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Results of an interlaboratory exercise for the analysis of 15 organic priority substances at ng/L levels in whole water samples

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Abstract

The European Water Framework Directive 2000/60/EC requires monitoring of organic priority pollutants in so called “whole water” samples, i.e. in aqueous non-filtered samples that contain natural colloidal and suspended particulate matter. Colloids and suspended particles in the liquid phase constitute a challenge for sample homogeneity and stability. Within the joint research project ENV08 “Traceable measurements for monitoring critical pollutants under the European Water Framework Directive 2000/60/EC” whole water test materials were developed by spiking defined amounts of aqueous slurries of ultra-finely milled contaminated soil or sediment and aqueous solutions of humic acid into a natural mineral water matrix. This paper presents the results of a European-wide interlaboratory comparison (ILC) using this type of test materials. Target analytes were tributyl tin (TBT), polybrominated diphenyl ethers (PBDEs) and polycyclic aromatic hydrocarbons (PAHs) in the ng/L concentration range. Results of the ILC indicate that the produced materials are sufficiently homogeneous and stable to serve as samples for e.g. proficiency testing or method validation. To our knowledge, this is the first time that ready to use water materials with a defined amount of suspended particulate and colloidal matter have been applied as test samples in an interlaboratory exercise.

Keywords

Water Framework Directive (WFD), interlaboratory comparison (ILC), whole water sample, suspended particulate matter (SPM), polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), tributyl tin (TBT)

Introduction

1
2 The Water Framework Directive (WFD) 2000/60/EC [1] establishes a legal framework for protecting
3 the quality of surface and coastal waters in the European Union (EU). It defines chemical substances
4 for priority remediation and their Environmental Quality Standards (EQS) in Directive 2008/105/EC
5 [2]. Two types of EQSs were set: annual average concentrations (AA-EQS) for protection against long-
6 term and chronic effects, and maximum allowable concentrations (MAC-EQS) to avoid serious
7 irreversible consequences for eco-systems due to acute exposure in the short-term. EQSs for organic
8 pollutants refer to whole water samples, i.e. water with colloidal and suspended particulate matter
9 (SPM) which can pose an additional difficulty to analysis, particularly of non-polar hydrophobic
10 compounds that strongly adsorb to particles [3-5]. Therefore the WFD requires monitoring methods
11 which allow the analysis of whole water bodies.
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16 All laboratories involved in the analysis and monitoring under the WFD should work according to
17 internationally accepted quality assurance and quality control (QA/QC) schemes and should be
18 obliged to demonstrate their competence by participating in appropriate proficiency testing (PT)
19 programmes on a regular basis [6, 7]. Several PT schemes have been organized for WFD regulated
20 contaminants at EQS levels in aqueous samples by e.g. PT-WFD [7], the network of PT providers to
21 support the implementation of the WFD, IMEP [8, 9], the International Measurement Evaluation
22 Programme of the Institute for Reference Materials and Measurements (IRMM) or within the SWIFT-
23 WFD project "Screening methods for water data information in support of the implementation of the
24 EU Water Framework Directive" [10]. However, these intercomparisons mostly used filtered waters
25 fortified with a spike of the target analytes in a water-miscible organic solvent. An exception was the
26 IMEP-23 intercomparison conducted in 2007/2008. Groundwater spiked with humic acid as a model
27 for the colloidal substances that are present in natural inland waters was used as matrix for the eight
28 WFD priority polycyclic aromatic hydrocarbons (PAHs) in this PT exercise [11]. However, the
29 groundwater, humic acid solution and a PAH spike solution were supplied to the participants as a kit.
30 The final test samples had to be reconstituted by the IMEP-23 participants. To our knowledge, ready
31 to use water test materials with a defined amount of SPM and/or humic acid have not been applied
32 for PT so far. Such materials are not easy to produce because SPM and colloidal matter in the water
33 phase pose a particular challenge in terms of sample homogeneity and stability.
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42 A feasibility study for the preparation of aqueous reference and test materials that contain colloidal
43 matter and SPM was performed as part of the joint research project ENV08 "Traceable
44 measurements for monitoring critical pollutants under the European Water Framework Directive
45 2000/60/EC" within the European Metrology Research Programme [12]. The concepts developed for
46 the preparation of the materials as well as their homogeneity and stability assessment are described
47 in detail elsewhere [13]. This paper presents the results and conclusions of a European-wide
48 interlaboratory comparison (ILC) using the ENV08 whole water materials. The ILC aimed to test the
49 concepts for whole water reference materials developed in the project. Recently, these types of
50 materials have also been used in a validation intercomparison for CEN TC230 "water analysis" draft
51 standards. Results of this CEN intercomparison will be published as part of the standards and
52 technical specification prEN 16691 Water quality - Determination of polycyclic aromatic
53 hydrocarbons (PAH) in whole water samples using liquid solid extraction combined with gas
54 chromatography mass spectrometry (GC-MS), prEN 16694 Water quality — Determination of
55 polybromodiphenyl ether (PBDE) in whole water samples using solid phase extraction (SPE) with SPE-
56 disks combined with gas chromatography - mass spectrometry (GC-MS) and FprCEN/TS 16692 Water
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1 quality - Determination of tributyl tin (TBT) in whole water samples using solid phase extraction (SPE)
2 and gas chromatography with triple quadrupole mass spectrometry. The two standards and the
3 technical specification are currently under approval and will be released in 2015.
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7 **Materials and methods**

8 *Test materials*

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11 The ENV08 project focused on three analytes or groups of analytes listed as priority hazardous
12 substances in the WFD: 1. tributyl tin TBT cation, 2. polybrominated diphenyl ethers PBDEs (BDE 28,
13 BDE 47, BDE 99, BDE 100, BDE 153, BDE 154), 3. PAHs (naphthalene (N), anthracene (A), fluoranthene
14 (F), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3,-
15 cd)pyrene (I), benzo(ghi)perylene (BghiP)). For each group of analytes two types of samples were
16 prepared: Sample 1 contained humic acid and SPM, sample 2 contained only SPM. Test materials
17 were prepared by spiking defined amounts of aqueous slurries of ultra-finely milled contaminated
18 soil or sediment materials into brown glass bottles pre-filled with 1 L natural mineral water (SPA
19 Reine still mineral water). The soil and sediment raw materials used are listed in Table 1. The milled
20 soil and sediment materials serve as model-SPMs in the water samples. Their top particle size was in
21 the range from 9 µm to 12.5 µm which corresponds to the average particle size of natural SPM in
22 many respects [14]. ERM®-CZ 100 was used without further milling for the preparation of PAH-2
23 samples since the particle size of this material was already in the desired range. The analytes are
24 strongly bound to the model-SPMs and therefore mimic the situation in natural waters. No spike of
25 neat target analytes was added. Samples did not contain any organic solvent or stabilizing agent.
26 Additional to the SPM an aqueous solution of commercial humic acid (Fluka, technical grade) was
27 added to some of the samples to imitate natural colloids in the liquid phase. The dissolved organic
28 carbon (DOC) of these samples was about 5 mg/L, i.e. in the range that naturally occurs in surface
29 waters. In total six different sample materials were prepared and distributed as listed in Table 1. The
30 analyte concentrations in the samples are defined by the distribution of the compounds in the
31 naturally contaminated SPM materials and therefore do not exactly meet the EQS values.
32 Concentrations in the milled SPM were determined by several analytical methods [13]. From these
33 data, the exact volume of the sample and the exact mass of SPM spiked an estimate of the analyte in
34 the final aqueous test materials was calculated (estimated concentrations in Table 1). For ERM®-CZ
35 100 the concentrations listed in the certificate were used to calculate estimated concentrations in
36 PAH sample 2. Estimated concentrations were in the ng/L range, for PBDEs in sample 2 even
37 considerably lower than 1 ng/L.
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49 More details on the preparation procedures are given in reference [13] together with data for the
50 characterization of the model-SPMs and for the homogeneity and stability testing of the final
51 aqueous test samples. Furthermore, a systematic study of the interaction of the target analytes with
52 different container materials (glass, aluminium, fluorinated polyethylene) has been conducted in
53 order to find the most suitable type of bottles. Results are published in [15].
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57 *Outline of the ILC*

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59 The ILC was conducted within a period of about 6 weeks in June/July 2014. All samples were
60 prepared, packed and finally dispatched from IRMM. Samples were shipped immediately after
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1 preparation with over-night courier. Participants were instructed to store them in the refrigerator at
2 4°C after arrival. All samples were provided in triplicate except PAH-2 which was provided in
3 duplicate. Participants were requested to shake the samples rigorously before extraction. The whole
4 1 L sample volume had to be extracted at once, sub-sampling was not allowed. At least one blank
5 sample should be analysed for each analyte group. It was recommended to use a natural mineral
6 water for the determination of blanks. Participants were asked to report blank values and details of
7 their analytical method.
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10 Thirteen expert labs from eight European countries participated in the ILC together with 11
11 institutions involved in the ENV08 project. The expert labs are engaged in water monitoring under
12 the WFD in their countries. ENV08 institutes are mainly National Metrology Institutes and Designated
13 Institutes. A list of participants is given in the electronic supplementary material, Table S1. In total 10
14 datasets each were returned for TBT and PBDEs, 12 for PAHs.
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17 *Analytical methods*

18 Participants could use a method of their choice. However, both the liquid and the particulate matter
19 phase should be included in the analysis. All methods are listed in Table 2 and in more detail in the
20 electronic supplementary material, Tables S2 to S4. All participants except Lab 18 (TBT samples only)
21 extracted the liquid and particulate matter phase together within one step. Lab 18 filtered the TBT
22 samples and analysed the liquid and SPM phases separately.
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28 *Statistical analysis*

29 Statistical analysis of the ILC results was done according to ISO 5725-5:2002 [16] using the QuoData
30 PROLab™ software for interlaboratory tests [17]. A robust approach (algorithm A + S) was used to
31 calculate the mean and standard deviations, i.e. outlier suspected values were not excluded.
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37 **Results**

38 As an example for each group of analytes, Figures 1 to 3 display the results of the ILC for TBT in
39 sample 2, BDE 47 in sample 1 and benzo(ghi)perylene in sample 2. Data for all other
40 analytes/samples are included in the electronic supplementary material Figures S1 to S27. Table 3
41 summarizes the key ILC performance parameters obtained from the statistical analysis. Recoveries in
42 Table 3 were calculated relative to the estimated values in Table 1.
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49 **Discussion**

50 *Reproducibility and repeatability standard deviations, recovery rates*

51 For 24 out of the 30 analyte/sample combinations the relative reproducibility standard deviation $C_{V,R}$
52 was found to be < 60%. With one exception (anthracene in sample 2), the relative repeatability
53 standard deviation $C_{V,r}$ was found to be < 15%, and recovery rates η were between 70% and 130% for
54 22 out of the 30 analyte/sample combinations (Table 3). The estimated value is within the (mean \pm
55 $2 \cdot C_{V,R}$) interval (black dashed line in Figures 1 to 3) for all analytes/samples except TBT in sample 1
56 and fluoranthene in both samples. Taking into account the complexity of the test samples, the low
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1 concentrations, the variety of analytical methods and the relative low number of data sets these
2 performance data are acceptable. The good repeatability furthermore confirms that the samples
3 were sufficiently homogeneous for the purpose of this study, thereby confirming the findings
4 available at the time of preparation of the test samples.
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6 The ILC was conducted within a period of about 6 weeks. For none of the analytes a dependency of
7 the measured values on the date of extraction was observed. Results scatter but there is no trend
8 towards lower values with time as it is shown in Figure 4 for benzo(b)fluoranthene in sample 1. This
9 is a further verification of a sufficient short-term stability of the whole water samples, thereby
10 confirming the findings available at the time of preparation of the test samples.
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13 In general, there seems to be a tendency towards lower recovery rates with higher analyte
14 concentration. Fluoranthene for instance is the analyte with the highest estimated concentration and
15 the one with the lowest recovery (34%) in both samples. This trend is somewhat surprising, and
16 currently no satisfactory explanation can be given. The physico-chemical interactions taking place
17 when adding model-SPM to pre-filled water bottles are not known in detail. They may depend on the
18 bottle material, the concentration, polarity and solubility of the analyte as well as pH, ionic strength
19 and other properties of the water phase [18]. Lab 18 performed a series of TBT measurements with
20 freshly prepared whole water samples containing SPM. Recovery rates were significantly higher (112
21 ± 11 %), 6 replicate measurements) compared to the ones found in the ILC (66%). This finding
22 indicates that the concentration or distribution of TBT in the whole water sample changes to some
23 extent within a very short time after addition of the SPM. Afterwards the samples remain sufficiently
24 stable for at least the course of the ILC, i.e. a few weeks. Results of a short term stability study [13]
25 verify the latter.
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32 The presence of humic acid in sample 1 led to slightly lower recovery rates, particularly for the 5 and
33 6 ring PAHs, and slightly higher standard deviations for PAHs and PBDEs. The humic acid apparently
34 hampers extraction of the analytes and phase separation in the liquid/liquid extraction (LLE) process.
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37 *Dependence of ILC results on the analytical methods*

38 TBT

39 For TBT two different detection methods were applied: 1. GC-MS or -MS/MS and 2. GC-ICP-MS, the
40 latter often in combination with isotope dilution calibration using ^{119}Sn enriched TBT. GC-ICP-MS
41 results were found to be higher compared to GC-MS based results (Figure 5) which, probably, can be
42 explained by the higher sensitivity of ICP-MS. The majority of participants applied LLE, one
43 participant (Lab 5) used SPE, one (Lab 9) headspace solid phase microextraction and one participant
44 (Lab 18) analysed the liquid phase by LLE and separately the filtered solid phase by ultrasonication.
45 All these extraction methods appear to be equivalent.
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51 PBDEs

52 For the PBDEs no systematic difference was observed between the results obtained by LLE and SPE as
53 shown for BDE 99, sample 1, in Figure S28 in the electronic supplementary material. Furthermore,
54 different detection/calibration modes (GC-EI-MS based methods with ^{13}C labeled internal standards,
55 GC-NCI-MS based methods with fluorinated or ^{13}C labeled internal standards, GC-ICP-MS with
56 isotope dilution calibration using ^{81}Br labeled PBDEs) did not lead to systematic differences in the
57 results (Figure S29 in the electronic supplementary material).
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PAHs

1 There was no difference observed in the results obtained by LLE and SPE (Figure S30 in the electronic
2 supplementary material). For detection and quantification, GC-MS based methods were used by all
3 but one participant (Lab 17) who applied LC-APPI-MS/MS.
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Conclusion

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9 For the first time, an interlaboratory comparison was conducted with whole water test materials
10 which contained defined amounts of suspended particulate matter and organic colloidal matter and
11 therefore mimicked the composition of natural surface waters. The concentration of the target
12 analytes TBT, PBDEs and PAHs was in the ng/L range, i.e. in the range of EQS set by the WFD.
13 Analytes were strongly bound to the suspended particle phase as in natural waters. Performance
14 parameters of the ILC such as recovery rates, reproducibility and repeatability standard deviations
15 indicate that the test materials prepared were indeed suitable, i.e. sufficiently homogeneous and
16 stable for proficiency testing. This is a step forward to the production of realistic whole water test
17 and reference materials as required by the European WFD.
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23 ILC participants applied different analytical procedures. For TBT the results of GC-ICP-MS in
24 combination with isotope dilution calibration were closer to the estimated values than GC-MS based
25 results. For PBDEs and PAHs the results obtained with different extraction and/or separation and
26 detection techniques did not vary significantly.
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7 **References**

8
9 [1] European Commission (2000) Directive 2000/60/EC of the European Parliament and of the
10 Council of 23 October 2000 establishing a framework for Community action in the field of water
11 policy. Official Journal of the European Communities L 327:1-72
12
13

14 [2] European Commission (2008) Directive 2008/105/EC of the European Parliament and of the
15 Council on environmental quality standards in the field of water policy and amending Directive
16 2000/60/EC. Official Journal of the European Union L 348:84-97
17
18

19 [3] Lepom P, Hanke G, Wollgast J, Loos R, Duffek A (2009) Common Implementation Strategy for the
20 Water Framework Directive (2000/60/EC) Guidance Document, n. 19 – Guidance on Surface Water
21 Chemical Monitoring under the Water Framework Directive. Office for Official Publications of the
22 European Communities, Luxembourg
23
24

25 [4] Lepom P, Brown B, Hanke G, Loos R, Quevauviller P, Wollgast J (2009) Needs for reliable analytical
26 methods for monitoring chemical pollutants in surface water under the European Water Framework
27 Directive. J Chromatogr A 1216:302-315
28
29

30 [5] Ademollo N, Patrolecco L, Polesello S, Valsecchi S, Wollgast J, Mariani G, Hanke G (2012) The
31 analytical problem of measuring total concentrations of organic pollutants in whole water. Trends
32 Anal Chem 36:71-81
33
34

35 [6] European Commission (2009) Directive 2009/90/EC of 31 July 2009 laying down, pursuant to
36 Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for
37 chemical analysis and monitoring of water status. Official Journal of the European Union L 201: 36-38
38
39

40 [7] Baumeister F, Borchers U, Koch M (2010) PT-WFD: the network of PT providers to support the
41 implementation of the European water framework directive. Accred Qual Assur 15:193–198
42
43

44 [8] <https://ec.europa.eu/jrc/en/interlaboratory-comparisons/IMEP/about> Assessed 19 January 2015
45

46 [9] Noergaard J, Van Nevel L, Aregbe Y, Papadakis I, Taylor, P (2001) IMEP: Bringing SI-traceable
47 values to field laboratories. VAM Bulletin 24: 26-27
48
49

50 [10] Brunori C, Morabito R, Ipolyi I, Pellegrino C, Ricci M, Bercaru O, Ulberth F, Sahuquillo A,
51 Rosenberg E (2007) The SWIFT-WFD Proficiency Testing campaigns in support of implementing the
52 EU Water Framework Directive. Trends Anal Chem 26:993-1004
53
54

55 [11] Van de Kreeke J, de la Calle B, Held A, Bercaru O, Ricci M, Shegunova P, Taylor P (2010) IMEP-23:
56 The eight EU-WFD priority PAHs in water in the presence of humic acid. Trends Anal Chem 29:928-
57 937
58
59

60 [12] <http://www.emrponline.eu/> Assessed 19 January 2015
61
62
63
64
65

1 [13] Elordui-Zapatarietxe S, Fettig I, Philipp R, Gantois F, Lalere B, Swart C, Petrov P, Goenaga-Infante
2 H, Vanermen G, Boom G, Emteborg H (2015) Novel concepts for preparation of reference materials
3 as whole water samples for priority substances at ng L⁻¹ level using model suspended particulate
4 matter and humic acids. Anal Bioanal Chem. Doi: 10.1007/s00216-014-8349-8
5

6 [14] Ran Y, Fu JM, Sheng GY, Beckett R, Hart BT (2000) Fractionation and composition of colloidal and
7 suspended particulate materials in rivers. Chemosphere 41:33–43
8

9 [15] Elordui-Zapatarietxe S, Fettig I, Richter J, Philipp R, Gantois F, Swart C, Emteborg H Interaction of
10 15 priority substances for water monitoring at ng L⁻¹ levels with glass-, aluminium- and fluorinated
11 polyethylene bottles for the containment of water reference materials. Accred Qual Assur, submitted
12
13

14 [16] ISO 5725-5:2002 Accuracy (trueness and precision) of measurement methods and results - Part
15 5: Alternative methods for the determination of the precision of a standard measurement method
16 (ISO 5725-5:1998). (2002) ISO, Geneva
17
18

19 [17] [https://quodata.de/en/software/for-interlaboratory-tests/software-for-interlaboratory-studies-
20 prolab.html](https://quodata.de/en/software/for-interlaboratory-tests/software-for-interlaboratory-studies-prolab.html) Assessed 19 January 2015
21
22

23 [18] Hoch M, Schwesig D (2004) Parameters controlling the partitioning of tributyltin (TBT) in aquatic
24 systems. Appl Geochem 19:323-334
25
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Tables and Figures:

Tab. 1

sample	humic acid concentration (DOC) in the whole water sample [mg/L]	SPM raw material	mass of SPM in the whole water sample [mg/L]	estimated analyte concentration in the whole water sample ^a [ng/L]	AA-EQS (2008/105/EC) [ng/L]
TBT-1	5	BCR 646 organotin compounds in river sediment	8.2	4.07	0.2
TBT-2		BCR 646 + TBT blank sediment ^b	21.1 (8.2 BCR 646 + 12.9 blank SPM)		
PBDE-1	5	freshwater sediment, IRMM candidate reference material	193.5	BDE 28: 0.03 BDE 47: 2.54 BDE 99: 5.90 BDE 100: 0.88 BDE 153: 1.20 BDE 153: 0.56	Σ 6 PBDEs: 0.5
PBDE-2			25.2	BDE 28: 0.004 BDE 47: 0.33 BDE 99: 0.77 BDE 100: 0.11 BDE 153: 0.16 BDE 153: 0.07	
PAH-1	5	industrial soil, BAM PT material	38.6	N: 46.1 A: 20.6 F: 367 BbF: 120 BkF: 89 BaP: 90 I: 101 BghiP: 118	N: 2400 A: 100 F: 100 BbF+BkF: 30 BaP: 50 I + BghiP: 2
PAH-2		ERM®-CZ 100 PAH in fine dust	20.2	N: - A: 5.7 F: 94.5 BbF: 28.7 BkF: 13.5 BaP: 14.6 I: 21.4 BghiP: 35.6	

DOC: dissolved organic carbon

^a: calculated from the analyte concentration determined in the milled SPM and the mass of SPM spiked

^b: blank sediment obtained by jet-milling of ERM[®]-CC141 (calcareous loam soil) to a top particle size of 10 µm; with TBT concentration < detection limit of method used.

Tab. 2

	TBT	PBDE	PAH
derivatisation	ethylation with NaBEt ₄	-	-
extraction	liquid/liquid extraction (LLE) with hexane or isooctane; solid phase extraction (SPE) with speediscs; headspace solid phase microextraction (HS-SPME) ; ultrasonic extraction of the SPM	LLE with hexane, isooctane or dichloromethane; speedisk SPE	LLE with dichloromethane, petrolether or hexane; speedisk SPE
clean-up of extract	none; Al ₂ O ₃ column	none; multi-layer silica column; H ₂ SO ₄	none; silica column; drying with Na ₂ SO ₄ or goretex membrane
separation/detection	GC-MS; GC-MS/MS; GC-ICP-MS	GC-MS or –MS/MS with electron impact or negative chemical ionization; GC-HR-MS; GC-ICP-MS	GC-MS; GC-MS/MS; LC-APPI-MS/MS
calibration	species specific isotope dilution (ID) with ¹¹⁹ Sn enriched TBT; calibration curve with deuterated TBT or tripropyltin as internal standard	species specific ID with ⁸¹ Br labeled isotopes; calibration curve with ¹³ C BDEs or fluorinated analogues	calibration curve without internal standard or deuterated or ¹³ C labeled internal standards

Tab. 3

Analyte	Sample 1 (with humic acid)					Sample 2 (without humic acid)				
	<i>n</i>	\bar{x} ng/L	η %	$C_{V,R}$ %	$C_{V,r}$ %	<i>n</i>	\bar{x} ng/L	η %	$C_{V,R}$ %	$C_{V,r}$ %
TBT	10	2.66	65	21	6.4	10	2.69	66	29	5,8
BDE 28	8	0.05	155	82	7.9	6	0.009	225	72	12
BDE 47	10	2.65	104	30	5.7	10	0.41	125	24	13
BDE 99	10	6.35	108	40	6.9	10	0.78	102	38	12
BDE 100	10	1.11	127	54	10	9	0.15	135	36	9.0
BDE 153	10	1.13	94	57	11	9	0.15	97	30	5.9
BDE 154	10	0.61	109	46	11	8	0.08	107	27	7.0
N	9	32.2	70	79	14	9	21.6	*	117	11
A	10	20.3	98	66	9.9	10	4.0	70	54	32
F	11	125	34	50	7.3	11	32.3	34	55	9.5
BbF	11	91.7	76	44	6.8	11	26.7	93	41	4.9
BkF	11	49.7	56	52	6.4	11	11.6	86	47	5.8
BaP	12	67.8	75	45	8.3	12	13.5	93	47	6.4
I	11	82.0	82	56	11	11	20.9	97	35	8.2
BghiP	12	80.9	70	63	12	12	25.9	73	22	8.2

n: number of data sets

$C_{V,R}$: coefficient of variation of reproducibility

\bar{x} : robust mean

$C_{V,r}$: coefficient of variation of repeatability

η : recovery rate, calculated relative to the estimated values in Table 1

*: Naphthalene was not certified in the raw SPM used, therefore no estimated value and recovery rate could be calculated.

Fig. 1

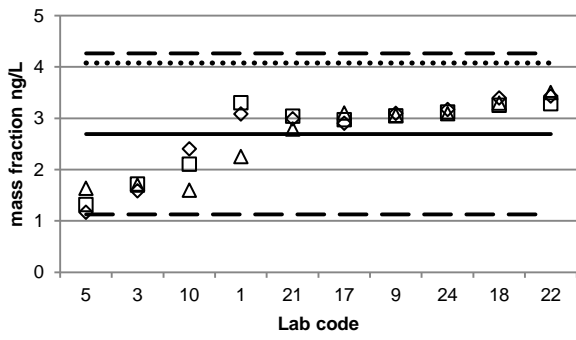


Fig. 2

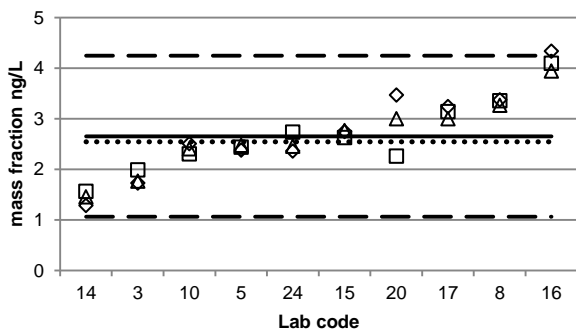


Fig. 3

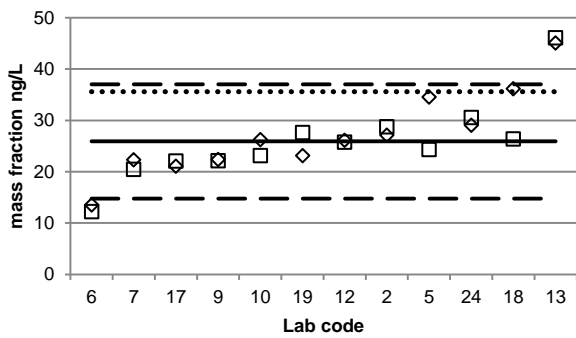


Fig 4

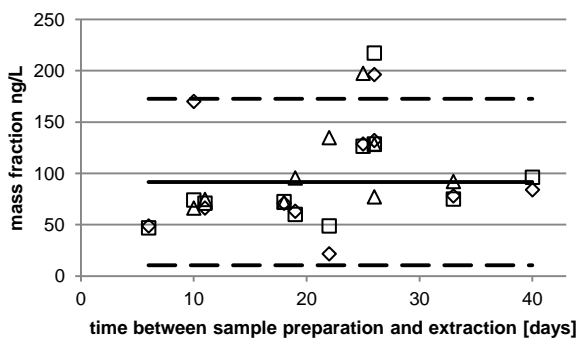
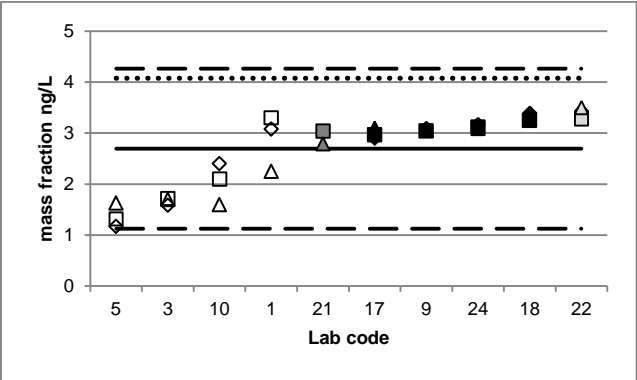


Fig. 5



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Captions for Figures and Tables:

Tab. 1 Composition of the test samples and annual average Environmental Quality Standards (AA-EQS) for the target analytes

Tab. 2 Analytical methods applied in the ILC

Fig. 1 ILC results for an estimated concentration of 4.1 ng/L of TBT, sample 2; solid line: robust mean, dashed lines: range of tolerance ($|Z\text{-score}| \leq 2$), dotted line: estimated concentration, \diamond bottle 1, \square bottle 2, Δ bottle 3

Fig. 2 ILC results for an estimated concentration of 2.5 ng/L of BDE 47, sample 1; solid line: robust mean, dashed lines: range of tolerance ($|Z\text{-score}| \leq 2$), dotted line: estimated concentration, \diamond bottle 1, \square bottle 2, Δ bottle 3

Fig. 3 ILC results for an estimated concentration of 36 ng/L of benzo(ghi)perylene, sample 2; solid line: robust mean, dashed lines: range of tolerance ($|Z\text{-score}| \leq 2$), dotted line: estimated concentration, \diamond bottle 1, \square bottle 2, Δ bottle 3

Fig. 4 ILC results for benzo(b)fluoranthene in sample 1 as a function of the extraction date; solid line: robust mean, dashed lines: range of tolerance ($|Z\text{-score}| \leq 2$), \diamond bottle 1, \square bottle 2, Δ bottle 3

Fig. 5 ILC results for TBT, sample 2, influence of the detection/calibration method; solid line: robust mean, dashed lines: range of tolerance ($|Z\text{-score}| \leq 2$), dotted line: estimated concentration, \diamond bottle 1, \square bottle 2, Δ bottle 3, unfilled symbols: GC-MS based results, no isotope dilution; dark gray symbols: GC-MS/MS with isotope dilution; black symbols: GC-ICP/MS with isotope dilution; light gray symbols: GC-ICP/MS, internal standard tripropyltin

Electronic supplementary material

Tab. S1

Institution	Location
Administratia Nationala Apele Romane, National Laboratory (LN-AITM)	Bucharest, Romania
Administration de la gestion de l'eau - Division du Laboratoire	Esch-sur-Alzette, Luxemburg
Agenzia Regionale Protezione Ambiente Ligure, Dipartimento della Spezia, U.O. Laboratorio	La Spezia, Italy
APPA Trento, Settore Laboratori	Trento, Italy
ARPAM	Ascoli Piceno, Italy
ARPAM, Dipartimento Provinciale di Ancona	Ancona, Italy
BAM Bundesanstalt für Materialforschung und –prüfung	Berlin, Germany
Biroul Roman de Metrologie Legala	Bucuresti, Romania
CNR-IRSA Istituto di Ricerca Sulle Acque	Brugherio, Italy
CTC	Lyon, France
Finnish Environment Institute	Helsinki, Finland
HZG Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research	Geesthacht, Germany
Jozef Stefan Institute, Department of Environmental Sciences	Ljubljana, Slovenia
LNE Laboratoire national de métrologie et d'essais	Paris, France
PTB Physikalisch-Technische Bundesanstalt	Braunschweig, Germany
Ramboll Analytics	Lahti, Finland
Regional Environmental Agency of Marche (ARPAM), Macerata Department	Macerata, Italy
RWS laboratory	Lelystad, The Netherlands
Serbian Agency for Environmental Protection	Beograd, Serbia
TUBITAK UME, Chemistry Group Laboratory	Gebze, Turkey
UBA Umweltbundesamt , FG II 2.5, Labor für Wasseranalytik	Berlin, Germany
UNIOVI, University of Oviedo	Oviedo, Spain
Vlaamse Milieumaatschappij, Afdeling Rapportering Water	Sint-Denijs-Westrem, Belgium
Material preparations, coordination and shipment: JRC-IRMM, Geel, Belgium	

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Tab. S2

Lab-Code	Extraction date	Sample pre-treatment	Derivatization	Extraction	Preconcentration	Clean-up	Injection	Separation/detection	Calibration	Calibration standards	Special observations
1	25/07/2014	none	pH 4.5, 1 M acetic acid/sodium acetate buffer, ethylation with 20% w/w NaBEt ₄ in THF	LLE according to ISO 17353:2004, n-hexane, 30 min	evaporation to 50 µL	none	4 µL splitless	GC-MS/MS, J&W HP-5MS column, transitions m/z 287>175, 291>235, 289>177	6 point calibration curve, calibration solutions prepared in 1 L mineral water	OTC mixture Ultra CUS-9993 and o2Si 0102288-02, deuterated internal standards	TBT-1A and TBT-3A samples were extracted twice because of emulsion formed. TBT-1A, TBT-1B and TBT-1C: signal intensities below LOQ, no results reported
3	23/06/2014	none	pH 5, 500 µl NaBEt ₄ 10%, over night	LLE, hexane, 4 ml, 20 min, magnetic stirrer	none	column with activated Al ₂ O ₃ , neutral	large volume	GC-MS, column HP5 MS	calibration curve 5 points	Custom Standard Ultra scientific 1000 µg/ml in MeOH, mix of mono-, bi-, tri-, tetra butyltin chloride	none
5	26/06/2014	none	NaBEt ₄	SPEDEX 4790 , automated SPE extraction , DVB disk , 47mm, hexane -MeOH	evaporation	none	20 µL	GC-MS/MS Thermo TSQ, column RXI 5 sil MS	calibration curve, deuterated internal standard	organotin standard mixture, 9 tin ethyl derivatives, S-4547-K-IO , Chiron	none
9	24/06/2014	acidification with 1 mL HCl (38%)	NaBEt ₄ , 1 mg/L, pH 4.8 (acetate buffer), online derivatisation	addition of isotopic spike (119Sn enriched TBT) and shaking for 20 hours,	HS-SPME	none	SPME, splitless (250 °C)	GC-ICP-MS; column DB1-MS, Sn @ m/z 119 and 120	IDMS	119Sn-enriched Butyltin Mix, ISC Science	none

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Lab-Code	Extraction date	Sample pre-treatment	Derivatisation	Extraction	Preconcentration	Clean-up	Injection	Separation/detection	Calibration	Calibration standards	Special observations
			/SPME	online HS-SPME: shake 10 min, extraction 30 min							
10	26/06/2014	not specified	not specified	not specified	not specified	not specified	not specified	not specified	not specified	not specified	not specified
17	01/07/2014		10 mL 1M acetate buffer, pH 4.9, 500 µL 1% NaBEt ₄ in THF	LLE, 5 mL hexane, 30 min	none	none	1 µL splitless	GC-ICP-MS, column Thermo Trace TR-5	Double IDMS	TBTCl, Sigma-Aldrich (T50202), ¹¹⁹ Sn-enriched Butyltin Mix, ISC Science (IES-MDT119)	none
18	02/07/2014	acidification (HCl, pH2) and filtration, water and filtered phase were analysed separately	1 mL 1% NaBEt ₄ , pH 4,5, 20 min	water phase: pH adjustment (pH 5, NaOH), derivatisation, extraction with 2 mL n-hexane (shaking 30 min), SPM phase: addition of 20 mL HAc/MeOH 3:1 (30 min ultrasonic), pH adjustment (pH 5, NaOH), derivatisation, extraction with 2 mL n-hexane (shaking 30 min)	none	none	2 µL, splitless	GC-ICP-MS, column Agilent DB-5 MS UI	Reverse IDMS	TBTCl Sigma Aldrich, ¹¹⁹ Sn-enriched Butyltin Mix, ISC Science	very small peak areas for samples containing HA, Blank solutions prepared with Evian water (glass bottles), peak areas of the blanks subtracted from peak areas of the samples during data processing
21	24/06/2014	acidification, 0.1 % (v/v) acetic acid	pH 5.4, 500 µL 2 % (w/v) NaBEt ₄ in MilliQ water	LLE, 1 mL hexane, 10 min manual shaking	under N ₂ to 75 µL	none	25 µL PTV injection	GC-MS/MS, column DB-5MS	IDMS	¹¹⁹ Sn-enriched Butyltin Mix, ISC-Science (Oviedo, Spain)	none

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Lab-Code	Extraction date	Sample pre-treatment	Derivatization	Extraction	Preconcentration	Clean-up	Injection	Separation/detection	Calibration	Calibration standards	Special observations
22	06/08/2014	acidification, 0.5 mL HNO ₃ (suprapure), shaking for 24 h	pH 5, 10 mL 1 M acetate buffer, 2.5 mL of 2 % NaBEt ₄	LLE, 1 mL isooctane, 60 min	none	none	2 µL splitless	GC-ICP-MS, column DB 5ms	calibration curve, internal standard TPrTCl	TBTCl, 96 %, Sigma Aldrich, TPrTCl, 98 %, from Merck	Sample 1: compact foam formed during extraction
24	22/06/2014 sample1, 24/06/2014 sample2	addition of 30 mL of (HAc:MeOH:H ₂ O) (1:1:1) (v/v), agitation on a rotary table at 100 rpm for 24h.	pH 5, 20 mL 1 M sodium acetate buffer, 2 mL NaBEt ₄ , 1% in mQ water	LLE, 20 mL hexane, 2 mL derivatization agent, shaking for 30 min at 200 rpm, let stand for 20 min, recover foam on the top of the bottle and centrifuge it for 4 min at 8500 rpm, recover hexane phase	vortex evaporation by Multivapor to 1 mL	none	2 µL, splitless	GC-ICP-MS, column HP-5	Species-specific IDMS, reverse ID used to quantify the isotope-enriched TBT mass fraction	TBTCl from Sigma-Aldrich, ¹¹⁹ Sn-enriched TBT from ISC Science (Spain)	Blank solutions were prepared in Evian mineral water. Blank signal was subtracted from sample signal during data processing.

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Tab. S3

Lab-Code	Extraction date	Sample pre-treatment	Extraction	Preconcentration	Clean-up	Injection	Separation/detection	Calibration	Calibration standards	Special observations
3	23/06/ 2014	none	SPE, elution with 6 mL CH ₂ Cl ₂ :EtAc 50:50, 4 ml/min	none	none	large volume	NCI GC-MS, NCI, column HP5 MS	5 point calibration curve	Accustandard BDE-CALEWS, internal standard BDE 209 C13 Well Lab 209L	none
5	01/07/ 2014	none	SPEDEX 4790, automated SPE, DVB disk, 47 mm, hexane - methanol	evaporation	none	10 µL	HR GC-MS Waters Autospec, column Rtx-1614	calibration curve, internal standard	individual standards BDE 28 - 47 - 100-99 - 154 - 153 - 183 and 209 from Wellington laboratories, internal standards ¹³ C labelled BDE 47 - 99 - 153 - 183 -209 from Wellington laboratories	none
8	24/06/ and 25/06/ 2014	none	SPE automated extractor HORIZON TECHNOLOGY SPE-DEX 4790, DVB disks 47 mm. Elution first with methanol (to eliminate the water) and second with n-hexane. Methanol was discharged and hexane was	to 1 mL under N ₂ stream, 40 °C	prEN 16694: Water quality - Determination of pentabromodiphenyl ether (PBDE) in whole water samples using solid phase extraction (SPE) with SPE-disks combined with gas chromatography - mass spectrometry (GC-MS), annex D, D.1 Multilayer silica clean-up	PTV, splittless, 2 µL	GC-MS/MS Thermo Electron ION-TRAP PolariQ, signal acquisition in MS/MS mode, column Restek rxi-5MS	4 level multipoint calibration	AccuStandard BDE-CM mix, 2.5 mg/L, internal standard ¹³ C ₁₂ BDE-28, 47, 99, 154, 153	no blank correction

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Lab-Code	Extraction date	Sample pre-treatment	Extraction	Preconcentration	Clean-up	Injection	Separation/detection	Calibration	Calibration standards	Special observations
			collected							
10	14/07/ 2014	not specified	not specified	not specified	not specified	not specified	not specified	not specified	not specified	not specified
14	23/06/ 2014	none	automated SPE, C18 disks, ethyl acetate and dichloromethane solvents	nitrogen stream	SPE silica-H ₂ SO ₄	PTV splitless, 5 µL	GC-MS/MS. column ZB-5HT Inferno	calibration curve with at least 6 points and species-specific isotope dilution	BFR calibration solutions, Cambridge Isotope Laboratories, internal standards ¹³ C-labeled BDEs 3, 15, 28, 47, 99, 153, 183 and 209, Wellington Laboratories	PBDE 1C Sample no. 07: Despite vigorous shaking of the sample before extraction, hard (cemented) precipitation was observed at the bottom of the bottle after extraction
15	10/07/ and 11/07/ 2014	none	LLE, hexane: dichloromethane (1:1), 3 x 30 mL, mechanical shaking (20 min)	rotary evaporator/and N ₂ evaporator system	H ₂ SO ₄	cool on column injector, 1µL	GC-ICP-MS, column DB5MS	IDMS	81Br labelled analogues to the target PBDEs	

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Lab-Code	Extraction date	Sample pre-treatment	Extraction	Preconcentration	Clean-up	Injection	Separation/detection	Calibration	Calibration standards	Special observations
16	08/07/ 2014	none	SPE Bakerbond Speedisk C18, elution: 2 x 4 mL acetone/n-hexane (50:50; v/v), followed by 8 ml of n-hexane	preconcentration with TurboVap in a N ₂ stream at about 35°C to 1 ml. preconcentration of the final extract (after clean-up) with a sensor controlled evaporator (Barkey; Flowtherm optocontrol) to 100 µL	multilayer silica column (wet filled from bottom to top): Sodium sulfate, 1 g silica-NaOH 33%, Sodium sulfate, 5 g silica-H ₂ SO ₄ 44%, Sodium sulfate	PTV-LVI, 20 µl	GC/ECNI-MS in SIM mode; column Rtx-CL Pesticides	in total 15 calibration standards (from 0 pg/µL to 150 pg/µL), full calibration range split into low and high concentration range (0 pg/µL to 10 pg/µL and 10 to 150 pg/µL); all calibration standards with IS concentration of 10 pg/µL; quadratic regression	native PBDE: Wellington Laboratories: BDE-28, -47, -99, -100, -153 - 154 ; 50 µg/mL each in nonane; F-BDE (IS): CHIRON (Norway): F-BDE 28, FF-BDE 47, and F-BDE 100; 50 µg/mL each in iso-octane	water samples with humic acid needed more time after sample loading to dry filter
17	17/07/ 2014	none	water samples were spiked with 1250 µl of 0.05 µg/kg labelled standard solution and agitated for 24 hrs, LLE with 150 mL n- hexane, 2 times	evaporation, final amount of extract was gravimetrically adjusted to 50mg	anhydrous sodium sulphate	PTV splitless	GC-MS/MS, column DB-5MS	IDMS	native PBDEs from Wellington Lab, internal standards from Cambridge Isotope Lab	blank solutions prepared with distilled water spiked with 5 mg/L humic acid

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Lab-Code	Extraction date	Sample pre-treatment	Extraction	Preconcentration	Clean-up	Injection	Separation/detection	Calibration	Calibration standards	Special observations
20	02/07/ to 10/07/2014	addition of mixture of BDE enriched in ⁸¹ Br prior to extraction	LLE with 30 mL iso-octane over night, phase separation, remaining water phase again extracted with 30 mL iso-octane for 1h	evaporation to 200 µL	none	PTV, 8 µL	GC-ICP-MS, column DB 5MS	double IDMS	⁸¹ Br labeled BDEs from ISC Science Oviedo	BDE 28 was very near or below the LOQ; for BDE 100 there was trouble with the spike solution so for some samples no BDE 100 concentration could be determined, the other values are very uncertain as the enrichment of the ⁸¹ BDE 100 spike is only 69 %
24	26/06/ 2014	none	LLE, 2 x 50 mL of DCM (Sigma Aldrich)	rotary evaporation to few mL, further evaporation under N ₂ to dryness, addition of 100µL iso-octane	none	10 µL, MMI injector	GC-MS/MS, column DB 5-MS	6 point calibration curve	PBDE congeners 50 µg/mL in nonane (Accustandard, USA) and NIST SRM 2257, ¹³ C-labeled PBDE in nonane (Cambridge Isotope laboratories)	blank solution prepared with mineral water

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Tab. S4

Lab-Code	Extraction date	Sample pre-treatment	Extraction	Pre-concentration	Clean-up	Injection	Separation/detection	Calibration	Calibration standards	Special observations
2	05/07/ 2014	none	LLE, dichloromethane, automatic shaker, 50 ml for 10 min, 25 ml for 10 min and 25 ml for 10 min	addition of internal standard, evaporation with N ₂ to 1 ml	anhydrous sodium sulphate	splitless, 1 µL	GC-MS/MS column 5% polar phase	Calibration curve with deuterated internal standards	mix standard 45 PAH (Dr Ehrenstorfer), concentration levels: 5, 10, 25, 50, 100, 250 ppb; IS are at level 50 ppb, naphthalene D8 for naphthalene, Phenanthrene D10 for anthracene and fluoranthene, perylene D12 for other PAHs; Mix 31 PAH Dr Ehrenstorfer	the sample 1C gave a different emulsion from 1A and 1B
5	23/06/ 2014	none	SPEDEX 4790 Horizon technologie; DVB-disk 47mm dichloromethane and acetone	evaporation by N ₂ stream	none	1 µL Gerstel MPS pulsed splitless	GC-MS, column Rxi-5sil MS	Calibration curve with deuterated internal standards	ERS011, PAH-mix 9 deuterated Dr Ehrenstorfer	
6	24/06/ 2014	none	SPE HLB discs solvent: 1x 5 ml acetone 5x 5 ml dichloromethane	in Dryvap from 40 ml to 0.9 ml dichloromethane	drying by goretex membrane (dryvap)	1 µL	TSQ MS/MS, column Varian select PAH	bracket standard single point forced by 0 (50 ppb)	restek standards 16 PAH mix, 10 ng of labeled PAH standard each	
7	21/07/ 2014	none	LLE, dichloromethane		TLC	splitless	GC-MS, column DB 5ms	calibration curve, perylene-d12	certified liquid standard,	same analytical procedure for samples 1 and 2

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Lab-Code	Extraction date	Sample pre-treatment	Extraction	Preconcentration	Clean-up	Injection	Separation/detection	Calibration	Calibration standards	Special observations
								as internal standard		
9	19/06/ 2014	none	LLE, 2x 40ml preroleum ether (40-60) for 10 minutes	evaporation, 14 mL to 2 mL	none	large volume 50 µL	GC-MS/MS with 50m specific PAH column	calibration curve, 3 points in duplicate, 2 calibration check standards at the begin and end of GC-run	standards were diluted from a custom mix purchased from accustandard and LGC (independence standard check), internal standards antracene-d10, naphthalene-d8, BghiPe-d12	
10	09/07/ 2014	not specified	not specified	not specified	not specified	not specified	not specified	not specified	not specified	not specified
12	01/07/ and 02/07/ 2014	none	LLE with hexane: dichloromethane, ratio 4:1, v/v, 60 min, time of phase separation 10 min	rotary evaporator	anhydrous sodium sulphate	direct injection at room temperature	according to EN ISO 17993:2004	7 point calibration curve, linearity range from 0.8 µg/L to 32 µg/L	external standard PAH Mix 64 (2 mg/ml -Dr. Ehrenstorfer, solution in Benzen:DCM, 1:1, v/v)	
13	16/07/ 2014	none	EPA 3610, LLE, CH ₂ Cl ₂ , 30min		solvent exchange CH ₂ Cl ₂ to hexane	splitless, 2 µL	GC-MS, column HP-5MSI	calibration curve, no internal standard	LGC standard, 16 EPA Priority PAHs in toluene, concentration 100 µg/mL	
17	23/07/ 2014	none	LLE	rotary evaporation to 500 µL, addition of 500 µL milliq water	none	50 µL	UPLC and LC-APPI-MS/MS XE PREMÝER (waters)	6 point calibration curve	Cambridge Isotope Lab. (CIL)	

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Lab-Code	Extraction date	Sample pre-treatment	Extraction	Preconcentration	Clean-up	Injection	Separation/detection	Calibration	Calibration standards	Special observations
18	08/07/ and 09/07/2014	internal standard spike 24 h before extraction	Speedisk, elution: acetone 5 mL, cyclohexane 5 X 5 mL	final volume 1 mL	none	large volume, 20 µl	GC-MS, column DB-EUPAH	7-point-calibration, 0,5 - 500 ng/mL, linear regression, ¹³ C labeled internal standards	16 EPA PAHs, Dr. Ehrenstorfer PAH-Mix 9, ¹³ C PAHs, CIL	benzo(j)fluoranthene separated from benzo(b,k)fluoranthene
19	02/07 – 05/07/ 2014	none	LLE	rotary evaporation	none	large volume, 5 µL	GC-MS	calibration curve	LNE stock solution distributed within ENV08 WP3, internal standard perylene	
24	09/07/ 2014	none	SPE Disk, speedisk C18 JT Baker, automatic system SPEDEX 4790, acetone:hexane (1:5)	rotary and N ₂ evaporation	sample 1: silica column (450°C, 4 hours) and sodium sulfate	5 µL in solvent vent mode	GC-MS, column DB-EUPAH	6 point calibration curve, ¹³ C labeled internal standards	neat compounds, Dr Ehrenstorfer (CIL) + NIST SRM 1647e, ¹³ C labelled compounds (CIL, individual compounds in nonane at 100 µg/mL)	blank solutions prepared in mineral water

Fig. S1

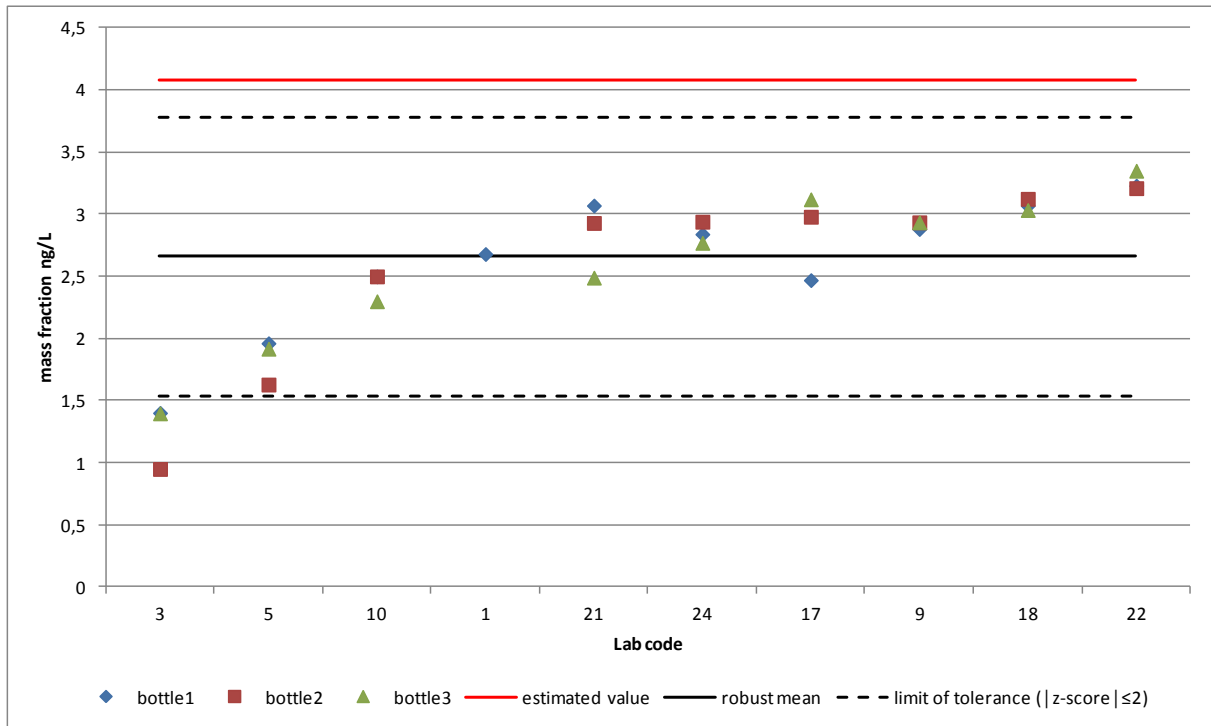


Fig. S2

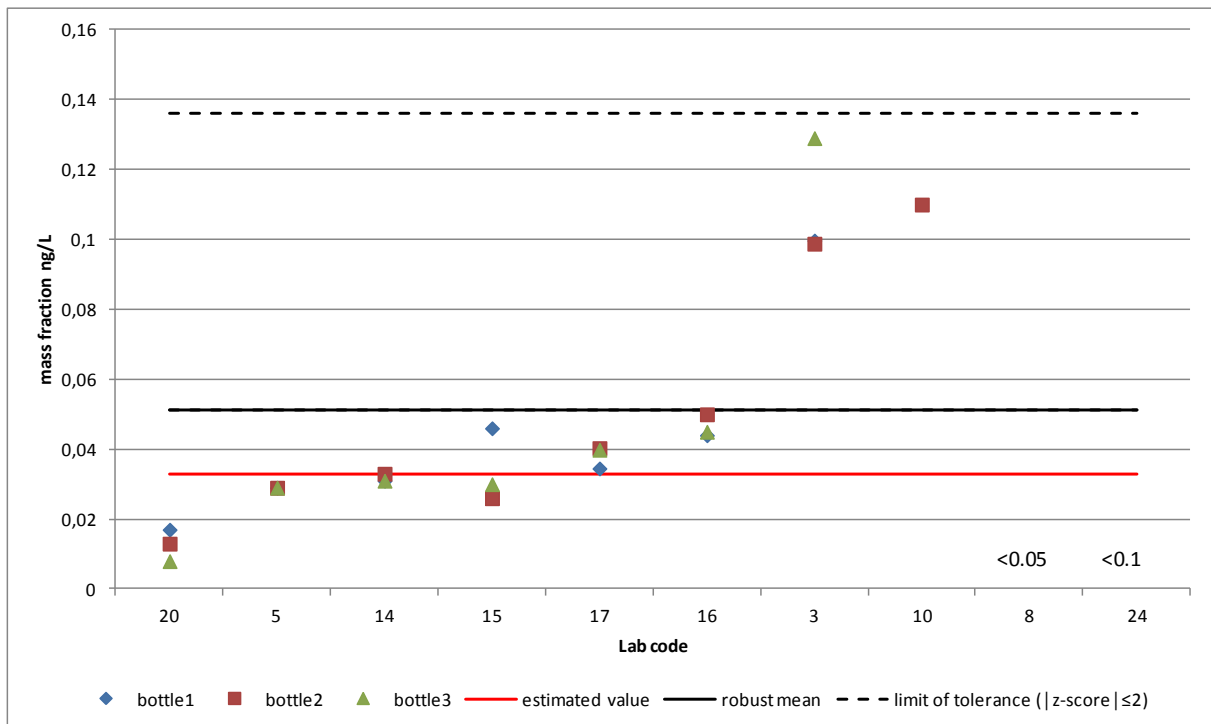


Fig. S3

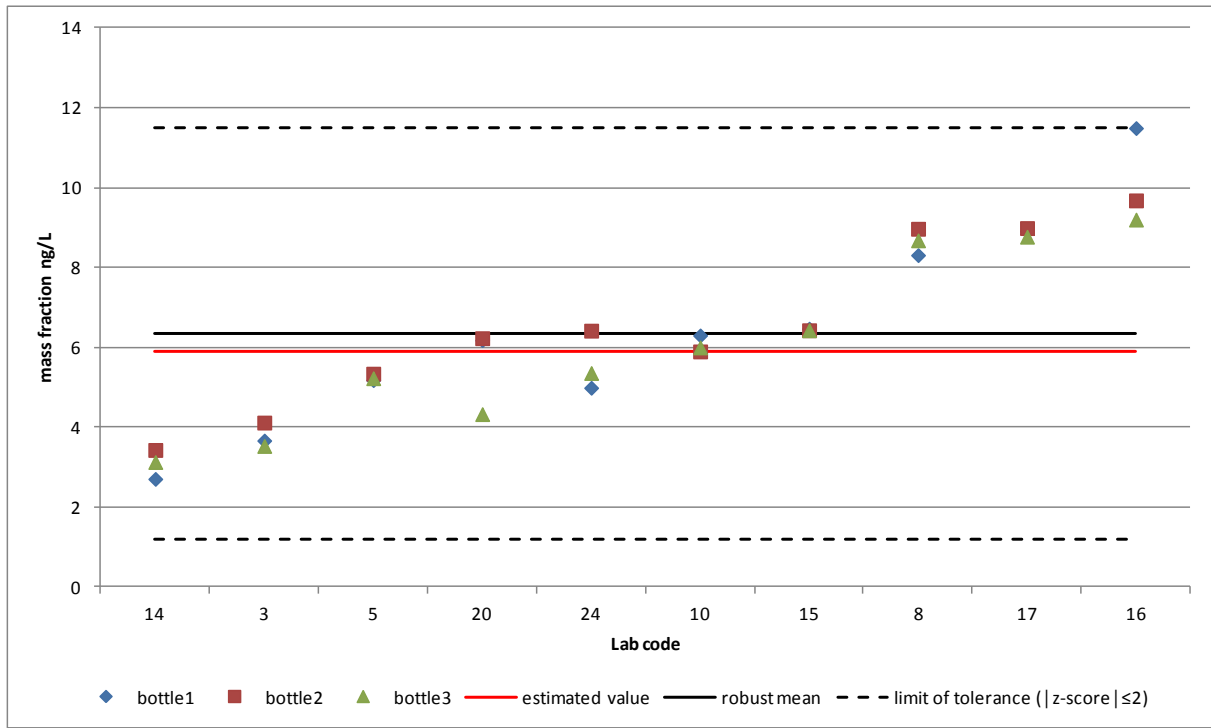


Fig. S4

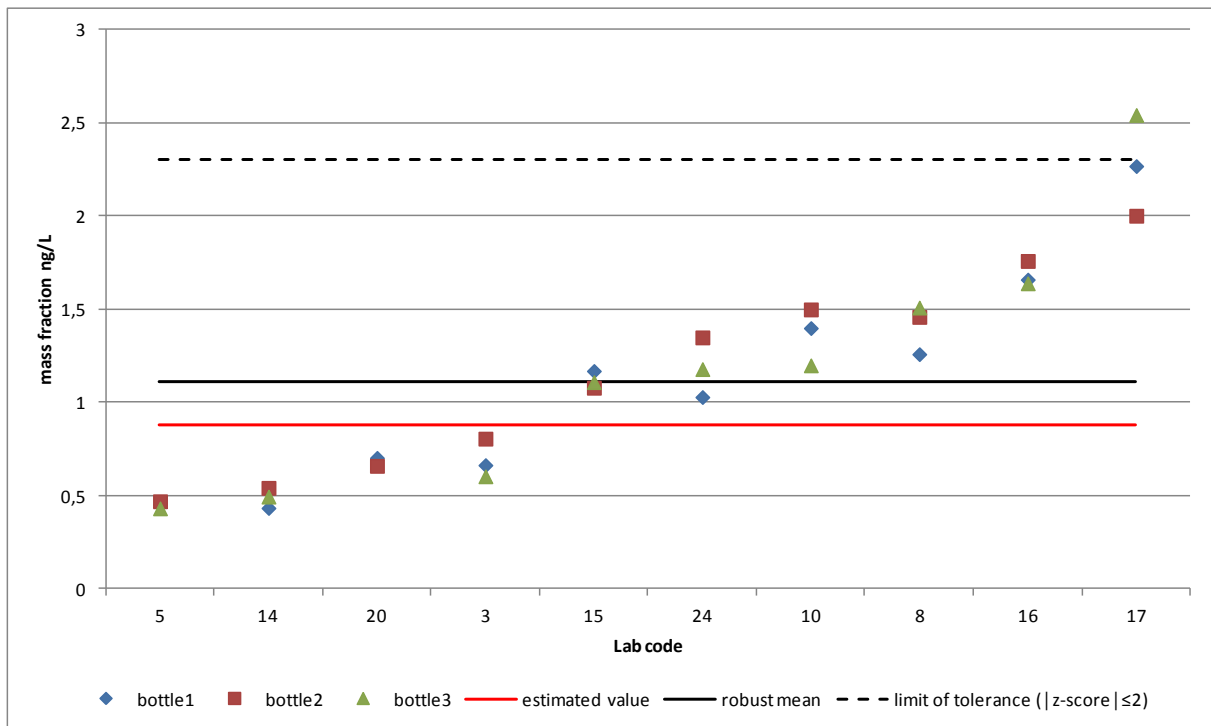


Fig. S5

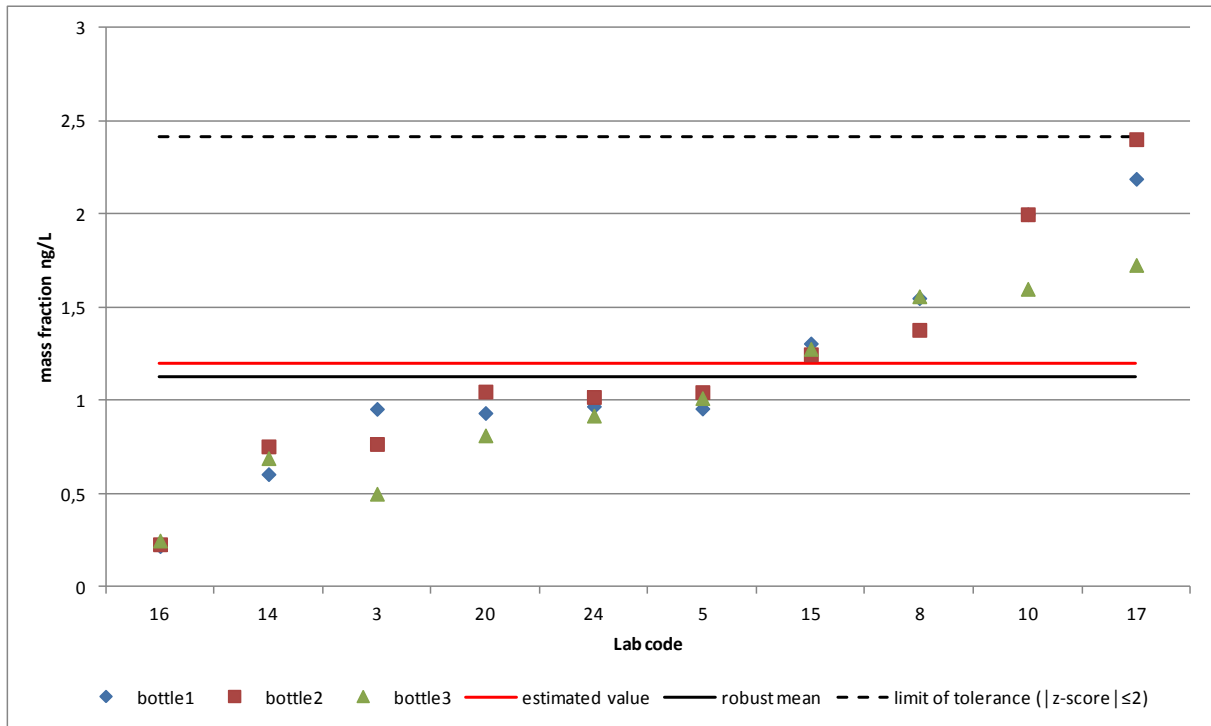


Fig. S6

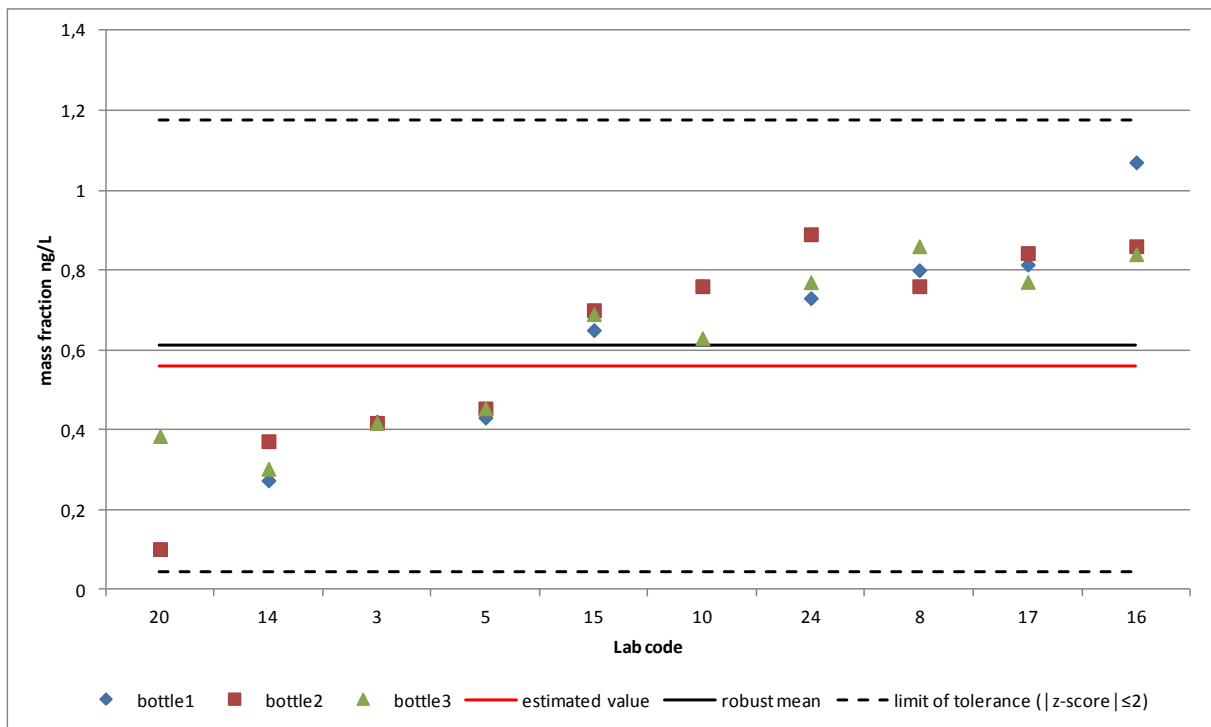


Fig. S7

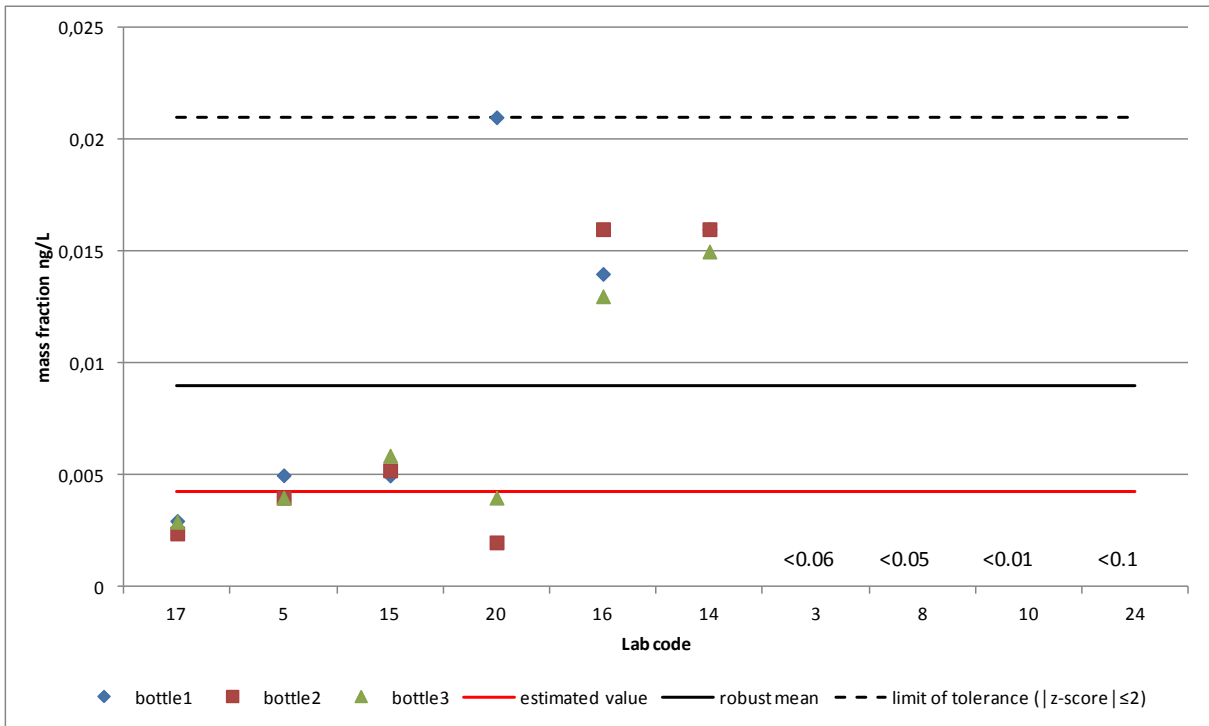
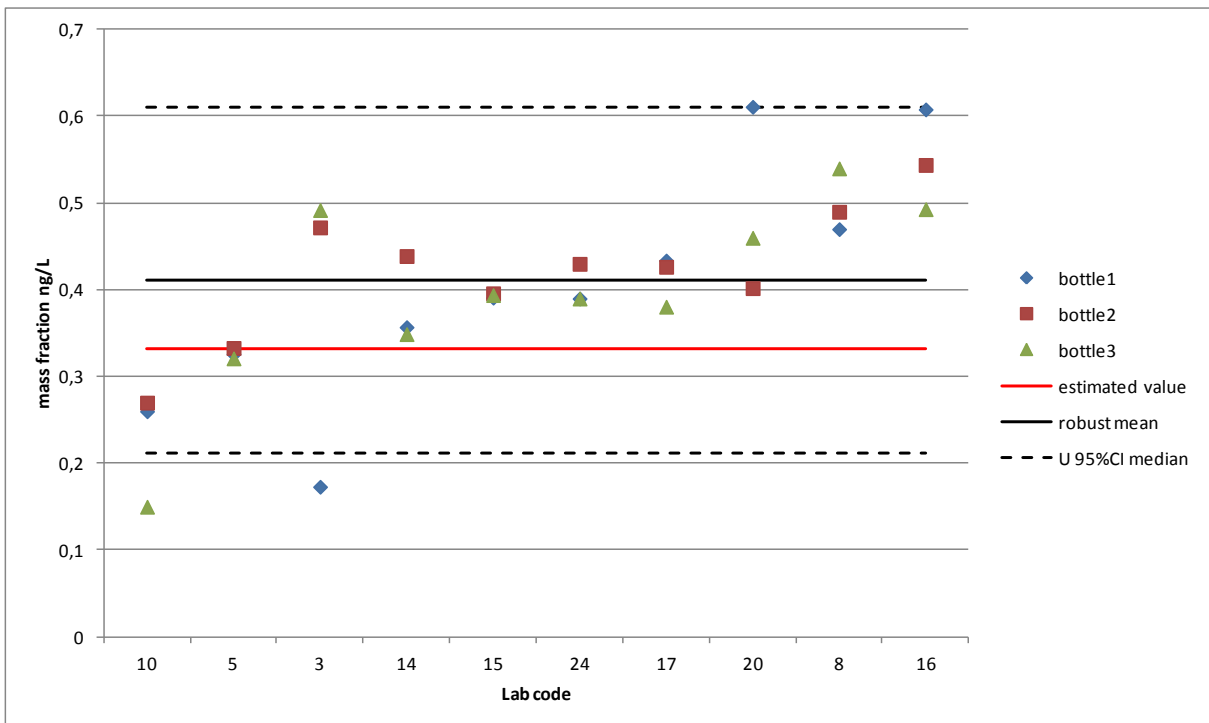
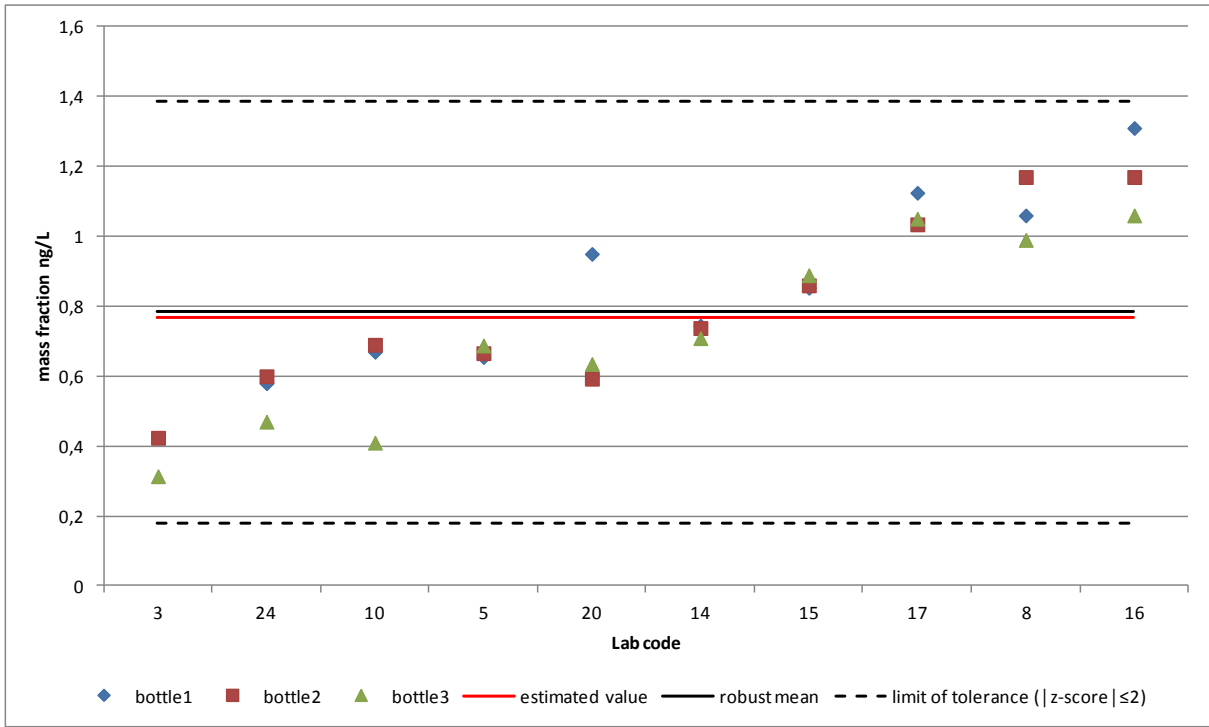


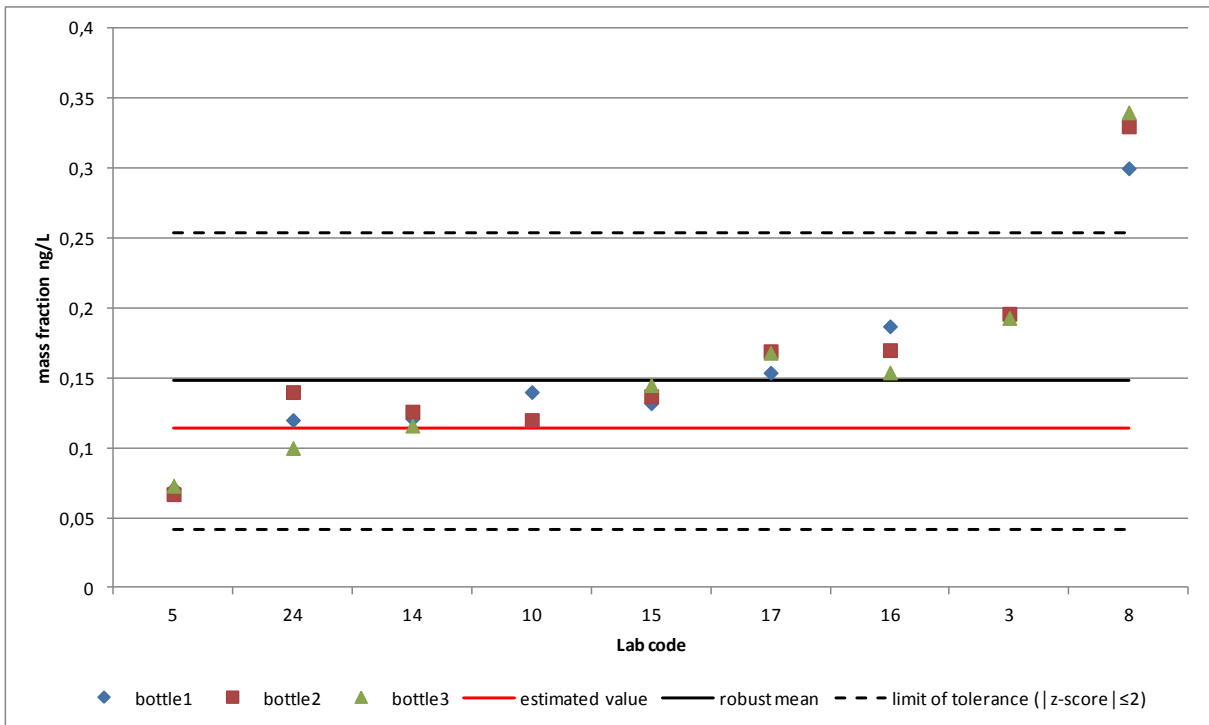
Fig. S8



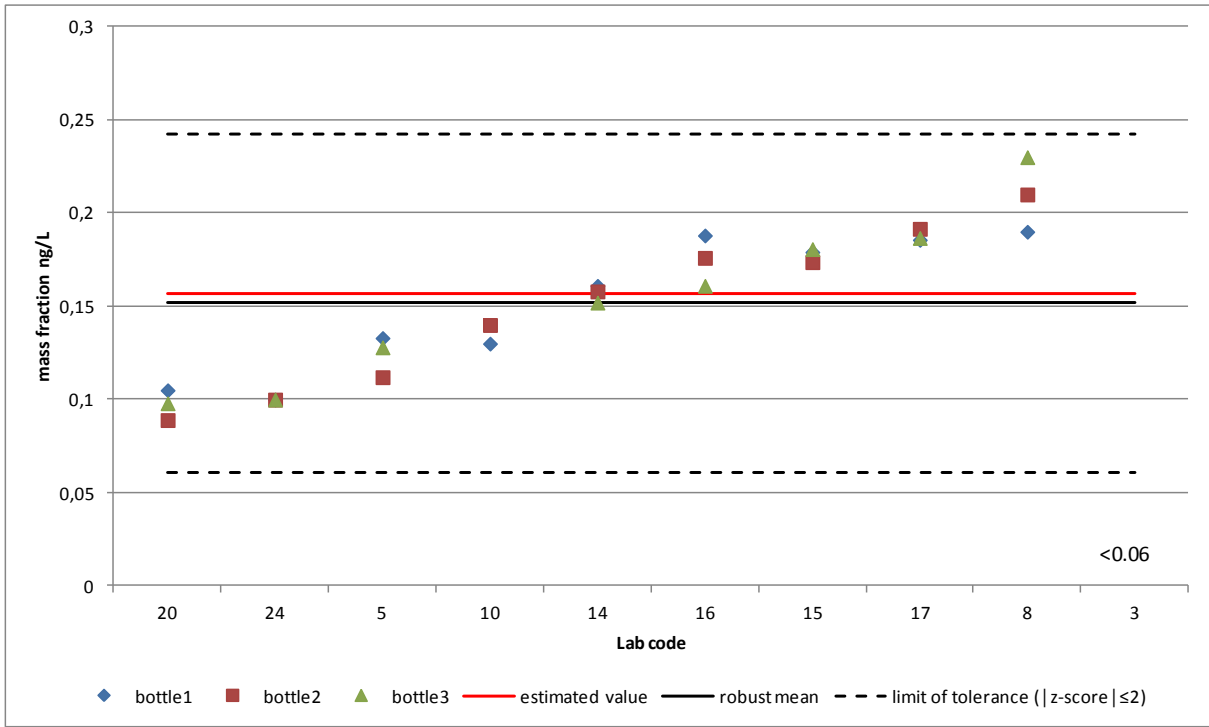
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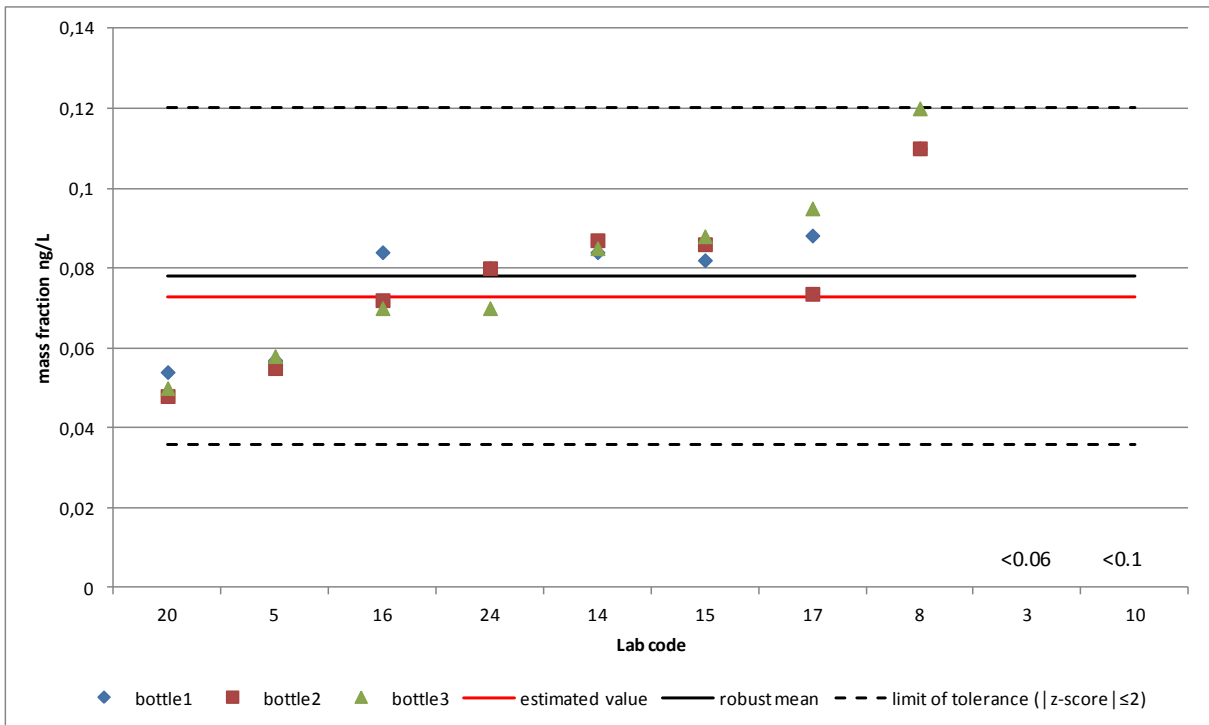
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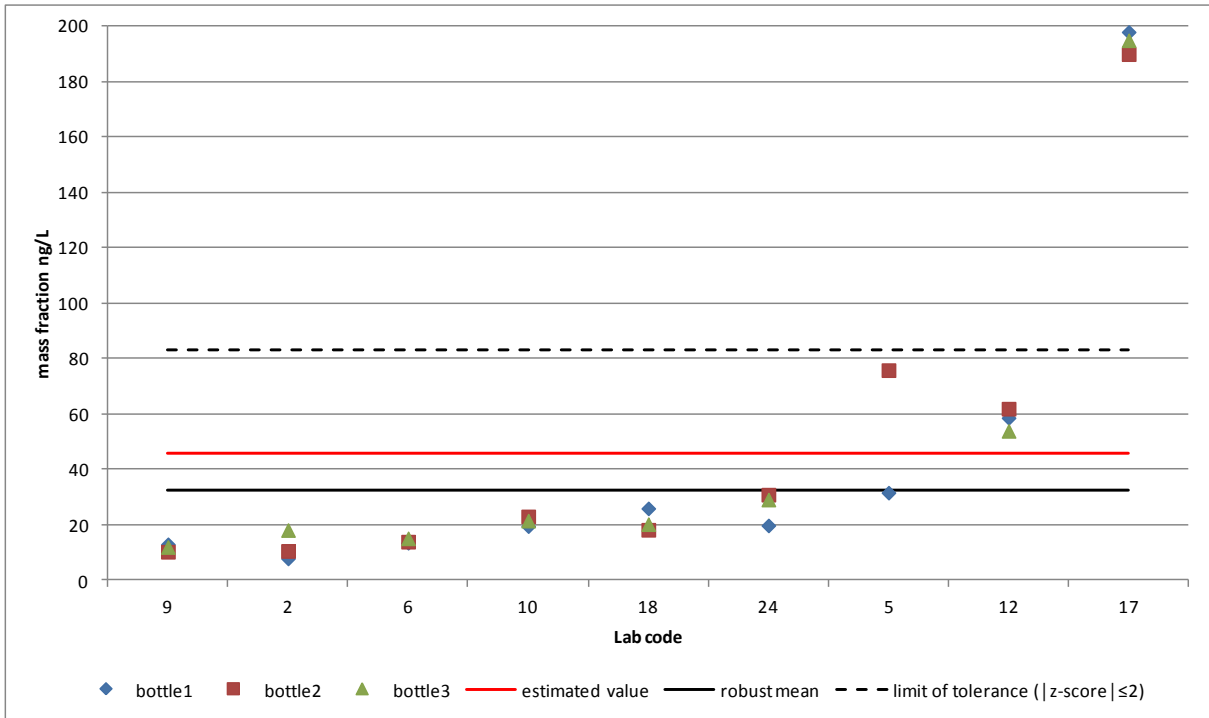
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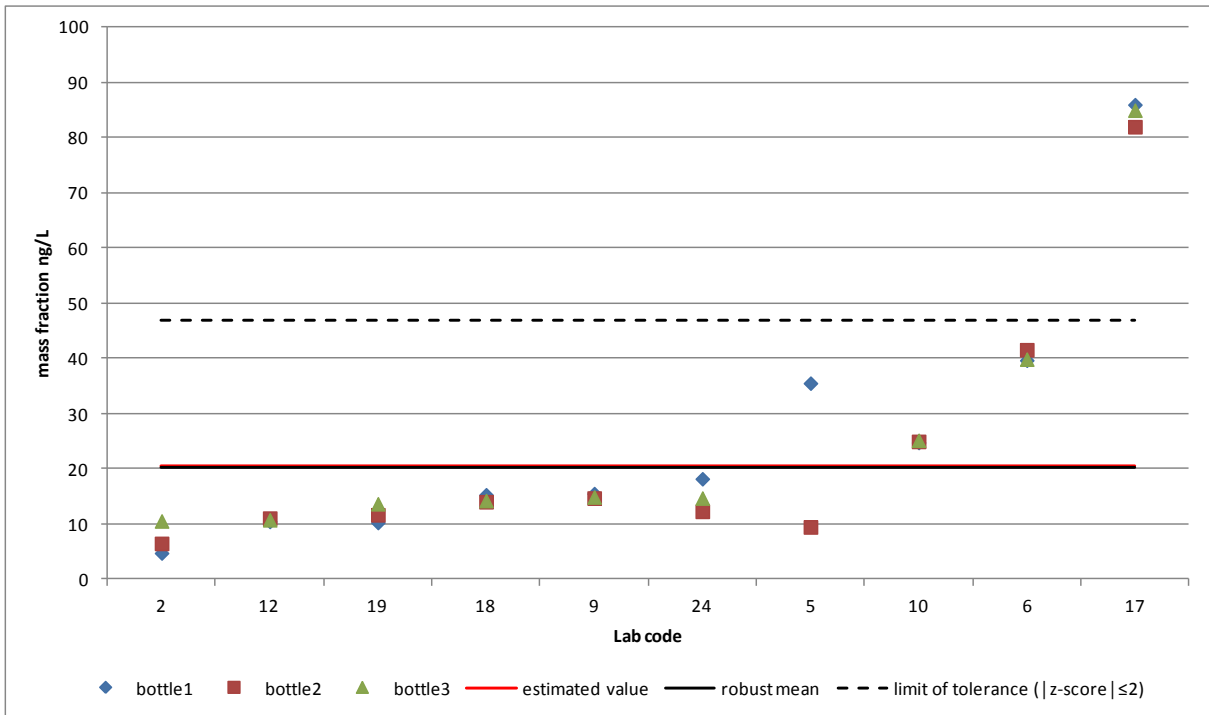
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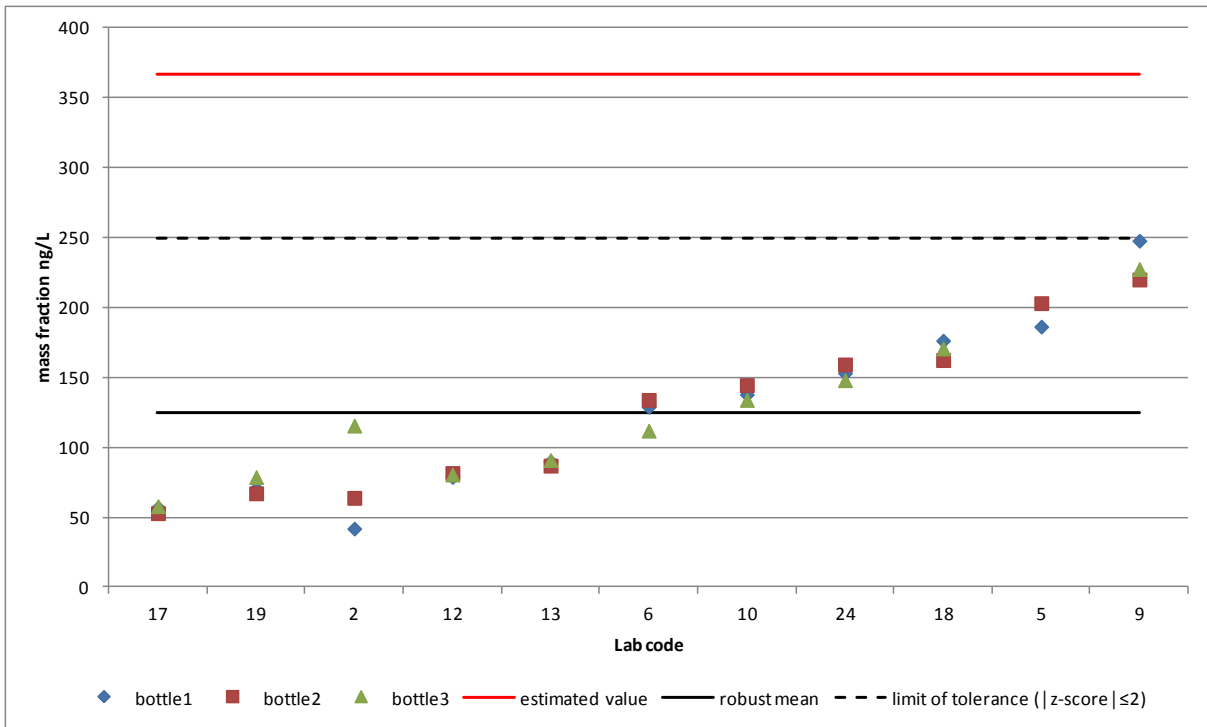


Fig. S16

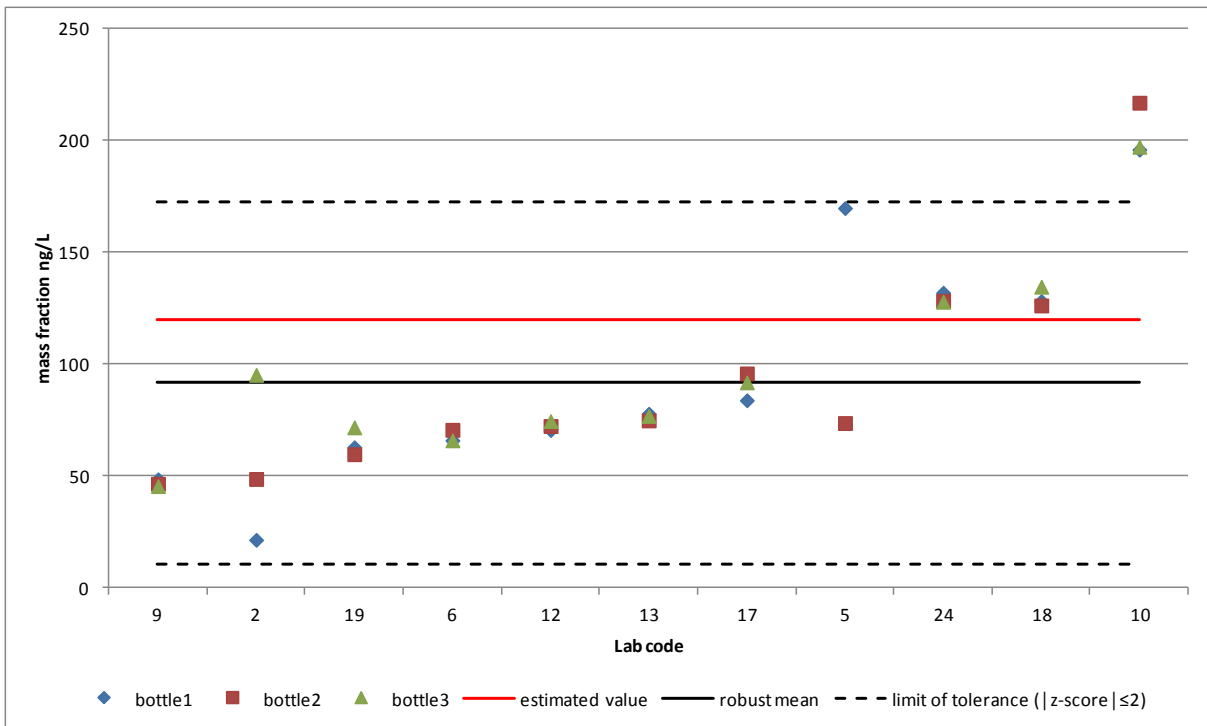


Fig. S17

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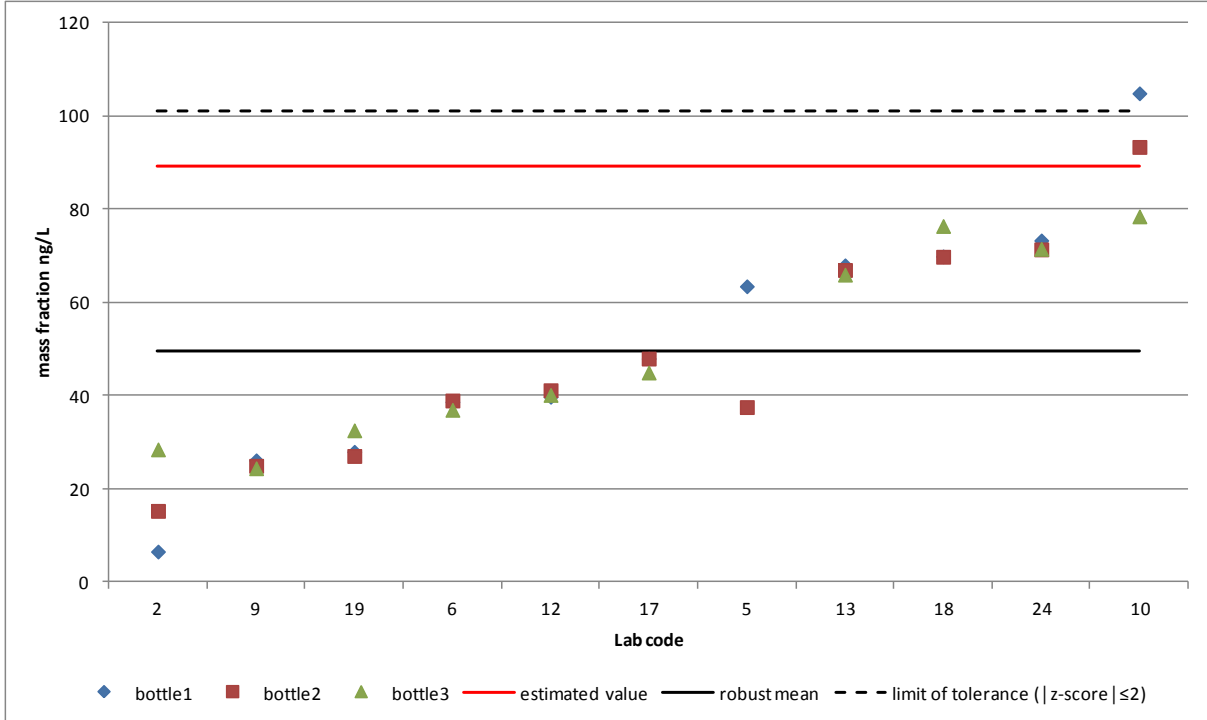


Fig. S18

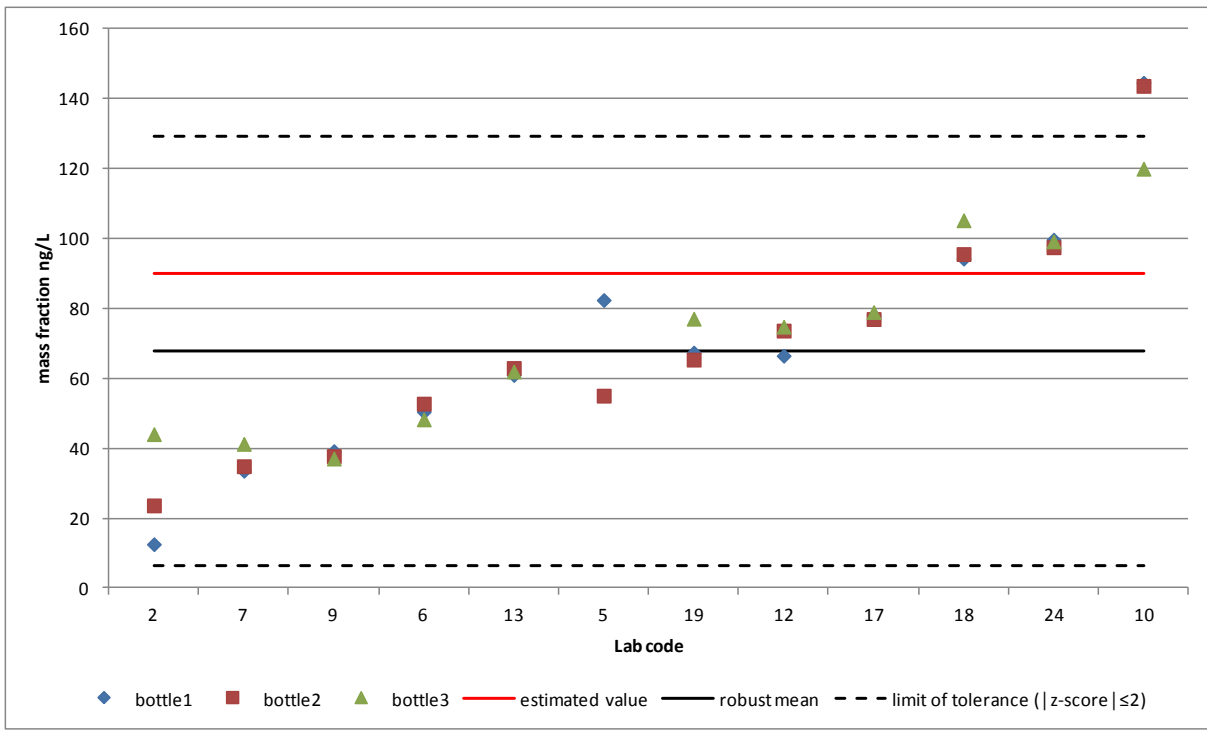


Fig. S19

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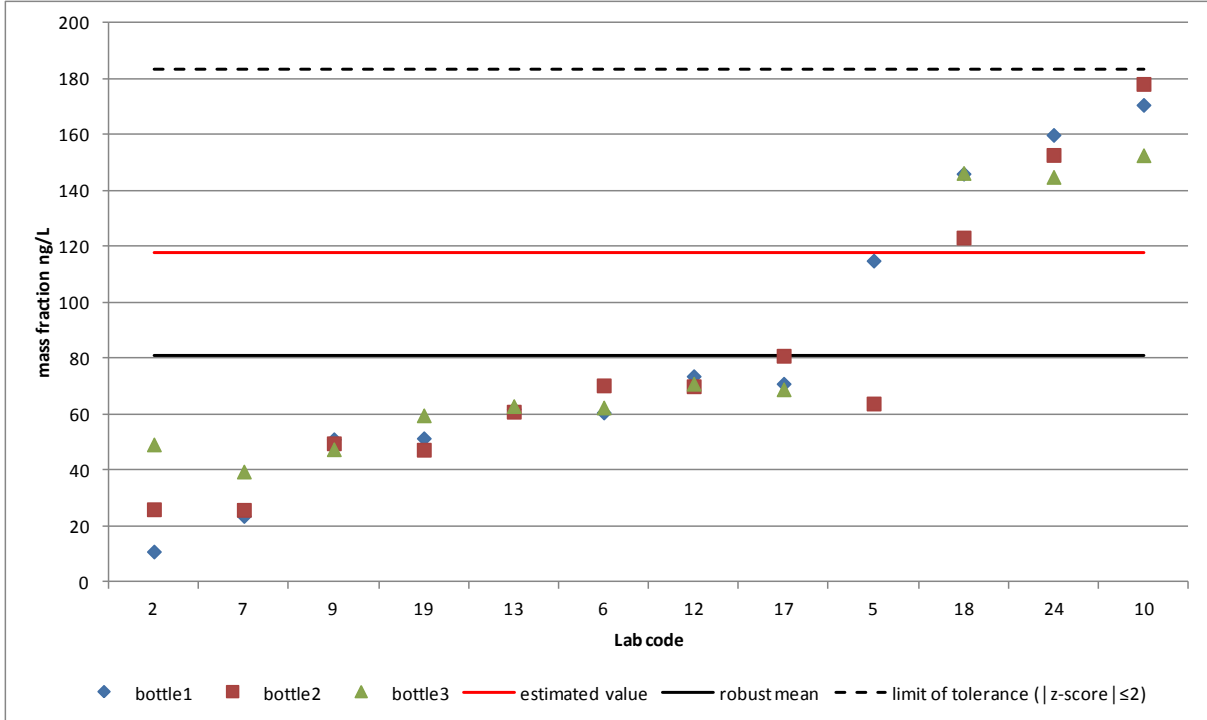


Fig. S20

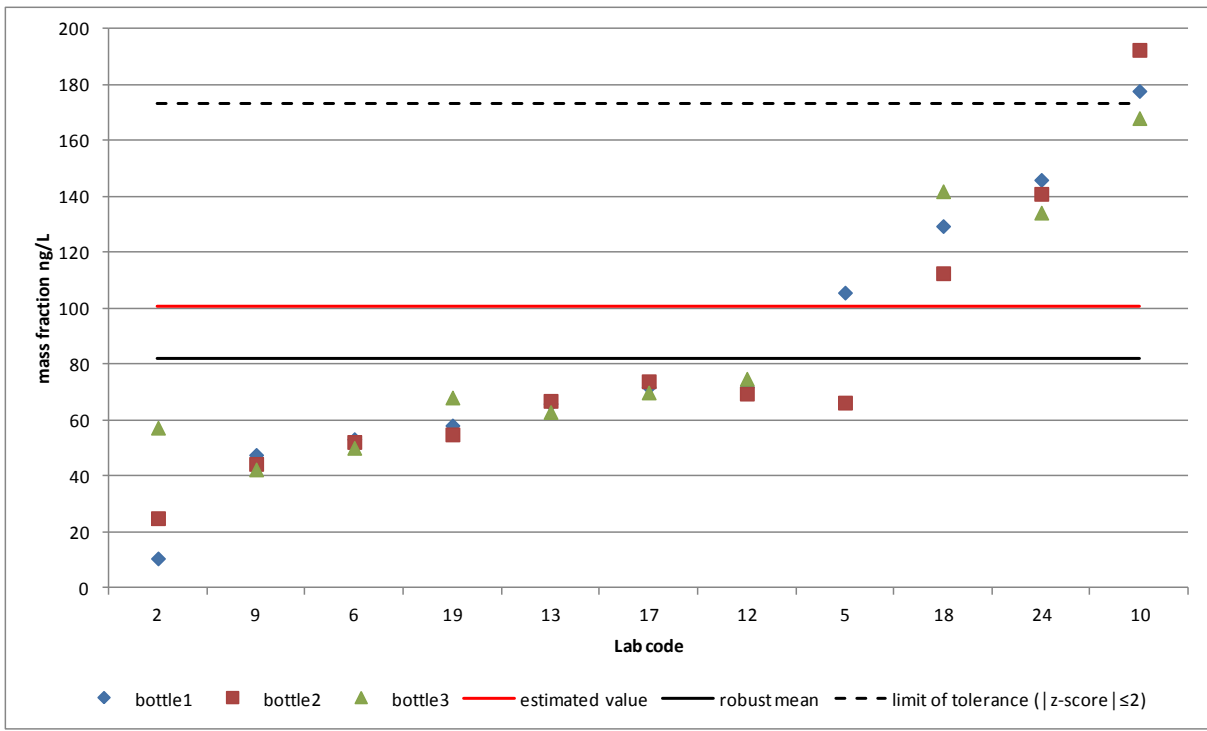


Fig. S21

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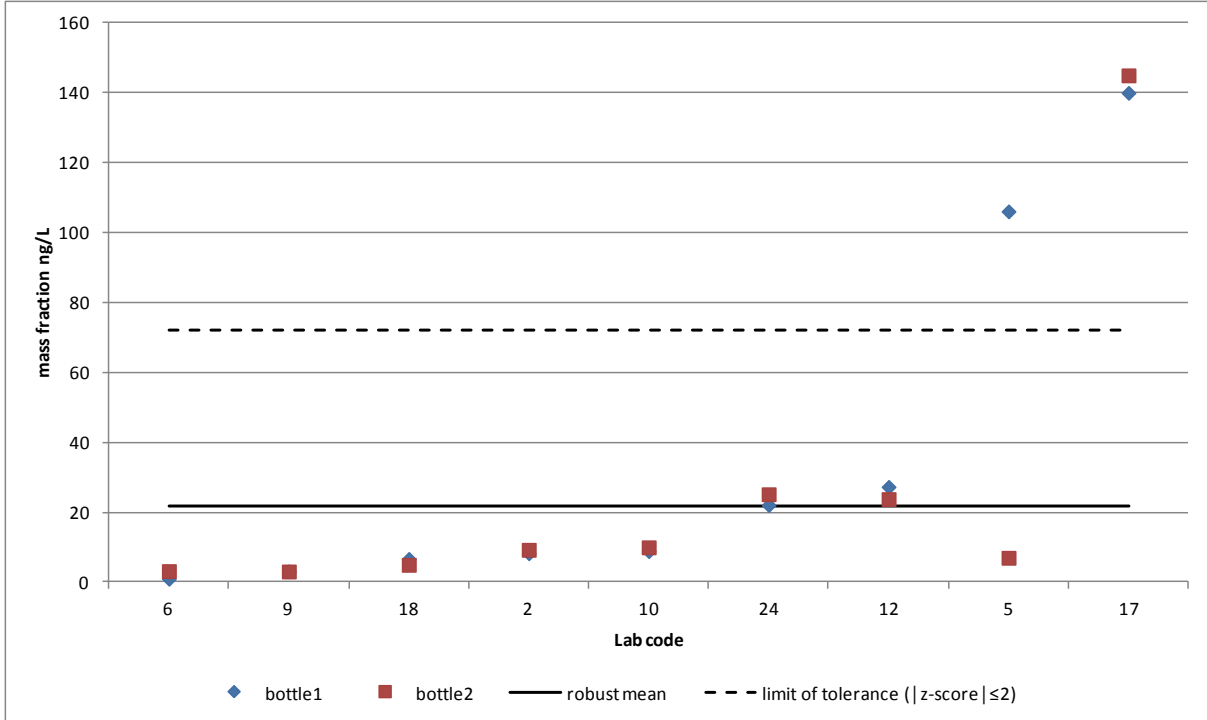


Fig. S22

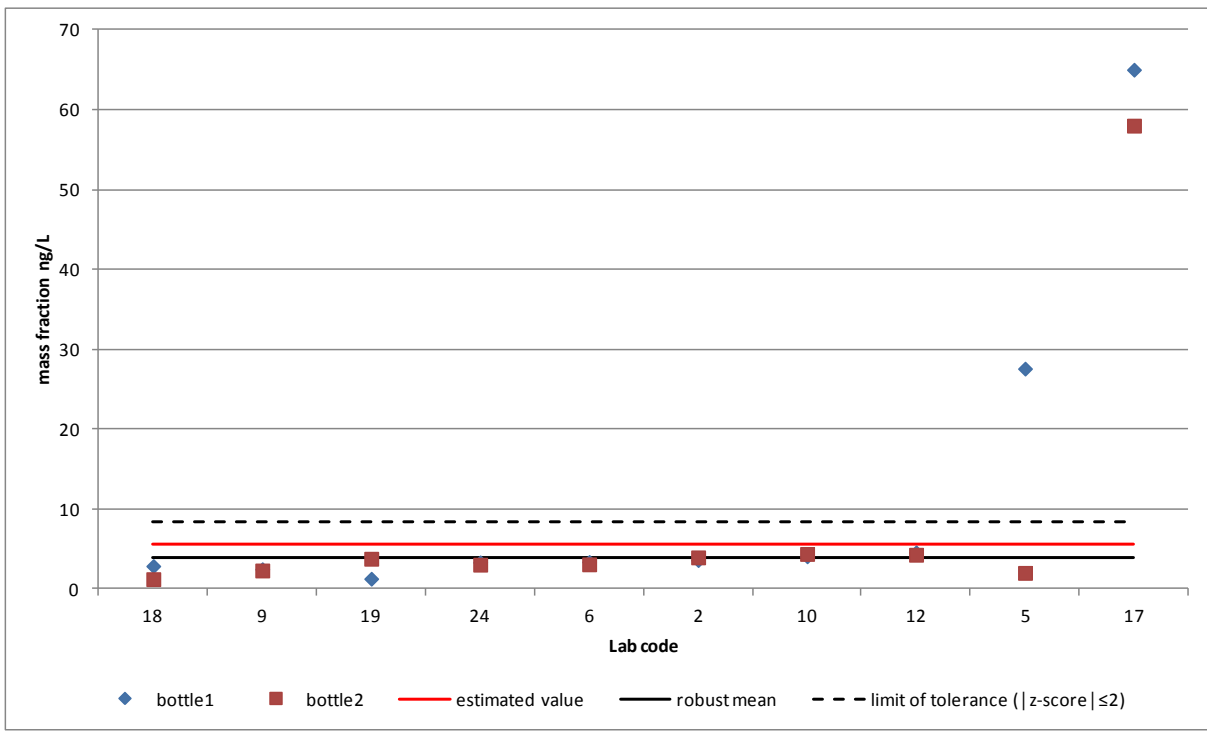


Fig. S23

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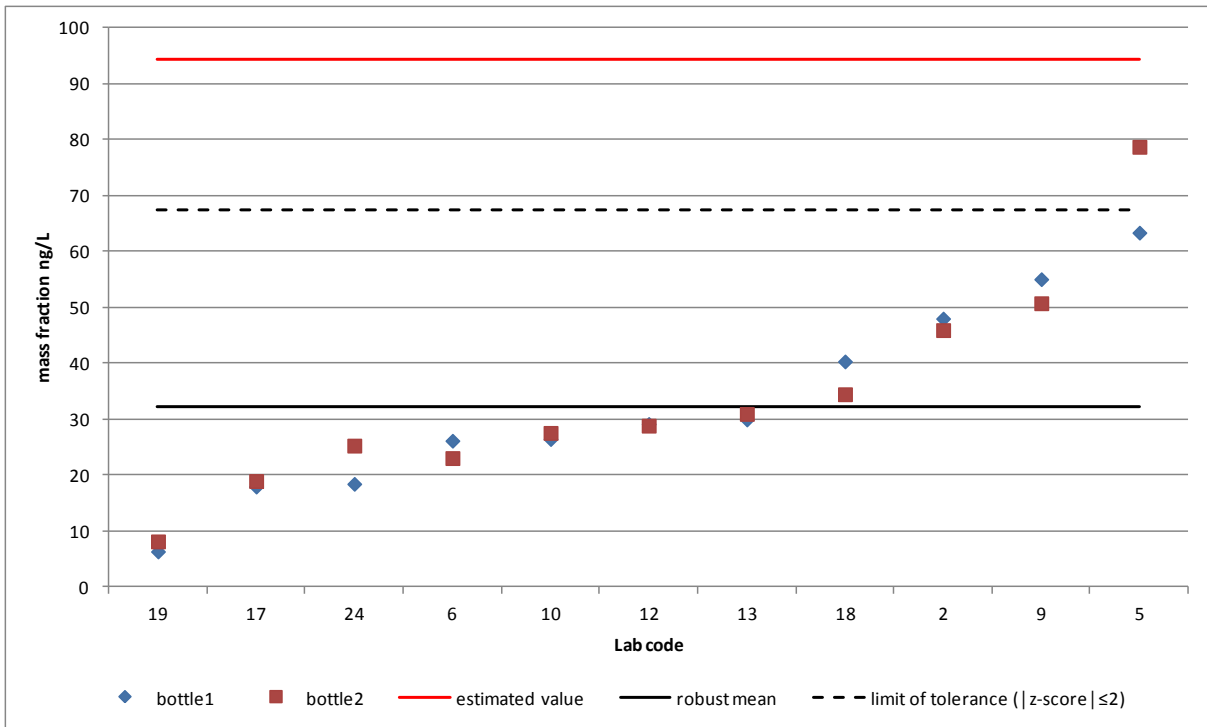


Fig. S24

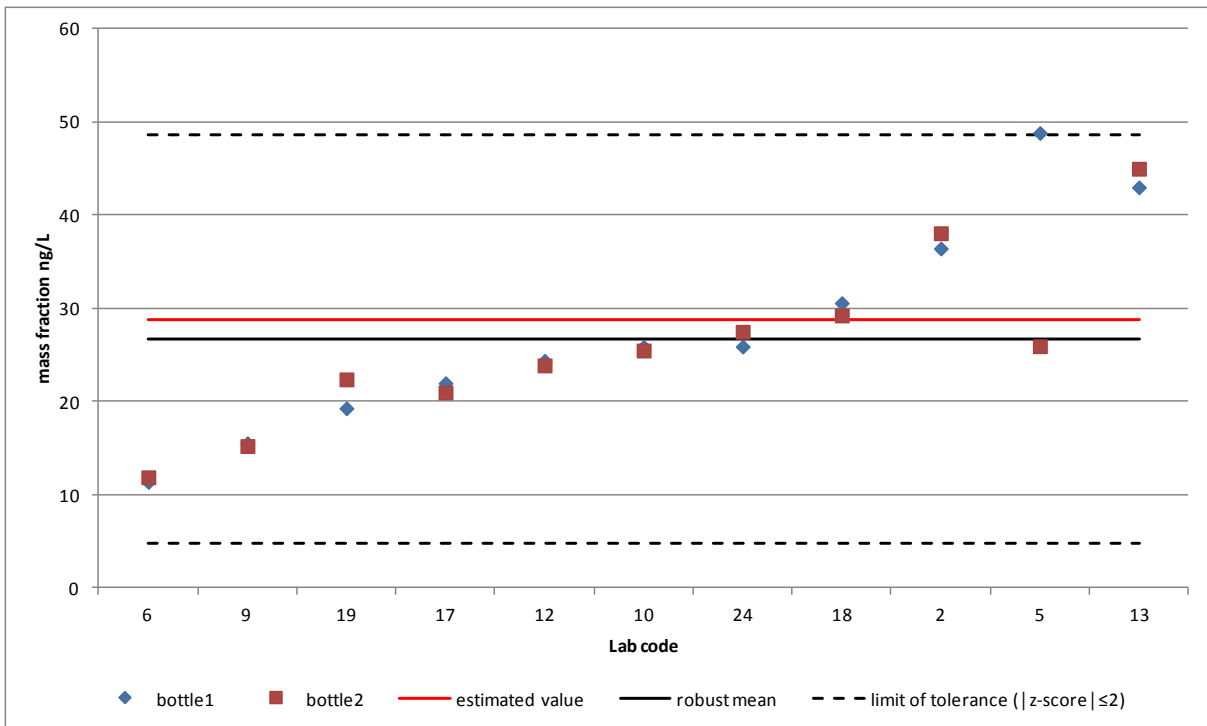


Fig. S25

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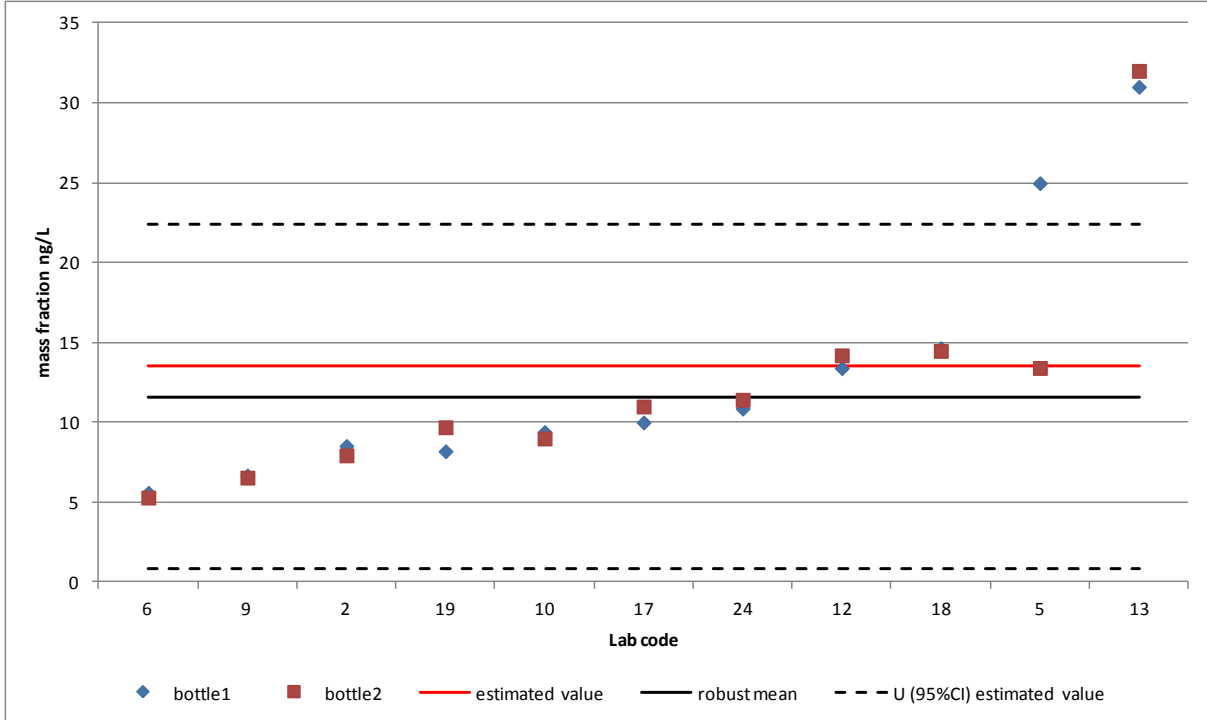


Fig. S26

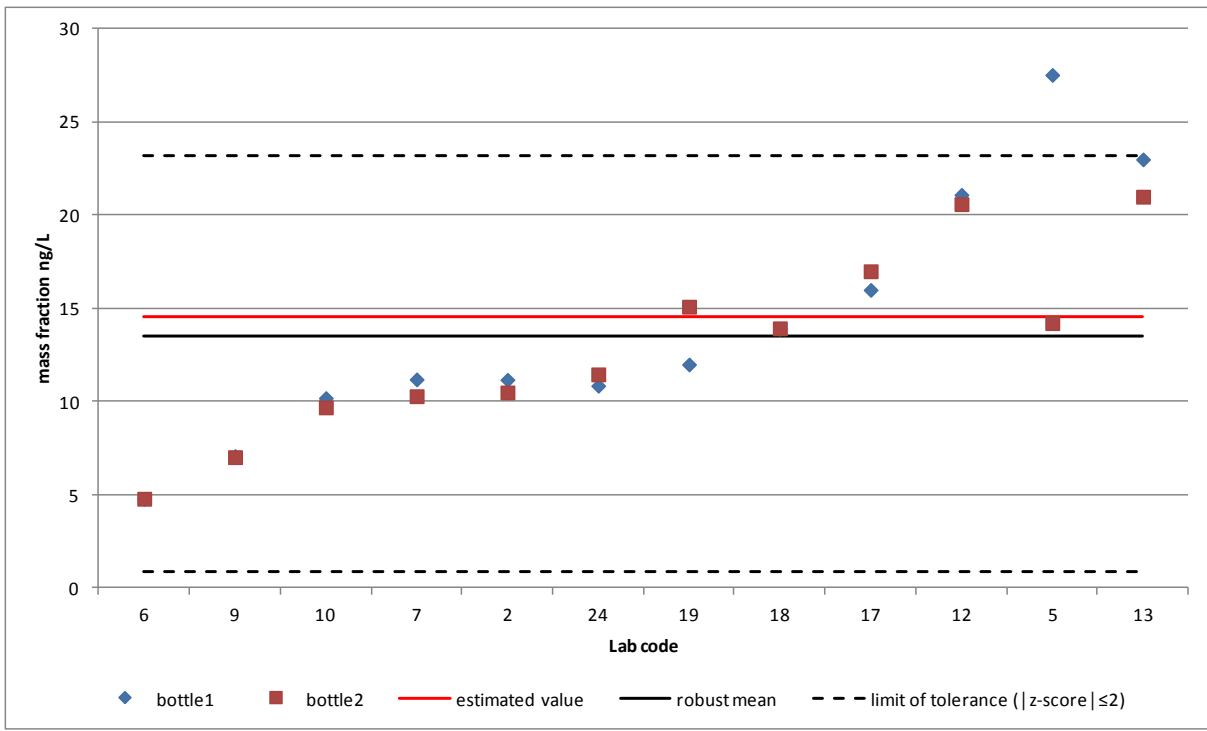


Fig. S27

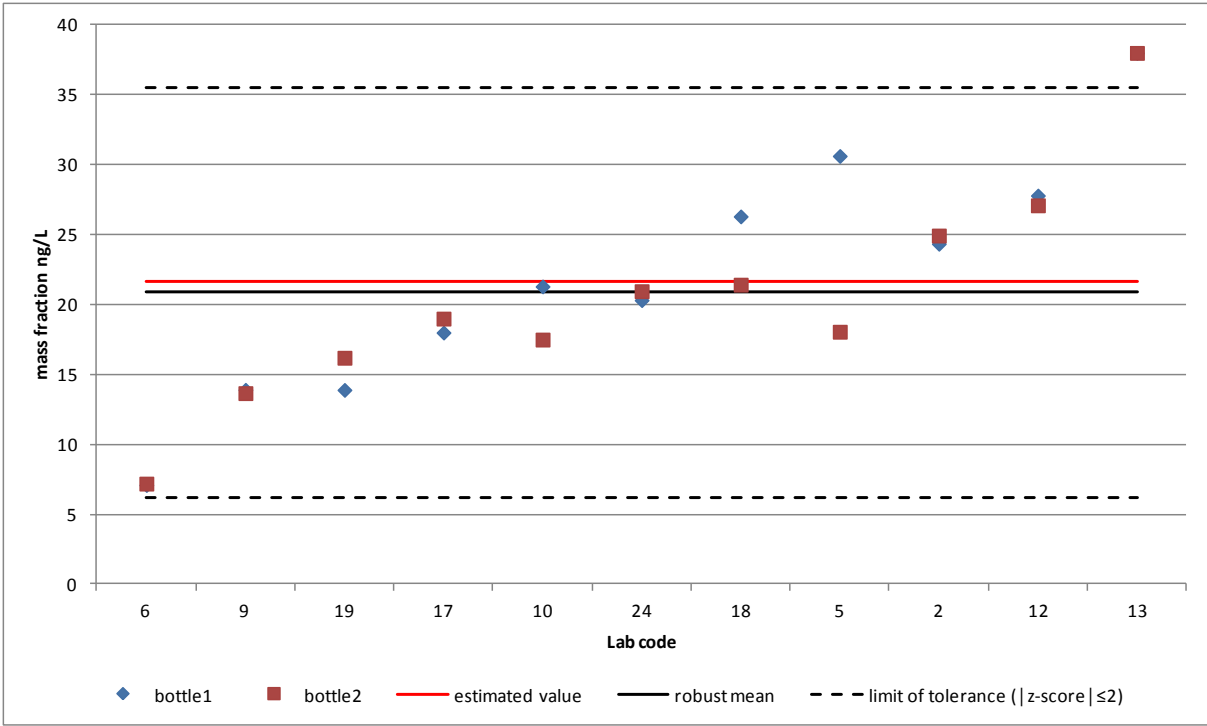


Fig. S28

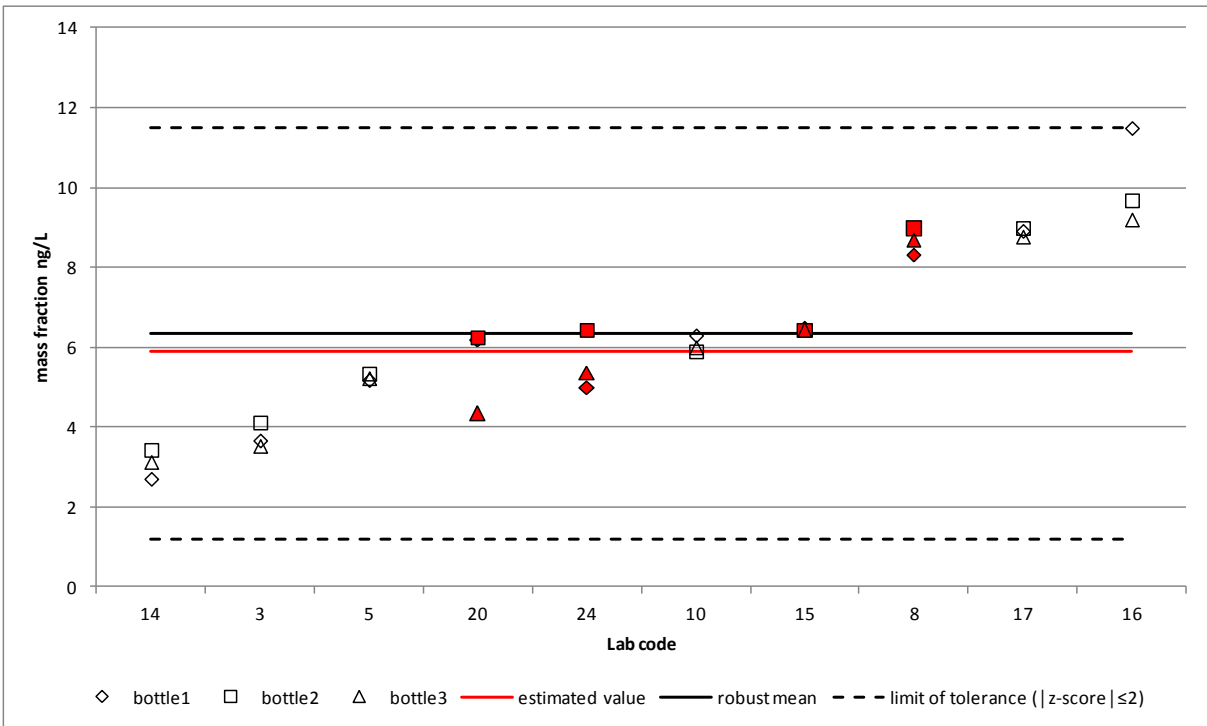


Fig. S29

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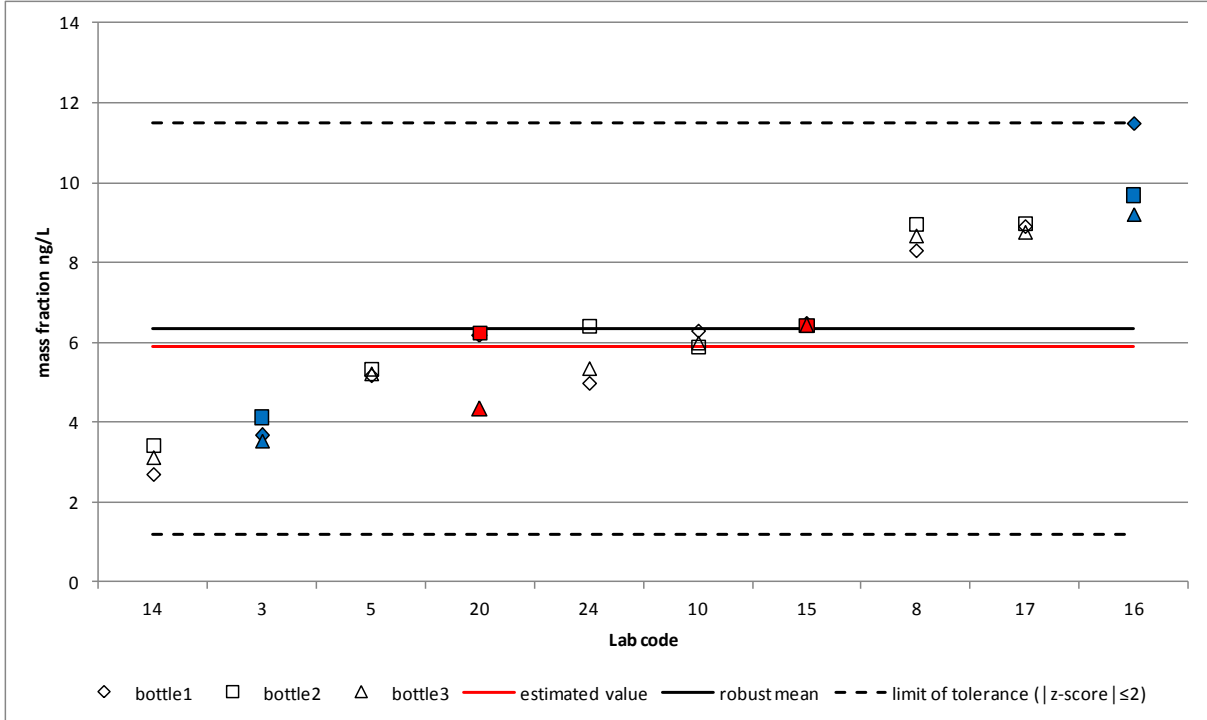
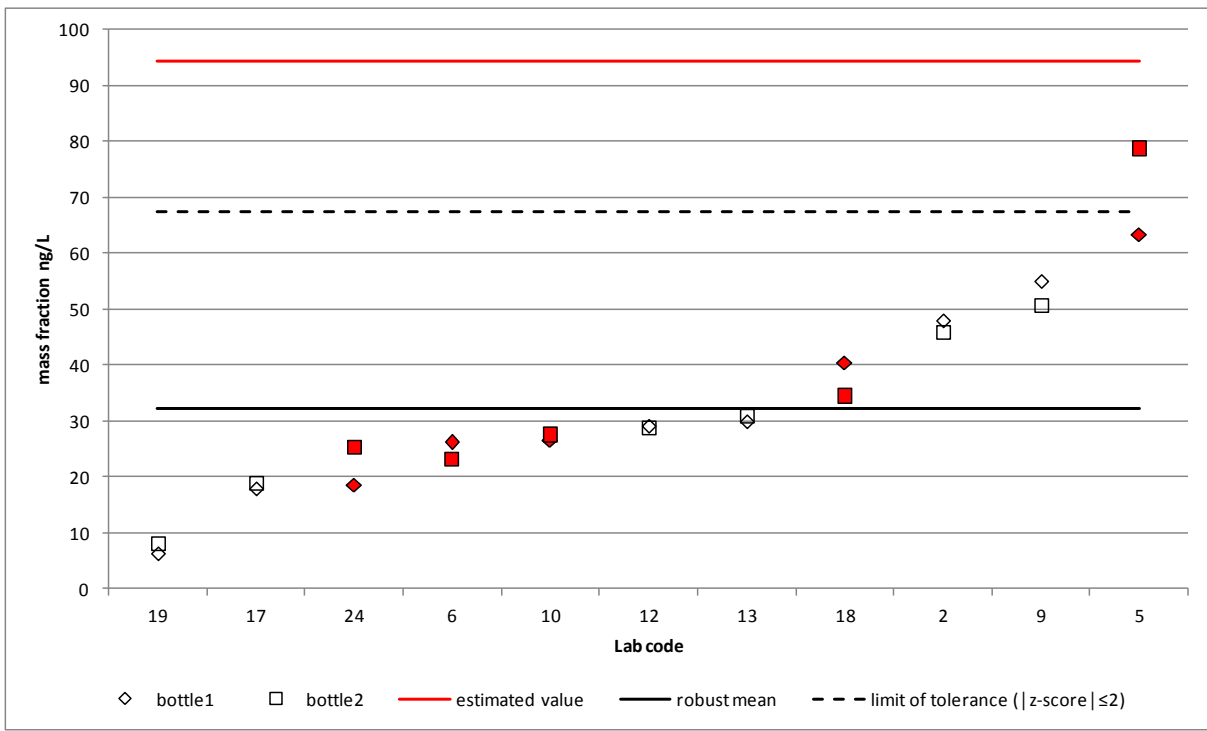


Fig. S30



Captions to Tables and Figures in the electronic supplementary material

Tab. S1 List of participants registered for the ILC (in alphabetical order)

Tab. S2 Details of the analytical method for TBT as reported by the ILC participants

Tab S3 Details of the analytical method for PBDEs as reported by the ILC participants

Tab. S4 Details of the analytical method for PAHs as reported by the ILC participants

Fig. S1 ILC results for an estimated concentration of 4.1 ng/L of TBT, sample 1

Fig. S2 ILC results for an estimated concentration of 0.03 ng/L of BDE 28, sample 1

Fig. S3 ILC results for an estimated concentration of 5.9 ng/L of BDE 99, sample 1

Fig. S4 ILC results for an estimated concentration of 0.88 ng/L of BDE 100, sample 1

Fig. S5 ILC results for an estimated concentration of 1.2 ng/L of BDE 153, sample 1

Fig. S6 ILC results for an estimated concentration of 0.56 ng/L of BDE 154, sample 1

Fig. S7 ILC results for an estimated concentration of 0.004 ng/L of BDE 28, sample 2

Fig. S8 ILC results for an estimated concentration of 0.33 ng/L of BDE 47, sample 2

Fig. S9 ILC results for an estimated concentration of 0.77 ng/L of BDE 99, sample 2

Fig. S10 ILC results for an estimated concentration of 0.11 ng/L of BDE 100, sample 2

Fig. S11 ILC results for an estimated concentration of 0.16 ng/L of BDE 153, sample 2

Fig. S12 ILC results for an estimated concentration of 0.07 ng/L of BDE 154, sample 2

Fig. S13 ILC results for an estimated concentration of 46 ng/L of naphthalene, sample 1

Fig. S14 ILC results for an estimated concentration of 21 ng/L of anthracene, sample 1

Fig. S15 ILC results for an estimated concentration of 367 ng/L of fluoranthene, sample 1

Fig. S16 ILC results for an estimated concentration of 120 ng/L of benzo(b)fluoranthene, sample 1

Fig. S17 ILC results for an estimated concentration of 89 ng/L of benzo(k)fluoranthene, sample 1

Fig. S18 ILC results for an estimated concentration of 90 ng/L of benzo(a)pyrene, sample 1

Fig. S19 ILC results for an estimated concentration of 118 ng/L of benzo(ghi)perylene, sample 1

Fig. S20 ILC results for an estimated concentration of 101 ng/L of indeno(1,2,3-cd)pyrene, sample 1

Fig. S21 ILC results for naphthalene, sample 2

Fig. S22 ILC results for an estimated concentration of 5.7 ng/L of anthracene, sample 2

Fig. S23 ILC results for an estimated concentration of 94 ng/L of fluoranthene, sample 2

1 **Fig. S24** ILC results for an estimated concentration of 29 ng/L of benzo(b)fluoranthene, sample 2

2 **Fig. S25** ILC results for an estimated concentration of 13 ng/L of benzo(k)fluoranthene, sample 2

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4 **Fig. S26** ILC results for an estimated concentration of 15 ng/L of benzo(a)pyrene, sample 2

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6 **Fig. S27** ILC results for an estimated concentration of 21 ng/L of indeno(1,2,3-cd)pyrene, sample 2

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9 **Fig. S28** ILC results for BDE 99 sample 1, influence of the extraction method. Unfilled symbols: solid
10 phase extraction (mostly Speedisk); red symbols: liquid/liquid extraction

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12 **Fig. S29** ILC results for BDE 99 sample 1, influence of the detection/calibration mode. Unfilled
13 symbols: GC-EI-MS based methods, ¹³C labeled internal standards; red symbols: GC-ICP-MS, ⁸¹Br
14 labeled internal standards; blue symbols: GC-NCI-MS, ¹³C labeled (Lab 3) or fluorinated (Lab 16)
15 internal standards
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19 **Fig. S30** ILC results for fluoranthene sample 2, influence of the extraction method. Unfilled symbols:
20 liquid/liquid extraction; red symbols: speedisk solid phase extraction
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