

Long-term monitoring of persistent organic pollutants (POPs) at the Norwegian Troll station in Dronning Maud Land, Antarctica

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Appendix A: Analytical method description

This method covers the following groups of components:

- α -, and γ -HCH
- HCB
- *o,p'*- and *p,p'*-DDT, DDD, DDE
- *trans*- and *cis*-chlordanes
- *trans*- and *cis*-nonachlor
- PCB (congeners No. 18, 28, 31, 33, 37, 47, 52, 66, 74, 99, 101, 105, 114, 118, 122, 123, 128, 138, 141, 149, 153, 156, 157, 167, 170, 180, 183, 187, 189, 194, 206, and 209)

Solvents and adsorbents were of ultra-trace analysis grade (SupraSolv, Merck, Darmstadt, GER), all gases were provided by Hydro (N₂ and He, 6.0 quality, Porsgrunn, NO).

Preparation of sampling equipment: New plugs are extracted in a 2000 ml Soxhlet extractor with toluene (24 h), acetone (8 h) and with toluene (8 h). Plugs, which have been

1 previously extracted after sampling, are cleaned using Soxhlet extraction with acetone (8 h)
2 and toluene (8 h). After extraction the bulk of the solvent is removed by squeezing the plugs
3 using solvent resistant lab gloves. The plugs are transferred into a desiccator and placed in an
4 oven for drying at 60° C and 100–200 mbar vacuum. Following drying two plugs are placed
5 in a custom-designed PUF sampling support (DIGITEL, Hegenau, Switzerland) and sealed
6 with lids which are connected with flate-ground joint and clamps (see Figure S1). For
7 transport and storage the PUF supports are stored in aluminium boxes with tailor-made plastic
8 foam inlays.

9 Glass fibre filters (GFF: 150 mm id, CaNo 1822-150, Whatman, Buckinghamshire, UK) are
10 heated in an oven to 450 °C (8 h). After cooling they are mounted into the filter support
11 (DIGITEL, Hegenau, Switzerland) and the support with the mounted filter were packed in
12 aluminium foil and zip-lock bag.

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14 **Sample collection:** For the monitoring, continuous integrated weekly/7-days samples were
15 collected with a flow rate of 10 - 15 m³/h resulting in sample volumes between 2200 and 2500
16 m³. A commercially available high volume air sampling device (DHA-80, DIGITEL,
17 Hegenau, Switzerland) for separate particle and gas phase collection was used for the
18 monitoring of POPs. The particle phase was collected on glass fiber filters whereas the gas
19 phase was collected on pre-cleaned polyurethane foam plugs (PUF). Gas- and particle phase
20 samples were collected simultaneously. Flow-rate and sampling conditions were digitally
21 monitored and documented (e.g., power failures, etc) as integrated part of the sampling and
22 quality control procedure. Sector controlled sampling was performed where air masses
23 passing over the main research station were not collected in order to minimize the potential
24 for local contamination.

25 **Sample storage:** After the sampling was completed, the exposed filters (GFF and PUF) were
26 packed again in aluminium/zip lock bag (GFF) or sealed with glass lids (PUF). All exposed
27 filters/PUFs were registered and stored frozen (-20 °) between sampling and analysis,
28 however, not during air transport between Troll station and quantification. The yearly sample
29 set was shipped on the first flight every austral summer (November) to the analytical
30 laboratory in Norway by combined ship and airfreight transport.

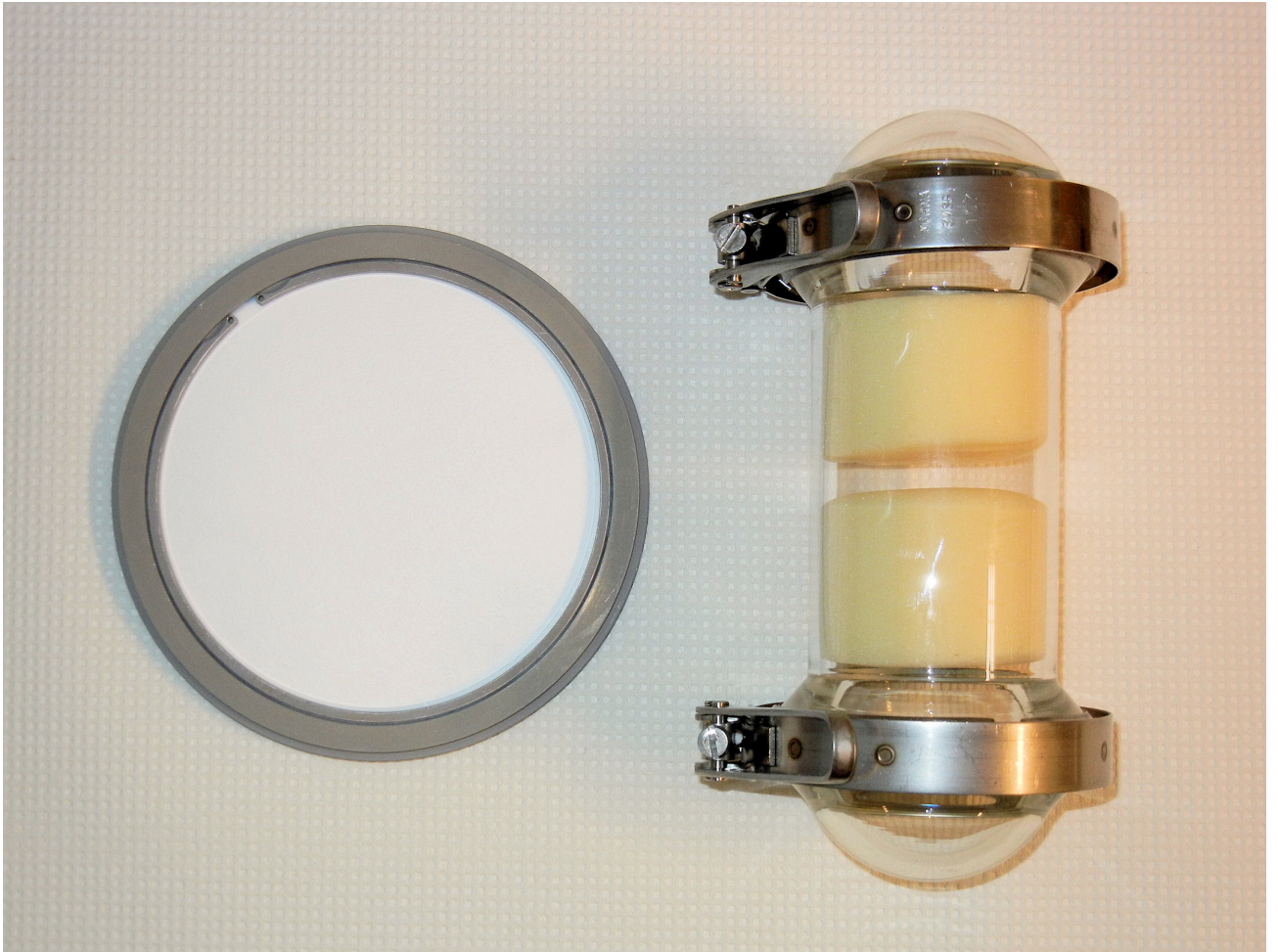
Sample preparation: All samples were Soxhlet extracted for 12 h with *n*-hexane/diethylether (90:10, v:v), firstly the GFF part of a given sample in a 50 mL Soxhlet extractor and secondly the two PUFs of the same sample in a 250 mL Soxhlet extractor mounted on the same round-bottom flask. Prior to extraction a mixture of 10 ng of different ¹³C Internal Standards (IST) for all congener and isomer groups analysed was added to the GFF. Volume reduction to ca. 500 µl was performed on a Turbovap (Caliper-Zymark, Hopkinton, MA, USA). The concentrated sample was transferred to a 10–15 mL centrifuge tube, 8-10 mL conc. sulphuric acid added, and placed in a rack until the next day. The hexane fraction was transferred to a new centrifuge tube and 1 mL MilliQ water added drop by drop. The water phase was removed and the hexane phase dried with ½ teaspoon precleaned sodium sulfate. After volume reduction, the extract was transferred to a 15 cm glass column (with stop cock) filled with precleaned and preconditioned Silica (2%-w water) and a top layer of pre-cleaned sodium sulfate for clean-up. After clean-up, volume of the eluate was reduced to 500 µL (Turbovap) and further reduced to 100 µL under a gentle N₂ stream. Before quantitative analysis, 10 ng of 1,2,3,4-tetrachloronaphthalene (TCN) was added as recovery standard (RecStd, table S1-S3).

Quantitative analysis: After sample preparation, the eluates were quantitatively analysed using high-resolution gas chromatography coupled to a high-resolution sector field mass spectrometer as detector (HRGC/HRMS). A 6890N Agilent gas chromatograph (Agilent, Palo Alto CA, USA) was coupled to an Autospec Ultima sector field mass spectrometer (Waters, Milford, MA, USA). An aliquote of 2 µL of the eluate was injected into the gas chromatograph in splitless mode (280 °C and 2 min splitless time). The analyses were performed with maximum resolution (ca. 10 000) in Electron Impact (EI: PCBs, HCB, DDT derivatives) and Negative Ion Chemical Ionisation mode NICI: OCP) for the respective compounds groups. For highest sensitivity grouped single ion monitoring (SIM) was applied. The detailed GC and MS parameters are given in Table S1 to S2 and the SIM groups are listed in Table S3 to S5. The isotope dilution method using ¹³C-labeled internal standards was applied for identification and quantification of the target compounds.

Quality control: Sampling and sample storage was an integral part of the overall quality control program. The responsible technicians at the Troll research station followed detailed

1 routines developed by NILU in order to avoid unwanted contamination during field work.
2 The analytical procedure used for the study was accompanied by a comprehensive quality
3 control program based on the requirements of NILU's accreditation, according to NS-EN/ISO
4 IEC 17025 (2005). The instrument limit of detection was determined (LOD) by calculating
5 the signal to noise ratio (S/N) > 3 for solvent blanks (using *n*-hexane). Extensive field and
6 laboratory blank values were analysed in order to monitor and control possible contamination
7 during sample transport and laboratory work. No evidence for contamination during sample
8 processing was found for the data presented here (no elevated values in field- and laboratory
9 blanks). All raw data are openly accessible from the NILU database (ebas.nilu.no) for
10 thorough examinations. As a general survey, monthly arithmetic mean values are listed in
11 table S4. All values below LOD were excluded from further statistical treatment (treated as
12 not detected = n.d.).

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15 Figure S1: Custom made PUF support (DIGITEL, Heggenau, Switzerland) with lids connected
16 with flange-ground joint and clamps and GFF support (DIGITEL, Heggenau, Switzerland).



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Table S1: GC parameters for the different compound groups.

Compound groups	Carrier gas	Stationary phase	Length [m]	Inner diameter [mm]	Film thickness [μm]	Gas velocity [mL/min]	Inj. temp. [°C]	Temp 1 [°C]	Hold time 1 [min]	Ramp 1 [°C/min]	Temp 2 [°C]	Hold time 2 [min]	Ramp 2 [°C/min]	Temp 3 [°C]	Hold time 3 [min]	Ramp 3 [°C/min]	Temp 4 [°C]	Hold time 4 [min]	Interface temp. [°C]
DDT	He	HP-1	25	0,2	0,25	1	220	60	2	20	270	4							260
PCB	He	HT-8	50	0,22	0,15	1	280	90	2	25	170	0	3	300	3				260
OCP	He	Ultra-II	25	0,2	0,11	0,9	260	70	2	20	170	3	5	240	0	30	280	5	260

Table S2: MS parameters for the different compound groups

Compound groups	Ionization mode	Ion source temp. [°C]	Lock substance	Acceleration voltage [V]	Electron energy [eV]	Mass resolution	CI gas	CI gas pressure [torr]
DDT	EI	260	PFK*	8000	35	10 000		
PCB	EI	260	PFK	8000	35	10 000		
OCP.	NICI	260	PFK	7000	90 - 150	10 000	CH ₄	0,4 – 0,6

*) PFK = Perfluorokerosene

Table S3: SIM-program for PCB-compounds

*) All masses provided appear as the masses of the [M⁺] ion.

SIM function	Isomer group	¹² C mass 1* (m/z)	¹² C mass 2 (m/z)	¹³ C mass 1 (m/z)	¹³ C mas 2 (m/z)
1	HCB	283,8102	285,8072	293,8244	295,9214
	PFK	292,9825			
2	TCN	263,9067	265,9038		
	Trichloro CB	255,9613	257,9584	268,0016	269,9986
	Tetrachloro-CB	289,9224	291,9194	301,9226	303,9597
	PFK	280,9825			
3	Tetrachloro-CB	289,9224	291,9194		
	Pentachloro-CB	325,8804	327,8775	337,9207	339,9177
	PFK	342,9792			
4	Pentachloro-CB	325,8804	327,8775	337,9207	339,9177
	Hexachloro-CB	359,8415	361,8385	371,8817	373,8788
	Heptachloro-CB	393,8025	395,7995		
	PFK ⁺	342,9792			
5	Hexachloro-CB	359,8415	361,8385	405,8428	407,8398
	Heptachloro-CB	393,8025	395,7995		
	PFK	380,9760			

TCN = 1,2,3,4-Tetrachloronaphthalene used as recovery standard.

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Table S4: SIM-program for DDT- and HCH-compounds

SIM function	Isomer group	¹² C mass 1 (m/z)	¹² C mass 2 (m/z)	¹³ C mass 1 (m/z)	¹³ C mas 2 (m/z)
1	PFK ⁺	218,9856			
	HCH	216,915	218,912	222,935	224,932
2	TCN	263,907	265,904		
	PFK ⁺	242,9856			
	DDE	246,000	247,997	258,041	260,038
	DDD	235,008	237,005		
	DDT	235,008	237,005	249,045.	247,049
	DDT(control)	246,000	247,997		

5 Internal standards used for HCH were ¹³C α- and γ-HCH. For the DDT-group ¹³C *p,p'*-DDE
6 was used for *o,p'*-DDE and *p,p'*-DDE and ¹³C *p,p'*-DDT was used as internal standard for the
7 compounds *o,p'*-DDT, *p,p'*-DDT, *o,p'*-DDD and *p,p'*-DDD.

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Table S5: SIM-program for other chlorinated pesticidesds

SIM function	Isomer group	¹² C mass 1 (m/z)	¹² C mass 2 (m/z)	¹³ C mass 1 (m/z)	¹³ C mas 2 (m/z)
1	PFK	280,9825			
	TCN	263,9067	265,9038		
2	PFK	411,974			
	<i>Trans/cis</i> -chlordane	407,7948	409,7919	417,8284	419,8254
		441,7558	443,7529	451,7894	453,7864
	<i>Trans/cis</i> -nonachlor				

1 Table S6: Organochlorine Pesticides selected for quantitative analysis in the Troll
2 atmospheric samples.

Common name	Abbreviation	Structure/ IUPAC	CAS-Number
α -hexachlorocyclohexane	α -HCH	(1a,2a,3b,4a,5b,6b)-1,2,3,4,5,6-hexachlorocyclohexane,	319-84-6
γ -hexachlorocyclohexane	γ -HCH	(1a,2b,3a,4b,5a,6b)-1,2,3,4,5,6-hexachlorocyclohexane	58-89-9
Hexachlorobenzene	HCB	1,2,3,4,5,6-hexachlorobenzene	118-74-1
<i>cis</i> -chlordane	<i>cis</i> -CD	(1a,2a,3aa,4b,7b,7aa)-1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-indene	5103-71-9
<i>trans</i> -chlordane	<i>trans</i> -CD	(1a,2b,3aa,4b,7b,7aa)-1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-indene	5103-74-2
<i>cis</i> -nonachlor	<i>cis</i> -NO	(1a,2a,3a,3aa,4b,7b,7aa)-1,2,3,4,5,6,7,8,8-nonachloro-2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-indene	5103-73-1
<i>trans</i> -nonachlor	<i>trans</i> -NO	1a,2b,3b,4,5,6,7,8,8-Nonachloro-2,3,3a,4,7,7a-hexahydro-4,7-methano-1H-indene	39765-80-5
<i>o,p'</i> -dichlorodiphenyltrichloroethane	<i>o,p'</i> -DDT	1,1,1-trichloro-2-[<i>o</i> -chlorophenyl]-2-[<i>p</i> -chlorophenyl]ethane	789-02-6
<i>p,p'</i> -dichlorodiphenyltrichloroethane	<i>p,p'</i> -DDT	1,1,1-trichloro-2,2-bis(<i>p</i> -chlorophenyl) ethane	50-29-3
<i>o,p'</i> -dichlorodiphenyldichloroethene	<i>o,p'</i> -DDE	1,1-dichloro-2-(<i>o</i> -chlorophenyl)-2-(<i>p</i> -chlorophenyl) ethene	3424-82-6
<i>p,p'</i> -dichlorodiphenyldichloroethene	<i>p,p'</i> -DDE	1,1-dichloro-2,2-bis(<i>p</i> -chlorophenyl) ethene	72-55-9
<i>o,p'</i> -dichlorodiphenyldichloroethane	<i>o,p'</i> -DDD	1,1-dichloro-2-(<i>o</i> -chlorophenyl)-2-(<i>p</i> -chlorophenyl)ethane	53-19-0
<i>p,p'</i> -dichlorodiphenyldichloroethane	<i>p,p'</i> -DDD	1,1-bis (4-chlorophenyl)-2,2-dichloroethane	72-54-8

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1 Table S7: Limit of quantification (LOQ) for the target POPs analysed in atmospheric samples
2 from Troll [pg/m³]

Structure	Name	LOQ*
<i>trans</i> -Chlordane	tr-CD	0.00
<i>cis</i> -Chlordane	cis-CD	0.01
<i>trans</i> -Nonachlor	tr-NO	0.01
<i>cis</i> -Nonachlor	cis-NO	0.00
α -HCH		0.04
γ -HCH		0.08
<i>o,p'</i> -DDE		0.02
<i>p,p'</i> -DDE		0.08
<i>o,p'</i> -DDD		0.01
<i>p,p'</i> -DDD		0.01
<i>o,p'</i> -DDT		0.02
<i>p,p'</i> -DDT		0.02
HCB		0.38
2,2',5-TriCB	18	0.46
2,4,4'-TriCB	28	0.13
2,4',5-TriCB	31	0.17
2',3,4-TriCB	33	0.09
3,4,4'-TriCB	37	0.01
2,2',4,4'-TetCB	47	0.08
2,2',5,5'-TetCB	52	0.14
2,3',4,4'-TetCB	66	0.03
2,4,4',5-TetCB	74	0.02
2,2',4,4',5-PenCB	99	0.04
2,2',4,5,5'-PenCB	101	0.06
2,3,3',4,4'-PenCB	105	0.03
2,3,4,4',5-PenCB	114	0.00

Structure	Name	LOQ*
2,3',4,4',5-PenCB	118	0.08
2'3,3',4,5-PenCB	122	0.00
2',3,4,4',5-PenCB	123	0.01
2,2',3,3',4,4'-HexCB	128	0.04
2,2',3,4,4',5'-HexCB	138	0.18
2,2',3,4,5,5'-HexCB	141	0.02
2,2',3,4',5,6-HexCB	149	0.06
2,2',4,4',5,5'-HexCB	153	0.22
2,3,3',4,4',5-HexCB	156	0.01
2,3,3',4,4',5'-HexCB	157	0.01
2,3',4,4',5,5'-HexCB	167	0.01
2,2',3,3',4,4',5-HepCB	170	0.05
2,2',3,4,4',5,5'-HepCB	180	0.11
2,2',3,4,4',5,6-HepCB	183	0.02
2,2',3,4',5,5',6-HepCB	187	0.05
2,3,3',4,4',5,5'-HepCB	189	0.00
2,2',3,3',4,4',5,5'-OctCB	194	0.01
2,2',3,3',4,4',5,5',6-NonCB	206	0.00
DecaCB	209	0.00

1 *) LOQ: The limit of quantification is calculated as average concentration in all blank values
2 and 3 times signal/ noise ratio is added as safety margin.

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