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Supplementary Information

Diurnal Variability of Persistent Organic Pollutants in the Atmosphere over the Remote Southern Atlantic Ocean. *Atmosphere* 2014, *5*, 622–634

Rosalinda Gioia [1,2,*], Matthew MacLeod [3,†], Javier Castro-Jiménez [4], Luca Nizzetto [1,5], Jordi Dachs [4], Rainer Lohmann [6] and Kevin C. Jones [1]

1 Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, UK; E-Mails: luca.nizzetto@niva.no (L.N.); k.c.jones@lancaster.ac.uk (K.C.J.)

2 The Centre for Environment, Fisheries and Aquaculture Science, Cefas Lowestoft Laboratory, Pakefield Road, Lowestoft, Suffolk NR33 0HT, UK

3 Swiss Federal Institute of Technology, CH-8093 Zurich, Switzerland; E-Mail: matthew.macleod@itm.su.se

4 Department of Environmental Chemistry, CSIC-IDAEA, Jordi Girona 18-24, E-08034 Barcelona, Spain; E-Mails: jcjqam@idaea.csic.es (J.C.-J.); jordi.dachs@idaea.csic.es (J.D.)

5 Norwegian Institute for Water Research, Gaustadalleen 21, NO-0349 Oslo, Norway

6 Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882, USA; E-Mail: Lohmann@gso.uri.edu

† Current Affiliation: Department of Applied Environmental Science, Stockholm University, SE-11418 Stockholm, Sweden.

* Author to whom correspondence should be addressed; E-Mail: rosalinda.gioia@cefas.co.uk; Tel.: +44-1502-524-393.

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This supplementary supports the main text as follows:

Table S1. PCB air concentrations in pg·m^{-3} from 3-N to 27-S, mean air and water temperature and mean latitude and longitude for each sample location. NA = not available.

Time of the Day	Air T	Water T	Latitude	Longitude	PCB_22	PCB_28	PCB_52	PCB_90/101	PCB_118	PCB_138	PCB_153	PCB_180	Sum of PCBs
day	27	28	3N	15W	4.1	9.1	5.8	14	2.4	8.2	5.7	1.2	50
night	27	27	2N	13W	2.2	5.0	2.3	3.0	1.1	2.7	2.39	0.82	20
day	26	26	0.7N	11.7W	2.8	11	3.5	5.1	1.4	4.7	3.23	0.89	32
night	25	26	0.5S	10W	3.1	5.8	2.6	5.4	0.89	2.8	4.84	0.59	26
day	25	26	2S	9.7W	2.7	6.8	3.1	5.6	0.89	3.7	2.28	0.75	26
night	24	25	3.5S	8.7W	3.1	6.1	2.4	4.0	0.73	2.8	4.24	0.52	24
day	23	24	5.5S	7W	12	28	10	8.4	1.52	4.5	3.54	1.07	70
night	23	24	7.5S	5.5W	3.2	6.0	2.8	3.5	0.77	2.0	1.35	0.29	20
day	22	23	9S	4.7W	3.7	12	3.8	3.3	0.71	2.3	1.44	0.44	28
night	21	22	10S	3W	1.4	3.5	1.9	2.4	0.35	1.1	0.75	NA	11
day	21	22	11S	2.5W	8.2	15	8.3	9.8	NA	5.4	4.97	NA	52
night	20	22	12S	1W	1.1	3.9	1.7	2.2	NA	1.0	0.63	NA	11
day	19	21	14S	0E	1.2	2.5	1.5	1.9	0.25	1.1	0.77	NA	9.2
night	19	19	16 S	1E	0.95	2.4	1.2	1.5	NA	0.55	0.50	NA	7.0
day	18	19	18.8S	2E	0.97	2.7	1.2	1.2	NA	0.75	0.48	NA	7.3
night	18	19	19S	3E	1.3	3.1	1.1	1.2	NA	0.57	0.85	NA	8.2
day	18	19	21S	5E	0.94	2.4	0.76	0.77	NA	0.49	0.43	NA	5.7
night	18	18	22S	6E	1.3	3.0	1.2	1.1	NA	0.61	0.41	NA	7.6
day	18	18	24S	7.5E	1.2	2.8	1.3	0.86	NA	0.83	0.43	NA	7.5
night	18	18	25.22S	8.41E	0.87	2.3	1.1	0.92	NA	0.66	0.52	NA	6.4
day	18	18	26S	9E	1.2	2.5	1.0	0.72	NA	0.58	0.48	NA	6.5
night	18	18	27S	11E	0.72	2.2	0.64	0.34	NA	0.54	NA	NA	4.4

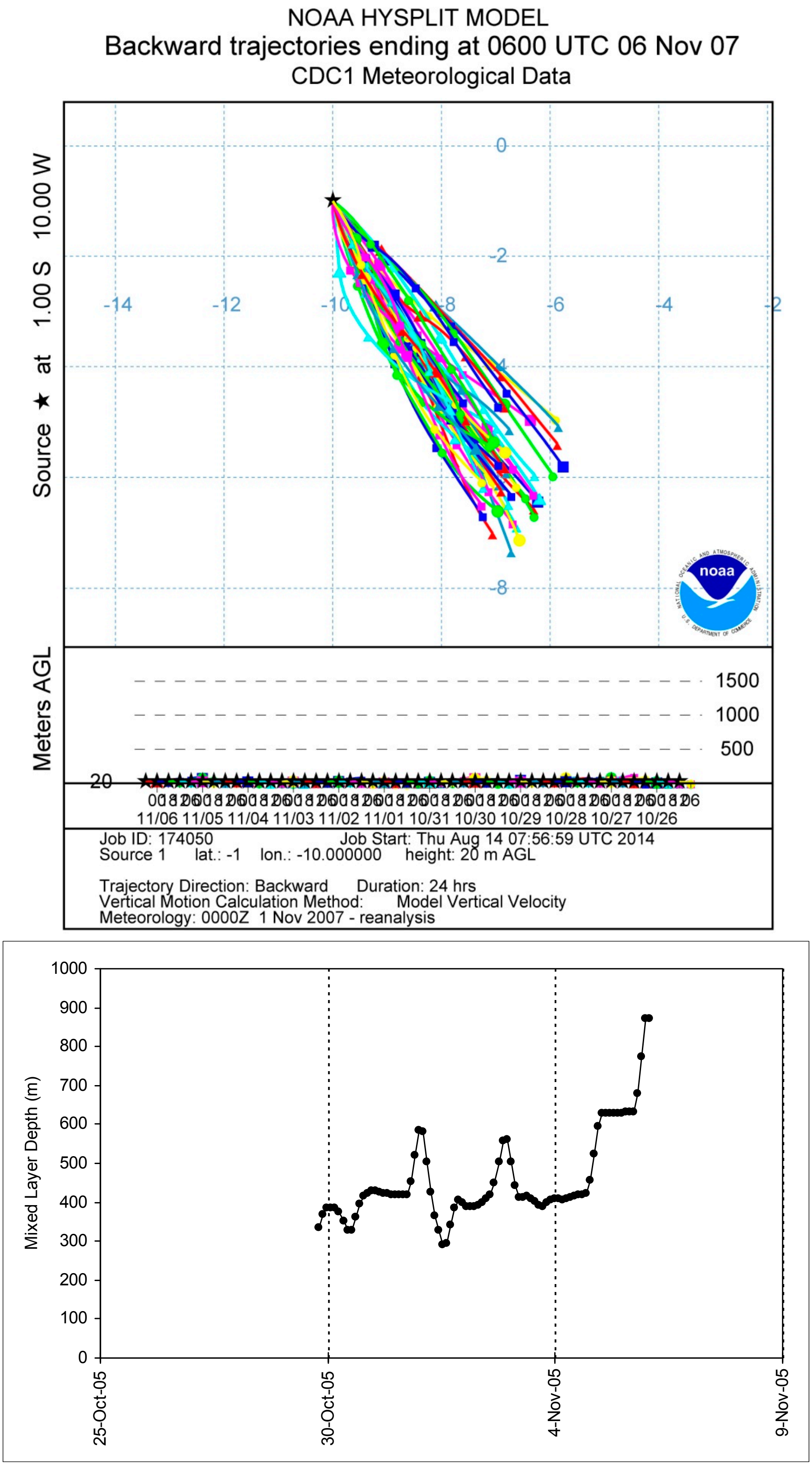
Table S2. Phenanthrene and fluoranthene air concentrations in pg·m^{-3} from 3-N to 25-S, mean air and water temperature and mean latitude and longitude for each sample location. NA = not available.

Time of the Day	Latitude	Longitude	Phenantrene	Fluoranthene
night	3.5	−14.5	34	15
day	−0.4	−11.2	160	45
night	−2.4	−10.1	211	80
day	−3.4	−8.6	41	13
night	−5.2	−7.4	147	NA
day	−7.2	−6.2	25	7.6
night	−8.4	−4.6	394	61
day	−10.2	−3.5	57	18
night	−11.4	NA	NA	NA
day	−12.3	−2.3	34	8.8
night	−14.1	−0.4	76	16
day	−15.5	0.4	15	<5
night	−17.4	2.9	54	13
day	−19.1	3.3	20	5.0
night	−25.0	8.2	84	28

Table S3. Selected PCB congeners water concentrations in pg·L^{-1} in the area where PCB cycle was observed. NA = not available.

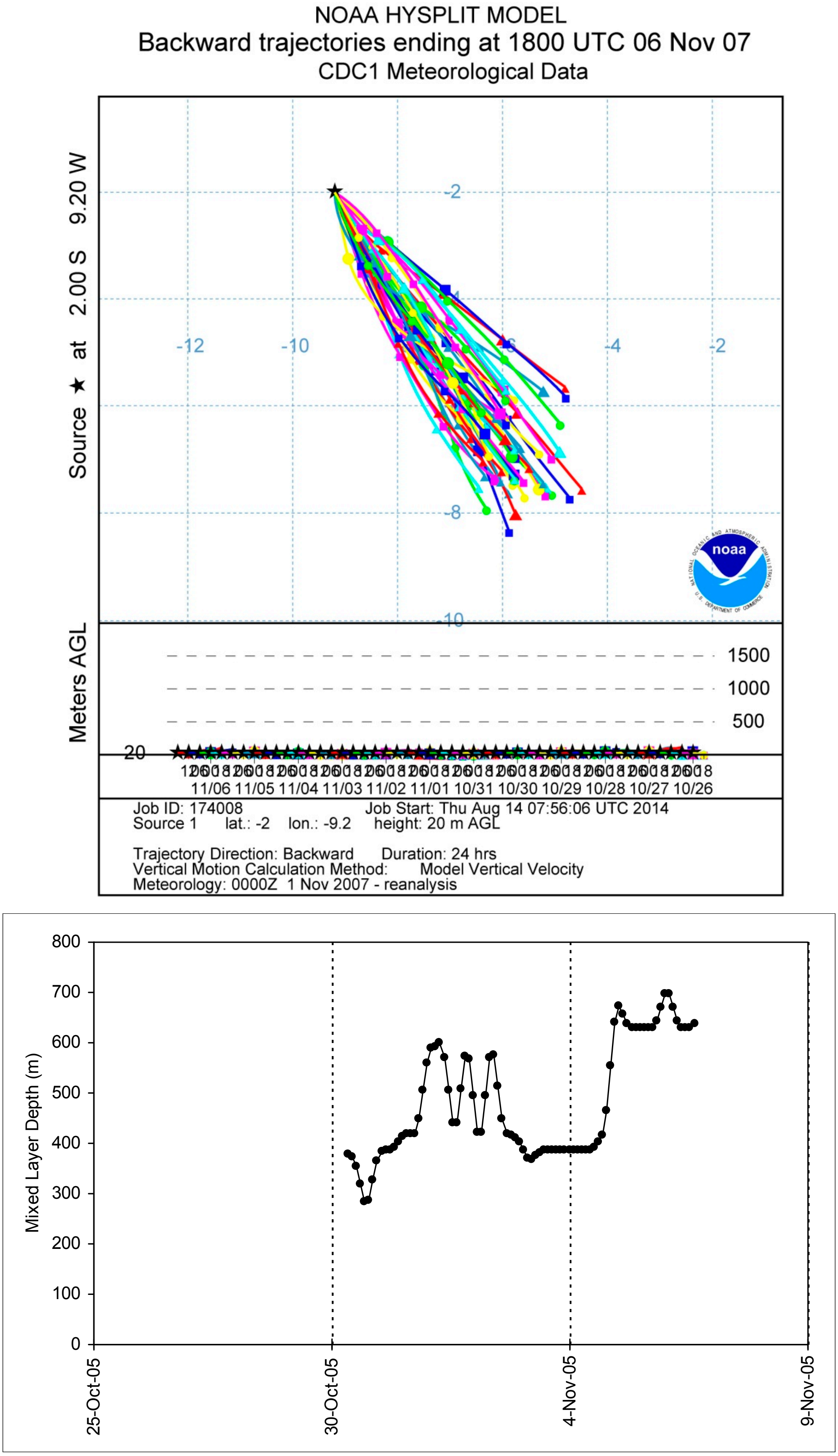
Time of the Day	Latitude	Longitude	PCB_22	PCB_28	PCB_52	PCB_90/101	PCB_118	PCB_138	PCB_153	PCB_180	Sum of PCBs
day	0N	11.7W	0.16	0.37	0.36	0.42	0.062	0.21	0.20	0.053	1.82
night	0.39S	10W	0.11	0.19	0.10	0.11	0.033	0.061	0.045	0.035	0.67
day	1.3S	9.7W	0.13	0.31	0.094	0.11	0.057	0.058	0.062	NA	0.82
night	3S	8.7W	0.052	0.12	0.041	NA	0.00076	NA	NA	NA	0.22

Figure S1. Seven days back trajectories and atmospheric mixing layers for three days sampling. (**A**) 5 November 2005, night sample; (**B**) 6 November 2005, day sample; (**C**) 6 November 2005, night sample.



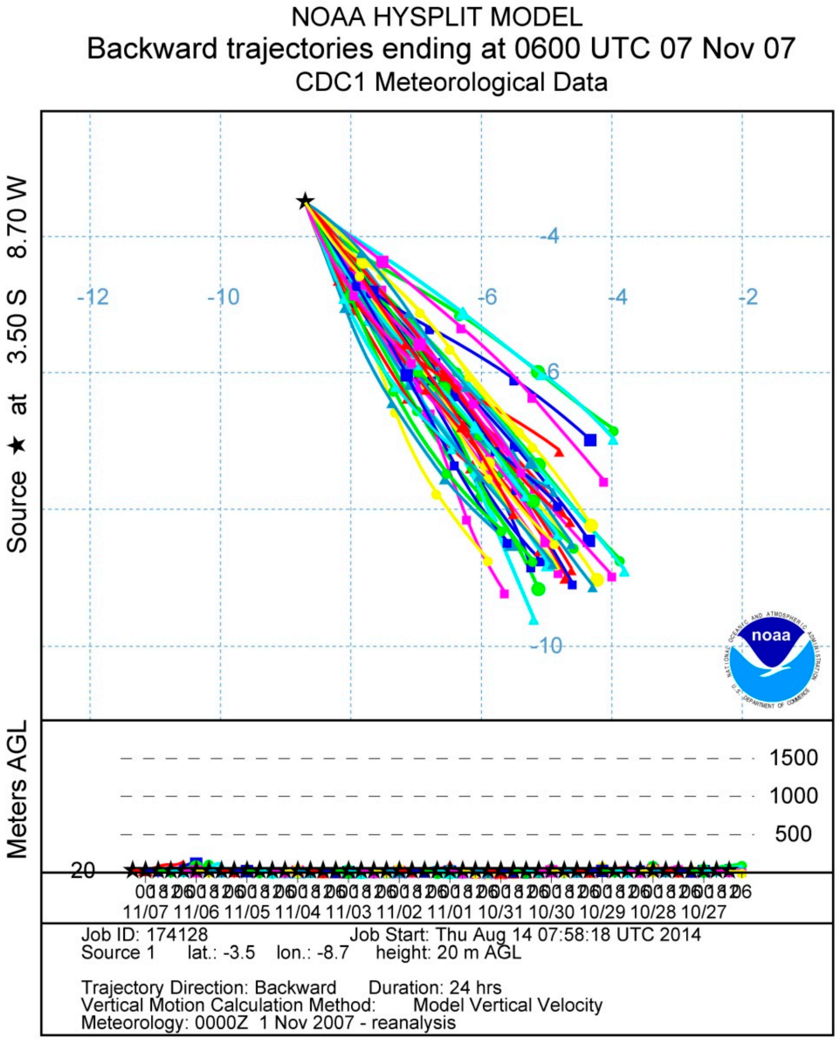
(**A**)

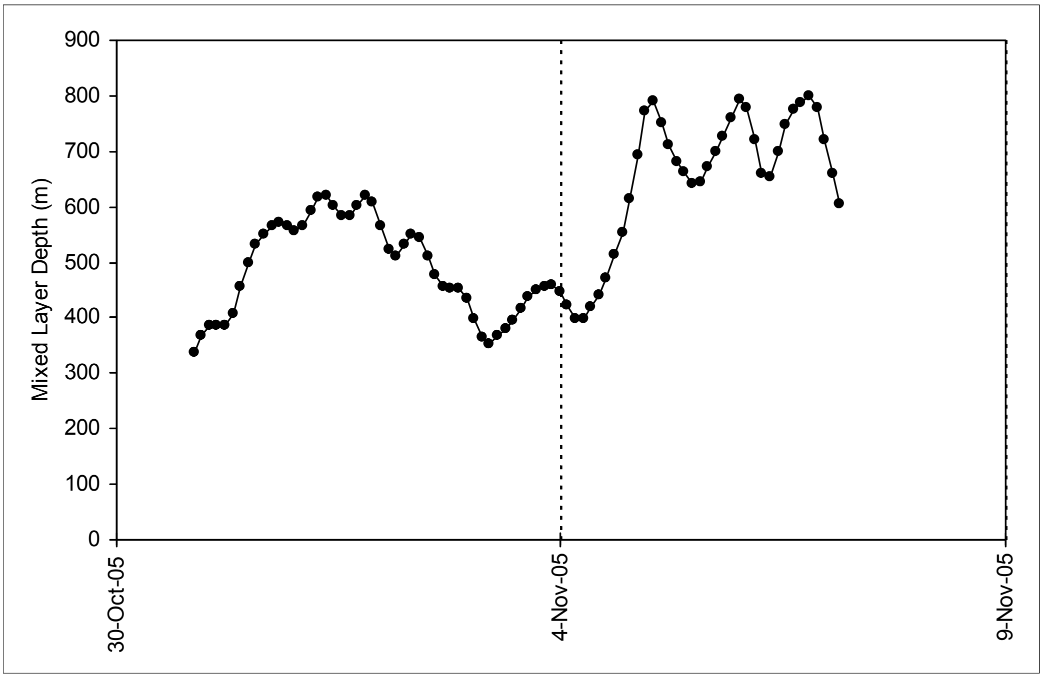
Figure S1. *Cont.*



(**B**)

Figure S1. *Cont.*





(**C**)

Modeling the Influence of Diel Variable Processes in the Ocean (Process-Level Description of the Two Scenarios)

Scenario 1. The Ocean as a Net Sink

The dynamic simulation starts from an assumed steady-state situation, in which the only source is a constant background inflow in air. The total sink is about equally divided between net deposition to ocean water and advection out of the system in air. The calculated air/water fugacity ratio was 3.6, indicating near equilibrium condition with a thermodynamic gradient favoring net deposition to water. If all other processes were stopped and only air-water deposition was occurring, the air concentration would reach half its initial value in 14 h. However, the response time of the atmosphere in the model is attenuated by diffusive feedback from the water. The net deposition rate is 25% smaller than gross deposition at steady state, and the air compartment is constantly re-supplied by PCBs from the background source.

Variability in the OC concentration in ocean water had a larger effect on air concentrations than variability in OH radical concentrations, but under this scenario the magnitude of the induced variability was small compared to what was observed in the field. Air concentrations varied only by about 20% in response to variability in ocean parameters (see Figure 3 in the main text). This corresponds to a factor of 1.2, which cannot account for the factor of 2 variability observed in the field measurements. The magnitude of the induced variability is limited by the relatively slow response of the air compartment to changes in the ocean compartment, and by the dynamic coupling and near-equilibrium conditions between air and water, which limit the magnitude of the net flux of PCBs from air to water.

Scenario 2. The Ocean as a Net Source

When the background concentration in air is reduced at the start of the dynamic model run, the model moves towards a new steady state. The lower-air compartment responds quickly to the change in inflow concentration, so if the background air concentration is lowered enough, the fugacity gradient switches and the ocean becomes a net source of PCB to the air (rather than a net sink). The ocean can be a net source to the atmosphere under two different scenarios: (1) If the ocean is "loaded up" with PCBs during the winter, which are then outgassed during the spring/summer (when the cruises took place); or (2) if the area where the diel variability was observed normally had higher PCB concentrations in air, but sampling occurred on days when the air concentration was unusually low (e.g., due to the arrival of relatively uncontaminated oceanic air masses). When the OC content of ocean water is high, the fugacity capacity of the surface ocean is also high, and the fugacity in the ocean water is low. At these times the fugacity gradient is downward, there is net deposition and air concentrations in the lower atmosphere fall. When the OC content of the ocean falls, the fugacity in this compartment rises above that of the lower air compartment and there is net volatilization so that air concentrations rise.