFRs in ESD in our study.

An additional explanation for the higher concentrations of BFRs in ESD compared to FD is because elevated surface dust samples included dust that had been in direct contact with products such as electronics and soft furnishing. Previous studies have shown that both direct source:dust contact and abrasion are highly effective pathways via which BFRs may transfer from products to dust [62,63] and thus ESD sampled from such product surfaces will likely contain elevated concentrations of BFRs.

3.3. Relationship between concentrations of different BFRs

Significant positive linear correlation between concentrations of different contaminants in paired samples of FD and ESD indicates that similar factors likely influence the observed concentrations. One such factor may be common sources. We therefore evaluated our data for the existence of such correlations.

To do so, we subjected log-transformed concentrations of each of our target BFRs in ESD with those in the corresponding FD samples to Pearson correlation analysis. These analyses revealed that concentrations of several of our target PBDEs and NBFRs in FD samples were significantly correlated with those in ESD samples. Significant correlation ($p < 0.05$) was found for: BDE-47, BDE-99, BDE-154, BDE-209, BEH-TEBP, EH-TBB, and DBDPE, with respective

Table 4
Estimated Exposure (ng/kg body weight/day) of Adults and Toddlers of PBDEs and NBFs via Dust Ingestion in Basrah, Iraq.

Compound	Adult				Toddler		
	Exposure scenario				Exposure scenario		
	Dust	Low-end	“Typical”	High-end	Low-end	“Typical”	High-end
BDE-47	ESD	0.00	0.00	0.04	0.01	0.03	0.83
BDE-47	FD	0.00	0.00	0.02	0.00	0.01	0.47
BDE-99	ESD	0.00	0.00	0.05	0.00	0.05	1.2
BDE-99	FD	0.00	0.00	0.03	0.00	0.03	0.60
BDE-183	ESD	0.00	0.00	0.01	0.00	0.03	0.25
BDE-183	FD	0.00	0.00	0.03	0.01	0.03	0.63
BDE-209	ESD	0.10	0.25	2.3	1.5	3.5	54
BDE-209	FD	0.09	0.17	1.14	1.2	2.5	27
∑tri-hexa BDE	ESD	0.00	0.01	0.12	0.02	0.10	2.7
∑tri-hexa BDE	FD	0.00	0.00	0.07	0.01	0.06	1.52
∑PBDE	ESD	0.11	0.26	2.4	1.6	3.8	55
∑PBDE	FD	0.10	0.18	1.2	1.4	2.6	27
EH-TBB	ESD	0.00	0.00	0.01	0.00	0.03	0.33
EH-TBB	FD	0.00	0.00	0.01	0.00	0.02	0.28
BTBPE	ESD	0.00	0.00	0.03	0.02	0.06	0.72
BTBPE	FD	0.00	0.00	0.02	0.02	0.06	0.54
BEH-TEBP	ESD	0.01	0.02	0.26	0.19	0.34	6.1
BEH-TEBP	FD	0.00	0.02	0.07	0.01	0.26	0.18
DBDPE	ESD	0.02	0.05	0.08	0.26	0.74	0.21
DBDPE	FD	0.01	0.04	0.06	0.13	0.51	0.15

correlation coefficient values of 0.855, 0.838, 0.780, 0.793, 0.803, 0.656, and 0.652. Note that correlation analyses were conducted only for those samples from homes in which the target BFR was detected in both ESD and FD. Similar results were obtained when we examined our data for correlations between organic-normalised concentrations of BFRs in the 12 sample pairs for which such data were available. This suggests that sources of these contaminants in ESD and FD are similar.

3.4. Human exposure to BFRs via dust ingestion

We used our data on concentrations of BFRs in indoor dust to generate preliminary estimates of human exposure to our target contaminants via ingestion of dust. To evaluate the likely range of exposure we examined three scenarios for ESD and FD separately [10]. The three scenarios are: 1) low-end exposure, in which we assume the exposed individual ingests the “typical” quantity of dust (20 mg and 50 mg/day for adults and toddlers respectively) and that dust contains the target BFR at the 5th percentile concentration; 2) “typical” exposure, which is the multiple of the typical daily dust ingestion rate and the median BFR concentration; and 3) high-end exposure, whereby dust ingestion of dust contaminated at the 95th percentile concentration occurs at the high rate (50 mg and 200 mg/day for adults and toddler respectively). For consistency with most other studies, we assumed 100% absorption of intake [64] and body weights of 70 kg and 12 kg for adults and toddlers respectively [65]. The resultant exposure estimates in ng/kg body weight/day for BDE-47, BDE-99, BDE-183, BDE-209, ∑tri-hexaBDE, ∑BDE, EH-TBB, BTBPE, BEH-TEBP, and DBDPE are shown in Table 4. Reassuringly, in no instance did exposure exceed the currently health based limit values listed in Table S7.

Given the higher concentrations of most target BFRs in ESD compared to FD, we calculated the ratio of exposure estimates obtained assuming ingestion of: (a) ESD only, and (b) FD only. The obtained ratios ranged between 0.7 for BDE-183 and 1.99 for BDE-99. While this may suggest that previous exposure estimates based on ingestion of floor dust alone may underestimate exposure, it is plausible that this applies only to adults, who we hypothesise are more likely to ingest elevated surface dust than floor dust. In contrast, it is reasonable to suggest that crawling toddlers will

ingest mainly floor dust, and as such, we believe that the elevated concentrations detected in elevated surface dust will exert little impact on toddler exposure.

4. Conclusions

This study reveals concentrations of several of our target BFRs to be significantly higher in dust collected from elevated surfaces like chairs and tables than in floor dust from the same rooms. This suggests that previous studies that base estimates of adult exposure via dust ingestion on floor dust, may underestimate exposure. Such underestimation is less likely for toddlers as observation suggests they are far more likely to ingest floor dust. Concentrations of PBDEs and NBFs in dust from both elevated surfaces and floors in Basrah, Iraq were at the lower end of contamination levels reported elsewhere in the world. In line with other studies from outside North America, the PBDE contamination pattern suggests that use in Iraq of the Deca-BDE formulation, exceeds substantially that of Penta-BDE. Our data also suggest that use of the Octa-BDE formulation has been higher in Iraq than in some other regions. Our data represent a valuable baseline against which responses to actions designed to limit exposure to PBDEs may be evaluated in future. Our estimates of exposure to our target BFRs via dust ingestion for the Iraqi population fall well below the relevant health-based limit values.

Acknowledgements

The authors express their thanks to all the dust donors from Basrah, Iraq. Layla Salih Al-Omran acknowledges gratefully the Iraqi government for a PhD Scholarship, the Iraqi Establishment of Martyrs for financial support and the Ministry of Higher Education and Scientific Research (MOHESR) for administrative support.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.emcon.2015.10.001>.

References

- [1] L.S. Birnbaum, D.F. Staskal, *Environ. Health Perspect.* 112 (2004) 9–17.
- [2] M. Alaei, R.J. Wenning, *Chemosphere* 46 (2002) 579–582.
- [3] WHO, *Environmental Health Criteria*, 192, 1997.
- [4] USEPA, 2006, <http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/proj-plan32906a.pdf>.
- [5] M. Alaei, P. Arias, A. Sjödin, A. Bergman, *Environ. Int.* 29 (2003) 683–689.
- [6] M.L. La Guardia, R.C. Hale, E. Harvey, *Environ. Sci. Technol.* 40 (2006) 6247–6254.
- [7] S. Newton, U. Sellström, C.A. de Wit, *Environ. Sci. Technol.* 49 (2015) 2912–2920.
- [8] S. Harrad, R. Wijesekera, S. Halliwell, R. Baker, *Environ. Sci. Technol.* 38 (2004) 2345–2350.
- [9] J.G. Allen, M.D. McClean, H.M. Stapleton, J.W. Nelson, T.F. Webster, *Environ. Sci. Technol.* 41 (2007) 4574–4579.
- [10] S. Harrad, C. Ibarra, M.A. Abdallah, R. Boon, H. Neels, A. Covaci, *Environ. Int.* 34 (2008a) 1170–1175.
- [11] S. Harrad, C. Ibarra, M. Diamond, L. Melymuk, M. Robson, J. Douwes, L. Roosens, A.C. Dertu, A. Covaci, *Environ. Int.* 34 (2008b) 232–238.
- [12] H.M. Stapleton, N.G. Dodder, J.H. Offenberger, M.M. Schantz, S.A. Wise, *Environ. Sci. Technol.* 39 (2005) 925–931.
- [13] H.M. Stapleton, S. Eagle, A. Sjödin, T.F. Webster, *Environ. Health Perspect.* 120 (2012) 1049–1054.
- [14] D. Muenhor, S. Harrad, N. Ali, A. Covaci, *Environ. Int.* 36 (2010) 690–698.
- [15] J. Wang, Y.-J. Ma, S.-J. Chen, M. Tian, X.-J. Luo, B.-X. Mia, *Environ. Int.* 36 (2010) 535–541.
- [16] B.-L. Wang, S. Pang, X. Zhang, X. Li, Y. Sun, X. Lu, O. Zhang, *Archives Environ. Contam. Toxicol.* 68 (2015) 9–16.
- [17] S. Brommer, S. Harrad, N. Van den Eede, A. Covaci, *J. Environ. Monit.* 14 (2012) 2482–2487.
- [18] G. Suzuki, K. Nose, H. Takigami, S. Takahashi, S. Sakai, *Organohalogen Compd.* 68 (2006) 1843–1846.
- [19] H. Fromme, B. Hilger, E. Kopp, M. Miserok, W. Völkel, *Environ. Int.* 64 (2014) 61–68.
- [20] Y. Hassan, T. Shoeib, *Sci. Total Environ.* 505 (2015) 47–55.
- [21] N. Ali, A.C. Dertu, N.V. Eede, E. Goosey, S. Harrad, H. Neels, A.A. T. Mannetjé, J. Coakley, J. Douwes, A. Covaci, *Chemosphere* 88 (2012) 1276–1282.
- [22] S. Harrad, M.A. Abdallah, A. Covaci, *Environ. Int.* 35 (2009) 573–579.
- [23] T. Shi, S.-J. Chen, X.-J. Zhang, C.-M. Tang, Y. Luo, Y.-J. Ma, J.-P. Wu, X.-Z. Peng, B.-X. Mai, *Chemosphere* 74 (2009) 910–916.
- [24] Z.-W. Zhang, Y.-X. Sun, K.-F. Sun, X.-R. Xu, S. Yu, T.L. Zheng, X.-J. Luo, Y. Tian, Y.-X. Hu, Z.-H. Diao, B.-X. Mai, *Chemosphere* 123 (2015) 26–32.
- [25] F. Zhang, G. Lu, J. Liu, Z. Yan, Z. Zhang, *Ecotoxicol. Environ. Saf.* 108 (2014) 16–22.
- [26] X. Hu, D. Hu, *Anal. Chem. Res.* 2 (2014) 1–14.
- [27] NICNAS, 2007, http://www.nicnas.gov.au/_data/assets/pdf_file/0003/4944/Final-Interim-Report-PBDE-March.pdf, accessed September 2012.
- [28] Health Canada, 2009, <http://www.cetesb.sp.gov.br/userfiles/file/laboratories/feia/retardant.pdf>, accessed March 2012.
- [29] S.D. Shaw, M.L. Berger, D. Brenner, K. Kannan, N. Lohmann, O. Pöpke, *Sci. Total Environ.* 407 (2009) 3323–3329.
- [30] EFSA, *Eur. Food Saf. Auth.* 10 (2012) 2908.
- [31] M. Fang, H.M. Stapleton, *Environ. Sci. Technol.* 48 (2014) 13323–13330.
- [32] Q. Chen, L. Yu, L. Yang, B. Zhou, *Aquat. Toxicol.* 110–111 (2012) 141–148.
- [33] UNEP, 2007, online, <http://chm.pops.int/default.aspx>.
- [34] UNEP, 2013, online, <http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-POPRC.9-2>.
- [35] A. Covaci, S. Harrad, M.A. Abdallah, N. Ali, R.J. Law, D. Herzke, C.A. de Wit, *Environ. Int.* 37 (2011) 532–556.
- [36] P. López, S.A. Brandsma, P.E.G. Leonards, J. de Boer, *Anal. Bioanal. Chem.* 400 (2011) 871–883.
- [37] G. Poma, C. Roscioli, L. Cuzzella, *Environ. Monit. Assess.* 186 (2014) 7683–7692.
- [38] N. Ali, S. Harrad, E. Goosey, H. Neels, A. Covaci, *Chemosphere* 83 (2011a) 1360–1365.
- [39] N. Ali, N. Van den Eede, A.C. Dertu, H. Neels, A. Covaci, *Indoor Air* 22 (2012) 200–211.
- [40] N. Ali, L. Ali, T. Mehdi, A.C. Dertu, F. Al-Shammari, H. Neels, A. Covaci, *Environ. Int.* 55 (2013) 62–70.
- [41] M. Shoeib, T. Harner, G.M. Webster, E. Sverko, Y. Cheng, *Environ. Pollut.* 169 (2012) 175–182.
- [42] P.I. Johnson, H.M. Stapleton, B. Mukherjee, R. Hauser, J.D. Meeker, *Sci. Total Environ.* 445–446 (2013) 177–184.
- [43] D.M.V. Saunders, E.B. Higley, M. Hecker, R. Mankidy, J.P. Giesy, *Toxicol. Lett.* 223 (2013) 252–259.
- [44] A. Besis, C. Samara, *Environ. Pollut.* 2012 (2012) 217–229.
- [45] B. Gevao, M. Al-Bahloul, A. Al-Ghadban, A. Al-Omair, L. Ali, J. Zafar, M. Helaleh, *Chemosphere* 64 (2006) 603–608.
- [46] S. Harrad, E. Goosey, J. Desborough, M.A. Abdallah, L. Roosens, A. Covaci, *Environ. Sci. Technol.* 44 (2010) 4198–4202.
- [47] C.A. de Wit, J.A. Björklund, K. Thuresson, *Environ. Int.* 39 (2012) 141–147.
- [48] K. Thuresson, J.A. Björklund, C.A. de Wit, *Sci. Total Environ.* 414 (2012) 713–722.
- [49] J.A. Björklund, K. Thuresson, C.A. de Wit, *Environ. Sci. Technol.* (2009) 2276–2281.
- [50] A.J. Björklund, U. Sellström, C.A. de Wit, M. Aune, S. Lignell, P.O. Darnerud, *Indoor Air* 22 (2012) 279–288.
- [51] E. Cequair, A.C. Ionas, A. Covaci, R.M. Marce, G. Becher, C. Thomsen, *Environ. Sci. Technol.* 48 (2014) 6827–6835.
- [52] Q. Wu, S.-Y. Baek, M. Fang, Y.-S. Chang, *Indoor Air* 20 (2010) 263–270.
- [53] USEPA, 2007, http://water.epa.gov/scitech/methods/cwa/upload/M1614A_11June10.pdf [accessed 12.02.13].
- [54] F. Mercier, P. Glorennec, O. Thomas, B. Le Bot, *Environ. Sci. Technol.* 45 (2011) 6716–6727.
- [55] H. Wei, M. Turyk, S. Cali, S. Dorevitch, S. Erdal, A. Li, *J. Environ. Sci. Health, Part A* 44 (2009) 1353–1361.
- [56] Z.-G. Cao, G. Yu, Y.-S. Chen, Q.-M. Cao, H. Fielder, S.-B. Deng, J. Huang, B. Wang, *Environ. Int.* 49 (2012) 24–30.
- [57] S.S. Que Hee, B. Peace, C.S. Clark, J.R. Boyle, R.L. Bornschein, P.B. Hammond, *Environ. Res.* 38 (1985) 77–95.
- [58] R.D. Edwards, P.J. Liroy, *J. Expo. Analysis Environ. Epidemiol.* 9 (1999) 521–529.
- [59] N. Yamamoto, Y. Takahashi, J. Yoshinaga, A. Tanaka, Y. Shibata, *Archives Environ. Contam. Toxicol.* 51 (2006) 157–163.
- [60] N. Ali, S. Harrad, D. Muenhor, H. Neels, A. Covaci, *Anal. Bioanal. Chem.* 400 (2011b) 3073–3083.
- [61] N.V. den Eede, A.C. Dertu, N. Ali, H. Neels, A. Covaci, *Talanta* 89 (2012) 292–300.
- [62] C. Rautert, S. Harrad, G. Suzuki, H. Takigami, N. Uchida, K. Takata, *Sci. Total Environ.* 393 (2014) 639–648.
- [63] C. Rautert, S. Harrad, *Sci. Total Environ.* 536 (2015) 568–574.
- [64] H.A. Jones-Otazo, J.P. Clarke, M.L. Diamond, J.A. Archbold, J.A. Ferguson, G. Harner, G.M. Richardson, J.J. Ryan, B. Wilford, *Environ. Sci. Technol.* 39 (2005) 5121–5130.
- [65] EFSA, *Eur. Food Saf. Auth.* 10 (2012) 2579.
- [66] Y. Kang, H.S. Wang, K.C. Cheung, M.H. Wong, *Atmos. Environ.* 45 (2011) 2386–2393.
- [67] N.-Z. Zhu, H. Qi, F. Zhang, W.-L. Ma, L.-Y. Liu, Y.-F. Li, *Bull. Environ. Contam. Toxicol.* 91 (2013) 640–644.
- [68] Sjödin, O. Pöpke, E. McGahee, J.-F. Focant, R.S. Jones, T. Pless-Mulloli, L.-M.L. Toms, T. Herrmann, J. Müller, L.L. Needham, D.G. Patterson, *Chemosphere* 73 (2008) 131–136.
- [69] N.M. Tue, S. Takahashi, G. Suzuki, T. Isobe, P.H. Viet, Y. Kobara, N. Seike, G. Zhang, A. Sudaryanto, S. Tanabe, *Environ. Int.* 51 (2013) 160–167.
- [70] H.M. Stapleton, J.G. Allen, S.M. Kelly, A. Konstantinov, S. Klosterhaus, D. Watkins, M.D. McClean, T.F. Webster, *Environ. Sci. Technol.* 42 (2008) 6910–6916.