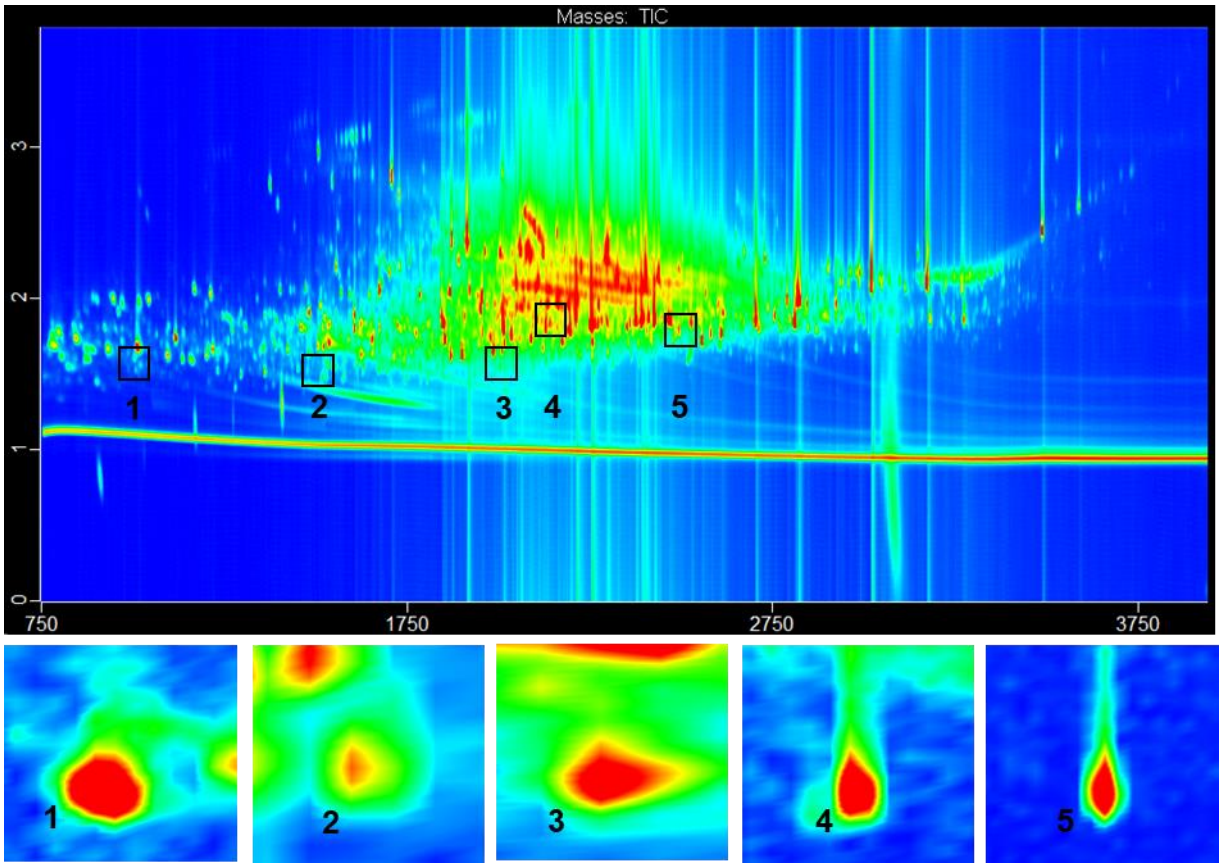

Figure S1: GC×GC 2-dimensional plot of PUF S2 extract
1: 2-Nitrotoluene; 2: 2-Nitroanisol; 3: Benzensulfonamide; 4: Triallate; 5: Dichlorfluanid

Used chemicals and equipment

Table S1: Used chemicals and equipment.

Chemical/ Equipment	Purchased
Aceton	VWR Pestinorm® for Pesticide residue analysis, VWR, Oslo, Norway
n-Hexane	VWR Pestinorm® for Pesticide residue analysis, VWR, Oslo, Norway
Cyclohexane	VWR Pestinorm® for Pesticide residue analysis, VWR, Oslo, Norway
Acetonitrile	LiChrosolv, isocratic grade for LC, Merck, Darmstadt, Germany
Toluene	EMSURE® for analysis, Merck, Darmstadt, Germany
Isooctane	EMSURE® for analysis, Merck, Darmstadt, Germany
Extran®	Merck, Darmstadt, Germany

Sodium sulphate	anhydrous, EMSURE® for analysis, Merck, Darmstadt, Germany
Discovery DSC-18	Supelco, Bellefonte, PA, USA
Supel™QuE Z-Sep^{+}	Supelco, Bellefonte, PA, USA
Florisil® 60-100 Mesh	Sigma Aldrich Chemie GmbH, Schnelldorf, Germany
Citric acid	anhydrous, puriss., Sigma Aldrich Chemie GmbH, Schnelldorf, Germany
Cotton	Mediq Norge AS, Oslo, Norway
Polyurethane foam (PUF) plugs (7 cm in diameter and 4 cm in height)	Sunde Skumplast A/S, Gan, Norway
Glass fibre filters (150 mm in diameter)	GF/C standard, Whatman®, GE Healthcare Life Sciences, Oslo, Norway
KNF vacuum pump	Laboport, N86KT.18, Village-Neuf, France
Nitrogen gas	5.0 quality, Nippon gases Norge AS, Oslo, Norway

All used glassware was washed with Extran®, heated to 450 °C for 8 h and rinsed with acetone prior use.

Florisil, glass fibre filters and sodium sulphate were heated to 450°C for 8 h prior use.

Cotton was Soxhlet extracted with n-hexane for 24h, rinsed with acetone and dried prior use.

PUF plugs were pre-cleaned by Soxhlet extraction prior use: 8 h with acetone followed by 8 h with cyclohexane.

Standards used for spiked surrogate method evaluation samples

$^{13}C/^{2}H$-labeled and native standards for used for standard mixtures ‘POP’ and ‘BFR’ were purchased from Wellington Laboratories, Guelph, ON, Canada.

Native standards for mixtures CUP A-C were purchased from AccuStandard, New Haven, CT, USA.

Table S2: Overview of spiked compounds, recovery and RSD for method evaluation samples 'POP', spiked with 'POP'.

Target compound	Native/ $^{13}C/^{2}H$ - labelled	Spike [ng]	POP (n = 3)	
			Rec [%]	RSD [%]
Dieldrin	^{13}C	24	112	12
Aldrin	^{13}C	12	63	3
Endrin	^{13}C	9	95	6
Mirex	^{13}C	15	92	2
Isodrin	^{13}C	46	74	4
Trifluralin	^{13}C	2	70	10
Cis-Chlordane	^{13}C	1	82	3
Trans-Chlordane	^{13}C	1	76	3
Oxychlordane	^{13}C	13	78	4
Trans-nonachlor	^{13}C	1	81	3
Cis-nonachlor	^{13}C	1	81	2
Heptachlor	^{13}C	14	67	4
Heptachlor *exo* epoxide	^{13}C	16	81	4
Endosulfan sulphate	^{13}C	1	117	5
Endosulfan I	^{13}C	2	90	5
Endosulfan II	^{13}C	3	105	5
α-HCH	^{13}C	20	96	4
β-HCH	^{13}C	4	48	17
γ-HCH	^{13}C	20	91	3
p,p'-DDE	^{13}C	6	59	4
o,p'-DDD	^{13}C	6	78	4
p,p'-DDT	^{13}C	7	83	10
δ-HCH	^{13}C	9	65	8
PCB-28	^{13}C	5	80	4
PCB-52	^{13}C	5	91	3
PCB-101	^{13}C	5	68	3
PCB-105	^{13}C	5	62	3
PCB-114	^{13}C	5	63	3
PCB-118	^{13}C	5	62	4
PCB-123	^{13}C	5	64	3
PCB-138	^{13}C	5	59	3
PCB-153	^{13}C	5	65	3
PCB-156	^{13}C	5	57	3
PCB-157	^{13}C	5	57	4
PCB-167	^{13}C	5	63	4
PCB-180	^{13}C	5	61	2
PCB-189	^{13}C	5	55	11
PCB-209	^{13}C	5	55	4
HCB	^{13}C	2	83	5
PeCB	^{13}C	2	58	6

Table S3: Overview of spiked compounds, recovery and RSD for method evaluation samples 'Brominated', spiked with 'BFR'.

Target compound	Native/ $^{13}C/^{2}H$ - labelled	Spike [ng]	Brominated, BFR (n = 3)	
			Rec [%]	RSD [%]
PBDE-28	^{13}C	5	48	11
PBDE-99	^{13}C	5	59	16
PBDE-47	^{13}C	5	62	4
PBDE-153	^{13}C	5	85	4
PBDE-197	^{13}C	5	92	11
PBDE-183	^{13}C	5	92	7
EHTBB	^{2}H	2	46	14
γ/δ-TBECH	native	48	57	6
PBBZ	^{13}C	2	60	2
BTBPE	^{13}C	2	60	7
α-TBECH	native	25	63	12
β-TBECH	native	25	61	10
TBP-AE (ATE)	native	49	62	9
BEHTBP	native	98	70	25
DPTE	native	49	74	5
BATE	native	50	74	4
PBEB	native	49	81	5
PBT	native	49	82	5
HBB	^{13}C	2	80	3

Table S4: Overview of spiked compounds, recovery and RSD for method evaluation samples CUP A, spiked with 'Mix 1'.

Target compound	Native/ $^{13}C/^{2}H$ - labelled	Spike [ng]	CUP A, Mix 1 (n = 3)	
			Rec [%]	RSD [%]
Alachlor	native	50	90	13
Atrazine	native	1012	50	5
Bromacil	native	51	14	46
Carbophenothion	native	50	129	16
Cis-chlordane (α-Chlordan)	native	51	108	5
Trans-chlordane (γ-Chlordan)	native	51	109	5
Chloroneb	native	50	19	10
Chlorothalonil	native	50	46[a]	141[a]
Chlorpyrifos	native	100	88	18
Chlorpyrifos-methyl	native	98	59	15
Chlorthal-dimethyl (Dacthal or DCPA)	native	51	78	3
cis-Permethrin	native	40	169	8
Cyanazine	native	152	86	27
Diazinon (Dimpylate)	native	50	50	14
Dieldrin	native	49	103	3
Endrin	native	10	131	12
Endrin ketone	native	10	139	5
Ethion	native	98	261	21
Fenitrothion	native	99	98	13
Heptachlor *exo*-epoxide	native	5	104	6
Malathion	native	50	108	14
Methidathion	native	49	200	21
Methoxychlor	native	25	103	10
Metolachlor	native	50	127	16
Metribuzine	native	25	79	18
p,p'-DDT	native	49	110	5
Pentachloronitrobenzene (PCNB or Quintozene)	native	49	41	0
Phosalone	native	99	103	11
Pirimiphos-methyl	native	48	26	23
Propachlor	native	51	32	6
Simazine	native	1019	56	9
Tecnazene (TCNB) 2,3,5,6-Tetrachloronitrobenzene	native	49	29	4
trans-Permethrin	native	59	157	15
Trifluralin	native	55	51	6
Chlorfenvinphos	native	49	0	-
Chlorobenzilate	native	51	0	-
Dichlorvos	native	99	0	-
Endine aldehyde	native	10	0	-
Etridiazole	native	51	0	-

[a]: This recovery is not sure, 2 samples with no recovery and one sample with 139 % recovery

Table S5: Overview of spiked compounds, recovery and RSD for method evaluation samples 'CUP B' and 'CUP C', spiked with 'Mix 2' and 'Mix 3'.

Target compound	Native/ $^{13}C/^{2}H$ - labelled	Spike [ng]	CUP B, Mix 2 (n = 3)		CUP C, Mix 3 (n = 3)	
			Rec [%]	RSD [%]	Rec [%]	RSD [%]
Octachlorostyrene	native	46	43	9	-	-
2,3,5,6-Tetrabromo-*p*-xylene	native	52	64	16	-	-
Musk ketone	native	81	83	58	-	-
Musk xylene	native	44	44	3	-	-
Tonalide (AHTN)	native	50	29	18	-	-
Galaxolide (HHCB)	native	20	-	-	27	8
1,2,3,5,8-Pentachloronaphthalene (PCN 53)	native	20	-	-	110	8
1,2,3,5,6,7-Hexachloronapthalene (PCN 67)	native	19	-	-	135	8
1,2,3,4,5,6,7-Heptachloronaphthalene (PCN 73)	native	20	-	-	155	5
1,2,3,4,5,6,7,8-Octachloronaphthalene (PCN 75)	native	20	-	-	120	51

Standards used for real high-volume air samples

Internal standards were used for method quality control.

^{13}C-labeled standards were purchased from Wellington Laboratories, Guelph, ON, Canada.

$^{2}H_{10}$-labeled phenanthrene was purchased from Chiron AS, Trondheim, Norway.

1,2,3,4-Tetrachloronaphthalene was purchased from Ultra-Scientific, North Kingstown, RI, USA.

Table S6: Spiking amounts ISTDs for real high-volume samples.

Internal standard	Spiking amount [ng]
$^{2}H_{10}$ phenanthrene	2.08
$^{13}C_6$ HCB	4.78
$^{13}C_{12}$ *p,p'*-DDT	16.12
$^{13}C_{12}$ PCB-153	12,20
$^{13}C_6$ HBB	21.14
$^{13}C_{12}$ PBDE-28	5.28
$^{13}C_{12}$ PBDE-47	5.22
$^{13}C_{12}$ PBDE-99	5.30
Recovery standard	
1,2,3,4-Tetrachloronaphthalene (TCN)	7.96

GCxGC-LRMS analysis

Three microlitre (µL) of each extract was injected into a PTV (programmed temperature vaporiser) inlet, operating in solvent vent mode.

PTV solvent vent mode with 30 sec solvent vent time, 50 mL min^{-1} solvent vent flow at 0 psi, with a Gerstel PTV injector. Initial inlet temperature was 50 °C with a duration of 0.55 min, ramped with 200 °C min^{-1} to 280 °C with a duration of 6 min and ramped with 100 °C min^{-1} to 320 °C with a duration of 2 min.

The temperature program of the primary GC column was set as follows: 45 °C (hold time 0.55 min), ramped with 50 °C min^{-1} to 80 °C (hold time 1.5 min) and ramped with 4 °C min^{-1} to 300 °C (hold time 8 min). The secondary oven temperature was programmed 105 °C (hold time 2.25 min) and ramped at 4 °C min^{-1} to 315 °C (hold time 10.5 min). Modulation period was set to 4.5 s with 0.54 s hot pulse time and 19 °C modulator temperature offset relative to the primary oven temperature. Liquid N_2 (Nippon gases Norge AS, Oslo, Norway) was used as coolant for the GC×GC modulator. The ion source and the transfer line temperatures were set to 200 °C and 300 °C, respectively and the MS was operated in electron ionisation (EI) mode with an electron energy of 70 eV. A data acquisition rate of 100 spectra s^{-1} was used in combination with an acquired mass range

of *m/z* (mass to charge ratio) 45 – 1000. Autotuning was performed by using the *m/z* 219 perfluorotributylamine (PFTBA) ion instead of the default *m/z* 69 ion. In order to avoid system contamination and memory effects, clean solvent (Toluene followed by Acetonitrile) was injected after each sample run.

GC-HRMS analysis

Chlorinated pesticides (Table S2, dieldrin-endosulfan II):

An Agilent 7200 q-ToF GC/MS in NCI mode with an Agilent 7890B GC, a Gerstel PTV and a restrictor column (1.8 m, 0.150 mm) was applied in combination with an Agilent J&W HP-5MS UI (15 m, 0.25 mm x 0.25 µm) GC column.

PTV injection in solvent vent mode with 0.30 min solvent vent time, 15 mL min^{-1} solvent vent flow at 0.7 psi, with a Gerstel PTV injector was used.

The initial inlet temperature was set to 55 °C with a duration of 0.35 min, ramped with 500 °C min^{-1} to 320 °C with a duration of 3 min.

Oven temperature program was as follows:

45 °C (hold time 2 min), ramped with 70 °C min^{-1} to 170 °C (hold time 0.2 min), ramped with 5 °C min^{-1} to 200 °C (hold time 2 min) and ramped with 40 °C min^{-1} to 320 °C (hold time 1 min).

DDTs/HCHs (Table S2, α-HCH-δ-HCH):

A Waters (former Micromass) Autospec MS in EI mode with an Agilent GC 7890A or GC 6890N, a Gerstel PTV injector and Zebron ZB-MultiResidue-1 (30 m, 0.25 mm x 0.25 µm) GC column was applied.

PTV injection in solvent vent mode with 0.16 min solvent vent time, 10 mL min^{-1} solvent vent flow at 0.50 kPa, with a Gerstel PTV injector was used.

The initial inlet temperature was set to 60 °C with a duration of 0.2 min, ramped with 550 °C min^{-1} to 220 °C with a duration of 8 min and ramped with 100 °C min^{-1} to 240 °C with a duration of 7 min.

Oven temperature program was as follows:

40 °C (hold time 1 min) and ramped with 22 °C min^{-1} to 280 °C (hold time 3.8 min).

PCBs (Table S2, PCB-28-PeCB):

Waters (former Micromass) Autospec MS in EI mode with an Agilent GC 7890A or GC 6890N, a Gerstel PTV injector and Trajan (former SGE) HT-8 (50 m, 0.22 mm x 0.25 µm) GC column.

PTV injection in solvent vent mode with 0.25 min solvent vent time, 20 mL min^{-1} solvent vent flow at 0.55 kPa, with a Gerstel PTV injector was used.

The initial inlet temperature was set to 50 °C with a duration of 0.32 min, ramped with 300 °C min^{-1} to 285 °C with a duration of 3 min and ramped with 300 °C min^{-1} to 310 °C with a duration of 9 min.

Oven temperature program was as follows:

45 °C (hold time 3 min), ramped with 25 °C min^{-1} to 170 °C (hold time 1 min), ramped with 3 °C min^{-1} to 210 °C, ramped with 4 °C min^{-1} to 285 °C (hold time 3 min) and ramped with 100 °C min^{-1} to 320 °C (hold time 2.8 min).

Brominated (Table S3):

Waters (former Micromass) Autospec MS I EI mode with an Agilent GC 7890A or GC 6890N, a Gerstel PTV injector and Restek Rtx-1614 (15 m, 0.25 mm x 0.1 µm) GC column.

PTV injection in solvent vent mode with 0.50 min solvent vent time, 45 mL min^{-1} solvent vent flow at 0 kPa, with a Gerstel PTV injector was used. The initial inlet temperature was set to 50 °C with a duration of 0.55 min, ramped with 250 °C min^{-1} to 300 °C with a duration of 24 min.

Oven temperature program was as follows:

45 °C (hold time 2.5 min), ramped with 22 °C min^{-1} to 220 °C, ramped with 7 °C min^{-1} to 280 °C and ramped with 40 °C min^{-1} to 300 °C (hold time 4.4 min).

CUPs (Table S4-S5):

Agilent 7200 q-ToF GC/MS in EI mode with an Agilent 7890B GC, a Gerstel PTV and a restrictor column (1.8 m, 0.150 mm) in combination with an Agilent J&W HP-5MS UI (15 m, 0.25 mm x 0.25 µm) GC column.

PTV injection in solvent vent mode with 0.30 min solvent vent time, 15 mL min^{-1} solvent vent flow at 0.7 psi, with a Gerstel PTV injector was used. The initial inlet temperature was set to 55 °C with a duration of 0.35 min, ramped with 500 °C min^{-1} to 320 °C with a duration of 3 min.

Oven temperature program was as follows:

45 °C (hold time 2 min), ramped with 70 °C min^{-1} to 80 °C (hold time 0.2 min), ramped with 5 °C min^{-1} to 300 °C (hold time 2 min).

Data alignment for suspect lists, which MS are to find in NIST 14/customised self-build libraries and how to highlight findings of suspects in peak lists

This study applied pre-defined suspect lists with components relevant as potential Arctic atmospheric contaminants (Reppas-Chrysovitsinos et al., 2017; Brown and Wania, 2008; Coscollà et al., 2011; Hoferkamp et al., 2010; Howard and Muir, 2010; NORMAN-network, 2019).

In order to account for different CAS numbers and/or different names of compounds in the used suspect lists and available MS libraries, compound names from the suspect lists were transformed to CAS numbers and compared to the original CAS number in the suspect list. In case the transformed CAS number derived for the respective original CAS number stated in the chosen publications, a manual search was performed in SciFinder to identify the correct CAS number for a compound. After all compounds were assigned with corrected CAS numbers, SMILES stings were created of each compound, using JChem for Excel (ChemAxon, 2019).

Conditional formatting in Excel was used to create a merged suspect list, including the information from which list a suspect is originating (e.g. AMAP list or NORMAN list etc.).

To identify which of those suspects might be listed in the used MS libraries, all entries of the used MS libraries were exported to Excel (Name, CAS and molecular formula).

With conditional formatting in Excel, all suspects, of which a MS is available in the used MS libraries, were highlighted and copied to a separate column.

The mass spectra of these suspects were manually copied from the used MS libraries to a separate, customised self-build library.

This customised MS library, containing the selected mass spectra, was used beside other self-build MS libraries for suspect screening. During suspect screening, the first library search was only performed with self-build libraries. Here all peak markers in ChromaTOF were highlighted as suspects before further data processing and classification. The final peak list, L0–L2 compounds, was cross checked with the initial suspect list and the origin list of a suspect was included.

Table S7: Summary of PBT criteria.

	REACH (European Parliament, 2018)	Stockholm convention (UNEP, 2009)
Persistent (P)	$t_{1/2}$water fresh/marine ≥ 960/1440 h (40/60 days) (vP[1] ≥ 1440 h (60 days)) $t_{1/2}$soil ≥ 2880 h (120 days) (vP[1] ≥ 4320 h (180 days)) $t_{1/2}$sediment fresh/marine ≥ 2880/4320 h (120/180 days) (vP[1] ≥ 4320 h (180 days))	$t_{1/2}$water ≥ 2 months (1440 h) $t_{1/2}$soil ≥ 6 months (2880 h) $t_{1/2}$sediment ≥6 months (2880 h)
Bioaccumulative (B)	BCF[2] ≥ 2000 (vB[3] ≥ 5000)	BCF[2] ≥ 5000
Toxic (T)	NOEL or EC10 ≤ 0.01 mg/ L Or Carcinogen 1A, 1B or 2 Or mutagenic 1A or 1B Or reproduction toxic 1A, 1B or 2 Or evidence for chron. Tox. STORE cat. 1 or 2	Evidence of adverse effects to human health, or toxicity or ecotox. indicate potential damage to human health or the environment
Long-range transport potential (LRTP)	-[4]	Measured levels in distant of source of relevance Or monitoring data showing LRT with potential to transfer to a receiving environment Or environment fate properties/model results that show LRTP: $t_{1/2}$air ≥ 2 days

[1] vP: very persistent; [2] BCF: Bioconcentration factor; [3] vB: very bioaccumulative; [4] not applicable

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