SUPPLEMENTARY INFORMATION

Evidence for major emissions of polychlorinated biphenyls (PCBs) in the West African region

Rosalinda Gioia[1], Sabine Eckhardt[2], Knut Breivik[2,5], Foday Jaward[3], Ailette Prieto[4^], Luca Nizzetto [1,6] and Kevin C. Jones[1]*

S.1. High-volume air sampling

Twelve hours integrated air samples were collected with the four high-vols operating in parallel. The two samplers on the observation deck collected an average volume of 150-200 m^3 each and the two on the back deck collected an average volume of 600 m^3 each. Samples were collected while the ship was moving; in 12 hours the ship would have travelled approximately 200 km. Both particulate and gas-phase were captured on a Whatman glass fiber filter grade A (GFF/A) and polyurethane foam (PUF), respectively. The four air samplers were deployed to monitor potential ship contamination. Air sampling on ships needs to be consistent and respectful of strict quality control measures, in order to avoid ship contamination and detect low levels of POPs in remote regions (*20*). A total of ten 24 hours air samples were collected from 06/11/07 to 08/04/08 in Cape Verde (14.9 ºN, 24.9 ºW), 5 from 06/11/07 to 10/11/07 (one each day) while the ship was in the vicinity. Thereafter, one 24 hour sample was collected every month between 12/11/07 and 08/04/08 in Cape Verde (a total of 5 samples). Only results from samples collected from 06/11/07 to 10/11/07 are discussed for the purpose of the manuscript. The sampling in Cape Verde went on for six months (including the intensive sampling in November) to establish outflows from Africa although one sample per month does not allow to establish typical levels of these compounds; these are reported in Table SI.2 and results are not discussed in the text.

S.2. Passive air sampling

PUF disks were transferred to the sampling locations in airtight containers to avoid contamination from ambient air. Local volunteers were given guidance on choice of deployment locations. They were all remote and far from potential sources. At the end of the deployment

period, the samplers were retrieved by volunteers, re-sealed in their original transport containers and returned by courier to Lancaster University. Upon receipt, the PUF disks were stored in sealed, solvent rinsed glass jars at -20°C until extraction.

S.3. Analytical and instrumental procedures

F1 was reduced in volume under N_2 to a 0.5 mL and transferred to a multilayer 20 mm id acid silica column containing a small layer of sodium sulphate, 1 g activated silica (Merck Silica 60), 2 g of basic silica (Merck Silica 60), 1 g of activated silica (Merck Silica 60, 4 g of acid silica (Merck Silica 60), 1 g activated silica and a small layer of sodium sulphate (all baked at 450˚C overnight). F1 and F2 were eluted through gel permeation columns containing 6 g of Biobeads SX 3 and concentrated to 100 uL. F1 was solvent exchanged to 25 uL of dodecane containing PCB 30 [$^{13}C_{12}$] PCB 141 and [$^{13}C_{12}$] PCB 208 as internal standards for PCBs. F2 was then transferred to 100 ul of isooctane internal standard containing Naphthalene d8, Acenaphthene d10, Phenathrene d10, Fluoranthene d10, Benzo(a)anthracene d12, Perylene d12, 1 3 5 TPB.

F1 was analysed by gas-chromatography mass spectrometry (GC-MS) with an EI+ source operating in selected ion mode (SIM) for PCBs as described elsewhere (Gioia et al., 2008a). The following compounds were monitored in air and seawater samples: tri-PCBs 18, 22, 28, and 31; tetra-PCBs 44, 49, 53, 70 and 74; penta-PCBs 87, 90/101, 95, 99, 105,110,118 and 123; hexa-PCBs 138, 141, 149, 151, 153/132; hepta- PCBs 180, 183 and 187. F2 was analyzed PAHs with a HP 5890 series II GC equipped with a 30 m HP5MS column (0.25 mm i.d., 0.25 μm film thickness) and 3 m long deactivated HP retention gap (0.53 mm i.d.) Euskal Herriko Unibertsitatea in Bilbao, Spain. This was connected to a HP 5972 MSD operating SIM mode. Sixteen PAHs (fluorene, phenanthrene, anthracene, 1-methylphenanthrene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benz[e]pyrene,

benzo[a]pyrene, perylene, indeno[123-cd]pyrene, dibenzo(a)anthracene and benzo[ghi]perylene) routinely detected in samples were quantified.

S.4.Methods to derive PCB concentration at the sampling location

For each sampling interval, 50000 particles were released at the measurement point and followed backward in time for 20 days, forming what we call a retroplume, to calculate a emission sensitivity (ES) function, as described by Seibert and Frank (2004) and Stohl et al. (2003). The value of the ES function (in units of s) in a particular grid cell is the particle residence time in the respective grid cell. It is assumed that the uptake of the PCBs just takes place in the lowest layer 0-100m above the ground, which is referred as footprint layer Folding (i.e., multiplying) the ES footprint with the emission flux densities (in units of kg m^{-3} s^{-1}) from the PCB inventory yields so-called emission contribution (EC) maps, that is the geographical distribution of sources contributing to the simulated mixing ratio at the receptor.

$$EC(x, y) = PCB\_Emissions(x, y) \bullet ES(x, y) \quad (1)$$

Spatial integration finally gives the simulated concentration at the receptor.

$$Conc\_receptor = \sum EC(x = 1, ny = 1, m) \quad (2)$$

Time series of these mixing ratios, obtained from the series of backward simulations, are presented in Figure 3.

S.5. Methods to estimate CO from biomass burning

For estimating biomass burning (BB) emissions from these fires, we used active fire detections by the MODIS instruments onboard the Aqua and Terra satellites.These detections are based on MODIS Collection 4 data and the MOD14 and MYD14 algorithms (Giglio et al., 2003) (see http://maps.geog.umd.edu/products/MODIS Fire Users Guide 2.2.pdf). A number between 0 and

100 characterizes the confidence for every fire detection. We only used detections with a confidence level greater than 75. The algorithm uses data from pixels of about 1 km^2 size but the actual fire size is not known. Fires of 1000 m^2 or less can be detected under good observing conditions but even large fires can be obscured by clouds. Furthermore, detections can only be made at the time of the satellite overpasses and the number of detections also depends on the minimum confidence level requested. In the absence of better information, we assumed that every detection represents a burned area of 180 ha, based on a statistical analysis of MODIS fire detections with independent area burned data by Wotawa et al. (2006). This shall account both for the area burned by the detected fire itself and undetected fires in its vicinity on the same day. This obtained emission inventory was used in the same way as for the PCBs, which means that the fire emissions were folded with the ES maps.

References for this section:

Giglio, L., Descloitres, J., Justice, C. O., and Kaufman, Y.: An enhanced contextual fire detection algorithm for MODIS, Rem.Sens. Environ., 87, 273–282, 2003.

Stohl, A., Forster, C. Eckhardt, S., Spichtinger, N., Huntrieser, H., Heland, J., Schlager, H.,Wilhelm, S., Arnold, F., and Cooper, O.: A backward modeling study of intercontinental pollution transport using aircraft measurements, J. Geophys. Res., 108, 4370,doi:10.1029/2002JD002862, 2003.

Seibert, P. and Frank, A.: Source-receptor matrix calculation with a Lagrangian particle dispersion model in backward mode, Atmos. Chem. Phys., 4, 51–63, 2004, http://www. atmos-chem-phys.net/4/51/2004/.

Wotawa, G., De Geer, L.-E., Becker, A., D'Amours, R., Jean, M., Servranckx, R., and Ungar, K.: Inter- and intra-continental transport of radioactive cesium released by boreal forest fires, Geophys. Res. Lett., 33, L12806, doi:10.1029/2006GL026206, 2006.

Table SI.1. PCB concentrations (pg/m^3) measured on the Polarstern cruise in 2007 from starboard observation deck. ND= Not detected

LAT	25	22	17	14	11	10	10	7	6	4	5
MINUTE	29.467	33.491	3.101	27.649	23.328	5.207	5.207	13.375	28.485	49.38	43.161
LONG	-19	-20	-21	-21	-20	-20	-20	-18	-17	-16	-16
MINUTES	17.808	51.005	7.83	8.694	20.522	1.451	1.451	6.153	28.656	6.03	50.827
air volume	849	573	592	825	625	558	714	685	661	784	558
PCB/OC											
18	10	5.09	6.46	6.66	18	31	7.17	0.00	6.00	7.15	48
22	4.99	4.42	1.51	3.50	14	13	7.04	2.67	28	2.77	7.28
44	4.76	0.97	0.58	2.15	6.03	7.85	6.21	0.00	ND	3.01	6.76
49	2.73	0.97	0.00	1.73	4.91	9.03	3.31	1.96	28.66	2.01	6.15
52	6.01	2.26	0.71	3.16	10	11	6.24	0.91	269.66	4.21	8.90
70	2.34	0.63	ND	1.41	5.43	2.97	4.65	0.88	0.30	1.99	2.14
74	1.56	0.45	ND	0.77	3.47	1.80	2.47	0.00	ND	1.49	1.44
87	0.74	0.61	0.10	1.17	4.29	0.11	0.64	0.05	0.93	0.72	0.53
95	3.34	2.18	0.23	4.59	9.41	1.59	2.63	0.42	1.71	2.27	1.70
99	0.39	0.29	0.05	0.81	1.53	0.29	0.24	0.00	0.92	0.48	0.48
110	1.58	0.90	0.16	2.67	6.06	0.71	1.72	0.33	1.52	1.17	0.96
118	0.66	0.59	0.08	1.28	2.62	0.61	0.54	0.18	1.51	0.56	0.35
123	0.21	ND	0.00	0.32	ND	ND	ND	0.19	0.97	0.24	0.31
138	2.45	1.39	0.14	3.77	5.05	1.00	1.27	1.70	0.42	1.44	1.29
141	0.43	0.15	ND	0.93	0.69	0.32	ND	0.23	0.30	ND	0.04
149	3.45	1.67	0.11	4.33	7.40	1.54	1.74	2.31	0.20	0.97	2.60
151	1.29	0.67	0.12	1.54	2.86	0.66	0.45	1.04	ND	0.22	1.31
155	ND	ND	ND	ND	ND	3.77	3.18	3.07	0.80	ND	ND
158	ND	0.17	0.05	0.38	0.66	0.10	0.22	0.10	ND	ND	ND
167	ND	ND	ND	ND	ND	ND	ND	ND	0.46	ND	ND
170	0.33	ND	ND	1.29	0.62	0.26	ND	ND	ND	0.23	ND
174	0.63	0.40	0.15	1.02	2.66	0.54	ND	0.00	0.28	0.29	0.80
180	1.05	0.82	0.23	1.10	3.00	1.08	0.68	0.98	ND	0.44	0.66
183	0.40	0.43	0.16	0.34	0.96	0.29	ND	0.78	ND	0.21	0.54
187	0.76	0.41	ND	0.74	1.62	1.29	ND	0.75	ND	ND	1.42
189	ND	ND	ND	ND	ND	ND	ND	0.00	0.16	ND	ND
194	ND	ND	ND	ND	ND	ND	ND	6.81	ND	ND	ND
153+132	3.55	2.50	ND	ND	7.41	ND	0.29	2.43	ND	0.05	2.24
31+28	14.87	9.41	15.66	70.39	21.54	176.76	35.10	14.24	ND	9.32	27.19
41/64	4.68	1.30	5.98	32.00	3.51	89.20	5.03	0.57	0.18	1.46	5.71
60/56	2.04	0.35	ND	ND	2.58	ND	3.39	6.25	ND	ND	0.68
90/101	3.38	2.06	ND	ND	9.19	ND	2.12	0.93	ND	1.83	1.71
ICES PCBs	29	17	17	80	50	191	44	20	272	16	41
sum of PCBs	79	41	32	148	155	357	96	50	328	45	131

Table SI.2. PCB concentrations (pg/m^3) measured in Cape Verde from 07/11/07 to 08/04/08.

ND= Not detected

Date	07/11/2007	09/11/2007	10/11/2007	18/12/2007	24/01/2008	05/03/2008	25/03/2008	08/04/2008
PCB/OC								
18	9.33	12.16	1.60	0.59	2.56	0.95	1.23	3.25
22	5.42	4.19	0.75	0.56	1.48	0.44	0.60	2.98
44	5.27	3.32	0.77	0.17	0.62	0.61	0.59	1.81
49	3.85	2.69	0.36	0.46	0.34	0.40	0.47	1.35
52	6.19	4.71	0.64	1.39	0.83	0.69	1.03	1.96
70	4.51	2.89	0.48	0.40	0.80	0.74	0.60	1.56
74	1.80	1.66	0.21	0.31	0.31	0.35	0.48	0.88
87	1.11	0.87	0.12	ND	ND	0.28	ND	0.26
95	4.20	3.92	0.69	0.24	1.34	0.74	0.57	1.08
99	0.85	1.17	0.18	ND	ND	0.23	ND	0.29
110	0.00	0.00	0.00	ND	ND	ND	ND	ND
114	3.13	2.89	0.72	ND	0.72	0.91		0.75
118	ND	ND	ND	ND	ND	ND	ND	ND
123	1.70	2.09	0.38	ND	ND	ND	ND	0.24
138	3.61	3.75	0.67	ND	0.21	0.36	0.74	0.36
141	0.85	1.26	0.17	ND	0.04	ND	ND	ND
149	4.79	5.36	0.65	ND	1.38	0.86	0.49	0.76
151	1.65	3.03	0.26	ND	ND	0.30	0.33	0.19
158	0.41	ND	ND	ND	ND	0.03	0.13	ND
170	ND	ND	ND	ND	ND	ND	ND	ND
174	0.82	1.16	0.00	ND	ND	ND	ND	ND
180	1.11	1.48	0.19	ND	ND	ND	ND	0.23
183	0.30	1.13	0.00	ND	ND	ND	ND	ND
187	0.73	1.30	0.13	ND	ND	ND	ND	ND
189	ND	ND	ND	ND	ND	ND	ND	ND
194	ND	ND	ND	ND	ND	ND	ND	ND
199	ND	ND	ND	ND	ND	ND	ND	ND
203	ND	ND	ND	ND	ND	ND	ND	ND
153+132	5.21	6.53	0.86	ND	0.97	1.27		1.03
31+28	13.44	22.69	2.31	1.11	3.77	1.22	1.28	3.76
41/64	4.72	2.51	0.46	ND	0.56	ND	0.51	1.89
60/56	2.16	0.93	0.30	0.50	ND	0.60	0.29	0.92
90/101	3.87	5.01	0.88	ND	1.03	0.97	0.66	1.25
HCB	0.00	0.00	0.00	ND	ND	ND	ND	ND
ICES PCBs	33	44	5.5	2.5	6.8	4.5	3.7	8.6
Sum of PCBs	91.02	98.72	13.78	5.75	16.98	11.95	10.01	26.79

TABLE SI.3. PCBs concentrations (pg/m^3) in West Africa countries. ND=Not Detected

Latitude	5.14	3.91	5.49	5.2	5.68	13.45	13.45	13.46	13.27	8.29	7.46	5.5	5.55	6.35	6
Longitude	-3.44	-0.7	4.05	-1.12	-2.36	-16.57	-16.3	-16.69	-15.5	-13.14	0.48	-1.03	0.59	0.28	0.36
Country	**Ivory coast**	**Ivory coast**	**Ivory coast**	**Ivory coast**	**Ivory coast**	**Gambia**	**Gambia**	**Gambia**	**Gambia**	**Sierra Leone**	**Ghana**	**Ghana**	**Ghana**	**Ghana**	**Ghana**
PCBOC															
18	46.03	ND	1.96	3.23	3.03	6.75	3.82	4.60	4.25	0.98	1.18	0.74	1.18	1.95	1.47
22	33.70	ND	2.10	2.28	2.85	4.66	2.93	5.22	5.85	0.49	0.72	0.33	0.82	0.59	ND
44	15.44	0.43	3.66	3.37	2.10	9.69	2.99	3.38	5.06	0.57	0.75	0.68	1.63	0.47	0.63
49	12.89	0.49	2.28	2.76	2.17	5.76	3.21	4.13	3.47	0.56	0.59	0.51	1.20	0.57	0.90
52	17.84	0.77	6.02	5.91	3.18	20.35	4.19	4.49	7.00	0.59	1.11	0.86	2.05	0.77	1.48
54	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
70	9.01	0.40	3.01	2.38	2.16	8.12	3.33	5.53	4.41	0.82	0.86	0.78	2.26	0.42	1.10
74	10.10	0.50	3.91	2.53	1.97	11.29	2.91	4.05	6.37	0.42	0.30	0.39	0.98	0.26	0.49
87	1.82	ND	2.89	1.07	0.59	7.88	1.78	1.46	4.17	0.30	0.48	ND	1.12	ND	0.29
95	9.72	0.80	6.39	3.45	1.96	30.13	4.20	3.75	8.55	0.67	1.43	0.43	1.97	0.48	0.86
99	1.65	0.20	2.20	0.97	0.43	4.19	0.93	1.89	3.81	0.23	0.33	ND	0.72	ND	0.34
110	4.43	0.60	6.22	2.38	1.35	18.62	3.85	3.78	9.26	0.56	1.12	0.20	2.05	0.11	0.45
114	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
118	2.38	0.40	3.51	1.40	0.93	8.69	2.49	2.08	6.53	0.39	0.81	ND	1.53	ND	0.54
123	0.39	ND	0.33	0.20	ND	1.31	ND	ND	0.61	ND	ND	ND	ND	ND	ND
138	4.79	0.92	6.20	2.95	2.44	20.33	4.95	4.93	13.88	0.66	2.34	ND	ND	ND	ND
141	1.02	0.23	1.24	0.66	0.57	5.09	1.05	1.04	2.99	ND	0.37	ND	0.46	ND	ND
149	7.53	0.96	5.57	2.90	2.10	24.12	4.16	4.43	10.99	0.62	1.52	0.22	1.97	0.25	0.56
151	3.18	0.36	1.67	1.06	0.87	9.20	1.40	1.44	3.50	0.24	0.53	ND	0.65	ND	0.24
155	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
156	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
157	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
158	0.42	ND	0.46	0.30	0.29	1.87	0.56	0.48	1.07	ND	0.30	ND	0.27	ND	ND
167	ND	ND	ND	0.25	ND	ND	0.48	0.48	ND	ND	ND	ND	ND	ND	ND
170	0.73	ND	1.21	0.40	0.61	3.13	0.83	1.11	2.36	ND	ND	ND	ND	ND	ND
174	0.95	0.18	1.06	0.59	0.46	4.25	0.84	1.14	2.10	ND	0.43	ND	0.42	ND	ND
180	1.66	0.41	2.30	0.99	1.03	6.54	1.70	2.08	4.39	0.22	1.09	ND	0.81	ND	0.11
183	0.78	ND	0.85	0.33	0.32	3.09	0.58	0.73	1.45	ND	0.30	ND	0.32	ND	ND
187	1.79	0.39	1.50	0.88	0.66	5.49	1.17	1.24	2.72	0.16	0.47	ND	0.54	ND	0.12
188	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

189	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
194	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
199	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
203	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
153+132	8.94	1.37	9.29	4.44	3.38	31.85	6.86	6.79	17.28	0.83	2.80	0.19	3.10	0.22	0.62
31+28	62.25	1.37	4.28	5.22	3.86	8.28	5.04	7.24	5.94	1.48	1.93	1.64	2.18	2.69	3.03
41/64	17.26	0.58	3.67	2.86	2.51	7.57	2.95	4.07	4.62	0.72	0.62	0.77	1.57	0.59	0.59
60/56	ND	ND	ND	1.26	0.69	ND	ND	1.40	ND	0.40	0.40	0.45	1.83	0.28	ND
90/101	8.33	0.88	6.86	3.51	1.71	28.74	4.67	4.21	10.40	0.72	1.46	0.41	2.17	0.38	0.98
ICES PCBs	106	6	38	24	17	125	30	32	65	4.9	11.5	3.1	11.8	4.1	6.7
Sum of PCBs	285.06	12.25	90.65	60.55	44.22	296.99	73.85	87.19	153.05	12.64	24.25	8.58	33.78	10.03	14.81

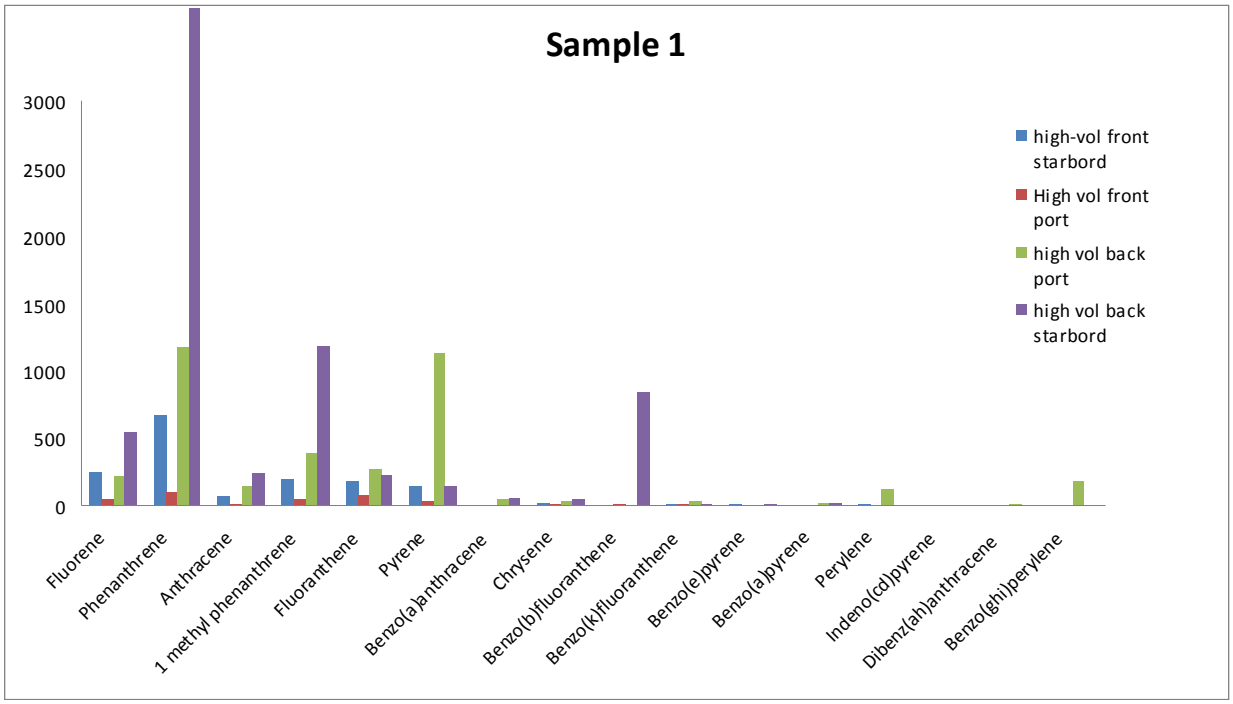


Figure SI.1. Differences in PAH concentrations among the 4 high-vols sampling simultaneously on the cruise.

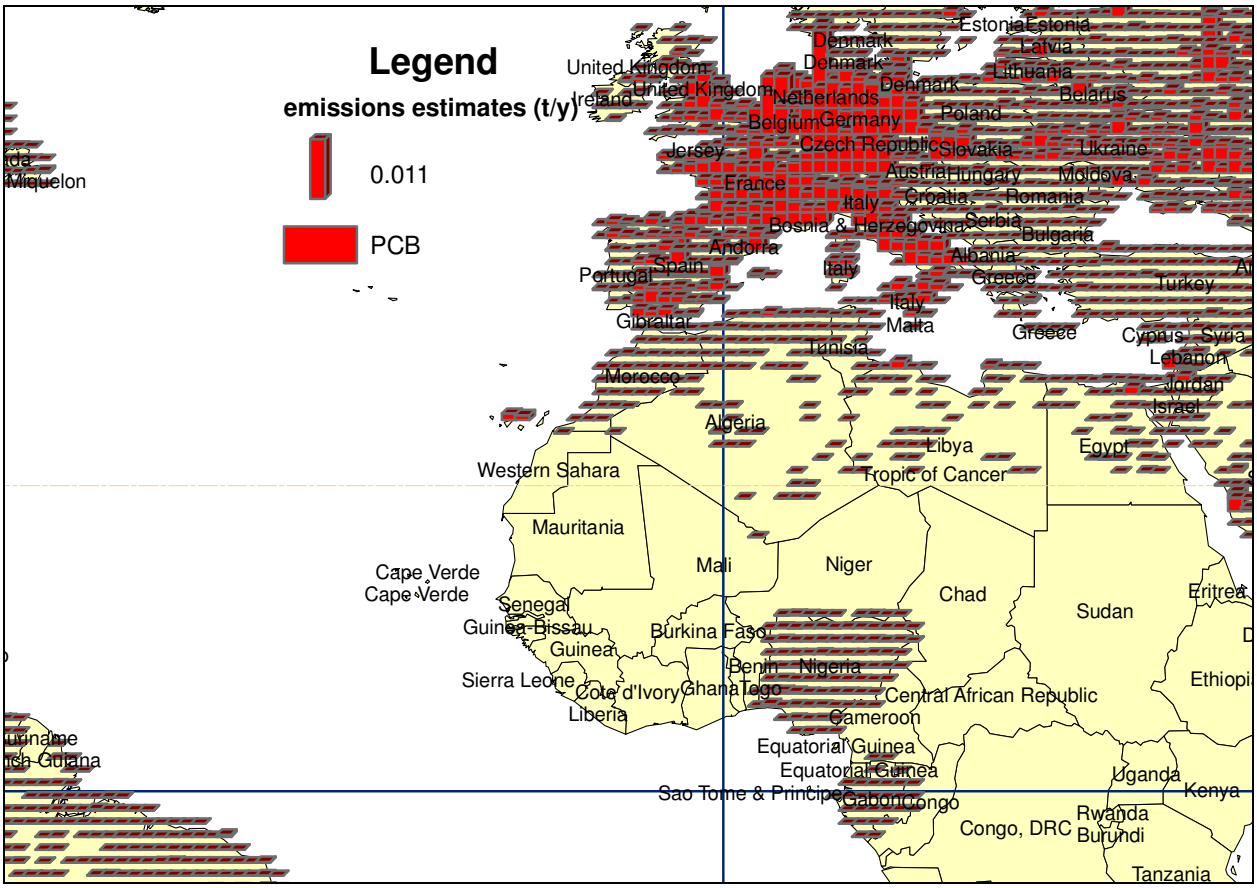


Figure SI.2. PCB emission estimates in t/year in Europe and Africa from Breivik et al. (2).

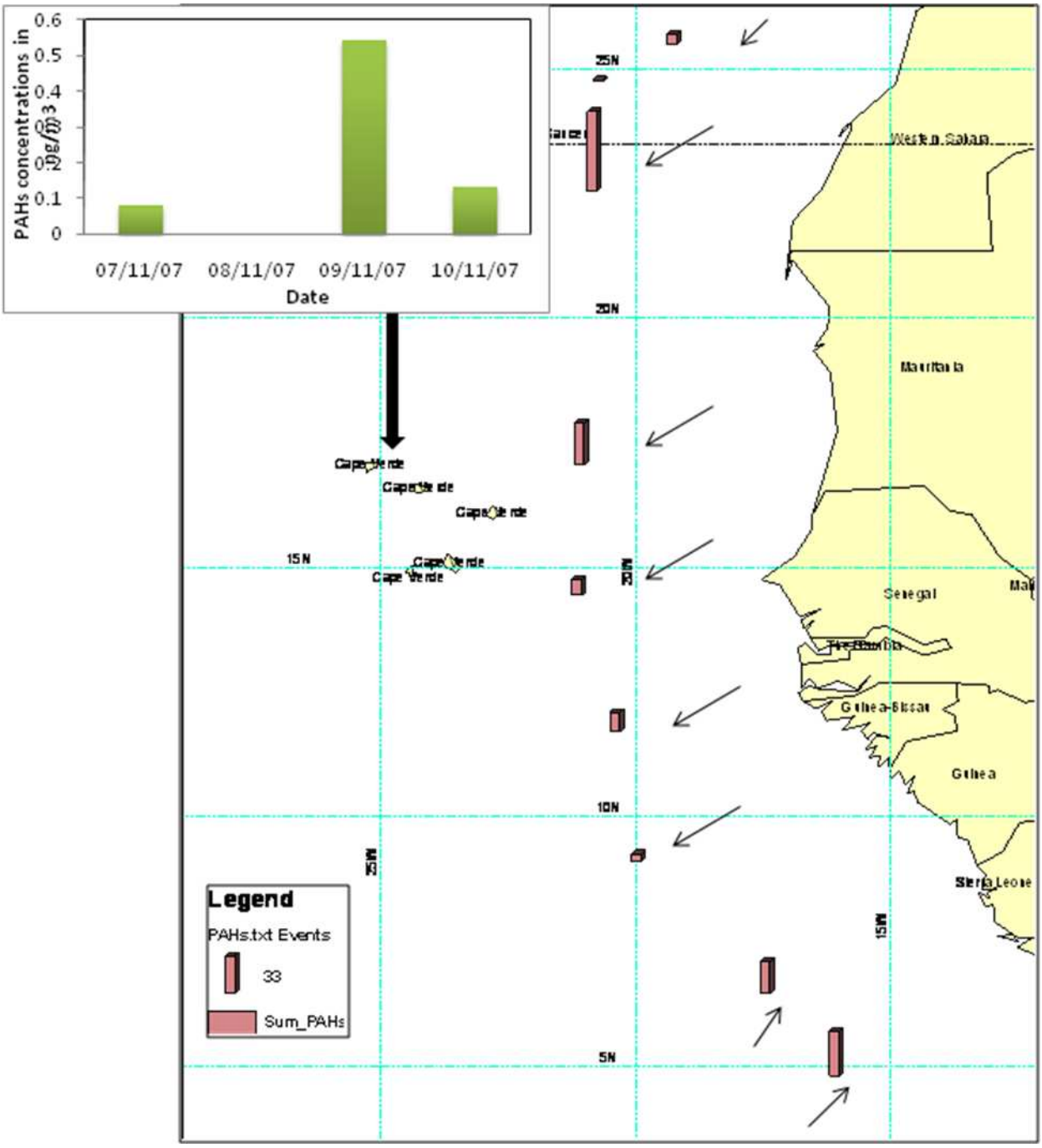


Figure SI.3: PAH concentrations in Cape Verde, cruise samples and West African countries in ng/m^3. Cape Verde is represented on a graph because is presented as a temporal series at a stationary sampling location. Black arrows represent broad air mass origins.

Figure SI.4 Satellite images from Moderate Resolution Imaging Spectroradiometer (Modis) on Nasa's Terra and Aqua satellites for the 10-day period between November 1 and November 17.The red and the yellow colour indicate high intensity fires.

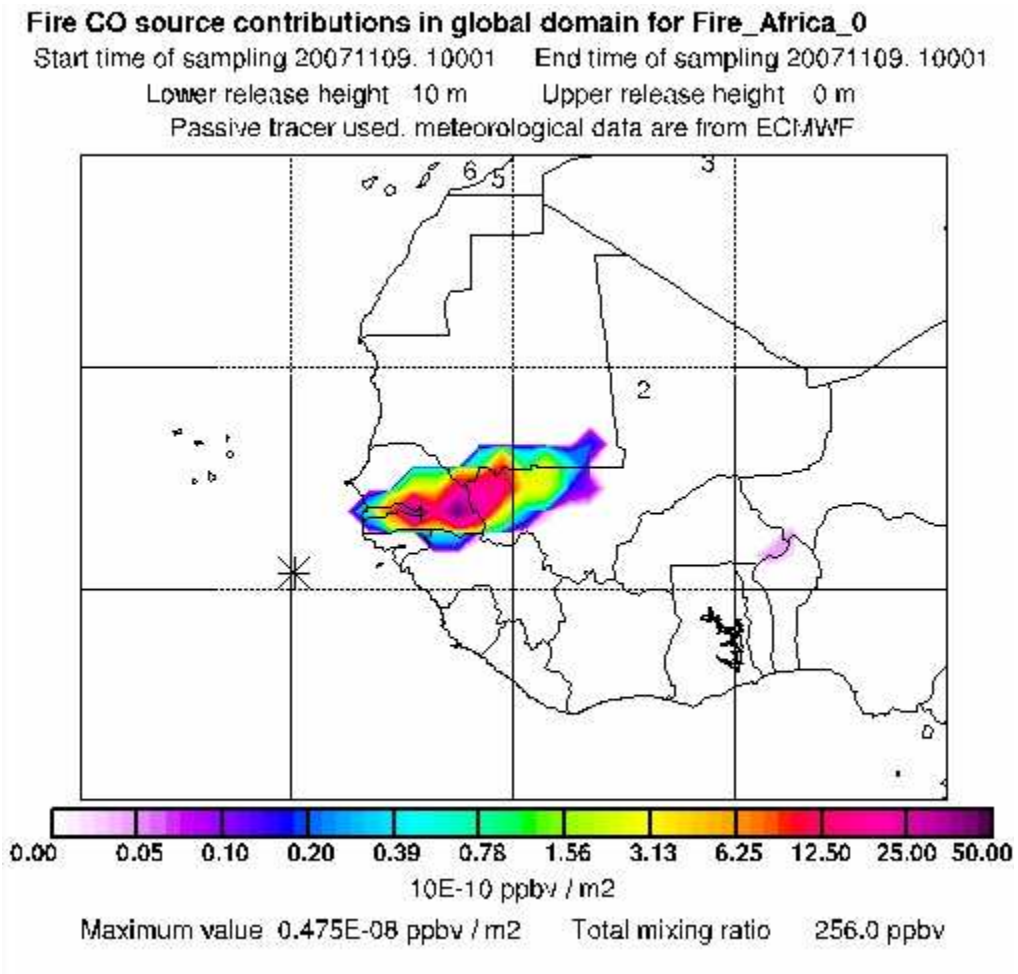
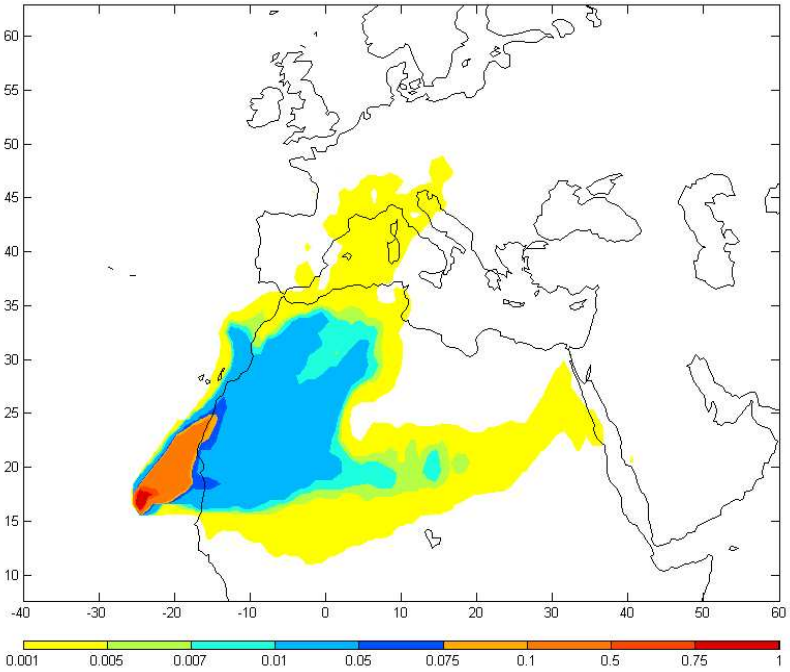


Figure SI.5. Fire source region for sample PS32 showing highest concentration of Σ_{29}PCBs and highest CO predictions.


60
55
50
45
40
35
30
25
20
15
10
-40
-30
-20
-10
0
10
20
30
40
50
60
0.001
0.005
0.007
0.01
0.05
0.075
0.1
0.5
0.75
1

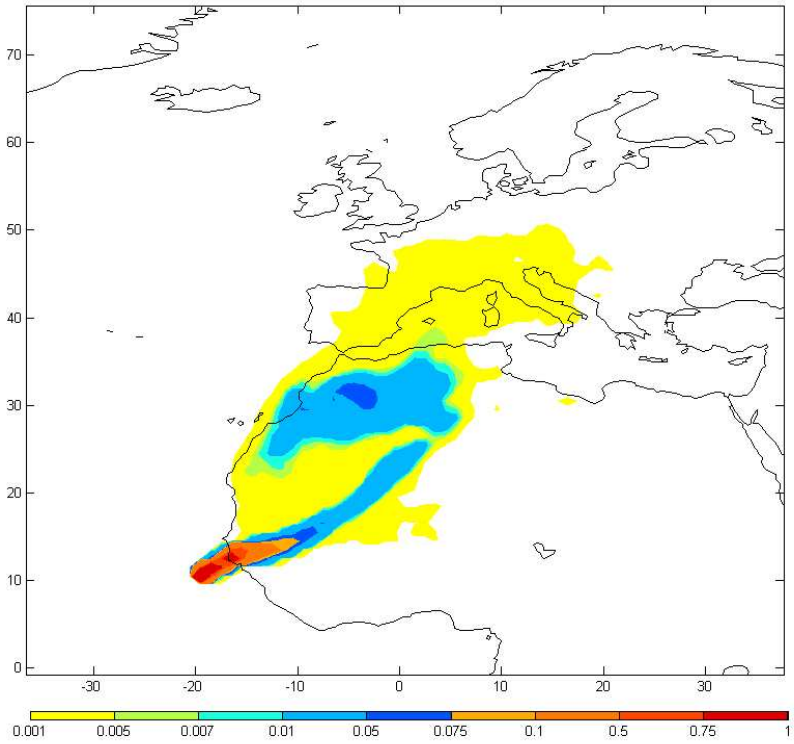


Figure SI.6. Source region (Footprint emission sensitivity [ns/m^3]) for the highest PCB sample measured in Cape Verde at 9.11. 7:00 to 10.11 19:00 (upper panel) and sample PS32 from the ship cruise on the 9.11 at 1:00 am.