- 1 Supplementary data
- 2 Endosulfan, pentachlorobenzene and short-chain chlorinated

## **3** paraffins in background soils from Western Europe

- 4
- 5 Anne Karine Halse<sup>1,2\*</sup>, Martin Schlabach<sup>1</sup>, Jasmin K. Schuster<sup>3</sup>, Kevin C. Jones<sup>3</sup>, Eiliv Steinnes<sup>4</sup>,
- 6 Knut Breivik<sup>1,5</sup>
- 7 <sup>1</sup>NILU Norwegian Institute for Air Research, Box 100, NO-2027 Kjeller, Norway
- <sup>2</sup> Norwegian University of Life Sciences, Department of Chemistry, Biotechnology and Food Science, P.O.
   Box 5003, NO-1432 Ås, Norway
- 10 <sup>3</sup> Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, UK
- <sup>4</sup> Norwegian University of Science and Technology, Department of Chemistry, NO-7491 Trondheim,
   Norway
- 13 <sup>5</sup> University of Oslo, Department of Chemistry, Box 1033, NO-0315 Oslo, Norway
- 14 \*Corresponding author. Norwegian Institute for Air Research, NO-2027 Kjeller, Norway.
- 15 Tel.: +47 63 89 80 00; fax: +47 63 89 80 50. E-mail: <u>akh@nilu.no</u> (A.K. Halse)
- 16

### **Table of Contents**

19	1.	Tab	es	4					
20 21		Tab sam	e A1: Information related to sample site, sample characteristics, geographical coordinates and ple amount (dry weight and amount of soil organic matter (SOM)).	4					
22		Tab	e A2: Instrumental parameters for analysis of the compounds	6					
23 24		Tab blar	e A3: Results for the recovery, i.e. range, average and standard deviation (SD) for soil and ks samples, respectively (in %)	6					
25 26 27	Table A4: Average $\pm$ standard deviation and ranges for the concentration of $\Sigma$ endosulfans, pentachlorobenzene (PeCB) and short chain chlorinated paraffins (SCCPs), in addition to blank values. All results are expressed as ng/g dry weight (dw).								
28 29		Tab (dw	e A5: Individual concentrations for each UK and Norwegian sites, expressed as ng/g dry weight ) and ng/g soil organic matter (SOM)	8					
30 31		Tab para	e A6: Results from correlation analysis with statistical significance for latitude, land use ameters and individual compounds for UK soils in 2008	0					
32 33		Tab indi	e A7: Results from correlation analysis with statistical significance for latitude, land use and vidual compounds for Norwegian soils in 20081	1					
34 35		Tab indi	e A8: Results from correlation analysis with statistical significance for latitude, land use and vidual compounds for GL soils in 2008	2					
36 37		Tab indi	e A9: Results from correlation analysis with statistical significance for latitude, land use and vidual compounds for WL soils in 2008	3					
38	2		Text	4					
39	2	.1.	Drying and sieving14	4					
40	2	.2.	Sample preparation14	4					
41		2.2.	1. Accelerated solvent extraction (ASE)14	4					
42		2.2.	2. Clean-up15	5					
43	2	.3.	Analysis15	5					
44	2	.4.	Method validation of the ASE extraction procedure1	7					
45	2	.5.	Blanks and method detection limit (MDL)	9					
46	2	.6.	Determination of soil parameters	9					
47	2	.7.	Partitioning and fate in soil20	D					
48	2	.8.	Statistical analysis22	1					
49		2.8.	1. Outliers22	1					

50	3.	Figures		22
51		Figure A1	Map showing sampling sites in UK and Norway.(Schuster et al., 2011)	22
52		Figure A2	ASE cell with sample and packing material (DE and florisil)	23
53		Figure A <sub>3</sub>	Flowchart for the clean-up and quantification.	23
54	4.	References		24

# **1. Tables**

	Latitude Longitude Sample amount
8	soil organic matter (SOM)).
7	Table A1: Information related to sample site, sample characteristics, geographical coordinates and sample amount (dry weight and amount of

Country	Site	Land use	Latitude [°]	Longitude [°]	Sample amount g dw	SOM g/g dw
United Kingdom	Bodwin	WL	50.58	-4.52	0.85	0.97
United Kingdom	Bodwin	GL	50.58	-4.52	2.04	0.29
United Kingdom	Okehamptons	WL	50.76	-4.00	0.73	0.87
United Kingdom	Okehamptons	GL	50.78	-3.91	3.04	0.20
United Kingdom	Tiverton	GL	51.03	-3.52	2.47	0.14
United Kingdom	Tiverton	WL	51.03	-3.51	2.01	0.36
United Kingdom	Aberystwyth	GL	52.20	-3.79	1.86	0.86
United Kingdom	Aberyswyth	WL	52.43	-4.03	2.56	0.18
United Kingdom	Corris	WL	52.64	-3.84	1.89	0.32
United Kingdom	Betsw-y-coed	WL	53.05	-3.80	2.61	<sup>1)</sup> 0.68
United Kingdom	Betsw-y-coed	GL	53.11	-3.78	2.41	<sup>1)</sup> 0.15
United Kingdom	Hazelrigg	GL	54.01	-2.78	2.35	0.17
United Kingdom	Hawkshead	WL	54.33	-3.00	1.74	0.52
United Kingdom	Hawkshead	GL	54.33	-3.00	1.97	0.25
United Kingdom	Ae, Dumfries	GL	55.20	-3.60	2.39	0.27
United Kingdom	Ae, Dumfries	WL	55.20	-3.61	3.20	0.24
United Kingdom	Clachan	GL	55.76	-5.54	0.75	0.77
United Kingdom	Clachan	WL	55.77	-5.53	1.80	0.66
United Kingdom	Colonsay	GL	56.08	-6.20	1.34	0.48
United Kingdom	Colonsay	WL	56.10	-6.18	2.75	0.13
United Kingdom	Tyndrum	WL	56.45	-4.71	1.18	0.92
United Kingdom	Glencoe	GL	56.66	-5.07	1.34	0.90
United Kingdom	Broadford	GL	57.28	-6.01	1.06	0.66
United Kingdom	Little Garv	GL	57.63	-4.70	1.79	0.26
United Kingdom	Little Garv	WL	57.63	-4.69	1.28	0.77
United Kingdom	Ullapool	GL	57.93	-5.19	0.93	0.93
United Kingdom	Ullapool	WL	57.99	-5.11	0.70	0.96
Norway	Birkenes	WL	58.48	8.29	0.74	0.94
Norway	Ualand	WL	58.56	6.46	0.79	0.97

Country	Site	Land use	Latitude [°]	Longitude [°]	Sample amount g dw	SOM g/g dw
Norway	Ualand	GL	58.56	6.46	1.23	0.89
Norway	Treungen	GL	59.10	8.63	3.20	0.15
Norway	Treungen	WL	59.10	8.63	0.75	0.97
Norway	Onsøy	GL	59.31	11.00	2.96	0.11
Norway	Onsøy	WL	59.31	11.00	0.77	0.96
Norway	Utbjoa	WL	59.76	5.80	0.99	0.96
Norway	Nordmoen	WL	60.30	11.18	2.51	0.24
Norway	Ulvik	WL	60.67	6.94	1.27	0.72
Norway	Osen	WL	61.25	11.75	0.77	0.97
Norway	Fureneset	peat/GL	61.29	5.04	1.44	0.82
Norway	Hovlandsdal	GL	61.51	5.51	2.46	0.22
Norway	Hovlandsdal	WL	61.51	5.51	2.49	0.34
Norway	Sollia/Enden	WL	61.79	10.30	1.26	0.65
Norway	Sollia/Enden	GL	61.79	10.30	2.83	0.23
Norway	Utvikfjellet	WL	61.80	6.50	0.92	0.98
Norway	Venabu	GL (heath)	61.88	10.35	2.10	0.49
Norway	Venabu	GL	61.88	10.35	1.51	0.64
Norway	Lom	WL	61.91	8.70	2.86	0.22
Norway	Gaulstad	WL	63.95	12.13	0.86	0.95
Norway	Gaulstad	GL	64.01	12.10	2.35	0.21
Norway	Momyra	WL	64.10	10.50	1.00	0.54
Norway	Namsvatn	WL	65.04	13.64	1.29	0.64
Norway	Balvatnet	GL	67.13	16.02	2.26	0.17
Norway	Balvatnet	WL	67.13	16.02	1.23	0.57
Norway	Innhavet	WL	68.11	15.99	0.70	0.96
Norway	Tamokdalen	WL	69.17	19.81	2.56	0.22
Norway	Tamokdalen	GL	69.17	19.81	1.18	0.67
Norway	Grøtfjord	WL	69.85	18.73	1.78	0.52
Norway	Skoganvarre	WL	69.95	25.20	1.06	0.81
Norway	Vestertana	WL	70.47	27.95	1.29	0.90

<sup>1)</sup> Data from (Schuster et al., 2011)

C	n
D	υ

### Table A2: Instrumental parameters for analysis of the compounds

Compound	Type of instrument	Type of column Column size		Carrier gas	Temperature interval	Target ion	
Endosulfan	GC/HRMS in ECNI mode, (Agilent 6890N GC coupled to VG Autospec)	Fused silica capillary column from J&W Scientific	Ultra 2, 25 m length, 0.2 mm I.D, 0.11 μm film thickness	Helium	Start°C: 70 (2 min.) Interval 1: 170°C/min by 20°C/min (3min.) Interval 2: 230°C/min by 5°C/min (3 min.)	[M] <sup>-</sup>	
					Injector temp. (°C): 260		
PeCB	GC/HRMS in El mode, (Agilent 6890N GC coupled to Autospec-Ultima)	Fused silica capillary column from J&W Scientific	Ultra 2, 25 m length, 0.11 mm I.D, 0.11 μm film thickness	Helium	Start°C: 45 (2 min.) Interval 1: 200°C/min by 15°C/min (3min.) Interval 2: 300°C/min by 15°C/min (5 min.)	[M] <sup>+</sup>	
			_		Injector temp. (°C): 260		
SCCPs	GC/HRMS in ECNI mode,(Agilent 6890N GC coupled to VG Autospec)	Fused silica capillary column from Restek	Rxi®-5ms, 15 m length, 0.25 mm I.D, 0.25 μm film thickness	Helium	Start°C: 90 (2 min.) Interval 1: 245°C/min by 20°C/min Interval 2: 300°C/min by 20°C/min (5 min.)	[M-Cl] <sup>-</sup>	
		_			Injector temp. (°C): 260		

61

### 62

### 63 Table A3: Results for the recovery, i.e. range, average and standard deviation (SD) for soil and blanks samples, respectively (in %).

		Soil samples		Blanks		
Internal standard	Range	Average ±SD	Range	Average ±SD		
$^{13}$ C $\alpha$ -endosulfan	10-109	60±25	18-70	52±20		
<sup>13</sup> C β-endosulfan	11-96	53±15	11-65	39±28		
<sup>13</sup> C-endosulfan sulfate	6-73	30±15	13-35	22±8		
<sup>13</sup> C-PeCB	11-107	34±14	9-48	34±15		
<sup>13</sup> C- <i>cis</i> -chlordane (SCCPs)	37-68	53±13	n.a.	n.a.		

Average ± standard deviation (SD)									
		Range (r	nin-max)						
$\Sigma$ endosulfans endosulfan sulfate $lpha$ -endosulfan $eta$ -endosulfan P									
All 2008	2±4	2±4	0.01±0.01	0.03±0.1	0.4±0.3	14±45			
n = 57/53/58 <sup>1)</sup>	<0.01-25	<0.002-24	<0.005-0.06	<0.002-0.7	<0.007-1	<0.8-281			
Norway	3±5	3±5	0.01±0.02	0.05±0.1	0.3±0.3	12±50			
n= 32/32/32 <sup>1)</sup>	0.02-25	0.01-24	<0.005-0.06	<0.002-0.7	<0.007-1	<0.8-281			
UK	1±2	1±2	0.007±0.005	0.009±0.03	0.4±0.3	16±38			
n= 25/21/26 <sup>1)</sup>	<0.01-9	<0.002-9	<0.005-0.02	<0.002-0.1	0.09-1	<0.8-179			
GL	0.4±0.8	0.4±0.8	0.006±0.004	0.005±0.01	0.3±0.3	18±58			
n= 23/20/24 <sup>1)</sup>	<0.01-4	<0.002-4	<0.005-0.02	<0.002-0.06	<0.007-1	<0.8-281			
WL	3±5	3±5	0.01±0.02	0.05±0.1	0.4±0.3	11±32			
n= 34/33/34 <sup>1)</sup>	0.05-25	0.04-24	<0.005-0.06	<0.002-0.7	0.07-1	<0.8-179			
Blanks (ng/g d.w)		0.002±0.0004	0.002±0.002	0.001±0.001	0.004±0.003	0.4±0.4			
n=5		< 0.002 <sup>2)</sup>	< 0.005 <sup>2)</sup>	< 0.0022)	0.007 <sup>2)</sup> -0.008	0.8 <sup>2)</sup> -1			
MDL		0.003	0.01	0.005	0.01	1.6			
Canada and UK <sup>3)</sup>	0.08-0.97	-	-	-	-	-			
Tajikistan <sup>4)</sup>	-	0.29-22.88	**nd-1.58	**nd-18.12	-	-			
Antarctic <sup>5)</sup>	-	-	-	-	0.38-1.3	-			
Estonia <sup>6)</sup>	-	-	-	-	<loq*-0.1< td=""><td>-</td></loq*-0.1<>	-			
China <sup>7)</sup>	-	-	-	-	-	0.42-210			

Table A4: Average ± standard deviation and ranges for the concentration of Σendosulfans, pentachlorobenzene (PeCB) and short chain
 chlorinated paraffins (SCCPs), in addition to blank values. All results are expressed as ng/g dry weight (dw).

66 <sup>1)</sup> Number (n) of sites for which  $\Sigma$ endosulfans, PeCB and SCCPs were analysed, respectively.

67 <sup>2)</sup> One or more samples were below MDL (½ MDL used for statistical treatment) value used for statistical treatment.

68 \* Limit of quantification, \*\* not detected

<sup>3)</sup> Wong et al., (2009)

<sup>4)</sup> Zhao et al., (2013)

<sup>5)</sup> Borghini et al., (2005)

<sup>6)</sup> Roots et al., (2010)

73 <sup>7)</sup> Wang et al., (2013)

			Σenc	losulfans	endosul	fan sulfate	a-end	losulfan	β-enc	losulfan	Р	eCB	so	CCPs
Country	Site	Landuse	ng/g dw	ng/g SOM	ng/g dw	ng/g SOM	ng/g dw	ng/g SOM	ng/g dw	ng/g SOM	ng/g dw	ng/g SOM	ng/g dw	ng/g SOM
United Kingdom	Bodwin	WL	4.978	4.345	4.971	4.338	<0.005	<0.004	<0.002	<0.002	0.225	0.196	9.800	8.600
United Kingdom	Bodwin	GL	0.028	0.200	0.021	0.149	<0.005	<0.034	<0.002	<0.017	N.D.*	N.D.*	<0.800	<5.600
United Kingdom	Okehamptons	WL	9.071	7.543	8.938	7.433	<0.005	<0.004	0.128	0.106	0.408	0.340	180.000	150.000
United Kingdom	Okehamptons	GL	0.025	0.377	0.018	0.268	<0.005	<0.072	<0.002	<0.037	N.D.**	N.D.**	N.D.**	N.D.**
United Kingdom	Tiverton	GL	0.010	0.179	0.003	0.056	<0.005	<0.081	<0.002	<0.042	0.092	1.570	<0.800	<14.000
United Kingdom	Tiverton	WL	0.922	5.158	0.908	5.080	<0.005	<0.027	0.009	0.051	0.288	1.610	1.800	9.900
United Kingdom	Abergwesyn	GL	N.D.**	N.D.**	N.D.**	N.D.**	N.D.**	N.D.**	N.D.**	N.D.**	1.313	2.836	<0.800	<1.700
United Kingdom	Abergwesyn	WL	0.123	1.702	0.115	1.602	<0.005	<0.066	<0.002	<0.034	0.147	2.040	<0.800	<11.000
United Kingdom	Corris	WL	0.305	1.820	0.295	1.764	0.007	0.042	<0.002	<0.015	0.280	1.672	<0.800	<4.700
United Kingdom	Betsw-y-coed	WL	0.116	0.443	0.108	0.416	<0.005	<0.018	<0.002	<0.009	N.D.*	N.D.*	46.000	175.000
United Kingdom	Betsw-y-coed	GL	0.020	0.315	0.012	0.199	<0.005	<0.076	<0.002	<0.039	0.103	1.654	6.600	106.000
United Kingdom	Hewelrigg	GL	0.034	0.478	0.026	0.376	<0.005	<0.068	<0.002	<0.035	0.168	2.382	4.200	60.000
United Kingdom	Hawkshead	WL	0.892	2.961	0.880	2.922	0.009	0.031	<0.002	<0.008	0.608	2.019	10.300	34.000
United Kingdom	Hawkshead	GL	0.036	0.281	0.014	0.108	0.019	0.153	<0.002	<0.019	0.772	6.064	4.500	35.000
United Kingdom	Ae, Dumfries	GL	0.052	0.468	0.045	0.403	<0.005	<0.043	<0.002	<0.022	N.D.*	N.D.*	<0.800	<7.000
United Kingdom	Ae, Dumfries	WL	0.111	1.504	0.104	1.406	<0.005	<0.065	<0.002	<0.033	0.180	2.440	<0.800	<10.700
United Kingdom	Clachan	GL	0.339	0.332	0.332	0.325	<0.005	<0.005	<0.002	<0.002	N.D.*	N.D.*	<0.800	<0.770
United Kingdom	Clachan	WL	0.411	1.115	0.409	1.108	N.D.**	N.D.**!	<0.002	<0.007	0.163	0.441	<0.800	<2.100
United Kingdom	Colonsay	GL	<0.009	<0.025	<0.002	<0.005	<0.005	<0.013	<0.002	<0.007	N.D.*	N.D.*	<0.800	<2.200
United Kingdom	Colonsay	WL	0.046	1.014	0.039	0.856	<0.005	<0.104	<0.002	<0.053	0.101	2.216	<0.800	<17.000
United Kingdom	Tyndrum	WL	3.749	4.833	3.699	4.769	0.024	0.031	0.026	0.033	1.182	1.524	25.000	32.000
United Kingdom	Glencoe	GL	0.322	0.482	0.304	0.456	0.015	0.022	<0.002	<0.004	0.377	0.564	4.900	7.300
United Kingdom	Broadford	GL	0.125	0.201	0.118	0.190	<0.005	<0.008	<0.002	<0.004	0.457	0.736	7.400	12.000
United Kingdom	Little Garv	GL	N.D.**	N.D.**	N.D.**	N.D.**	N.D.**	N.D.**	N.D.**	N.D.**	0.207	1.455	81.000	570.000
United Kingdom	Little Garv	WL	0.082	0.136	0.075	0.124	<0.005	<0.008	<0.002	<0.004	0.208	0.346	<0.800	<1.300
United Kingdom	Ullapool	GL	0.332	0.333	0.325	0.326	<0.005	<0.005	<0.002	<0.002	0.295	0.297	16.000	16.000
United Kingdom	Ullapool	WL	2.525	1.847	2.505	1.832	<0.005	<0.003	0.016	0.011	0.415	0.303	7.900	5.800
Norway	Birkenes	WL	10.922	8.567	10.755	8.436	<0.005	<0.004	0.162	0.127	1.359	1.066	8.000	6.200
Norway	Ualand	WL	5.584	4.581	5.346	4.385	0.047	0.039	0.191	0.157	0.229	0.188	4.000	3.300
Norway	Ualand	GL	3.579	4.942	3.518	4.858	<0.005	<0.007	0.056	0.077	0.579	0.800	<0.800	<1.100

Table A5: Individual concentrations for each UK and Norwegian sites, expressed as ng/g dry weight (dw) and ng/g soil organic matter (SOM).

			Σen	dosulfans	endosul	fan sulfate	α-end	losulfan	β-end	osulfan	P	eCB	sc	CPs
Country	Site	Landuse	ng/g dw	ng/g SOM	ng/g dw	ng/g SOM	ng/g dw	ng/g SOM	ng/g dw	ng/g SOM	ng/g dw	ng/g SOM	ng/g dw	ng/g SOM
Norway	Treungen	GL	0.077	1.699	0.070	1.540	<0.005	<0.105	<0.002	<0.054	0.076	1.670	<0.800	<17.000
Norway	Treungen	WL	5.065	3.883	4.909	3.763	0.033	0.025	0.123	0.094	0.613	0.470	2.400	1.900
Norway	Onsøy	GL	0.145	3.811	0.138	3.622	<0.005	<0.125	<0.002	<0.064	0.027	0.695	<0.800	<20.600
Norway	Onsøy	WL	24.671	19.661	23.902	19.049	0.063	0.050	0.706	0.562	0.495	0.394	8.000	6.500
Norway	Utbjoa	WL	2.746	2.840	2.713	2.807	<0.005	<0.005	0.028	0.029	0.945	0.978	53.000	55.000
Norway	Nordmoen	WL	0.815	8.480	0.799	8.319	0.005	0.050	0.011	0.111	0.372	3.876	<0.800	<8.200
Norway	Ulvik	WL	1.645	2.920	1.606	2.849	0.015	0.027	0.024	0.043	0.554	0.983	<0.800	<1.400
Norway	Osen	WL	3.723	2.956	3.656	2.903	<0.005	<0.004	0.062	0.049	0.844	0.670	9.900	7.900
Norway	Furunes	peat/GL	0.986	1.737	0.971	1.711	<0.005	<0.008	0.010	0.018	0.256	0.451	4.600	8.000
Norway	Hovelandsdal	GL	0.132	1.463	0.125	1.383	<0.005	<0.053	<0.002	<0.027	0.058	0.641	<0.800	<8.700
Norway	Hovelandsdal	WL	0.363	2.693	0.356	2.640	<0.005	<0.035	<0.002	<0.018	0.238	1.762	<0.800	<5.800
Norway	Sollia/Enden	WL	3.857	7.491	3.813	7.406	<0.005	<0.009	0.039	0.076	0.289	0.562	<0.800	<1.500
Norway	Sollia/Enden	GL	0.076	0.938	0.069	0.850	< 0.005	<0.059	<0.002	<0.030	0.051	0.626	<0.800	<9.700
Norway	Utvikfjellet	WL	5.514	5.208	5.376	5.078	0.061	0.058	0.076	0.072	0.332	0.313	2.800	2.700
Norway	Venabu	GL (heat)	0.513	2.183	0.506	2.153	<0.005	<0.020	<0.002	<0.010	0.085	0.361	<0.800	<3.400
Norway	Venabu	GL	1.490	3.513	1.481	3.492	0.007	0.016	<0.002	<0.006	0.140	0.330	<0.800	<1.900
Norway	Lom	WL	0.212	2.725	0.205	2.633	<0.005	<0.061	<0.002	<0.031	0.121	1.557	<0.800	<10.000
Norway	Gaulstad	WL	1.064	0.964	1.057	0.957	<0.005	<0.004	<0.002	<0.002	1.092	0.989	<0.800	<0.700
Norway	Gaulstad	GL	0.016	0.176	0.009	0.096	<0.005	<0.053	<0.002	<0.027	<0.007	<0.079	<0.800	<8.800
Norway	Momyr	WL	0.449	0.836	0.442	0.822	<0.005	<0.009	<0.002	<0.005	0.217	0.403	<0.800	<1.500
Norway	Namsvatn	WL	1.409	2.827	1.402	2.813	<0.005	<0.010	<0.002	<0.005	0.304	0.609	<0.800	<1.600
Norway	Balvatnet	GL	0.128	1.714	0.121	1.618	<0.005	<0.064	<0.002	<0.032	0.052	0.696	<0.800	<10.500
Norway	Balvatnet	WL	0.482	1.043	0.475	1.028	<0.005	<0.010	<0.002	<0.005	0.095	0.205	<0.800	<1.700
Norway	Innhavet	WL	2.758	2.031	2.751	2.026	<0.005	<0.004	<0.002	<0.002	0.399	0.294	<0.800	<0.580
Norway	Tamokdalen	WL	0.099	1.167	0.092	1.083	<0.005	<0.056	<0.002	<0.029	0.067	0.788	<0.800	<9.300
Norway	Tamokdalen	GL	0.335	0.588	0.328	0.576	<0.005	<0.008	<0.002	< 0.004	0.378	0.663	280.000	490.000
Norway	Grøtfjord	WL	0.506	1.732	0.498	1.707	<0.005	<0.016	<0.002	<0.008	0.279	0.955	<0.800	<2.700
Norway	Skoganvarre	WL	2.207	2.893	2.180	2.857	0.025	0.032	<0.002	<0.003	0.472	0.619	<0.800	<1.000
Norway	Vestertana	WL	1.254	1.802	1.228	1.764	<0.005	<0.007	0.022	0.031	0.149	0.213	<0.800	<1.100

<: refers to ½ MDL (method detection limit) used for statistical summaries. N.D.: not detected ( $\Sigma$ endosulfans (n=2), and SCCPs (n=1) due to matrix effects \*\*, PeCB (n=6):5

samples due to low % recovery \* and 1 sample due to matrix effects\*\*

Table A6: Results from correlation analysis with statistical significance for latitude, land use parameters and individual compounds for UK soils in 2008. Samples which either (i) failed to meet the QA/QC criteria (low recovery etc.), (ii) were below method detection limit (MDL), or

0	1
0	т

(iii) gualified as outliers were not considered (see text for details)  $\Sigma$ endosulfans  $\alpha$ -endosulfan  $\beta$ -endosulfan endosulfan sulfate BD(g/cm<sup>3</sup>) Latitude  $\Sigma_5 PBDEs$  $\Sigma_{31}$ PCBs SCCPs MOS PeCB нсв Variables ВС BD (g/cm<sup>3</sup>) -0.12 1 -0.02 -0.56\*\* 1 BC 0.64\*\*\* SOM 0.13 -0.83\*\*\* 1 0.80\*\*\* -0.75\*\*\*  $\Sigma$ endosulfans 0.21 0.47\* 1 0.79\*\*\* 1.00\*\*\* -0.75\*\*\* 0.46\* Endosulfan sulfate 0.23 1  $\alpha$ -endosulfan 0.24 -0.37 0.25 0.70 0.48 0.41 1 β-endosulfan -0.01 -0.28 0.16 0.60 0.92 0.92 0.86 1 -0.59\*\* 0.59\*\* 0.71\*\*\* 0.58\*\* 0.55\*\* 0.22 0.05 PeCB -0.17 1 0.17 SCCPs -0.19 -0.14 0.13 0.10 0.18 -0.35 0.14 0.19 1 -0.84\*\*\* 0.80\*\*\* 0.81\*\*\* 0.81\*\*\* 0.75\*\*\* 0.76\*\*\* 0.65\*\* -0.01 0.22 0.50\* 1 HCB -0.52\*\* 0.41\*  $\Sigma_5 PBDEs$ -0.44\* 0.30 0.39\* 0.38 0.46\* 0.39\* 0.49\* 0.27 0.49\* 1 0.56\*\* -0.76\*\*\* 0.50\*\* 0.73\*\*\* 0.73\*\*\* 0.73\*\*\* 0.76\*\*\* 0.63\*\*\* 0.87\*\*\* 0.70\*\*\* 0.06  $\Sigma_{31}$ PCBs 0.04 1

82 \*:p<0.05, \*\*: p<0.01,\*\*\*: p<0.001

83 n=27, except from:  $\Sigma$  endosulfans and endosulfan sulfate (n=24),  $\alpha$ -endosulfan (n=5),  $\beta$ -endosulfan (n=4), PeCB (n=21), SCCPs (n=14), HCB (n=22),  $\Sigma_5$ PBDE and  $\Sigma_{31}$ PCB (n=26)

84 All data were log-transformed with exception of latitude and land use.

Table A7: Results from correlation analysis with statistical significance for latitude, land use and individual compounds for Norwegian soils in 86 87 2008. Samples which either (i) failed to meet the QA/QC criteria (low recovery etc.), (ii) were below method detection limit (MDL), or (iii) qualified as outliers were not considered (see text for details)

Variables	Latitude	BD (g/cm³)	BC	SOM	Σendosulfans	Endosulfan sulfate	α-endosulfan	β-endosulfan	PeCB	SCCPs	HCB	$\Sigma_5$ PBDEs	Σ <sub>31</sub> PCBs
Latitude	1												
BD (g/cm <sup>3</sup> )	0.13	1											
BC	0.08	-0.56***	1										
SOM	0,01	-0.78***	0.71***	1									
$\Sigma$ endosulfans	-0.23	-0.75***	0.55**	0.86***	1								
Endosulfan sulfate	-0.22	-0.75***	0.54**	0.85***	1.00***	1							
$\alpha$ -endosulfan	-0.10	-0.68	0.51	0.85**	0.95***	0.95***	1						
$\beta$ -endosulfan	-0.41	-0.21	0.20	0.58*	0.94***	0.94***	0.90***	1					
PeCB	-0.09	-0.68***	0.60***	0.80***	0.77***	0.78***	0.31	0.14	1				
SCCPs	-0.09	-0.52	0.12	0.05	-0.17	-0.16	0.62	-0.34	0.65	1			
НСВ	-0.08	-0.89***	0.60**	0.88***	0.89***	0.89***	0.78***	0.68***	0.75***	0.03	1		
$\Sigma_5 PBDEs$	-0.55**	-0.60***	0.31	0.57**	0.74***	0.74***	0.80***	0.69***	0.52**	0.25	0.72***	1	
$\Sigma_{31}$ PCBs	-0.26	-0.79***	0.57**	0.73***	0.74***	0.72***	0.89***	0.75***	0.66***	-0.08	0.88***	0.77***	1
*:p<0.05, **: p<0.	.01,***: p<0	0.001	•	•	•	•	•	-	•		•		

89

90 n=32, except from: Σendosulfans and endosulfan sulfate (n=31), α-endosulfan (n=8), β-endosulfan (n=12), PeCB (n=30), SCCPs (n=8), HCB (n=26), Σ<sub>5</sub>PBDE and Σ<sub>31</sub>PCB (n=30)

91 All data were log-transformed with exception of latitude and land use. Table A8: Results from correlation analysis with statistical significance for latitude, land use and individual compounds for GL soils in 2008.
 Samples which either (i) failed to meet the QA/QC criteria (low recovery etc.), (ii) were below method detection limit (MDL), or (iii)

94
----

qualified as outliers were not considered (see text for details)  $\Sigma$ endosulfans  $\alpha$ -endosulfan  $\beta$ -endosulfan Endosulfan sulfate BD (g/cm<sup>3</sup>) Latitude  $\Sigma_5 PBDEs$  $\Sigma_{31}$ PCBs SCCPs SOM PeCB нсв Variables ВС Latitude 1 BD (g/cm<sup>3</sup>) 0.03 1 -0.64\*\*\* BC 0.001 1 -0.88\*\*\* 0.79\*\*\* SOM 0.13 1 0.77\*\*\* 0.47\* -0.71\*\*\* 0.44\*  $\Sigma$ endosulfans 1 -0.69\*\*\* 0.75\*\*\* 0.99\*\*\* endosulfan sulfate 0.50\* 0.41 1  $\alpha$ -endosulfan -1.00\* 0.35 -0.85 -0.50 -0.93 -0.90 1  $\beta$ -endosulfan --1 -----0.98\*\*\* -0.53\* 0.66\*\* 0.71\*\*\* PeCB -0.31 0.30 0.23 -1 0.25 1 SCCPs 0,23 -0.13 0.18 -0.05 0.21 -0.19 ---0.77\*\*\* 0.81\*\*\* 0.81\*\*\* 0.79\*\*\* 0.67\*\* HCB 0.14 0.52\* -0.24 1 ---0.45\* 0.82\*\*\* 0.52\* 0.50\* 0.51\* 0.27 0.24  $\Sigma_5 PBDEs$ -0.37 0.14 0.31 -1 -0.09 -0.64\*\* 0.27 0.58\*\* 0.55\*\* 0.53\* 0.65\*\* 0.13 0.82\*\*\* 0.68\*\*\*  $\Sigma_{31}$ PCBs 1 --

95 \*:p<0.05, \*\*: p<0.01,\*\*\*: p<0.001

96 n=24, except from: Σendosulfans and endosulfan sulfate (n=22), α-endosulfan (n=3), β-endosulfan (n=2), PeCB (n=19), SCCPs (n=8), HCB (n=20), Σ<sub>5</sub>PBDE and Σ<sub>31</sub>PCB (n=22)

97 All data were log-transformed with exception of latitude and land use).

1	2

Table A9: Results from correlation analysis with statistical significance for latitude, land use and individual compounds for WL soils in 2008.
 Samples which either (i) failed to meet the QA/QC criteria (low recovery etc.), (ii) were below method detection limit (MDL), or (iii)

1	0	2
- 1		( )
	•••	

qualified as outliers were not considered (see text for details)

Variables	Latitude	BD (g/cm <sup>3</sup> )	BC	SOM	$\Sigma$ endosulfans	endosulfan sulfate	α-endosulfan	β-endosulfan	PeCB	SCCPs	НСВ	$\Sigma_5$ PBDEs	$\Sigma_{31}$ PCBs
Latitude	1												
BD (g/cm <sup>3</sup> )	-0.15	1											
BC	-0.06	-0.41*	1										
SOM	0,13	-0.75***	0.42*	1									
$\Sigma$ endosulfans	0.04	-0.59***	0.35*	0.77***	1								
endosulfan sulfate	0.04	-0.60***	0.35*	0.77***	1.00***	1							
$\alpha$ -endosulfan	0.33	-0.69*	0.23	0.92***	0.92***	0.92***	1						
$\beta$ -endosulfan	-0.07	-0.25	0.20	0.63*	0.90***	0.90***	0.86***	1					
PeCB	-0.11	-0.51**	0.41*	0.61***	0.65***	0.65***	0.001	0.01	1				
SCCPs	-0.32	-0.11	0.08	0.18	-0.10	-0.10	-0.48	0.07	0.40	1			
НСВ	0.34	-0.80***	0.48*	0.83***	0,70	0.70***	0.72***	0.70***	0.49**	-0.04	1		
$\Sigma_5 PBDEs$	-0.72***	-0.31	0.31	0.37*	0.70***	0.30	0.33	0.35*	0.43*	0.20	0.27	1	
$\Sigma_{31}$ PCBs	-0.00009	-0.68***	0.60***	0.73***	0.64***	0.64***	0.67***	0.77***	0.43*	0.04	0.76***	0.40*	1
*:p<0.05, **: p<0.01,	***: p<0.00	1											

101

102 n=34, except from:  $\Sigma$  endosulfans and endosulfan sulfate (n=33),  $\alpha$ -endosulfan (n=10),  $\beta$ -endosulfan (n=14), PeCB (n=32), SCCPs (n=14), HCB (n=27),  $\Sigma_5$ PBDE and  $\Sigma_{31}$ PCB (n=33)

103 All data were log-transformed with exception of latitude and land use

#### 104 **2. Text**

#### 105 **2.1. Drying and sieving**

Wet soil samples from (18-89 gram) (see Table A1), were placed on alumina foil (WrapFilm 106 Systems Ltd, Telford, UK) and weighted prior to drying in an oven (Heraeus, UT 6120) WVR, 107 Hanau (Offenbach, Germany) at approximately 27 °C. In order to obtain completely dry 108 109 samples, the soil was regularly weighted until stable weight was reached, which were obtained within approximately two weeks. To further assure complete dryness, the soil 110 111 samples were placed in a desiccator for minimum one hour, and the weighting was repeated. Moreover, for evaluation of possible contamination during the drying process, 112 parallels of diatomaceous earth (DE) was "dried" with the soil samples, and analysed as 113 method blanks. There were no indications of contamination, hence the blank values were 114 115 low (Table A4 and A2.5). Completely dry soil samples were further sieved (mesh size 2 mm diameter, Retsch GmbH, Haan, Germany). The sieve was cleaned with acetone and *n*-hexane 116 117 between each sample. Dried, sieved soil samples were stored in brown glass bottle covered 118 with alumina foil and a PP-lid (VWR, Rommen, Norway) in order to protect potential light 119 sensitive compounds, and stored in a fridge until further sample preparation.

120 **2.2. Sample preparation** 

Solvents used for extraction and clean-up (aceton, *n*-hexane, and *iso*-octane) were of Suprapur grade from SupraSolv, Merck (Darmstadt, Germany). Diethyl ether (glass distilled grade), was obtained from Rathburn (Walkerburn, Scotland). Sulphuric acid and adsorbents used for clean-up and extraction, i.e. Florisil PR (0.15-0.25 mm (60/100 mesh), silica gel (0.063-0.20 mm) and anhydrous sodium sulfate was also obtained from Merck (Darmstadt, Germany). DE was purchased from Dionex, ASE<sup>®</sup> Prep DE (SunnyVale, CA, USA).

127

### 2.2.1. Accelerated solvent extraction (ASE)

Extraction of the soil samples were performed by use of a Dionex Accelerated Solvent Extractor unit (California, USA). The soil samples were placed in a 33 mL cells, and the cells were packed as shown in Figure A2. By use of florisil, the ASE procedure provides clean-up in addition to extraction of the samples. In order to achieve a porous sample for enhancement of the extraction, the soil samples should contain  $\geq$  25 % of DE, which were mixed with the individual soil samples, generating a soil/25% DE mixture. Furthermore, internal standards (A2.3) were added on top of the soil/25% DE mixture in the cell, before filling the cell with

only DE (Figure A2). The samples were extracted by use of acetone/n-hexane: 1/1 (w/w) as a
solvent. The samples were extracted with four cycles, 80 % flush volume and with pressure
(N<sub>2</sub> gas) and temperature, 1500 Psi and 100 °C, respectively.

#### 138 **2.2.2.** Clean-up

The samples were analysed for  $\Sigma$ endosulfans ( $\alpha$ -endosulfan,  $\beta$ -endosulfan and endosulfan 139 140 sulfate), pentachlorobenzene (PeCB) and short-chain chlorinated paraffins (SCCPs), and a comprehensive clean-up procedure were needed. As illustrated in Figure A3, the ASE 141 extracts were divided into two equal aliquots, with solely silica fractionation for compounds 142 degraded by concentrated sulphuric acid ( $\Sigma$ endosulfans), and acid treatment together with 143 silica fractionation for the acid stable fraction (PeCB and SCCPs). For endosulfan analysis 144 145 (see Figure A3) one aliquot was reduced to 0.5 mL followed by clean-up by fractionation 146 with a silica column. For more information concerning the silica method, see Halse et al., (2011). It was required to have two separate fractions to collect the various  $\Sigma$  endosulfans. 147 The first fraction was eluted with 30 ml *n*-hexane/10 % diethyl ether and was analysed for  $\alpha$ -148 endosulfan, while the second fraction was eluted with additionally 20 mL n-hexane/10 % 149 diethyl ether and was analysed for both  $\beta$ -endosulfan and endosulfan sulfate (see A2.4). 150

For analysis of PeCB and SCCPs, the respective aliquot (Fig. A3) was reduced to 0.5 mL by evaporation. Hereafter, the extract was transferred to a centrifuge tube, adjusted to 2 mL, and treated with 2 mL concentrated sulphuric acid (Halse et al., 2011). After final sulphuric acid treatment, the extracts were reduced to 0.5 mL for further clean-up by fractionation with a silica column (Halse et al., 2011). All final fractions were reduced to approximately 0.5 mL and solvent exchange to *iso*-octane and transferred to a small vial with a screw-cap.

Before analyses, the extracts were reduced to approximately 50 μL by nitrogen (5.0 Ultra, Yarapraxair, Haugenstua, Norway) and recovery standard (A2.3). Some extracts of the second fraction were exposed to precipitation, hence it was necessary to centrifuge (Jouan CR3, DJB Labcare Ltd, Buckinghamshire, UK) these samples at 1900 revolutions per minute (rpm) for 10 minutes prior to transferring the sample to a new vial.

#### 162 **2.3.** Analysis

163 For quantification and also for monitoring the recovery rates for the sample treatment, all 164 the samples were added a mixture containing 50  $\mu$ L of different internal standard prior to

extraction and clean-up. The internal standards consist of  ${}^{13}C-\alpha$ -endosulfan,  ${}^{13}C-\beta$ -165 endosulfan, <sup>13</sup>C-endosulfan sulfate, <sup>13</sup>C-pentachlorobenzene and <sup>13</sup>C-*cis*-chlordane, to 166 monitor the endosulfans, PeCB and SCCP, respectively. Several <sup>13</sup>C-labeled standards were 167 168 added for parallel analysis of other compounds. However since the method blanks prove that the <sup>13</sup>C-labeled compounds did not interfere with the measurements, the completed 169 list is not given here. All standards were purchased from LGC, formerly Promochem AB 170 171 (Borås, Sweden). In order to quantify the recovery of the internal standards, the extracts were added recovery standards. All extracts were added 20 µL of TCN (1,2,3,4-172 173 tetrachloronaphtalene), as recovery standard.

174 Analysis of the  $\Sigma$ endosulfans was carried out by a high resolution gas chromatography on an Agilent 6890N gas chromatograph coupled to an Autospec operating at accelerated voltage 175 of 6000 Volt in electron capture negative ion (ECNI) mode (80eV) (GC/HRMS(ECNI)). The 176 177 endosulfan isomers were separated using an Ultra 2 (25 m×0.2 mm inner diameter, 0,11 μm 178 film thickness (J&W Scientific)) fused silica capillary column (see Table A2). With helium as a 179 carrier gas (flow rate 0,9 mL/min), the GC operated in splitless mode (Halse et al., 2011). See 180 Table A2 for more detailed information concerning the temperature program. The 181 endosulfan isomers were monitored at mass/charge ratio (m/z) of the molecular ions [M]<sup>-</sup>. 182 The m/z ratio for the selected ions were 405.8139/407.8110 ( $^{12}$ C  $\alpha$ ,  $\beta$ -endosulfan), and 183 385.8322/387.8292 ( $^{12}$ C endosulfan sulfate) and 414.8441/416.8412 ( $^{13}$ C  $\alpha$ ,  $\beta$ -endosulfan) and 394.8624/396.8594 for <sup>13</sup>C labelled endosulfan sulfate. The sum of the area of the two 184 185 monitored ions was used in the quantification and the ratio between the two ions was used for verification. The ion ratio between the isotope signals should be within 20 % of the 186 187 theoretical value.

188 The PeCB was analysed with an Agilent 6890N gas chromatograph coupled to a high 189 resolution mass spectrometer operating with accelerating voltage of 8000 Volt (Autospec-190 Ultima) in electron impact (EI) mode (37eV) (GC/HRMS(EI)). The column used was an Ultra 2 191 (25 m×0.11 mm inner diameter, 0,11 µm film thickness (J&W Scientific)) fused silica capillary 192 column. Along with the endosulfans, PeCB was injected to the GC operating in a splitless 193 mode with helium as the carrier gas (1ml/min). See Halse et al., (2011) for more details concerning the operating parameters. The temperature program is given in Table A2. The 194 PeCB component was monitored at m/z of the molecule ion [M]<sup>+</sup>. m/z of the selected ions 195

were 249.8491/251.8462 and 255.8693/257.8663 for the <sup>12</sup>C PeCB and <sup>13</sup>C labelled PeCB,
respectively. As for the endosulfans, the sum of the area of the two monitored ions was
used in the quantification and the ratio between the two ions was used for verification.

SCCPs were analysed with an Agilent 6890 gas chromatograph coupled to a VG AutoSpec, 199 high resolution mass spectrometer, operating at 6000 V in ECNI mode (GC/HRMS-ECNI). To 200 201 achieve necessary separation a Restek Rxi<sup>®</sup>-5ms (15 m×0.25 mm inner diameter, 0,25 µm film thickness), fused silica capillary column was used with a constant helium flow of 1 202 203 mL/min. The injector temperature was 260°C, see Table A2 for more detailed information 204 concerning the operating parameters. The MS operated in ECNI mode (80-120 eV) using methane at a pressure of  $2 \times 10^{-5}$  mbar as moderating gas. The SCCPs were identified by use 205 of the following m/z values (monitoring the  $[M-Cl]^-$  ions), 277.0084 ( $C_{10}Cl_5$ ), 291.0241 206 (C11Cl5), 314.9636 (C10Cl6), 360.9432 (C11Cl7), 374.9588 (C12Cl7), 380.8886 (C10Cl8), 394.9042 207 208 (C<sub>11</sub>Cl<sub>8</sub>), 408.9199 (C<sub>12</sub>Cl<sub>8</sub>), 422.9355 (C<sub>13</sub>Cl<sub>8</sub>), 430.8623 (C<sub>11</sub>Cl<sub>9</sub>) and 444.8779 (C<sub>12</sub>Cl<sub>9</sub>), with 209 273.9403 (<sup>13</sup>C-*cis*-chlordane) as the internal standard. The quantification of the SCCPs was 210 performed according to a method described by Tomy and co-workers (1997).

#### 211

#### 2.4. Method validation of the ASE extraction procedure

In order to evaluate the efficiency of the ASE extraction, e.g. the number of cycles, adequate 212 flush volume by monitoring the recovery rates, four ASE cells were filled with dried 213 background soil (W.L soil, Harestua, Norway) and spiked with internal standard (see section 214 A2.3). The ASE was furthermore programmed to run each individual sample twice, in order 215 216 to generate two ASE extracts of each sample (E1 and E2). All extracts were cleaned and prepared according to the same procedure as the collected soil samples (section A2.2.2). 217 218 Furthermore, to evaluate the extraction pattern of the various endosulfans, three clean-up 219 sub fractions of E1 and E2 were executed by adding increasing amount of solvent volume (n-220 hexane/10 % diethyl ether to the column. Hence, the first fraction contained 30 mL of eluent, the second fraction contained 20 mL of eluent, while the last fraction was added a 221 222 final volume of 20 mL eluent (see Fig. A3). Clean-up of the PeCB and the SCCPs extracts was carried out in accordance to section A2.2.2. 223

The average percentage recovery and standard deviation (SD) for sum of the individual extracts for the endosulfans of the first ASE extracts (E1) were 46±5%, 70±8%, 80±7% and

for the second extract (E2) 1.5±0.7%, 1.1±0.6% and 1±0.4% (E2), for  $\alpha$ -,  $\beta$ -endosulfan and 226 endosulfan sulfate, respectively. Results from the recovery test for the individual 227 endosulfans revealed that the recovery for  $\beta$ -endosulfan and endosulfan sulfate was 228 229 improved by adding more eluent. Unfortunately, increasing the amount of eluent will also 230 increase the possibility to wash out matrix compounds, and hence require separation of 231 more interfering matrix compounds. It was therefore decided to limit the number of fractions for which the recovery was within an optimum range i.e. 38-52%, 49-70%, 23-38% 232 for  $\alpha$ -endosulfan,  $\beta$ -endosulfan and endosulfan sulfate, respectively. Consequently two 233 234 clean-up fractions (30 mL and 20 mL) was the final solution for the endosulfans.

The average percentage recovery and SD for E1 and E2 for PeCB was 25±3% and 0.5±0.3%. Samples which were recognized with recovery < 10%, was removed from the data set. A low recovery is attributed to the higher volatility of this compound.

238 As <sup>13</sup>C-labeled 1,5,5,6,6,10-hexachlorodecane was not available when these soil samples 239 were prepared, the recovery for the SCCPs was monitored by use of *cis*-chlordane as an internal standard (Tomy et al., 1997). It should be kept in mind that SCCPs is a complex 240 241 mixture of chlorinated paraffins and is eluting over a wide range along the capillary column. The uncertainty are caused by several factors e.g. i) impossible to achieve complete peak 242 separation and ii) the internal standard (i.e. *cis*-chlordane) used may not be adequate due to 243 lack of knowledge regarding the individual response factors. The uncertainty in the 244 measurement for the SCCPs may accumulate to  $\pm 50\%$  (Sverko et al., 2012). The average 245 percentage of recovery and SD for E1 of  ${}^{13}C$  cis-chlordane was 46 ± 15%, while the average 246 247 recovery and SD for E2 was  $0.6 \pm 0.1\%$ .

248 Results for all soil samples revealed that some results had to be discarded due to 249 matrix related disturbances, i.e. the ion ratio was not satisfying. Hence, results for 250 endosulfan sulfate (n=2),  $\alpha$ -endosulfan (n=3),  $\beta$ -endosulfan (n=2) within the  $\Sigma$ endosulfans in 251 addition to PeCBs (n=1) and SCCPs (n=1) was removed.

Recoveries for all samples, including soil samples (not the method development samples) and blanks are presented in Table A3. For the various endosulfans, the range in the percentage of recovery varied between soil and blank samples. The sometimes low recovery for endosulfan sulfate for some soil sites (~ 6%), may be caused by reduced amount of

eluent added together with matrix related effects disturbing the fractionation potential in 256 the column. However, all three individual <sup>12</sup>C endosulfans have been monitored by <sup>13</sup>C 257 labelled internal standards. Consequently, the low recovery does not influence the 258 259 measured concentrations, but may increase the uncertainty in the measurements. 260 Concerning PeCB, the range of percentage recovery for the soil samples (11-107%) which 261 was somewhat wider compared to the recovery found for the blanks (9-48 %) (Table A3). For PeCB, a few soil samples with recovery <10% (n=5) were removed from the data-set. 262 Recovery for the SCCPs was monitored by use of *cis*-chlordane, and it was assumed that loss 263 264 of SCCPs reflects loss of *cis*-chlordane. Selected soil samples were quantified for *cis*-clordane 265 and the average percentage recovery varied between 37-68% (see Table A3).

266

#### 2.5. Blanks and method detection limit (MDL)

Method blanks (n=5) consisting of DE were "dried", cleaned-up and analysed following the 267 same preparation and quantification method as used for the soil samples (section A2.1-268 A2.3). Table A4 provides information regarding the levels found in the blank samples. The 269 concentrations found in the DE samples were all at the same level. The method detection 270 271 limit (MDL) was calculated as the average concentration found in the blank samples plus 272 three times the SD. When the target compounds were not detected in the blank samples, an 273 instrumental detection limit (IDL) was used (Halse et al., 2011). Furthermore, when the target compounds were not detected in soil samples or fell below the calculated MDL, ½ of 274 the MDL value normalized on the site specific SOM values was used for statistical 275 summaries. See table A5 for the individual sites with concentrations below MDL. 276

277

### 2.6. Determination of soil parameters

The content of soil organic matter (SOM) was determined by loss on ignition (LOI) at 550 °C. 278 279 1-10 gram of the individual soil samples were weighed out and placed in a muffle furnace 280 for 4 hours. Further, after being cooled properly, the soil samples were placed in a desiccator and re-weighed after 30 minutes. Percentage LOI was determined using the ratio 281 between the loss and the initial weight of the sample. Other parameters of the soil samples 282 283 have been characterized in a former study, and information concerning the bulk density and black carbon (BC), together with temperature values was obtained from Schuster and co-284 285 authors (2011).

#### 286 **2.7. Partitioning and fate in soil**

Following Wong and Wania (2011), we have mapped the equilibrium distribution and 287 mobility potential in soils of selected POPs. Figure 1a) shows the equilibrium phase 288 289 distribution plot of log K<sub>OA</sub> vs log K<sub>AW</sub> (note: as log K<sub>OW</sub> = log K<sub>OA</sub> + log K<sub>AW</sub>, log K<sub>OW</sub> appears as 290 diagonal bands). Data on physical-chemical properties for selected POPs (PCBs, PBDEs, HCB, 291 individual endosulfans, PeCB and SCCPs) used to create these plots were taken from the 292 literature (European Commision Joint Research centre, 1999; Li et al., 2003; Shen et al., 293 2005; US EPA, 2011; Wania and Dugani, 2003). Concerning the phase distribution of the SCCPs, two sets of data was used. One was the EU risk assessment approach (EU-RAR) 294 (European Commision Joint Research centre, 1999), which contains of an average set of 295 296 SCCP properties, shown as RAR in Figure 1., and the other approach includes a wide range of 297 physical-chemical properties going from the  $C_{10}Cl_2$  to  $C_{13}Cl_{12}$ , using data from Gawor et al. 298 (2013). If found in soils, organic contaminants which are located in the upper left region in 299 Figure 1a) will favor the air-filled pores, while substances located in the lower left region will 300 have a preference to be solved in the water phase while chemicals located in the upper right region will have a strong affinity for sorption to organic solids. Figure 1b, presents the 301 302 mobility potential of selected POPs in soils. In Figure 1b, we have instead plotted log Koc vs log K<sub>AW</sub>, (assuming K<sub>OC</sub>=0.35\*K<sub>OW</sub> (Seth et al., 1999)). In this plot, components located in the 303 304 upper left are more prone to vaporization, whereas components located in the lower left 305 region are more prone to leaching, while components in the lower right are most prone to erosion. As demonstrated by Wong and Wania (2011) it is possible to use the equilibrium 306 phase distribution plot to estimate the percentages of chemical which resides in the air- and 307 308 water-filled pore space as well as the percentage sorbed to organic solids for a given soil with certain characteristics (e.g. SOM content) at a specific temperature and water content 309 310 (Wong and Wania, 2011). This can also be done for the mobility plot (Fig. 1b), yet requires various mass transfer coefficients to be specified. However, as our study deals with multiple 311 312 sites and soil conditions, such calculations have not been attempted as we are only interested in how these POPs are positioned relative to each other in order to compare how 313 314 different POPs are expected to distribute and behave in soils. For a more detailed discussion, we refer to Wong and Wania (2011). 315

#### 316 **2.8. Statistical analysis**

In order to evaluate any linear relationship between two variables, Persons correlation (r) 317 was estimated in Excel. Along with this, an significance value (p) for each correlation was 318 319 also calculated, based in Student's t-distribution. Various sample groups were tested in 320 order to evaluate if the correlation was significant or not, by testing the null hypothesis. The null hypothesis states that the difference in the mean of the datasets tested, was zero. A 321 322 two tailed t-test was implemented due to the datasets tested was both higher and lower compared to each other. If the p-value was lower than 0.05 (p<0.05), the datasets tested 323 was significantly different from each other, and the null-hypothesis could be rejected. 324 Similar, if the p-value was above 0.05 (p>0.05), the dataset tested was not significantly 325 326 different from each other and the null hypothesis could not be rejected.

#### 327 **2.8.1.Outliers**

The z-score was calculated for individual compounds as the ratio between the observed 328 value and the average value, divided by the standard deviation. Four sites were identified 329 with outliers for one or more compounds or compound groups. For Okehampton (WL, UK), 330 the concentration of  $\Sigma_5$ PBDEs was 1.817 ng/g dw (z=3.2). The concentration for PeCB at 331 Birkenes (WL, Norway) was 1.359 ng/g dw (z=3.02), and the concentration of SCCPs at 332 Tamokdalen (GL, Norway) was 280 ng/g dw (z=3.7). Onsøy (WL, Norway) was identified with 333 334 outliers for several compounds, i.e.  $\Sigma$ endosulfans, endosulfan sulfate,  $\beta$ -endosulfan, and 335  $\Sigma_{31}$ PCB was 24.671 ng/g dw (z=5.9), 23.902 (z=5.9) ng/g dw, 0.706 ng/g dw (z=3.6) and 25.130 ng/g dw (z=4.8), respectively. Consequently these observations were excluded from 336 the correlation analysis and the figures. 337

# 3. Figures



Figure A1 Map showing sampling sites in UK and Norway. (Schuster et al., 2011)

Figure A2 ASE cell with sample and packing material (DE and florisil)



Figure A<sub>3</sub> Flowchart for the clean-up and quantification.



### 4. References

- Borghini, F., Grimalt, J. O., Sanchez-Hernandez, J. C., and Bargagli, R. (2005). Organochlorine pollutants in soils and mosses from Victoria Land (Antarctica). *Chemosphere* **58**, 271-278.
- European Commision Joint Research centre (1999). "European Union Risk Assessment Report."
- Gawor, A., and Wania, F. (2013). Using quantitative structural property relationships, chemical fate models, and the chemical partitioning space to investigate the potential for long range transport and bioaccumulation of complex halogenated chemical mixtures. *Environmental Science-Processes & Impacts* **15**, 1671-1684.
- Halse, A. K., Schlabach, M., Eckhardt, S., Sweetman, A., Jones, K. C., and Breivik, K. (2011). Spatial variability of POPs in European background air. *Atmospheric Chemistry and Physics* 11, 1549-1564.
- Li, N. Q., Wania, F., Lei, Y. D., and Daly, G. L. (2003). A comprehensive and critical compilation, evaluation, and selection of physical-chemical property data for selected polychlorinated biphenyls. *Journal of Physical and Chemical Reference Data* **32**, 1545-1590.
- Roots, O., Roose, A., Kull, A., Holoubek, I., Cupr, P., and Klanova, J. (2010). Distribution pattern of PCBs, HCB and PeCB using passive air and soil sampling in Estonia. *Environmental Science and Pollution Research* **17**, 740-749.
- Schuster, J. K., Gioia, R., Moeckel, C., Agarwal, T., Bucheli, T. D., Breivik, K., Steinnes, E., and Jones, K. C. (2011). Has the Burden and Distribution of PCBs and PBDEs Changed in European Background Soils between 1998 and 2008? Implications for Sources and Processes. *Environmental Science & Technology* 45, 7291-7297.
- Seth, R., Mackay, D., and Muncke, J. (1999). Estimating the organic carbon partition coefficient and its variability for hydrophobic chemicals. *Environmental Science & Technology* **33**, 2390-2394.
- Shen, L., Wania, F., Lei, Y. D., Teixeira, C., Muir, D. C. G., and Bidleman, T. F. (2005). Atmospheric distribution and long-range transport behavior of organochlorine pesticides in north America. *Environmental Science & Technology* **39**, 409-420.
- Sverko, E., Tomy, G. T., Marvin, C. H., and Muir, D. C. G. (2012). Improving the Quality of Environmental Measurements on Short Chain Chlorinated Paraffins to Support Global Regulatory Efforts. *Environmental Science & Technology* **46**, 4697-4698.
- Tomy, G. T., Stern, G. A., Muir, D. C. G., Fisk, A. T., Cymbalisty, C. D., and Westmore, J. B. (1997). Quantifying C-10-C-13 polychloroalkanes in environmental samples by high-resolution gas chromatography electron capture negative ion high resolution mass spectrometry. *Analytical Chemistry* 69, 2762-2771.
- US EPA (2011). Estimation Programs Interface Suite(TM) for Microsoft WIndows, v 4.1.
- Wang, X. T., Zhang, Y., Miao, Y., Ma, L. L., Li, Y. C., Chang, Y. Y., and Wu, M. H. (2013). Short-chain chlorinated paraffins (SCCPs) in surface soil from a background area in China: occurrence, distribution, and congener profiles. *Environmental Science and Pollution Research* 20, 4742-4749.
- Wania, F., and Dugani, C. B. (2003). Assessing the long-range transport potential of polybrominated diphenyl ethers: A comparison of four multimedia models. *Environmental Toxicology and Chemistry* **22**, 1252-1261.
- Wong, F., Robson, M., Diamond, M. L., Harrad, S., and Truong, J. (2009). Concentrations and chiral signatures of POPs in soils and sediments: A comparative urban versus rural study in Canada and UK. *Chemosphere* **74**, 404-411.

- Wong, F., and Wania, F. (2011). Visualising the equilibrium distribution and mobility of organic contaminants in soil using the chemical partitioning space. *Journal of Environmental Monitoring* 13, 1569-1578.
- Zhao, Z., Zeng, H., Wu, J., and Zhang, L. (2013). Organochlorine pesticide (OCP) residues in mountain soils from Tajikistan. *Environmental Science-Processes & Impacts* **15**, 608-616.