

SUPPORTING INFORMATION

for

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Spatial variability of POPs in European background air

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Tables

Table S1 Site description and details.

Country	EMEP sites	Station name	Latitude	Longitude	M.a.s.l ⁵⁾	Sample start	Sample end	Sampling rate (m ³ day ⁻¹)	PRCs ¹⁾
Austria	X	Illmitz	N 47°46	E 16°46	117	27.07.06	02.11.06	4.93	5
Austria	X	Vorhegg	N 46°40	E 12°58	1020	18.07.06	23.10.06	4.69	5
Belgium	-	Koksijde	N 51°07	E 02°29	7	04.07.06	03.10.06	3.48	6
Bulgaria	-	Moussala	N 42°11	E 23°35	2925	06.07.06	05.10.06	11.07 ³⁾	5
Croatia	X	Zavizan	N 44°49	E 14°59	1594	10.07.06	10.10.06	17.88 ³⁾	6
Cyprus	-	Ayia Marina	N 33°02	E 33°03	532	29.06.06	02.10.06	5.30	6
Czech Rep	X	Košetice	N 49°35	E 15°05	534	12.07.06	12.10.06	3.59/3.97 ⁴⁾	5/5 ⁴⁾
Czech Rep	X	Svratouch	N 49°44	E 16°02	737	13.07.06	13.10.06	3.72	5
Denmark	X	Tange	N 56°21	E 09°36	13	07.07.06	06.10.06	3.03	5
Denmark	X	Keldsnor	N 54°44	E 10°44	10	11.07.06	19.10.06	3.12	6
Denmark	X	Anholt	N 56°43	E 11°31	40	06.07.06	06.10.06	4.52	6
Denmark	X	Lille Valby	N 55°41	E 12°08	10	13.07.06	13.10.06	4.32	6
Estonia	X	Laheema	N 59°30	E 25°54	32	06.07.06	10.10.06	3.83	6
Färoe Islands	-	Norðuri á Fossum	N 62°11	W 07°12	~300	01.07.06	02.10.06	4.61	3
Finland	X	Pallas	N 67°58	E 24°07	566	19.07.06	19.10.06	2.80/4.45 ⁴⁾	2/4 ⁴⁾
Finland	X	Ähtari	N 62°33	E 24°13	162	01.07.06	02.10.06	3.78	6
Finland	X	Utö	N 59°47	E 21°23	7	30.06.06	02.10.06	8.10	6
Finland	X	Virolahti	N 60°31	E 27°41	4	01.07.06	01.10.06	4.51	6
Finland	X	Oulanka	N 66°19	E 29°24	310	30.06.06	30.09.06	4.18	5
Finland	X	Hailuoto	N 65°00	E 24°41	4	04.07.06	03.10.06	4.19	6
France	X	Donon	N 48°30	E 07°08	775	05.07.06	05.10.06	3.95	6
France	X	Peyrusse Vieille	N 47°37	E 00°11	236	11.07.06	10.10.06	4.23	6
France	X	La Tardiere	N 46°39	W 00°45	133	04.07.06	03.10.06	4.03	6
France	X	Le Casset	N 45°00	E 06°28	1750	04.07.06	03.10.06	3.96	5
France	X	Porspoder	N 48°31	E 04°45	50	10.07.06	16.10.06	7.31	6
Germany	X	Westerland	N 54°56	E 08°19	12	07.07.06	09.10.06	5.01	6
Germany	X	Schmücke	N 50°39	E 10°46	937	10.07.06	10.10.06	2.99	4

Germany	X	Zingst	N54°26	E 12°44	1	10.07.06	09.10.06	4.01	6
Germany	X	Schauinsland	N 47°54	E 07°54	1205	10.07.06	10.10.06	3.75	5
Germany	X	Neuglobsow	N 53°09	E 13°02	62	24.07.06	24.10.06	3.29	6
Greece	X	Aliartos	N 38°22	E 23°05	110	11.07.06	12.10.06	3.42	6
Greenland	-	Nuuk	N 64°11	W 51°44	~5	04.07.06	08.10.06	3.50 ²⁾	-
Greenland	-	Summit	N 72°52	W 38°46	3250	28.07.06	20.10.06	3.50 ²⁾	-
Hungary	X	K-puszt	N 46°58	E 19°35	125	18.07.06	19.10.06	3.45	5
Iceland	X	Stórhöfði	N 63°27	W 20°15	118	11.07.06	08.10.06	11.53/10.90	6/6
Ireland	X	Mace Head	N 53°20	W 09°54	25	10.07.06	18.10.06	7.90	6
Ireland	-	Malin Head	N 55°22	W 07°20	22	06.07.06	08.10.06	5.86	6
Ireland	-	Carnsore Point	N 52°11	W 06°22	9	19.07.06	11.10.06	9.51	6
Italy	X	Ispra	N 45°48	E 08°38	209	07.09.06	04.12.06	4.13	2
Italy	X	Montelibretti	N 42°06	E 12°38	48	03.07.06	20.09.06	3.63	6
Italy	-	Longobucco	N 39°39	E 16°61	1379	28.07.06	07.11.06	3.02 ³⁾	4
Italy	-	San Lucido	N 39°19	E 16°02	49	27.07.06	13.11.06	2.88	6
Kazakhstan	-	Borovoye	N 44°08	E 75°51	~300	15.08.06	17.11.06	2.07	2
Latvia	X	Rucava	N 56°13	E 21°13	18	17.07.06	17.10.06	3.55	5
Latvia	X	Zoseni	N 57°08	E 25°55	183	17.07.06	17.10.06	3.49	5
Lithuania	X	Preila	N 55°21	E 21°04	5	22.07.06	01.10.06	4.91	6
Lithuania	-	Rugstelis	N 55°26	E 26°04	120	15.07.06	30.09.06	2.56	2
Malta	X	Giordan lighthouse	N 36°06	E 14°12	160	02.08.06	07.11.06	6.90	6
Moldova	X	Leovo	N 46°30	E 28°16	156	10.07.06	10.10.06	4.60	4
Netherlands	X	Kollumerwaard	N 53°20	E 06°17	0	26.07.06	22.11.06	5.77	6
Netherlands	X	Vredepeel	N 51°32	E 05°51	28	25.07.06	21.11.06	5.69	5
Norway	X	Birkenes	N 58°23	E 08°15	190	02.07.06	01.10.06	3.03/3.58 ⁴⁾	5/6 ⁴⁾
Norway	X	Tustervatn	N 65°50	E 13°55	439	28.06.06	09.10.06	4.03	4
Norway	X	Kårvatn	N 62°47	E 08°53	210	29.06.06	10.10.06	3.88	6
Norway	X	Spitsbergen	N 78°54	E 11°53	474	14.07.06	26.09.06	3.50/3.50 ²⁾	-/ ⁴⁾
Norway	X	Hurdal	N 60°22	E 11°04	300	01.07.06	02.10.06	3.59	5
Norway	X	Karasjok	N 69°28	E 25°13	333	26.06.06	29.09.06	4.34	6
Poland	X	Diabla Gora	N 54°09	E 22°04	157	06.07.06	06.10.06	4.92	5
Poland	X	Jarczew	N 51°19	E 21°59	180	01.07.06	02.10.06	4.05	6

Poland	X	Sniezka	N 50°44	E 15°44	1604	10.07.06	10.10.06	3.50 ²⁾	-
Poland	X	Leba	N 54°45	E 17°32	2	13.07.06	13.10.06	4.40	6
Portugal	X	Bragança	N 41°49	W 06°46	691	19.07.06	19.10.06	4.44	6
Portugal	X	Monte Velho	N 38°05	W 08°48	43	19.07.06	19.10.06	3.29	6
Slovakia	X	Chopok	N 48°56	E 19°35	2008	02.07.06	03.10.06	19.18 ³⁾	5
Slovakia	X	Starina	N 49°03	E 22°16	345	04.07.06	04.10.06	4.23	5
Slovenia	X	Iskrba	N 45°34	E 14°52	520	07.07.06	06.10.06	3.53	5
Spain	X	Víznar	N 37°14	W 03°32	1265	14.07.06	14.10.06	4.34	6
Spain	X	Niembro	N 43°27	W 04°51	134	12.07.06	12.10.06	5.63	6
Spain	X	Els Torms	N 41°24	E 00°43	470	15.07.06	15.10.06	3.55	6
Spain	X	Risco Llamio	N 39°31	W 04°21	1241	13.07.06	13.10.06	3.63	6
Sweden	X	Råö	N 57°24	E 11°55	5	04.07.06	02.10.06	8.33/6.24 ⁴⁾	6/6 ⁴⁾
Sweden	X	Aspvreten	N 58°48	E 17°23	20	06.07.06	06.10.06	1.66	2
Sweden	X	Vavihill	N 56°01	E 13°09	172	11.07.06	08.10.06	3.47	5
Sweden	X	Bredkälen	N 63°51	E 15°20	404	06.06.06	06.09.06	2.56	3
Sweden	X	Hoburg	N 56°55	E 18°09	58	30.06.06	03.10.06	6.71	6
Sweden	-	Abisko	N 68°21	E 18°49	~385	06.07.06	11.10.06	6.11	6
Sweden	X	Vindeln	N 64°15	E 19°46	225	28.06.06	28.09.06	3.41	6
Switzerland	X	Jungfrauoch	N 46°33	E 07°59	3573	06.07.06	13.10.06	8.0 ³⁾	5
Switzerland	X	Payerne	N 46°48	E 06°57	510	05.07.06	11.10.06	3.42	5
Ukraine	-	Zmeiny Island	N 45°15	E 30°12	n.a.	17.07.06	08.11.06	7.58	5
United Kingdom	X	Harwell	N 51°34	W 01°19	137	05.07.06	09.10.06	3.92	6
United Kingdom	-	Auchencorth Moss	N 55°80	W 03°20	255	03.07.06	13.10.06	3.75	4
United Kingdom	X	Lough Navar	N 54°26	W 07°54	126	03.07.06	11.10.06	3.97	6
United Kingdom	X	Yarner Wood	N 50°36	W 03°43	119	30.06.06	02.10.06	3.90	6
United Kingdom	X	High Muffles	N 54°20	W 00°48	267	05.07.06	04.10.06	2.89	4
United Kingdom	X	Strath Vaich Dam	N 57°44	W 04°46	270	30.06.06	02.10.06	4.25	6

1) Number of PRCs with more than 40 % loss during deployment. 2) No significant loss of PRCs, default value used. 3) Adjusted temperature as detailed in section 2. 4) Results for two PAS parallels: Sample A / Sample B. 5) Meters above sea level.

Table S2 Range in recoveries for the internal standard for exposed samples, field blanks, method blanks as well as PRCs for field and method blanks, respectively (in %).

Internal standards and PRCs	Range		
	Exposed samples	Field blank	Method blank
Metylnaphtalene-d ₁₀	24-45	29-40	31-40
Acenaphtene- d ₁₀	34-77	33-44	33-61
Antracene- d ₁₀	40-78	52-64	34-69
Pyrene- d ₁₀	49-91	61-71	51-83
Benz(a)anthracene- d ₁₂	53-137	75-93	27-111
Benz(e)pyrene- d ₁₂	54-126	76-85	66-96
Benzo(ghi)perylene- d ₁₂	50-114	64-81	41-96
¹³ C-PeCB	21-49	22-31	23-37
¹³ C-PCB (28)	48-89	55-72	62-79
¹³ C -PCB (52)	48-89	58-78	65-82
¹³ C -PCB (101)	59-104	74-90	80-97
¹³ C -PCB (105)	69-127	90-112	98-115
¹³ C -PCB (114)	66-124	85-105	90-110
¹³ C -PCB (118)	68-119	86-108	92-114
¹³ C -PCB (123)	64-127	88-108	92-112
¹³ C -PCB (153)	70-119	86-107	87-114
¹³ C -PCB (138)	74-125	93-115	100-116
¹³ C -PCB (167)	72-136	96-122	104-127
¹³ C -PCB (156)	73-137	103-124	107-129
¹³ C -PCB (157)	74-140	103-123	108-130
¹³ C -PCB (180)	76-129	99-120	100-125
¹³ C -PCB (189)	81-132	108-124	108-128
¹³ C -PCB (209)	76-129	102-119	107-127
¹³ C -HCB	30-63	27-37	34-47
¹³ C - <i>p,p'</i> -DDE	55-139	78-119	68-115
¹³ C - <i>p,p'</i> -DDT	32-218 ¹⁾	85-198 ¹⁾	77-119

¹³ C -α-HCH	32-118	31-48	35-67
¹³ C -β-HCH	19-117	45-76	61-88
¹³ C -γ-HCH	44-136	51-75	57-88
¹³ C -trans-Chlordane	42-122	70-94	71-122 ²⁾
¹³ C -trans-Nonachlor	29-121	33-44	43-121 ²⁾
¹³ C Mirex	11-132	74-116	73-160 ²⁾
PRCs			
d6-γ-HCH	-	86-103	72-106
PCB-12	-	73-94	76-107
PCB-14	-	61-80	69-100
PCB-23	-	72-85	74-103
PCB-30	-	57-74	66-90
PCB-32	-	78-91	81-105
PCB-107	-	87-100	75-110
PCB-198	-	80-93	75-116

- 1) Two sites showed higher recovery. Highest % recovery for the deployed samples was for one of the parallels at the Spitsbergen site, while the highest % recovery for the field blanks occurred for the Košetice site.
- 2) The higher recovery originates from one method blank

Table S3 Instrumental parameters for analysis of the compound groups.

Compound groups	Type of instrument	Type of column	Column size	Carrier gas	Operational parameters	
					Temp.interv.	Target ion
PCBs & HCB	GC/HRMS in EI mode (Agilent6890 GC coupled to Waters AutoSpec)	Fused silica capillary column from SGE	HT-8, 50 m length, 0.22 mm I.D, 0.15 mm film thickness	Helium	Start (°C): 90 (2 min.) Intervall 1: 25°C/min to 170°C Intervall 2: 308°C by 3°C/min Injector temp. (°C): 280	[M] ⁺
HCHs & DDTs	GC/HRMS in EI mode (Agilent6890 GC coupled to Micromass AutoSpec).	Fused silica capillary column from J&W Scientific	HP-1, 25 m length, 0.2 mm I.D, 0.33 mm film thickness	Helium	Start (°C): 95 (1.5 min.) Intervall: 280°C by 20°C/min (5 min.) Injector temp. (°C): 220	[M] ⁺
PAHs	GC/LRMS in EI mode (Agilent6890 GC coupled to Agilent5973 MSD)	Fused silica capillary column from Zebron	ZB-5, 30 m length, 0.25 mm I.D, 0.10 mm film thickness	Helium	Start (°C):50 Intervall 1: 100°C/min by 20°C/min. Intervall 2: 320°C by 5°C/min Injector temp. (°C): 300	[M] ⁺
Chlordanes	GC/LRMS in ENCI mode, (Agilent6890 GC coupled to a Agilent5973 MSD)	Fused silica capillary column from J&W Scientific	Ultra 2, 25 m length, 0.2 mm I.D, 0.11 mm film thickness	Helium	Start (°C): 90 (2 min.) Intervall 1: 170°C by 20°C/min (3 min) Intervall 2: 235°C by 5°C/min (2 min.) Injector temp. (°C): 260	[M-Cl]- and [M-2Cl]-

Table S4 Relative deviations from the average value of two parallel PAS.

Compounds/compound- groups	Košetice CZ 0003R	Pallas FI 0096G	Stórhöfði IS 0019R	Birkenes NO 0001R	Spitsbergen NO 0042G	Råö SE 0014R
PCB-28	±1	±23	±8	±8	±46	±27
PCB-52	±1	±26	±7	±9	±19	±20
PCB-101	±6	±27	±5	±8	±10	±6
PCB-118	±7	±24	±1	±9	n.d.	±3
PCB-138	±7	±32	±1	±8	n.d.	±0,3
PCB-153	±8	n.d.	±3	±9	n.d.	±1
PCB-180	±12	±38	±12	±8	n.d.	±4
Σ_nPCBs	±4	±26 (n=6) ¹⁾	±4	±8	±30 (n=3) ¹⁾	±8
α-HCH	±7	±13	±1	±13	±6	±12
γ-HCH	±7	±15	±6	±13	±2	±18
<i>p,p'</i> -DDE	±9	n.d.	n.d.	n.d.	n.d.	±35
<i>p,p'</i> -DDD	±9	n.d.	n.d.	n.d.	n.d.	±23
<i>o,p'</i> -DDT	±6	n.d.	n.d.	±18	n.d.	±8
<i>p,p'</i> -DDT	±5	n.d.	n.d.	±13	n.d.	±24
Σ_nDDTs	±8	n.d.	n.d.	±15 (n= 2) ¹⁾	n.d.	±26
Fluorene	±9	±20	n.d.	±10	n.d.	±11
Phenanthrene	±2	±26	n.d.	±13	n.d.	±9
Anthracene	±0.02	n.d.	n.d.	n.d.	n.d.	n.d.
Fluoranthene	±8	±31	n.d.	±14	n.d.	±8
Pyrene	±8	±31	±15	±20	n.d.	±6
Benzo[a]pyrene	±12	n.d.	n.d.	n.d.	n.d.	n.d.
Benz[a]anthracene	±14	n.d.	n.d.	n.d.	n.d.	n.d.
Chrysene	±11	±36	n.d.	±8	n.d.	±10
Σ_nPAH	±2	±25 (n=5) ¹⁾	±15 (n=1) ¹⁾	±12 (n=5) ¹⁾	n.d.	±9 (n=5) ¹⁾
HCB	±2	±19	±1	±4	±22	±8

n.d.: one or both samples below MDL

¹⁾ Sum PCBs, DDTs and PAHs only include the sum of substances where both samples are above MDL (number in parantheses).

Table S5 Percentage deviation between PAS and AAS at EMEP sites $[(C_{PAS}-C_{AAS})/C_{AAS}]$. A positive deviation indicates higher concentrations in the PAS.

Compound/compound group	Košetice CZ CZ0003R		Birkenes NO 0001R		Stórhöfði IS 0019R		Spitsbergen NO 0042G	
		Råö SE 0014R		Aspvreten SE 0012 ¹⁾ R		Pallas FI 0096G		
PCB-28	69	49	-4	102	-77	-70	-54	
PCB-52	48	39	5	64	-48	-62	22	
PCB-101	178	40	24	-22	-37	-34	111	
PCB-118	56	47	-12	-30	50	-5	n.d.	
PCB-138	257	33	-13	4	11	-26	n.d.	
PCB-153	193	65	-24	34	35	n.d.	n.d.	
PCB-180	-27	66	-53	64	9	41	n.d.	
Σ_n PCB	86	47	-5	25	-51	-59 (n=6)	-35 (n=3)	
α -HCH	98	19	-43	154	318	-17	23	
γ -HCH	85	24	-48	54	-8	-30	22	
<i>p,p'</i> -DDE	264	63	n.a.	-34	n.d.	n.d.	n.d.	
<i>p,p'</i> -DDD	-39	-24	n.a.	n.a.	n.d.	n.d.	n.d.	
<i>p,p'</i> -DDT	577	10	n.a.	n.a.	n.d.	n.d.	n.d.	
Σ nDDTs	282 (n=3)	40 (n=3)	n.a.	-34 (n=1)	n.d.	n.d.	n.d.	
Phenanthrene	211	52	n.a.	109	n.a.	51	n.d.	
Anthracene	137	n.d.	n.a.	512	n.a.	n.d.	n.d.	
Fluoranthene	270	46	n.a.	13	n.a.	71	n.d.	
Pyrene	240	5	n.a.	-16	n.a.	32	n.d.	
Benzo[a]pyrene	-49	n.d.	n.a.	n.d.	n.a.	n.d.	n.d.	
Benz[a]anthracene	73	n.d.	n.a.	-47	n.a.	n.d.	n.d.	
Σ_n PAH	216 (n=6)	45 (n=3)	n.a.	76 (n=5)	n.a.	52 (n=3)	n.d.	
HCB	36	n.a.	-31	n.a.	1540	n.a.	34	
Sampling duration	1 day	2 weeks	1 day	1 week	2 weeks	1 week	2 days	
Sampling frequency	1x week	2x month	1x week	1x month	2x month	1x month	1x week	
Sampling coverage (%)	~14	~100	~14	~25	~100	~25	~29	

1) Only one PAS sample available for this site.

n.d. : Values below MDL in PAS. n.a. : no available data for the AAS

Table S6 Concentrations (pg/m³) of PCB-28 derived from AAS, PAS and the FLEXPART model for selected sites.

Country	Sites	AAS	PAS	Model	% deviation (Model/PAS)
Czech Republic	Košetice	6.51	10.98 ¹⁾	13.57	24
Finland	Pallas	4.12	1.25 ¹⁾	2.74	119
Iceland	Stórhöfði	4.22	0.96 ¹⁾	0.79	-18
Norway	Birkenes	2.13	2.04 ¹⁾	4.69	130
Norway	Spitsbergen	3.19	1.48 ¹⁾	0.26	-82
Sweden	Råö	3.15	4.68 ¹⁾	6.69	43
Sweden	Aspvreten	1.66	3.34	5.81	74
Ireland	Mace Head	n.d.	1.15	2.28	98
Ireland	Malin Head	n.d.	1.22	2.02	66
Italy	Longobucco	n.d.	1.58	10.36	556
Kazakhstan	Borovoye	n.d.	8.79	4.43	-50
Malta	Giordan lighthouse	n.d.	5.35	6.33	18
Poland	Jarczew	n.d.	6.85	9.81	43
Poland	Leba	n.d.	4.96	8.59	73
Spain	Víznar	n.d.	2.28	6.24	174
Spain	Els Torms	n.d.	2.67	7.11	166
United Kingdom	Strath Vaich Dam	n.d.	0.96	2.42	152

¹⁾ Average of two PAS

Text

S 1.1 Deployment and sample preparation

In the following, the solvents and sulfuric acid used for sample preparation and clean-up were of pesticide grade from Merck (Darmstadt, Germany), except diethyl ether which was purchased from Rathburn (Walkerburn, Scotland). Anhydrous sodium sulfate and silica gel were purchased from Merck (Darmstadt, Germany).

Prior to deployment, the PUF disks (14 cm in diameter, 1.35 cm thick, surface area 0.0364 m², density 2.47 10⁻² g/m³; Sunde Søm & Skumplast A/S, Gan, Norway) were pre-cleaned using Soxhlet extraction with toluene for 24 hours, with acetone for 8 hours and finally with toluene for new 8 hours. The PUF disks were then dried in desiccators at 40°C under vacuum until they were completely dry. The PUF disks were spiked with the following PRC mixture (PCBs 12, 14, 23, 30, 32, 107, 198 and d6 γ -HCH) by adding 25 μ L PRC mixture, with the respective concentrations; 189.4, 188.4, 188.4, 188.3, 193.6, 189.0, 187.9, 186.7 pg/ μ L, in 10 mL of pentane in a small vial. This solution was applied evenly on both sides of the PUF disk using a Pasteur pipette in a clean laboratory environment (class 100000 part/m³/ft). The PUF disks were placed on 3 short metal tubes to minimize the contact area during spiking. The spiked PUFs were next wrapped in double layers of alumina foil, double zip-lock bags and stored in a freezer until shipment. Pre-cleaning of the sampling chambers prior to shipment was carried out by soaking all the parts in soap solution over night, followed by rinsing in tap water and acetone. Each sampling kit was then packed in sealed plastic bags to avoid contamination during shipment.

S 1.2 Clean-up

In order to reduce sample contamination all laboratory equipment was rinsed with *n*-hexane immediately before use. The exposed PUF disks and field blanks were stored in a freezer until extraction and clean-up. Prior to extraction, the PUF disk were unwrapped in a clean-room laboratory environment, spiked with internal standards (see S 1.3), and placed in a Soxhlet

extractor. The disks were Soxhlet extracted for 8-10 hours in approximately 250 mL of *n*-hexane. Extracts were concentrated to about 0.5 mL on a TurboVap 500 System (Zymark, Hopkinton, MA, USA), and transferred to a graduated cylinder. Further sample treatment was done separately and the extracts were therefore divided into two identical aliquots.

The acid resistant part (PCBs, HCHs, DDTs, HCB, pesticides (trans-chlordane, cis-chlordane, trans-nonachlor, cis-nonachlor) of the extract was transferred to a centrifuge tube, adjusted to 2 mL, and treated with 2 mL concentrated sulfuric acid for mixing by vigorous whirling on a whirl mixer. During this treatment the extract turns color to dark yellow. The treatment was repeated until no more color change was visible (2-3 times). The extract was then transferred to an evaporation unit and reduced to 0.5 mL for further clean-up by fractionation with a silica column (15 mm in diameter and 200 mm in length). The column consists of 4 g of activated silica (Silica gel 60 Merck nr. 7734 0.063 – 0.200 mm pretreated 8 h at 550°C) topped with 1 cm anhydrous sodium sulfate (pretreated 12 h at 600°C). The column was prewashed with 30 mL *n*-hexane. The samples were eluted with 30 mL *n*-hexane/10 % diethyl ether. Extracts were reduced to 0.5 mL by evaporation and solvent exchanged into *iso*-octane and transferred to a small vial with a screw-cap.

The PAH part of the extract was solvent exchanged to cyclohexane and cleaned on a silica column (15 mm in diameter and 200 mm in length). This column consists of a slurry of 5 g deactivated silica (deactivated with 8% MilliQ water) and 15 mL cyclohexane overlaid with 1 cm anhydrous sodium sulfate. The column was prewashed with 40 mL cyclohexane. The sample was eluted with 100 mL cyclohexane, and the extract was reduced to 0.5 mL by evaporation and transferred to a small vial with a screw-cap.

Prior to analyses all extracts were further reduced to approximately 50 µL by a gentle stream of nitrogen.

S I.3 Analyses

In order to monitor recovery rates for the extraction and clean-up procedures, the PUF disk were added a mixture containing 20 µL of each internal standard prior to extraction and clean-up. This

standards consist of a range of ^{13}C – labeled polychlorinated biphenyls (PCB) congeners (^{13}C PCB-28,-52,-101,-105,-114,-118,-123,-138,-153,-156,-157,-167,-180,-189, -209) and organochlorine pesticides (OCPs) (^{13}C α , β , γ - hexachlorocyclohexane (HCH), ^{13}C -hexachlorobenzene (HCB), ^{13}C *p,p'*- dichlorodiphenyldichloroethylene (DDE) and ^{13}C *p,p'*-dichlorobiphenyldichloroethane (DDT), ^{13}C trans-nonachlor, ^{13}C trans-chlordane, ^{13}C dieldrine and ^{13}C Mirex). For the PAHs, a mixture of deuterium labeled polyaromatic hydrocarbons (PAH) congeners (2-methylnaphthalene- d_{10} , acenaphthene- d_{10} , anthracene- d_{10} , pyrene- d_{10} , benz(a)anthracene- d_{12} , benz(e)pyrene- d_{12} , benz(ghi)perylene- d_{12}), were added. All standards were purchased from LGC, formerly Promochem AB (Borås, Sweden). In order to quantify the recovery of the internal standards, the extracts were added recovery standards. 10 μL of recovery standard consisting of deuterated PAHs (biphenyl- d_{10} , fluorantene- d_{10} and perylene- d_{12}) were added to the PAH extracts, while 20 μL of a recovery standard (1.2.3.4-tetrachloronaphthalene) were added to the acid resistant extracts.

Analysis of the PCB congeners, α -HCH, β -HCH, γ -HCH, *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT and *p,p'*-DDT, HCB, together with the PRC compounds were performed with GC/HRMS on an Agilent 6890N gas chromatograph coupled to a Waters AutoSpec mass spectrometer in electron impact (EI) mode (Table S3). The different PCB congeners and some of the PRCs (PCB-23,-30,-32,-107,-198) were separated using a HT-8 (50 m \times 0.22 mm inner diameter (SGE)) fused silica capillary column (Table S3). The GC was operating in splitless mode with helium as a carrier gas. 1 μL was injected at an injector temperature on 280°C. See Table S3 for more detailed information concerning the temperature program. Separation of α -HCH, β -HCH, γ -HCH, *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT and *p,p'*-DDT, together with the PRCs (PCB-12,-14, D6 γ -HCH) compounds were done by use of a HP-1 (25 m \times 0.2 mm inner diameter (J&W Scientific)) fused silica column. 1 μL was injected by an autosampler on the split/splitless injection port in splitless mode with helium as a carrier gas (flow rate 1 mL/min). See Table S3 for detailed specification for the temperature program. During the GC run, *p,p'*-DDT could be thermally converted to *p,p'*-DDD and *p,p'*-DDE. This is eluded due to use of ^{13}C labeled *p,p'*-DDT as an internal standard. ^{13}C *p,p'*-DDT may format to ^{13}C -DDD/DDE, which are compounds that are not included in the internal standard. If the peak area of ^{13}C -DDD/DDE >5% of the peak area of ^{13}C *p,p'*-DDT, that result will be rejected.

Analysis of PAHs was carried out by a GC/LRMS on an Agilent 6890N gas chromatograph coupled to an Agilent 5973 mass spectrometer in an electron impact (EI) mode (Table S3). 1 µL was injected by an auto sampler on the split/splitless injection port in splitless mode with helium as a carrier gas (flow rate ~1 mL/min), with a temperature program as detailed in Table S3.

Analysis of the pesticides (trans-chlordane, cis-chlordane, trans-nonachlor, cis-nonachlor) was carried out by a GC/LRMS on a Agilent 6890N gas chromatograph coupled to a Agilent 5973 mass spectrometer in a electron capture negative ion (ENCI) mode. 1 µL was injected by an auto sampler on the split/splitless injection port in splitless mode with helium as a carrier gas (flow rate 1 mL/min). See Table S3 for the temperature program.

S 1.4 Internal standard recoveries

The internal standard recoveries for the deployed samples, field and method blanks, were to a large extent at the same level (Table S2), which address minimal matrix interferences from the deployed samples governed due to exposure. Nonetheless, some sites are experiencing higher recoveries for some of the internal standards. One of the parallels at the Spitsbergen site had a high percentage recovery for ¹³C *p,p'*-DDE. High recovery was also found for the field blank from Košetice for this internal standard.

S 1.5 PRC recoveries

The second recovery values were for the added mixture of PRCs. These values lie in the range of 57-116 % The range in percentage recovery is governed from each PRC (8) in the field and method blank individually (Table S2). The lower values in the range originates from PCB-30, which had to be corrected towards two internal standards (¹³C HCB and ¹³C PCB-28). The higher recovery values for one of the method blanks may be caused by adding too much of the PRC solution to the PUF-disk. i.e. when comparing the recoveries from the different compounds in the same sample, it seems to be over all a high compound recovery for this sample.

S 1.6 Duplicate passive air samplers at selected sites

Figure S2 (a-f) compares selected results for the six EMEP POPs sites where two samplers were co-located (Fig S1), while Table S4 additionally lists relative deviations, expressed as the percentage deviation from the average of these two parallels. The error bars in Fig. S2 are included to illustrate the uncertainty associated with the chemical analysis alone, which was estimated to be ~35 % (Section 3.4).

The relative deviation for PCBs between the two replicates was less than 10 % at four out of six sites and ranged from 4 % (Košetice, Stórhöfði) to 30 % for Σ_n PCBs (Spitsbergen) (Table S4). Among individual PCBs, larger differences tended to occur for substances and sites experiencing lower concentrations (Spitsbergen, Pallas). However, differences of 20% or more were also seen for PCB-28 and 52 at the Råö site (Table S4) in spite of the relatively high air concentrations at this site (Fig S2a). Differences in wind speed experienced between the two replicates may have contributed to some of the deviations observed (Tuduri et al., 2006). If the two parallels were subject to different effective windspeeds, then this would lead to differences in loss of PRCs and hence estimated sampling rates. The resulting site-specific sampling rates and ranges which could be determined for 5 out of 6 sites were: Košetice ($3.78 \text{ m}^3 \text{ day}^{-1} \pm 5.0\%$); Pallas ($3.63 \text{ m}^3 \text{ day}^{-1} \pm 22.8\%$); Stórhöfði ($11.22 \text{ m}^3 \text{ day}^{-1} \pm 2.8\%$); Birkenes ($3.31 \text{ m}^3 \text{ day}^{-1} \pm 8.3\%$) and Råö ($7.29 \text{ m}^3 \text{ day}^{-1} \pm 14.3\%$) (Table S1). Furthermore, sample A had a higher sampling rate than sample B for Stórhöfði and Råö, while sample B was higher than sample A for Košetice, Pallas and Råö. Among the sites for which site-specific sampling rates could be determined, larger differences in loss of PRCs were found at Pallas and Råö. Yet, while loss of 6 PRCs were used to estimate the sampling rate for both samples from Råö, only 2 and 4 PRCs were used for Pallas. Hence, we are less confident about the estimated sampling rate for Sample A from Pallas (Table S1) which, in turn, makes it difficult to conclude that the two parallels at Pallas were subject to significantly different windspeeds. The results for Råö rather suggest that the differences observed between the two parallels are more of an analytical character as sample A had a higher sampling rate in comparison to sample B while estimated air concentrations were consistently higher for sample A (Fig S2). Figure S2 (b,c) show results for α -HCH and γ -HCH. The relative deviations for α - and γ -HCH were always less than 20 % and ranged from 1 to 13 % and 2 to 18 %, respectively (Table S4). Figure S2d) shows the results for Σ_n DDTs where n varies between the sites. Both

replicates at Stórhöfði and Spitsbergen had concentrations below the MDL for all DDTs and are therefore not included in Fig. S2d). Concentrations under the MDL were also experienced at Birkenes and Pallas and hence a comparison for all four DDT isomers was only possible for Košetice and Råö. The larger deviations among the latter two sites were found for Råö where both the relative difference in sampling rates were larger and air concentrations much lower in comparison to Košetice (Fig. S2d). Figure S2e) shows the results for Σ_n PAHs, where n varies from 1 (Stórhöfði) to 8 (Košetice), while no comparison could be made for Spitsbergen. The relative deviation between the replicates ranged from 2 % (Košetice) to 25 % (Pallas) for Σ_n PAHs. The better agreement found for the Košetice (2 %) site (Table S4) may be attributed to the higher concentration of PAHs experienced at this site (Fig. S2e) in combination with a limited difference in sampling rates compared to Pallas. Figure S2f) shows the results for HCB. The difference between the two parallels ranged from 1 to 22 %. A very good agreement was found at Stórhöfði, Košetice, Birkenes and Råö with 1, 2, 4 and 8 % respectively, while larger discrepancies (~20 %) were observed at the northern sites at Pallas and Spitsbergen. In general, we conclude that there is a reasonable agreement between the two replicates for most substances, with a tendency for better agreement for those substances (e.g. HCHs, HCB) and sites (e.g. Košetice) which tend to experience higher concentrations in air.

160 **References**

161 Tuduri, L., Harner, T., and Hung, H.: Polyurethane foam (PUF) disks passive air samplers: Wind effect on
162 sampling rates, *Environmental Pollution*, 144, 377-383, 10.1016/j.envpol.2005.12.047, 2006.

163

164

Figures

Figure S1 EMEP POP measurement network, showing sites for which both air and precipitation measurements are carried out. Sites presented with names are localities for which POPs were monitored in air using AAS in 2006.

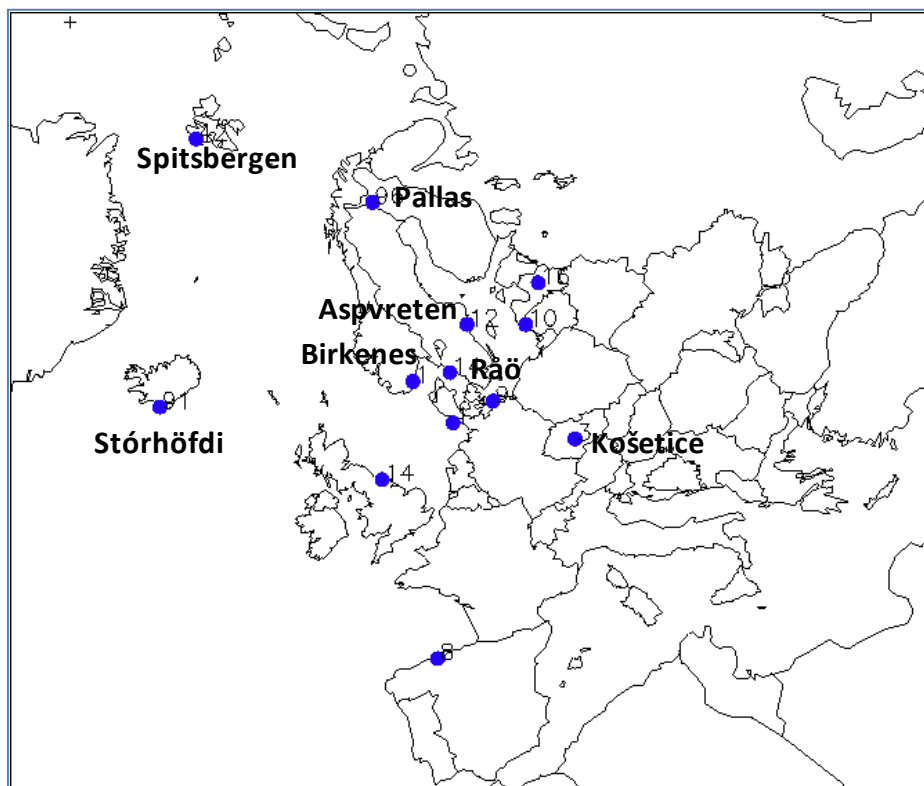


Figure S2 Comparison of selected PAS results for two parallels at six EMEP sites. Note that all results are expressed on a logarithmic scale due to large variability across sites. Secondly, the sum of PCBs, DDTs and PAHs only includes those substances (n) for which both samples at a given site were found to be above MDL. The error bars indicates an estimated uncertainty of +/-35% associated with the chemical analysis alone.

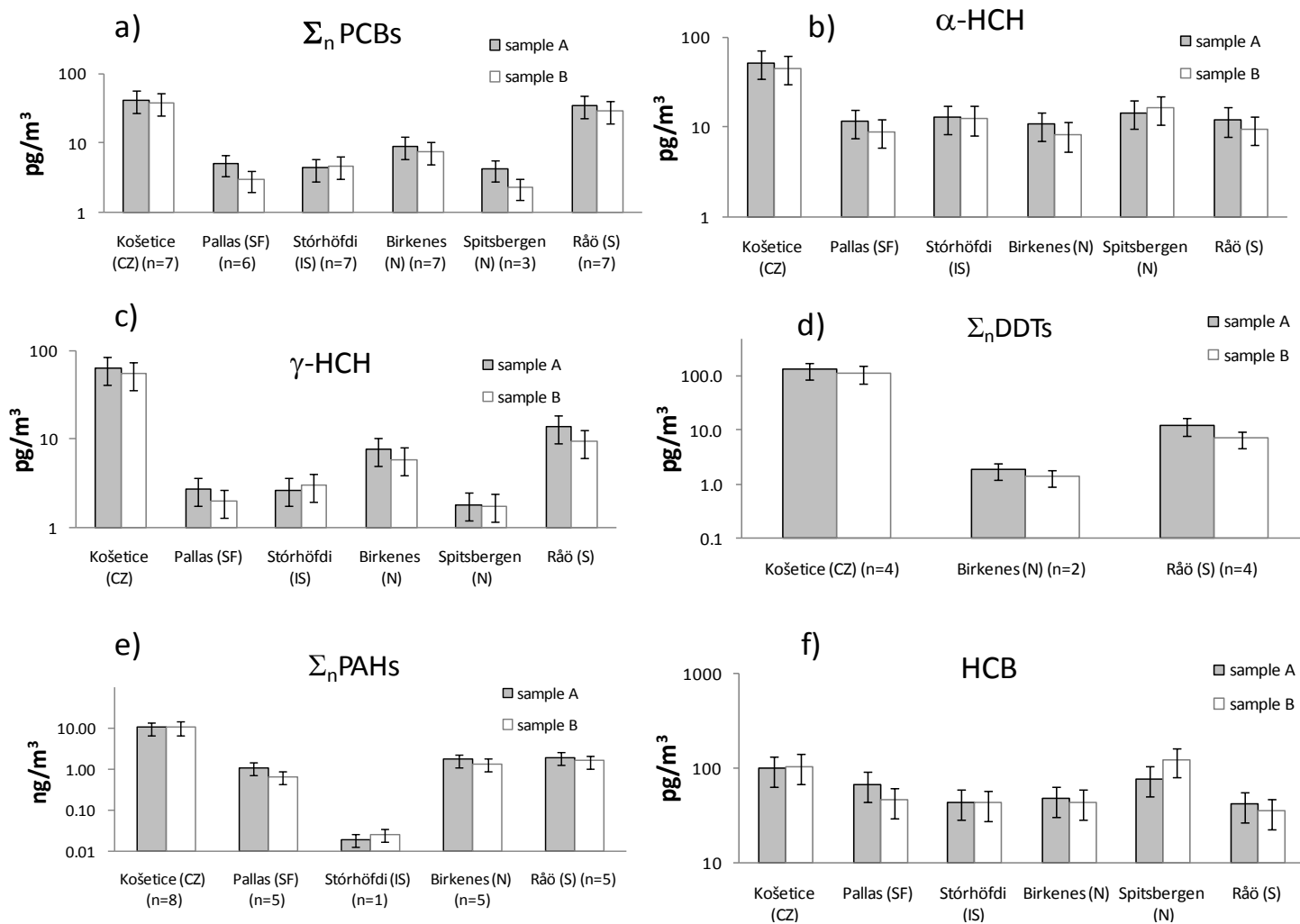
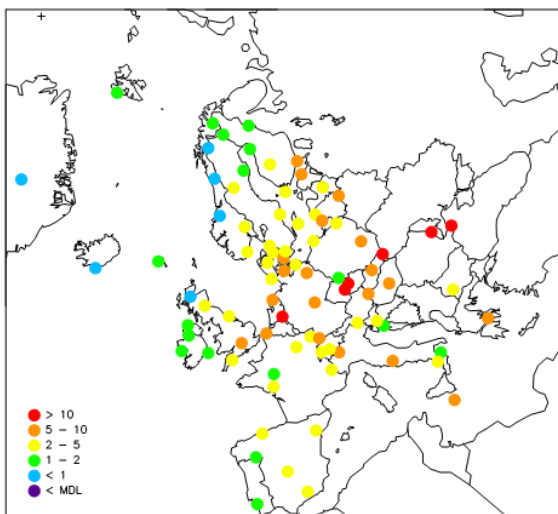


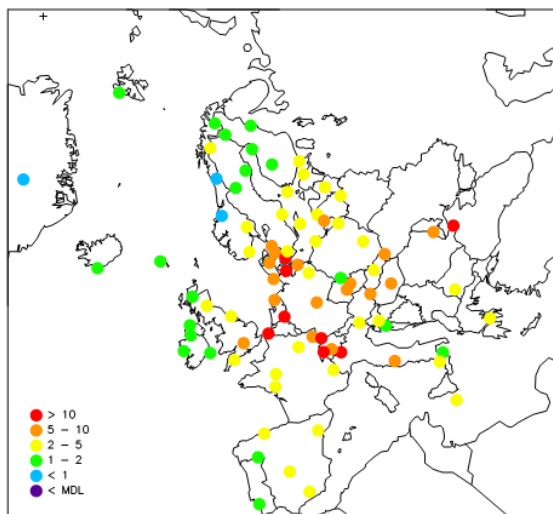
Figure S3 Spatial pattern of individual PCBs in European background air.

Figure S3a)



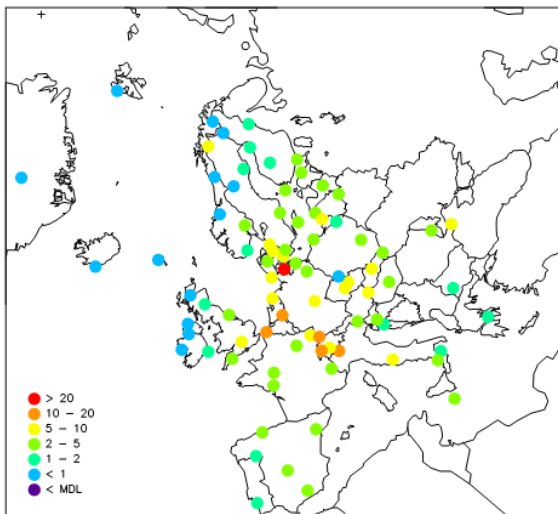
PCB-28 (pg/m³)

Figure S3b)



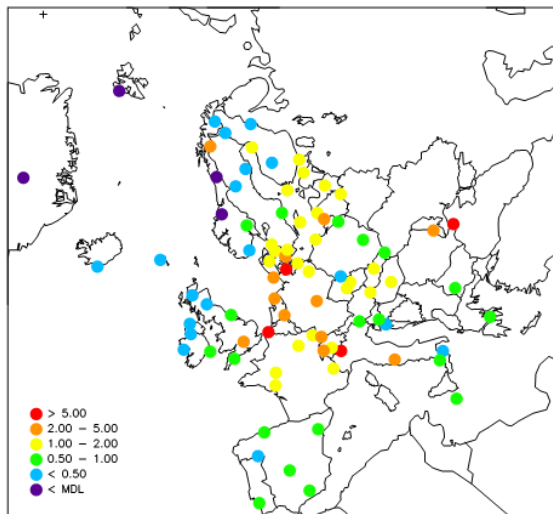
PCB-52 (pg/m³)

Figure S3c)



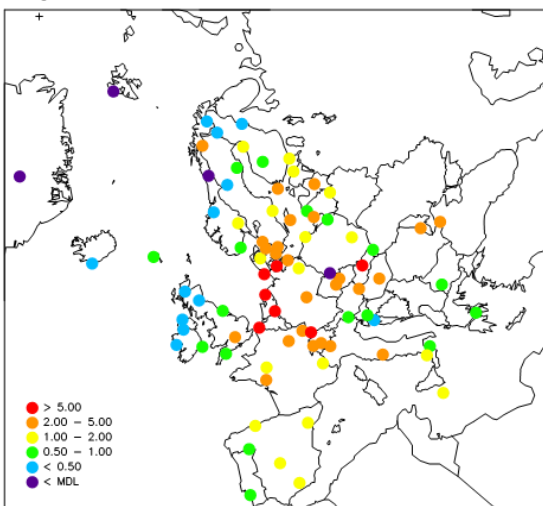
PCB-101 (pg/m³)

Figure S3d)



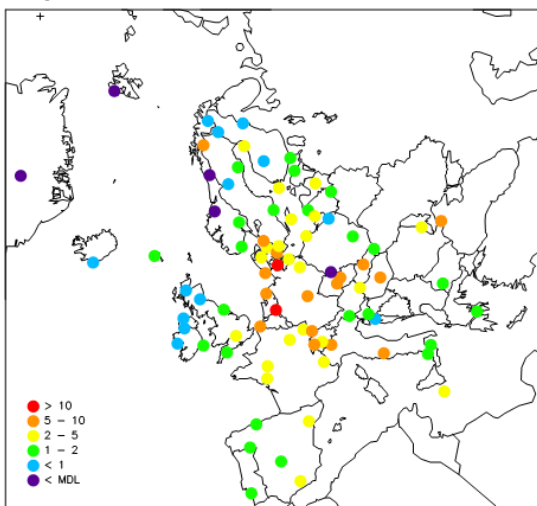
PCB-118 (pg/m³)

Figure S3e)



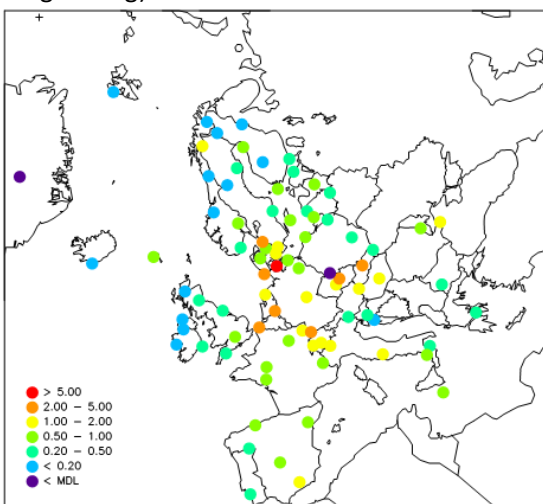
PCB-138 (pg/m³)

Figure S3f)



PCB-153 (pg/m³)

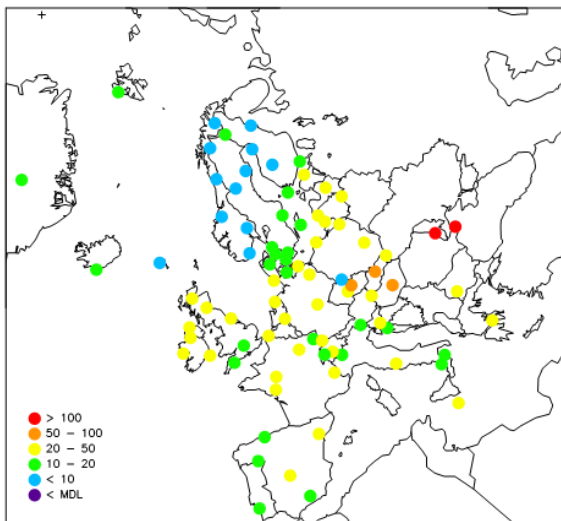
Figure S3g)



PCB-180 (pg/m³)

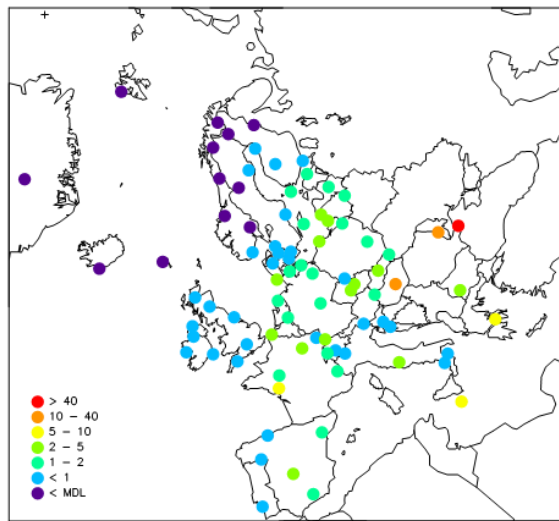
Figure S4 Spatial pattern of individual HCHs in European background air.

Figure S4a)



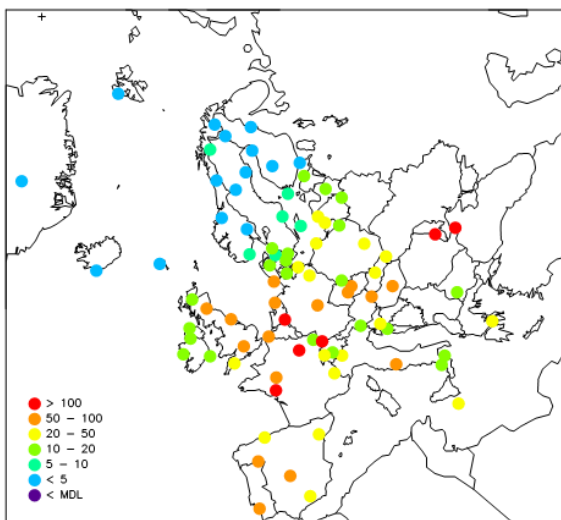
α -HCH (pg/m^3)

Figure S4b)



β -HCH (pg/m^3)

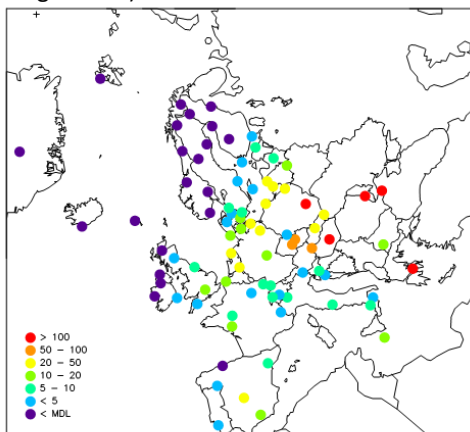
Figure S4c)



γ -HCH (pg/m^3)

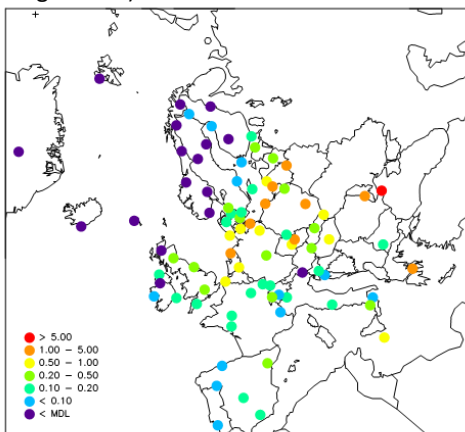
Figure S5 Spatial pattern of individual DDTs in addition to p,p' -DDT/ p,p' -DDE and o,p' -DDT/ p,p' -DDT ratios in European background air.

Figure S5a)



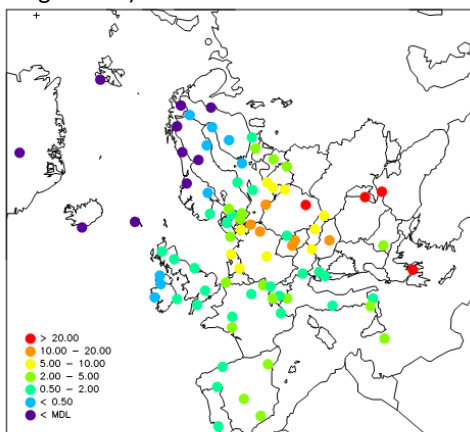
p,p' -DDE (pg/m³)

Figure S5b)



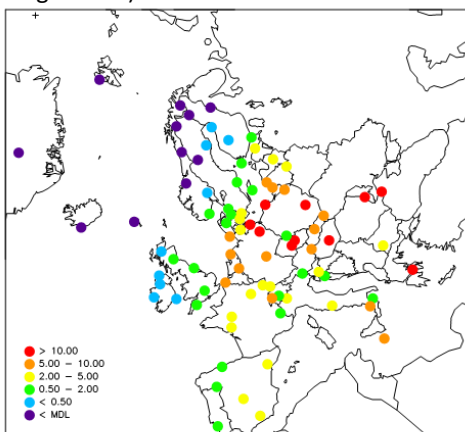
p,p' -DDD (pg/m³)

Figure S5c)



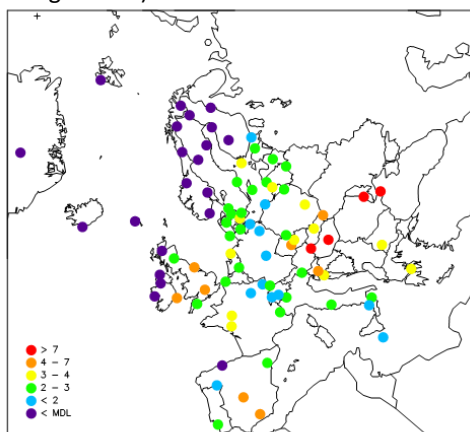
o,p' -DDT (pg/m³)

Figure S5d)



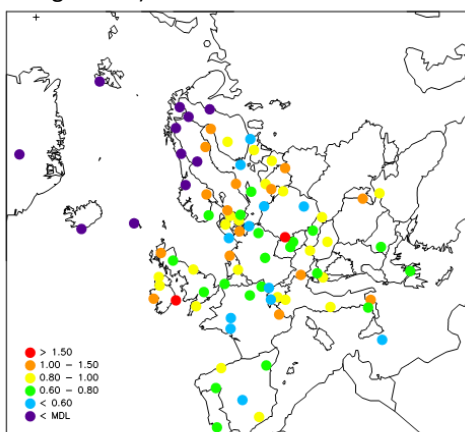
p,p' -DDT (pg/m³)

Figure S5e)



p,p' -DDE/ p,p' -DDT ratio

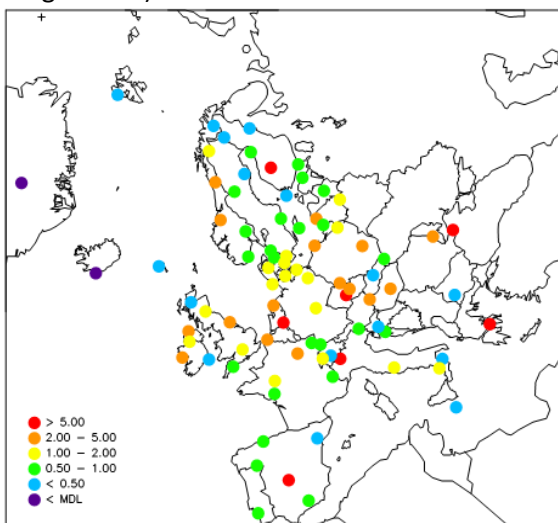
Figure S5f)



o,p' -DDT/ p,p' -DDT ratio

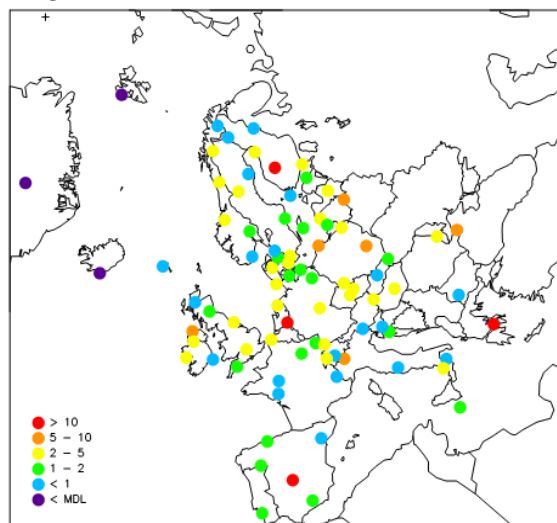
Figure S6 Spatial pattern of individual PAHs in European background air.

Figure S6a)



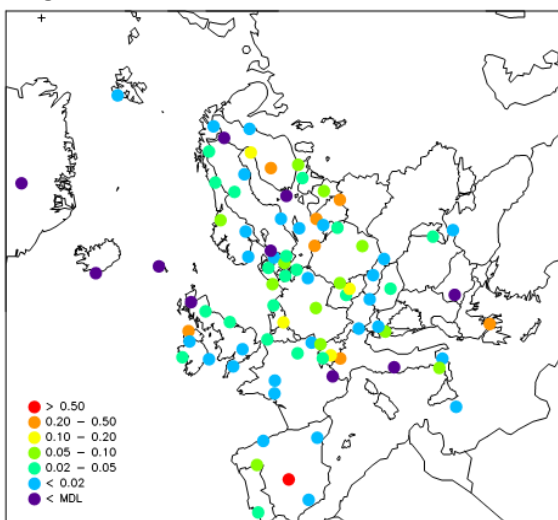
Fluorene (ng/m³)

Figure S6b)



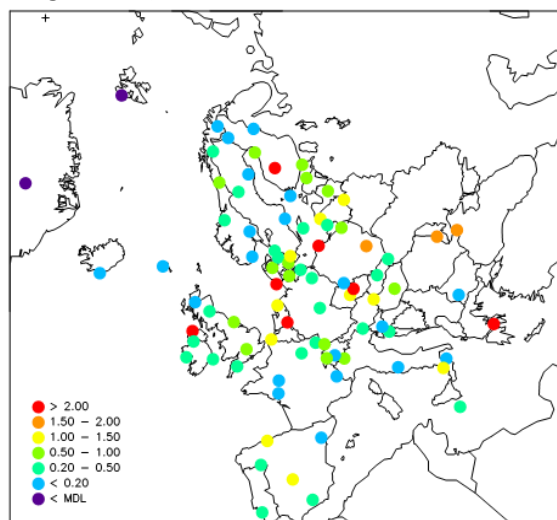
Phenanthrene (ng/m³)

Figure S6c)



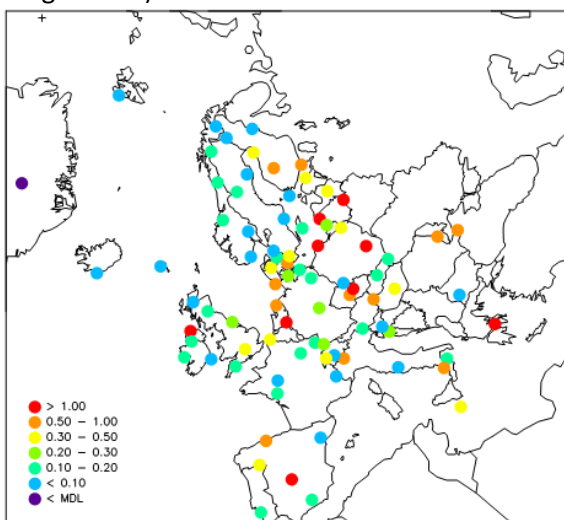
Anthracene (ng/m³)

Figure S6d)



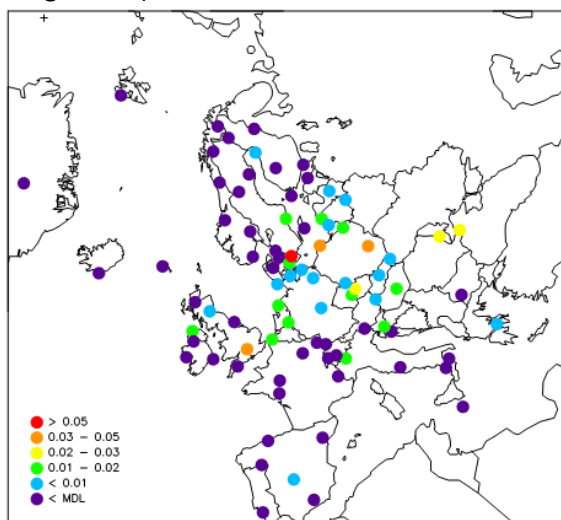
Fluoranthene (ng/m³)

Figure S6e)



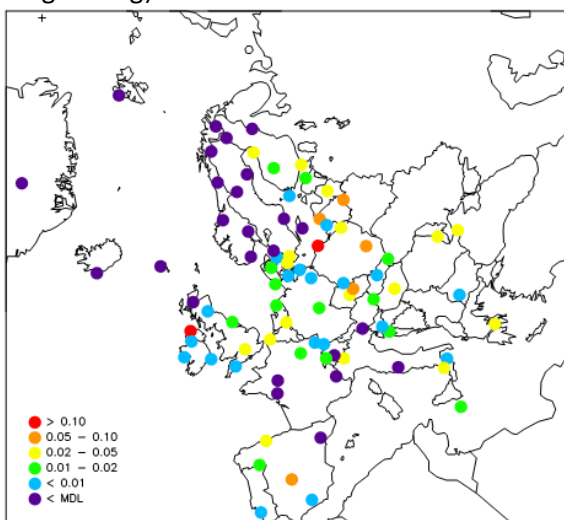
Pyrene (ng/m³)

Figure S6f)



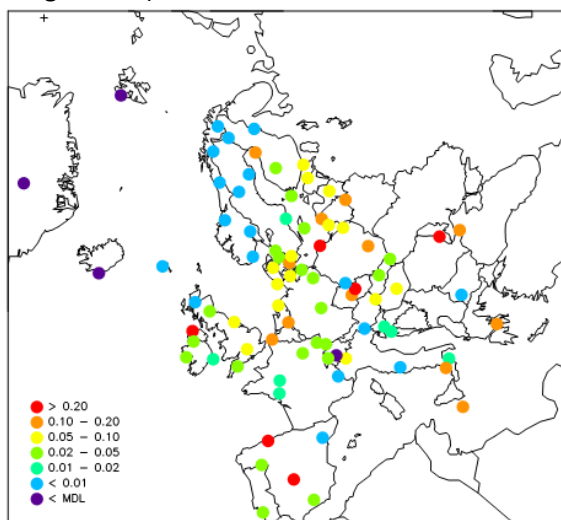
Benzo(a)pyrene (ng/m³)

Figure S6g)



Benzo(a)anthracene (ng/m³)

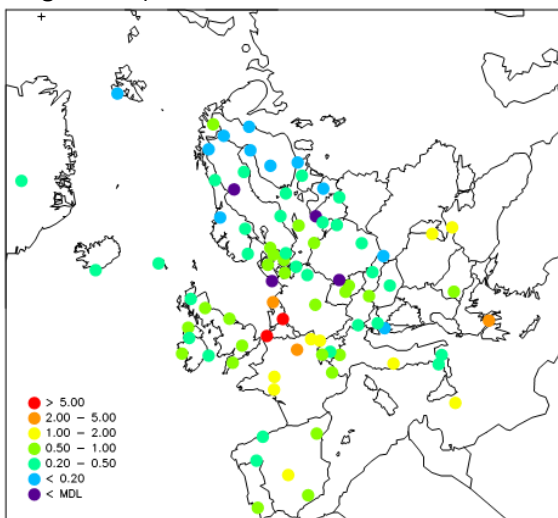
Figure S6h)



Chrysene (ng/m³)

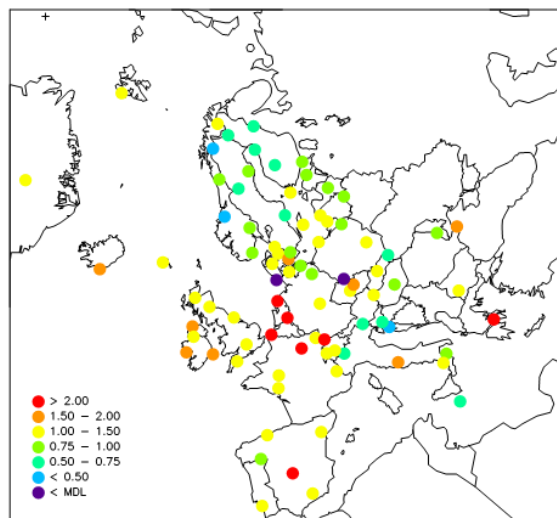
Figure S7 Spatial pattern of individual chlordanes in European background air.

Figure S7a)



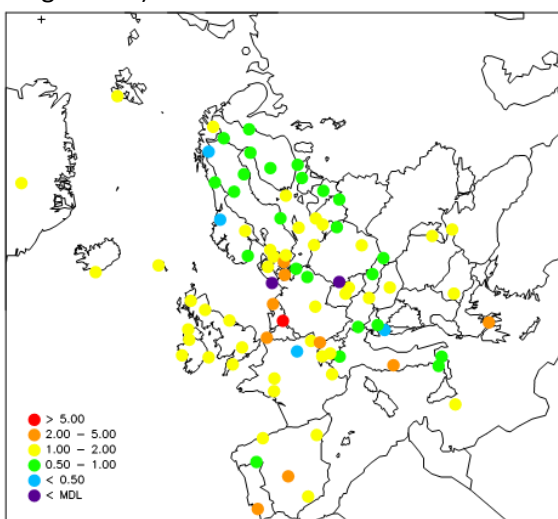
trans-chlordane (pg/m^3)

Figure S7b)



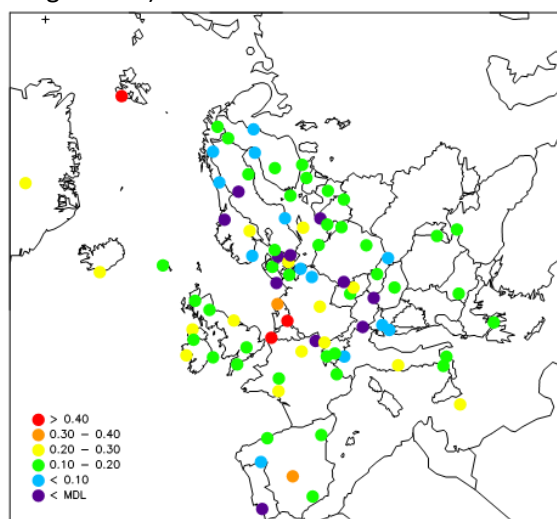
cis-chlordane (pg/m^3)

Figure S7c)



trans-nonachlor (pg/m^3)

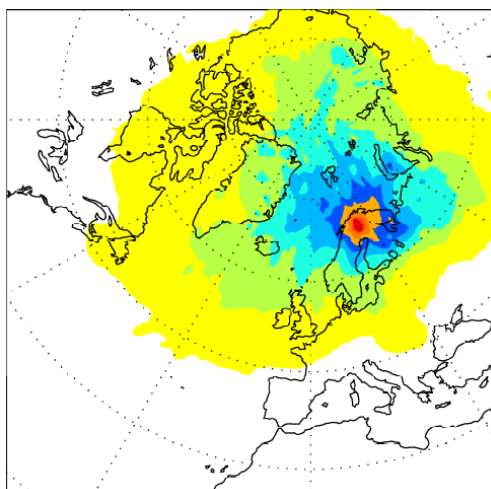
Figure S7d)



cis-nonachlor (pg/m^3)

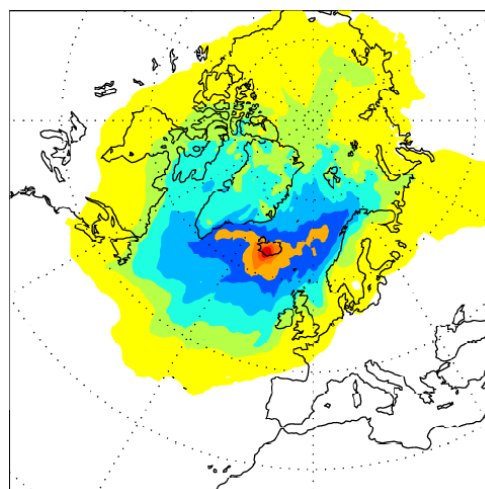
Figures S8-S22: Maps of Footprint ES (emission sensitivity) (a) and EC (emission contribution) (b) for PCB-28 for the PAS sampling period (see text) at selected sites.

Figure S8a)



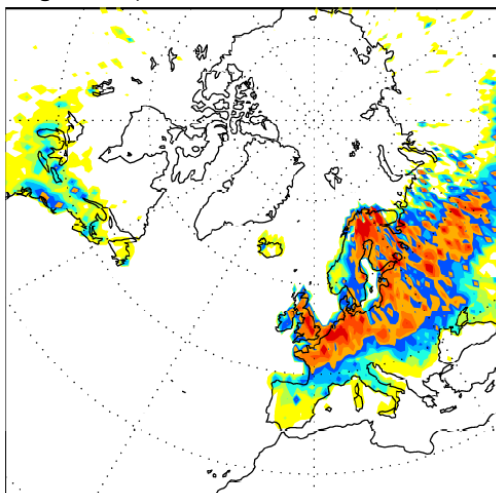
ES map [ns/m^3] Pallas

Figure S9a)



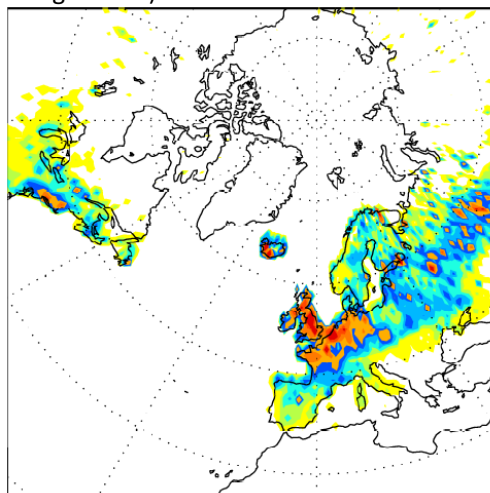
ES map [ns/m^3] Stórhöfði

Figure S8b)



EC map $1\text{E}-12$ [pg/m^5] Pallas

Figure S9b)



EC map $1\text{E}-12$ [pg/m^5] Stórhöfði

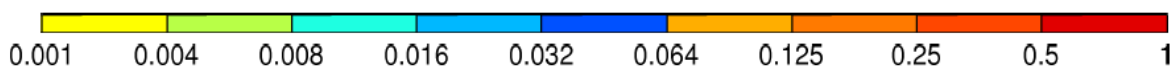
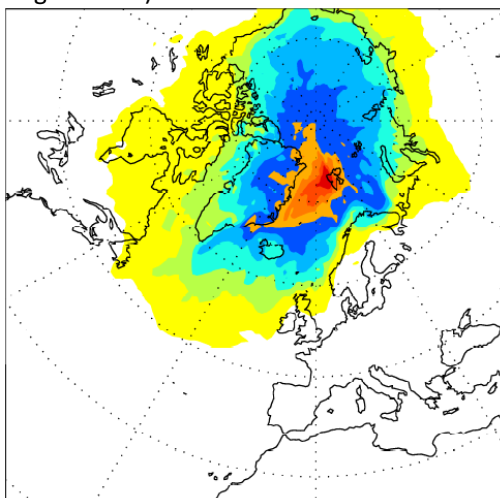
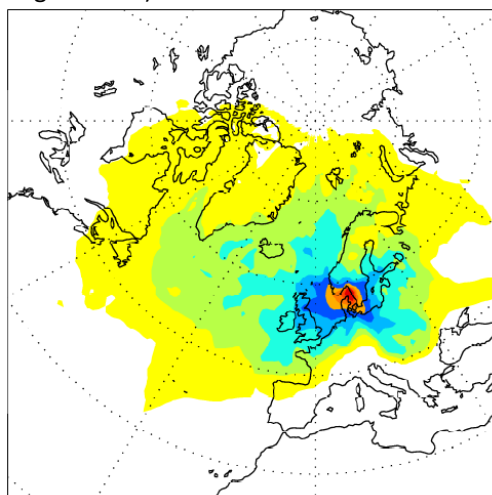


Figure S10a)



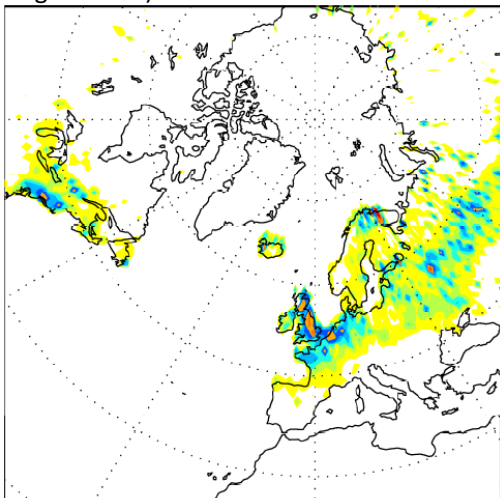
ES map [ns/m^3] Spitsbergen

Figure S11a)



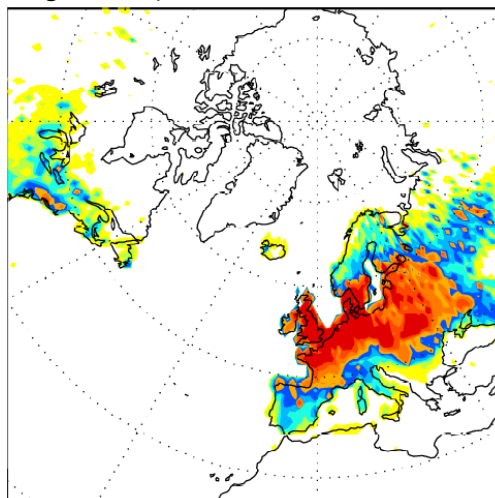
ES map [ns/m^3] Råö

Figure S10b)



EC map $10^{-12} \text{ [pg/m}^3\text{]}$ Spitsbergen

Figure S11b)



EC map $10^{-12} \text{ [pg/m}^3\text{]}$ Råö

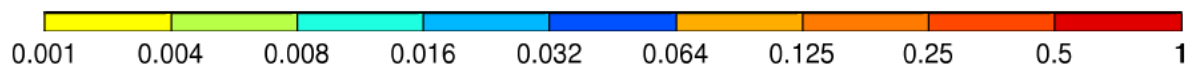
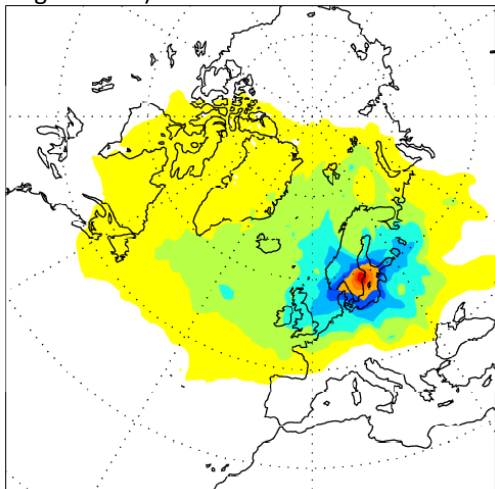
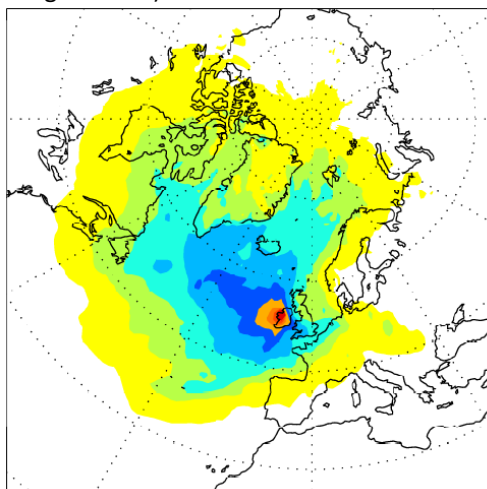


Figure S12a)



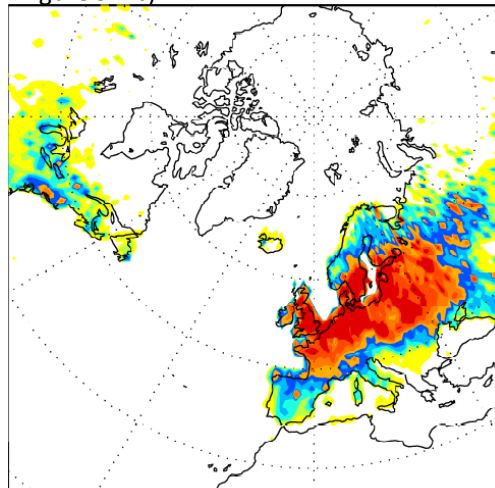
ES map [ns/m³] Aspvreten

Figure S13a)



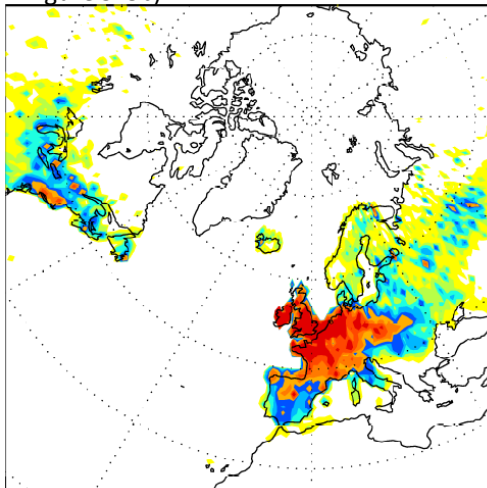
ES map [ns/m³] Mace Head

Figure S12b)



EC map 1E-12 [pg/m⁵] Aspvreten

Figure S13b)



EC map 1E-12 [pg/m⁵] Mace Head

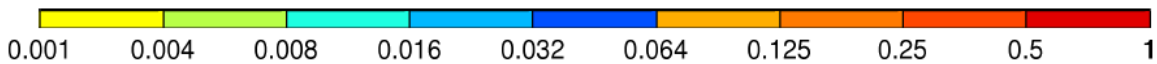
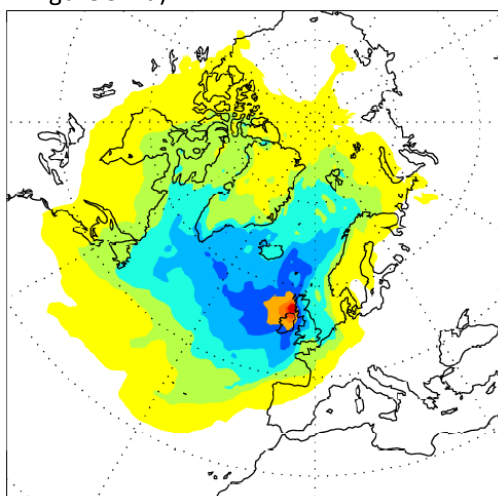
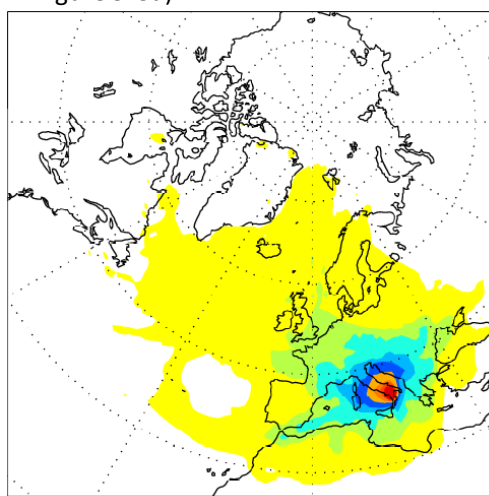


Figure S14a)



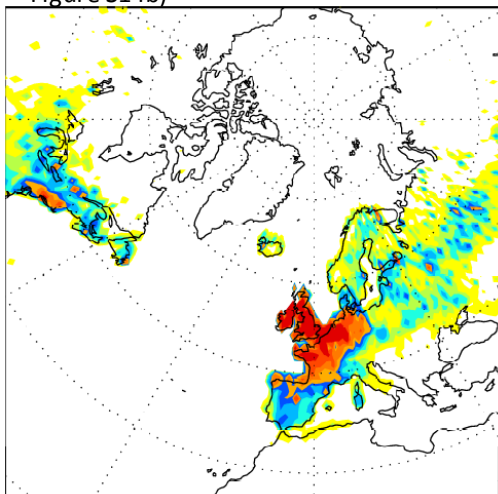
ES map [ns/m³] Malin Head

Figure S15a)



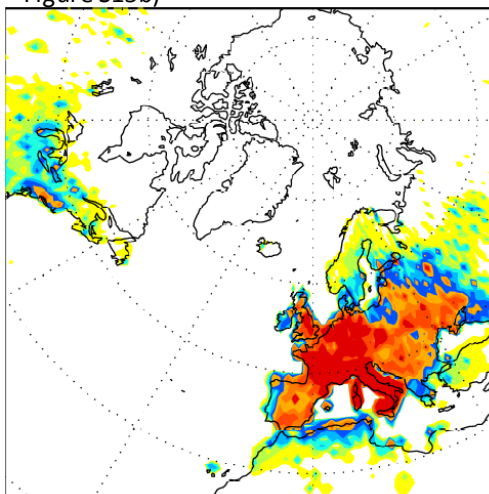
ES map [ns/m³] Longobucco

Figure S14b)



EC map 1E-12 [pg/m⁵] Malin Head

Figure S15b)



EC map 1E-12 [pg/m⁵] Longobucco

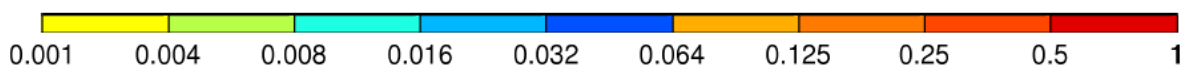
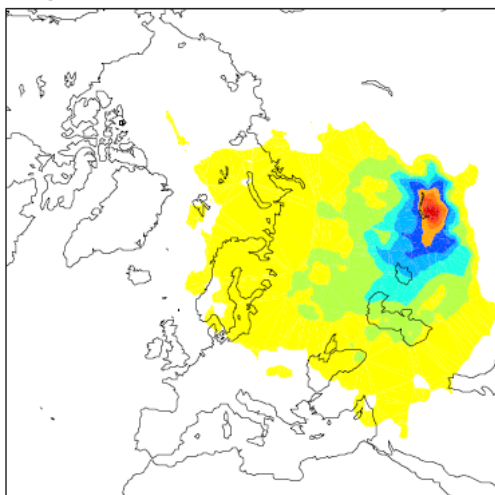
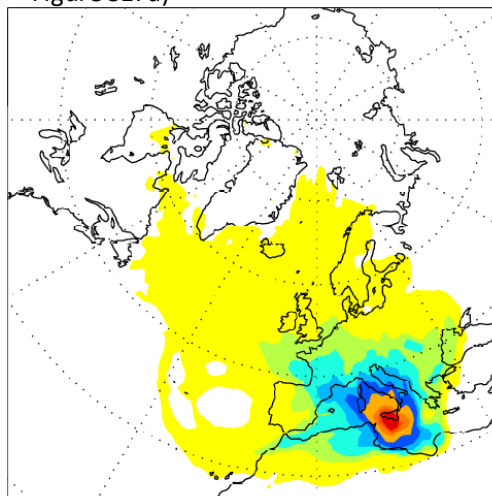


Figure S16a)



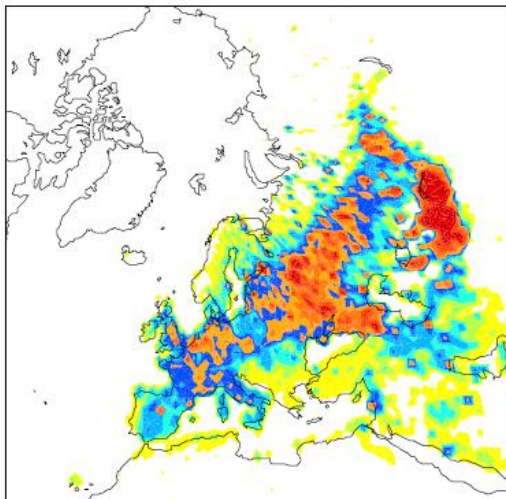
ES map [ns/m³] Borovoje

Figure S17a)



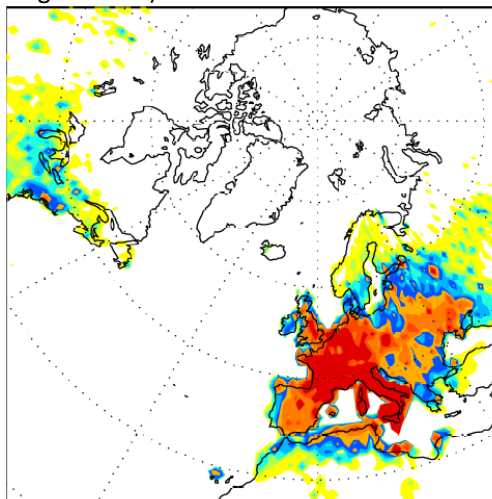
ES map [ns/m³] Giordan Lighthouse

Figure S16b)



EC map 1E-12 [pg/m⁵] Borovoje

Figure S17b)



EC map 1E-12 [pg/m⁵] Giordan Lighthouse

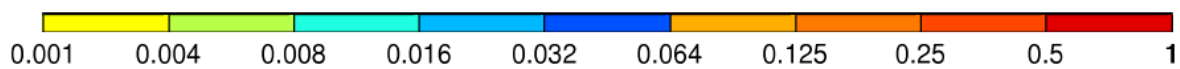
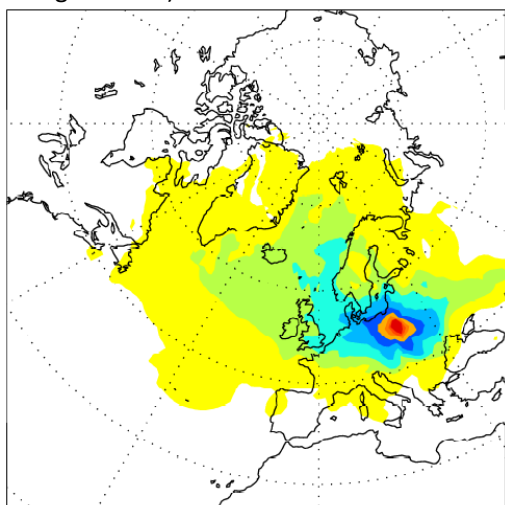
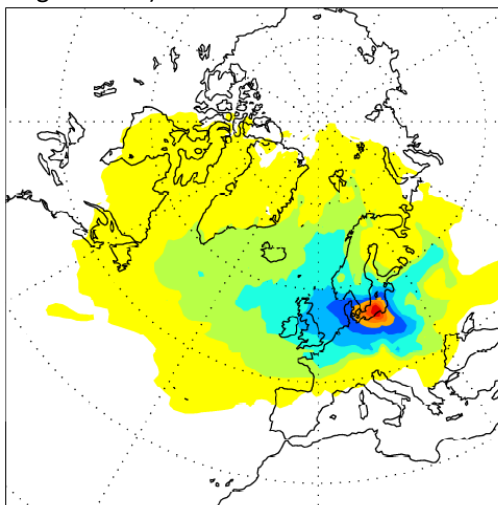


Figure S18a)



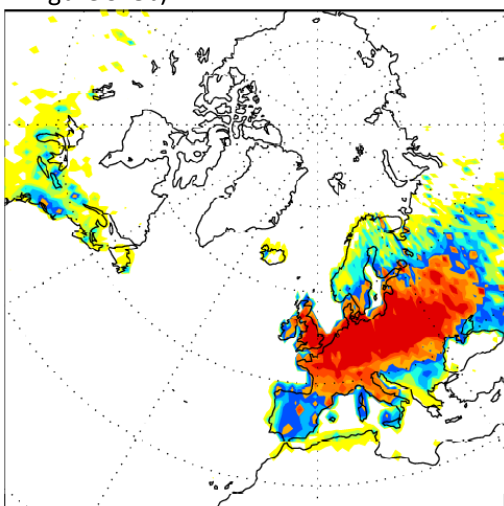
ES map [ns/m³] Jarczew

Figure S19a)



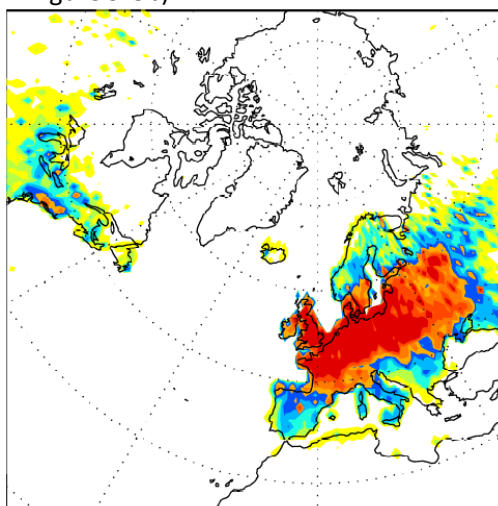
ES map [ns/m³] Leba

Figure S18b)



EC map 1E-12 [pg/m³] Jarczew

Figure S19b)



EC map 1E-12 [pg/m³] Leba

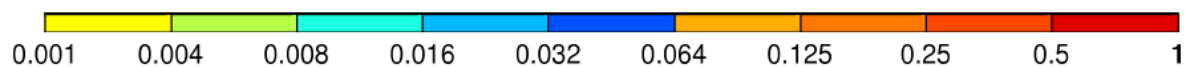
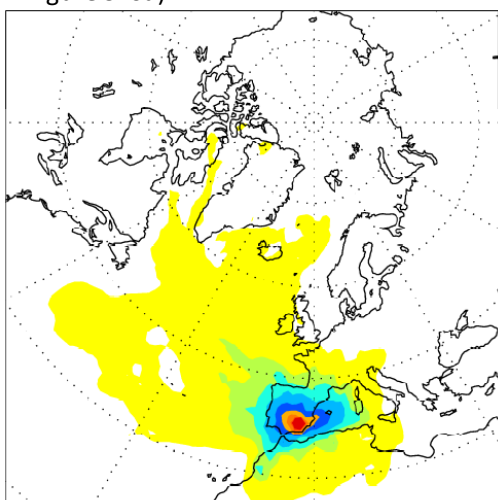
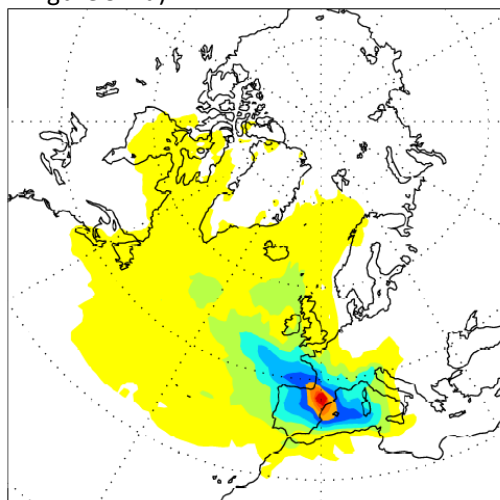


Figure S20a)



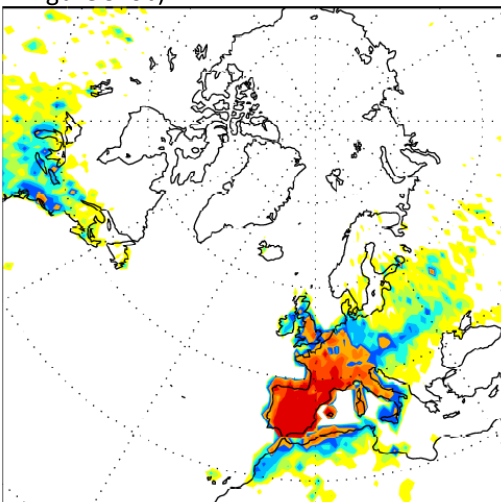
ES map [ns/m³] Viznar

Figure S21a)



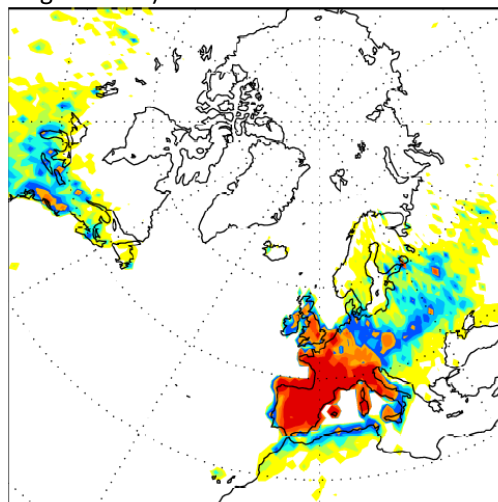
ES map [ns/m³] Els Torms

Figure S20b)



EC map 1E-12 [pg/m³] Viznar

Figure S21b)



EC map 1E-12 [pg/m³] Els Torms

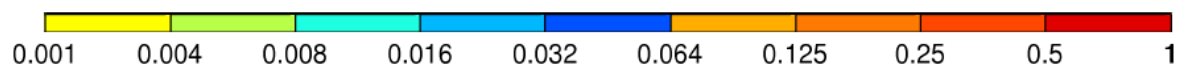
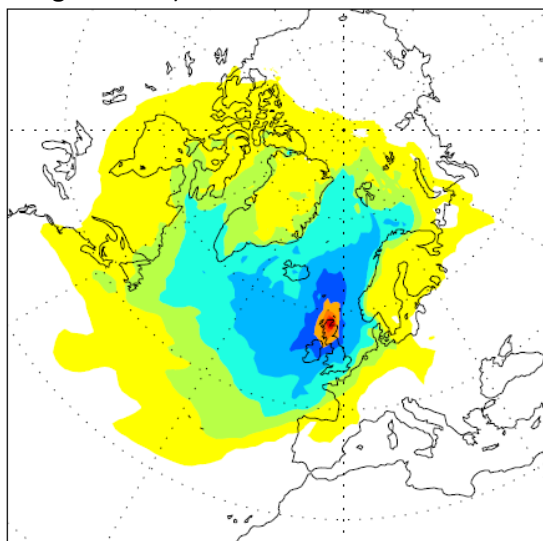
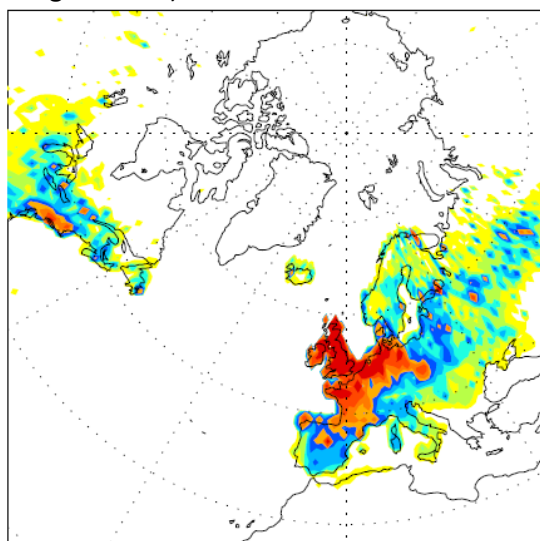


Figure S22a)



ES map [ns/m³] Strath Vaich Dam

Figure S22b)



EC map 1E-12 [pg/m³] Strath Vaich Dam

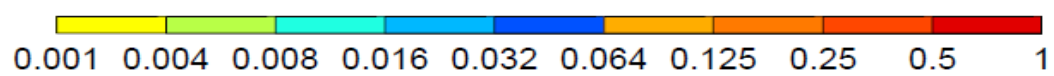
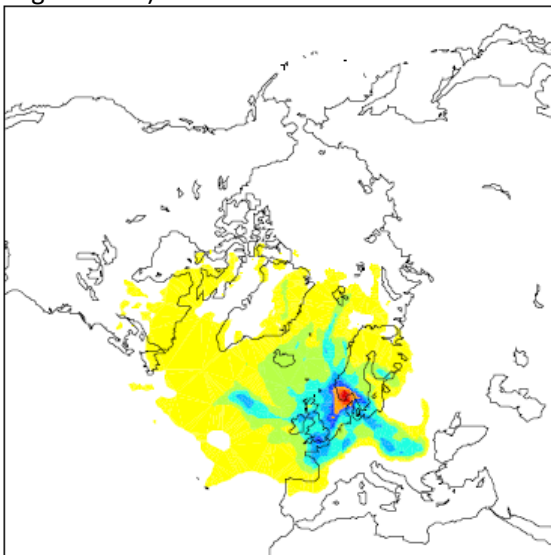


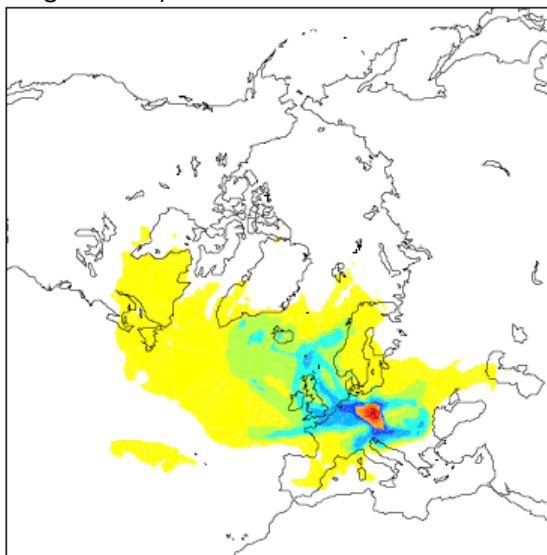
Figure S23-S24 Maps of Footprint ES (emission sensitivity) (a) and EC (emission contribution) (b) for PCB-28 for the AAS sampling period (see text) at Birkenes (23) and Košetice (24) respectively.

Figure S23a)



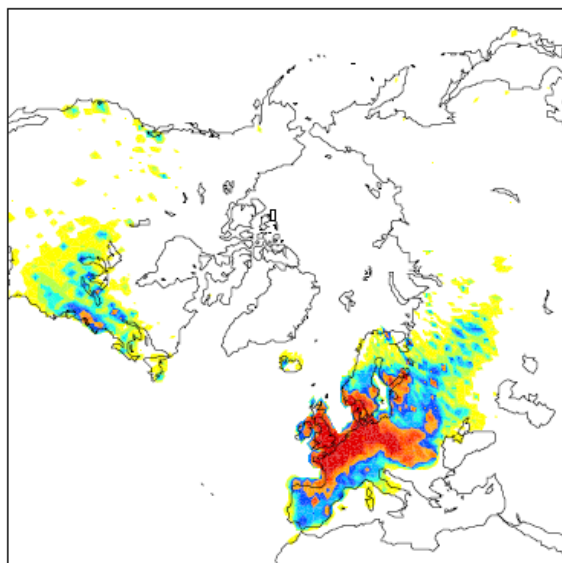
ES map [ns/m³] Birkenes

Figure S24a)



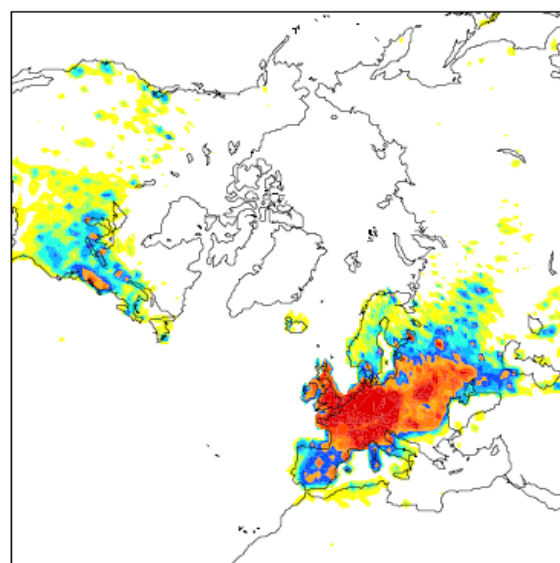
ES map [ns/m³] Košetice

Figure S23b)



EC map 1E-12 [pg/m⁵] Birkenes

Figure S24b)



EC map 1E-12 [pg/m⁵] Košetice

