

Table S1: List of acronyms used in this article

Acronym	Full name
AsB	Arsenobetaine
3-BaP	3-Hydroxybenzo(a)pyrene
BCEP	Bis(2-chloroethyl) phosphate
BCIPP	Bis(chloroisopropyl) phosphate
BDCIPP	Bis(1,3-dichloroisopropyl) phosphate
BDE-153	2,2',4,4',5,5'-Hexabromodiphenyl ether
BDE-209	Decabromodiphenyl ether
BDE-47	2,2',4,4'-Tetrabromodiphenyl ether
BP1	2,4-Dihydroxybenzophenone
BP2	2,2',4,4'-Tetrahydroxybenzophenone
BP3	2-Hydroxy-4-methoxybenzophenone
BP7	5-Chloro-2-hydroxybenzophenone
BPA	Bisphenol A
BPF	Bisphenol F
BPS	Bisphenol S
Cd	Cadmium
cis-DBCA	Cis-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylic acid
cis-DCCA	Cis-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-1-carboxylic acid
CIF3CA	Cis-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylic acid
Cr	Chromium
cx-MiDP	Mono(2,7-methyl-7-carboxy-heptyl) phthalate
cx-MINCH	Cyclohexane-1,2-dicarboxylate-mono-(7-carboxylate-4-methyl)heptyl ester
cx-MiNP	7-Carboxy-mono-methylheptyl phthalate
DBDPE	Decabromodiphenyl ethane
1,2-DHN	1,2-Dihydroxynaphthalene
DINCH	1,2-Cyclohexane dicarboxylic acid diisononyl ester
DMA	Dimethylarsinic acid
DON	Deoxynivalenol
DPHP	Diphenyl phosphate
2-FLUO	2-Hydroxyfluorene
3-FLUO	3-Hydroxyfluorene
9-FLUO	9-Hydroxyfluorene
GAMA	N-Acetyl-S-(2-carbamoyl-2-hydroxyethyl)cysteine
HFRs	Halogenated flame retardants
MBzP	Monobenzyl phthalate
MCHP	Monocyclohexyl phthalate
MEHP	Monoethylhexyl phthalate
MEP	Monoethyl phthalate
MiBP	Monoisobutyl phthalate
MMA	Monomethylarsonic acid
MnBP	Mono-n-butyl phthalate
MnOP	Mono-n-octyl phthalate
MnPeP	Mono-n-pentyl phthalate

1-naphthol	1-Hydroxynaphthalene
2-naphthol	2-Hydroxynaphthalene
OH-MiDP	6-OH-Mono-propyl-heptyl phthalate
OH-MINCH	Cyclohexane-1,2-dicarboxylate-mono-(7-hydroxy-4-methyl)octyl ester
OH-MiNP	7-OH-(Mono-methyl-octyl) phthalate
OPFRs	Organophosphorus flame retardants
PAHs	Polycyclic aromatic hydrocarbons
PFAS	Per- and polyfluoroalkyl substances
PFBS	Perfluorobutane sulfonate
PFDA	Perfluorodecanoic acid
PFDoDA	Perfluorododecanoic acid
PFHpA	Perfluoroheptanoic acid
PFHpS	Perfluoroheptane sulfonate
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexane sulfonate
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
PFPeA	Perfluoropentanoic acid
PFUnDA	Perfluoroundecanoic acid
1-PHEN	1-Hydroxyphenanthrene
2-PHEN	2-Hydroxyphenanthrene
3-PHEN	3-Hydroxyphenanthrene
4-PHEN	4-Hydroxyphenanthrene
9-PHEN	9-Hydroxyphenanthrene
1-PYR	1-Hydroxypyrene
Syn-DP	Syn-Dechlorane plus
TBBPA	Tetrabromobisphenol A
TCPy	3,5,6-Trichloro-2-pyridinol
trans-DCCA	Trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-1-carboxylic acid
α -HBCD	α -Hexabromocyclododecane
γ -HBCD	γ -Hexabromocyclododecane

Table S2. Criteria for selecting candidate laboratories to participate in scheme 1

KNOW – HOW	Exclusive	1st level	2nd level	Scoring system
Experience analysing human samples	X			
Experience in the target matrix/biomarker		x		5: experience in matrix and biomarker 3: experience in matrix or biomarker
Participation in human biomonitoring surveys/studies – sample size		x		5: >1000 participants 3: 250 - 1000 participants 1: <250 participants
Participation in human biomonitoring surveys/studies – target population		x		5: general population, mother/children 3: occupational, highly exposed
QA/QC AND BIOSAFETY				
Successful participation in Interlaboratory Comparison Exercises (ICIs) for the target matrix/biomarker		x		5: in the last 3 years 3: in > 3 years
Successful participation in External Quality Assurance Schemes (EQUAS) for the target matrix/biomarker in the last 3 years		x		5: in the 3 years 3: in 2 years
Accreditation by ISO/IEC 17025 norm			x	3: yes in human samples 1: in biological samples or others
Not accredited but there is a QA/QC system in the laboratory covering the: - Control of the instruments, standards, reagents, etc. - Traceability of the samples - Data protection - Biosafety practices and facilities (chemical fume hoods, biological safety cabinets, chemical hygiene plan, SOP for chemical handling, etc.)		x		5: if yes in all options 3: if yes in the 2 first options (control and traceability)
Existence of a SOP for the analysis of the target matrix/biomarker		x		5
CAPACITY				
Analysis capacity per month		x		Taking as 100% the maximum number of samples of the answers received: 5: 100-50% 3: <50%
Storage capacity			x	Taking as 100% the maximum capacity of the answers received: 3: 100-50% 1: <50%
Time required for starting the analysis considering the time for fulfilling the legal and/or the required internal procedures		x		5: ≤ 4 weeks 3: > 4 weeks
Cost of the analysis			x	Taking as 100% the maximum cost of the answers received: 3: <75% 1: 100-75%

Table S3. Criteria for selecting candidate laboratories to support the QA/QC programme

KNOW – HOW	Exclusive	1st level	2nd level	Scoring system
Experience in organizing Interlaboratory Comparison Investigations (ICIs) with biological matrices	X			
Experience in organizing External Quality Assurance Schemes (EQUAS) with biological matrices		x		5
Participation as reference laboratory in EQUAS			x	3
Experience in preparation of control material		x		5: at concentration found in lowest exposed subpopulation 3: native or spiked human samples 1: not human samples
QA/QC AND BIOSAFETY				
Accreditation as organiser of proficiency testing (UNE-EN ISO/IEC 17043)		x		5
If not accredited, existence of a QA/QC system in the laboratory covering the preparing control material, organising ICI/EQUAS, managing samples and results and data protection		x		5: if yes in all options 3: if yes in the 2 first options (preparing control material and organising ICI/EQUAS)
CAPACITY				
Capacity to prepare and distribute control material for ≥15 participants		x		5
Capacity for organising ICI/EQUAS during the whole HBM4EU project		x		Taking as 100% the maximum of the answers received: 5: 100-50% 3: <50
Tools for fluid communication with the participants			x	3: if yes in all options 1: if yes in > 2

Table S4. Criteria for selecting expert laboratories for the scheme 2

1. Experience in analysis of the ALL selected parameters in (the selected) human matrices at levels expected in general population (proven experience, papers, reports, etc.) **EXCLUSIVE CRITERION**

2. Capacity for analysis (number of samples/time for analysis), 300, 600, 900, 1200 in 2020

3. Limit of quantification of the method sufficiently low for HBM4EU samples (indicate how the LOQ was determined)

4. Historic data of the successful participation in interlaboratory comparison exercises for the target substance (s)

Table S5. Expert laboratories collaborating in the EQUAS of scheme 1.

COUNTRY	INSTITUTION	SUBSTANCE GROUP
Canada	Centre de Toxicologie du Québec (CTQ) / Institut National de Santé Publique du Québec (INSPQ)	Bisphenols, HFRs, PFAS
Japan	IDEA Consultants, Inc.	Cadmium
Japan	Otsuka Pharmaceutical Co., Ltd.	PAHs
Japan	Shimadzu Techno - Research, Inc.	PFAS
United States	Arizona Department of Health Services Laboratory	Phthalates
United States	Centers for Disease Control and Prevention (CDC)	DINCH, Phthalates, Bisphenols, PAHs
United States	New York State Department of Health Wadsworth Center	Phthalates
United States	New York State Department of Health Wadsworth Center	Cadmium
United States	Wisconsin State Laboratory of Hygiene	HFRs

Table S6. Registered laboratories, laboratories reporting results and laboratories consistently reporting satisfactory results per round and biomarker in scheme 1.

		ROUND 1		ROUND 2		ROUND 3		ROUND 4		no. reporting satisfactory results ¹	% reporting satisfactory results ¹ (among registered)	% reporting satisfactory results ¹ (among reported)
		no. registered	% reporting	no. registered	% reporting	no. registered	% reporting	no. registered	% reporting			
DINCH	OH-MINCH	11	100%	11	100%	11	100%	10	100%	8	67%	73%
	cx-MINCH	10	100%	10	100%	10	90%	8	100%	7	64%	70%
Phthalates	MEP	17	94%	19	100%	18	100%	14	100%	15	71%	75%
	MBzP	16	100%	18	100%	17	100%	12	100%	15	79%	88%
	MiBP	16	100%	18	100%	17	100%	14	100%	12	60%	67%
	MnBP	16	100%	18	100%	17	100%	14	100%	16	80%	89%
	MCHP	12	92%	12	100%	12	100%	11	100%	8	57%	62%
	MnPeP	9	100%	10	100%	9	100%	11	100%	5	42%	50%
	MEHP	18	100%	20	100%	18	100%	15	100%	11	50%	58%
	5OH-MEHP	18	100%	20	100%	18	100%	15	100%	18	82%	95%
	5oxo-MEHP	18	100%	20	100%	18	100%	15	100%	17	77%	89%
	5cx-MEPP	14	100%	17	100%	16	100%	13	100%	15	79%	94%
	MnOP	11	100%	12	100%	12	100%	12	100%	6	40%	46%
	OH-MiNP	9	89%	12	100%	12	100%	10	100%	4	31%	31%
	cx-MiNP	12	100%	14	100%	14	100%	12	100%	7	47%	50%
	OH-MiDP	11	91%	13	100%	13	100%	11	100%	7	50%	54%
cx-MiDP	8	50%	8	100%	8	100%	6	100%	6	75%	75%	
Bisphenols	BPA	24	100%	29	103%*	28	100%	24	100%	24	77%	83%
	BPF	23	91%	28	93%	25	96%	21	95%	13	45%	50%
	BPS	22	82%	29	90%	26	92%	21	90%	18	62%	72%

PFAS	PFPeA	16	81%	18	83%	17	100%	12	100%	14	68%	81%
	PFHxA	16	100%	19	95%	20	100%	14	93%	14	62%	65%
	PFHpA	16	100%	19	100%	19	100%	13	100%	20	95%	100%
	PFOA	17	100%	20	100%	20	100%	14	100%	21	95%	100%
	PFNA	17	100%	20	100%	20	95%	14	93%	21	95%	100%
	PFDA	16	100%	19	95%	20	95%	13	100%	20	90%	100%
	PFUnDA	15	100%	19	95%	18	106%*	13	100%	18	81%	89%
	PFDoDA	15	100%	18	100%	18	100%	12	100%	14	68%	72%
	PFBS	17	100%	20	100%	20	100%	13	108%	17	76%	80%
	PFHxS	17	100%	20	100%	20	100%	14	100%	21	95%	100%
	PFHpS	12	100%	15	100%	15	100%	10	100%	14	81%	87%
PFOS	17	100%	20	100%	20	100%	14	100%	21	95%	100%	
HFRS	BDE-47	11	91%	14	100%	14	100%	12	92%	14	88%	100%
	BDE-153	11	91%	14	100%	14	100%	12	92%	13	81%	93%
	BDE-209	10	100%	13	92%	13	85%	9	89%	7	47%	64%
	α-HBCD	7	86%	8	100%	8	100%	7	100%	7	70%	78%
	γ-HBCD	7	86%	8	100%	8	100%	7	100%	8	80%	89%
	DP-syn	6	83%	8	113%*	9	100%	8	88%	7	78%	78%
	DP-anti	6	83%	8	113%*	9	100%	8	88%	8	89%	89%
	TBBPA	4	50%	5	100%	5	100%	6	50%	1	17%	25%
	DBDPE	8	75%	9	67%	8	63%	6	50%	1	10%	17%
2,4,6-TBP	4	50%	4	125%*	5	80%	4	75%	1	17%	25%	
OPFRs	DPHP	7	71%	6	83%	5	100%	6	100%	5	63%	100%
	BDCIPP	7	71%	6	83%	5	100%	6	100%	5	63%	100%
	BCIPP	5	60%	5	80%	4	100%	6	100%	4	50%	100%
	BCEP	6	17%	4	25%	2	100%	3	133%	1	14%	50%
PAHs	1-naphthol	14	86%	18	94%	17	94%	17	88%	15	70%	74%
	2-naphthol	13	100%	20	100%	19	84%	19	74%	19	86%	86%

	1,2 DHN ²	3	0%	5	20%	-	-	-	-	1	0%	0%
	2-FLUO	9	78%	11	91%	11	73%	10	80%	9	62%	80%
	3-FLUO	5	60%	7	86%	8	75%	7	57%	4	33%	50%
	9-FLUO	5	40%	7	71%	5	100%	4	50%	1	0%	0%
	1-PHEN	8	88%	12	92%	13	85%	12	67%	9	57%	73%
	2-PHEN	9	78%	12	92%	11	100%	11	82%	9	62%	67%
	3-PHEN	9	78%	12	92%	11	100%	12	75%	10	64%	75%
	4-PHEN	8	88%	12	100%	12	92%	11	73%	11	77%	83%
	9-PHEN	7	71%	10	80%	10	60%	9	33%	2	9%	17%
	1-PYR	17	88%	26	100%	24	88%	22	86%	17	55%	64%
	3-BaP ²	10	50%	11	64%	-	-	-	-	1	0%	0%
Cd	U-Cd	21	100%	39	95%	42	100%	22	95%	37	70%	92%
	B-Cd	19	100%	35	94%	37	97%	20	90%	29	74%	82%
Cr	Cr urine	10	100%	25	96%	26	96%	18	89%	28	93%	100%
	Cr serum	8	100%	22	95%	22	95%	16	94%	23	85%	96%
	Cr blood	8	100%	22	95%	21	95%	16	88%	20	74%	87%

¹ achieving satisfactory z-scores for the biomarker in both control materials from a round, in at least two rounds from the QA/QC programme.

² biomarkers only in the 1st and 2nd rounds.

* percentages above 100 are because some laboratories reported results without having initially registered for these biomarkers.

Table S7. Concentration range of the sample in the HBM4EU QA/QC programme.

Chemical group	Biomarker	Concentration range
DINCH	OH-MINCH	1.09 - 23.0 ng/ml
	cx-MINCH	1.09 - 14.6 ng/ml
Phthalates	MEP	17.4 - 138 ng/ml
	MBzP	0.95 - 10.4 ng/ml
	MiBP	1.28 - 69.9 ng/ml
	MnBP	1.03 - 53.9 ng/ml
	MCHP	0.29 - 1.26 ng/ml
	MnPeP	1.32 - 2.50 ng/ml
	MEHP	0.57 - 10.1 ng/ml
	5OH-MEHP	3.01 - 40.6 ng/ml
	5oxo-MEHP	1.44 - 19.7 ng/ml
	5cx-MEPP	3.22 - 36.5 ng/ml
	MnOP	0.4 - 6.55 ng/ml
	OH-MiNP	1.07 - 17.5 ng/ml
	cx-MiNP	2.04 - 26.3 ng/ml
	OH-MiDP	1.55 - 32.0 ng/ml
	cx-MiDP	1.8 - 23.9 ng/ml
Bisphenols	BPA	0.58 – 8.40 ng/ml
	BPF	0.10 – 3.42 ng/ml
	BPS	0.10 – 8.51 ng/ml
PFAS	PFPeA	0.19 - 0.48 ng/ml
	PFHxA	0.13 - 0.52 ng/ml
	PFHpA	0.19 - 1.04 ng/ml
	PFOA	0.43 - 11.44 ng/ml
	PFNA	0.22 - 1.92 ng/ml
	PFDA	0.37 - 1.13 ng/ml
	PFUnDA	0.23 - 0.66 ng/ml
	PFDoDA	0.11 - 0.40 ng/ml

	PFBS	0.12 - 0.46 ng/ml
	PFHxS	0.39 - 2.73 ng/ml
	PFHpS	0.14 - 1.15 ng/ml
	PFOS	1.42 - 12.22 ng/ml
HFRs	BDE-47	0.15 – 1.00 ng/ml
	BDE-153	0.18 – 0.81 ng/ml
	BDE-209	0.71 – 2.09 ng/ml
	α-HBCD	0.50 – 5.19 ng/ml*
	γ-HBCD	0.32 – 7.64 ng/ml*
	DP-syn	0.38 – 1.22 ng/ml
	DP-anti	0.29 – 1.23 ng/ml
	TBBPA	-/-
	DBDPE	-/-
	2,4,6-TBP	-/-
OPFRs	DPHP	1.72 – 11.15 ng/ml
	BDCIPP	1.81 – 14.92 ng/ml
	BCIPP	2.48 – 32.65 ng/ml
	BCEP	-/-
PAHs	1-naphthol	2.01 - 10.62 ng/ml
	2-naphthol	1.28 - 14.27 ng/ml
	1,2 DHN	-/-
	2-FLUO	0.13 - 1.59 ng/ml
	3-FLUO	0.07 - 0.40 ng/ml
	9-FLUO	-/-
	1-PHEN	0.23 - 0.79 ng/ml
	2-PHEN	0.13 - 0.73 ng/ml
	3-PHEN	0.16 - 0.48 ng/ml
	4-PHEN	0.07 - 0.25 ng/ml
	9-PHEN	-/-
	1-PYR	0.04 - 0.26 ng/ml
	3-BaP	-/-
Cd	U-Cd	0.04 - 0.45 ng/ml

	B-Cd	0.13 - 0.77 ng/ml
Cr	U-Cr	1.10 - 25.60 ng/ml
	S-Cr	2.12 - 14.49 ng/ml
	B-Cr	1.54 - 7.15 ng/ml

U: urine; B: blood; S: serum.

** consensus values*