Supplementary Information

Investigating PAH Relative Reactivity using Congener Profiles, Quinone Measurements and Back Trajectories

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Sampling Analysis

List of chemicals

HPLC grade dichloromethane (DCM) was purchased from Fischer Scientific (Loughborough, UK) and nonane 99% purum, zinc powder 99% purum, pentane 99% GC grade and acetic anhydride 99% puriss were supplied by Sigma-Aldrich (Dorset, UK). Certified standard 16 EPA Priority PAH pollutant mixture CERTAN 100 µg/mL of each analyte in toluene was purchased from LGC Promochem (Teddington, UK). Coronene standard solution 100 µg/mL in toluene, acenaphthylene-d_8 200 µg/mL in isooctane, pyrene-d_{10} 500 µg/mL in acetone, chrysene-d_{12} 2000 µg/mL in dichloromethane, benzo[a]pyrene-d_{12} 200 µg/mL in isooctane, indeno[$1,2,3$-cd]pyrene-d_{12} 200 µg/mL in isooctane, benzo[ghi]perylene-d_{12} 200 µg/mL in toluene were supplied by Greyhound ChemService (Birkenhead, UK), benz[a]anthracene-d_{12} and phenanthrene-d_{10} 1000 µg/mL in DCM were purchased from UltraScientific (North Kingstown, RI, USA) whilst anthracene-d_{10} and p-terphenyl-d_{14} 2000 µg/mL in dichloromethane were purchased from Greyhound ChemService and UltraScientific. Quinone standards and internal standards were purchased as powders (>97% purity) from Sigma-Aldrich (Dorset, UK) with the exception of benzo[a]pyrene-1,6-dione and benzo[a]pyrene-6,12-dione, which were purchased from NCI Chemical Reference Standard Repository. Standard Reference Material SRM 1649a was supplied by Greyhound ChemService. Quinone powders were measured with a 0.1 µg balance enclosed in a fume cupboard to prevent inhalation.

Table S1. Number of trajectories (out of 24) assigned to each cluster during the winter and summer sampling campaigns. See Figure S1A and S1B for clusters.

Winter Sampling Campaign (03-Feb-2010 to 25-Feb-2010)			
Date	**GREEN** *(Eastern & Southern Europe)*	**BLUE** *(Southern England & mainland UK)*	**RED** *(North Sea & Scaninavia))*
03-Feb-2010	6	**18**	
05-Feb-2010		**24**	
06-Feb-2010	**15**	9	
07-Feb-2010	**24**		
08-Feb-2010	6		**18**
09-Feb-2010	3		**21**
10-Feb-2010	**24**		
11-Feb-2010			**24**
12-Feb-2010			**24**
13-Feb-2010			**24**
14-Feb-2010	3		**21**
15-Feb-2010	**19**	5	
16-Feb-2010	**15**	9	
17-Feb-2010	4	**20**	
18-Feb-2010	5	**19**	
19-Feb-2010	1	**23**	
20-Feb-2010	3	**21**	
21-Feb-2010	**16**	8	
22-Feb-2010	6	**18**	
23-Feb-2010		5	**19**
24-Feb-2010			**24**
25-Feb-2010		**24**	

Summer Sampling Campaign (06-Aug-2010 to 02-Sep-2010)			
Date	**RED** *(Mainland UK)*	**BLUE** *(Southern England)*	**GREEN** *(North Sea)*
06-Aug-2010	5	**19**	
07-Aug-2010		**19**	5
08-Aug-2010	3		**21**
09-Aug-2010	**18**	6	
10-Aug-2010	7	**17**	
11-Aug-2010	**24**		
13-Aug-2010			**24**
14-Aug-2010			**24**
15-Aug-2010			**24**
16-Aug-2010	5		**19**
17-Aug-2010	**20**	4	
18-Aug-2010	**24**		
19-Aug-2010	6	**18**	
20-Aug-2010		**24**	
21-Aug-2010		**24**	
22-Aug-2010		**24**	
23-Aug-2010	8	**16**	
24-Aug-2010	**24**		
25-Aug-2010	**24**		
27-Aug-2010	6		**18**
28-Aug-2010	**24**		
29-Aug-2010	5		**19**
30-Aug-2010			**24**
31-Aug-2010			**24**
01-Sep-2010			**24**
02-Sep-2010			**24**

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Table S2. Average quinone to parent-PAH ratios calculated at rural (Weybourne – winter and summer) and urban background sampling sites (EROS, see Alam et al., 2013)

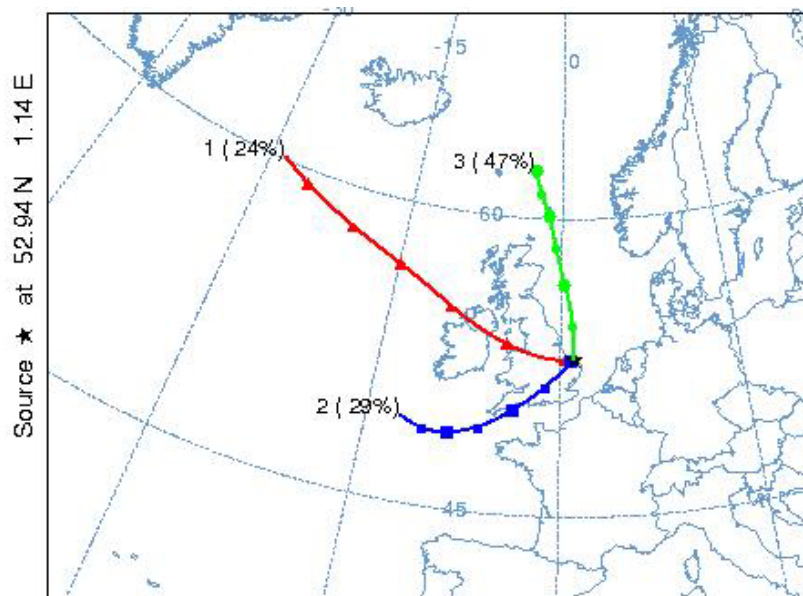| Quinone / parent-PAH	Average Ratios		
	Winter Weybourne	Summer Weybourne	EROS (urban background)
PQ / PHE	0.19	0.25	0.23
AQ / ANT	0.72	0.84	0.20
B(a)A-7,12 / B(a)A	0.59	0.69	0.18

(A)
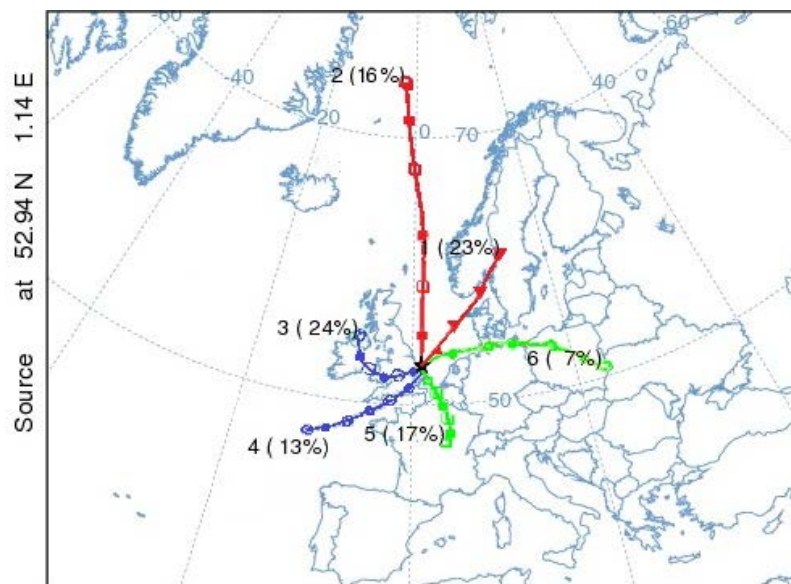
(B)

Figure S1. (A) Cluster analysis of 744 back trajectories, for winter campaign. **(B)** Cluster analysis of 720 back trajectories, for summer campaign. Both (A) and (B) indicate the rapid change in air mass direction at the Weybourne Observatory site. Simulations performed by HYSPLIT model