Supplementary Material

SI Materials and Methods

The pyrene fluorescence loss method is a novel approach to quantify a broader portion of the BC combustion continuum (Flores-Cervantes et al., 2009). BC concentrations were calculated from the loss of dissolved pyrene based on eq. 1 – 3.

$$f_w = \frac{C_f}{C_i} \qquad \text{(eq. 1)}$$

Where f_w is the fraction of pyrene lost from solution due to adsorption to the BC, i.e. ratio of the final (C_f) to the initial pyrene concentration (C_i).

$$K_d = \frac{(1-f_w)}{f_w r_{sw}} \qquad \text{(eq. 2)}$$

The solid-water partitioning coefficient (K_d) for pyrene was determined using eq. 2, where r_{sw} is the solid-water ratio (kg L^{-1}).

$$f_{BC} = \frac{[K_d - f_{OC}K_{OC}]}{K_{BC}\,C_W^{n-1}} \qquad \text{(eq. 3)}$$

The calculated K_d was used to determine the fraction of BC (f_{BC}) according to eq. 3. The K_{OC} and K_{BC} are the previously determined pyrene partitioning coefficients of $10^{4.7}$ (L $kgOC^{-1}$) for organic carbon (OC) and $10^{6.25}$ (L $kgBC^{-1}$) for BC (BC), respectively (Accardi-Dey and Gschwend, 2002). The C_w^{n-1} is the initial truly dissolved pyrene concentration, where n is the Freundlich exponent of 0.62. An initial concentration of 1 µg L^{-1} pyrene was purposely selected to allow the C_w term to approach 1 since the Freundlich exponent is the component with the highest degree of uncertainty. Finally, the f_{OC} is the fraction of the total organic carbon determined by the IRMS during the CTO-375 analysis. We assumed that BC would be a minor constituent so that the total organic carbon would be equivalent to the organic carbon concentration, as was done in Flores-Cervantes (2009).

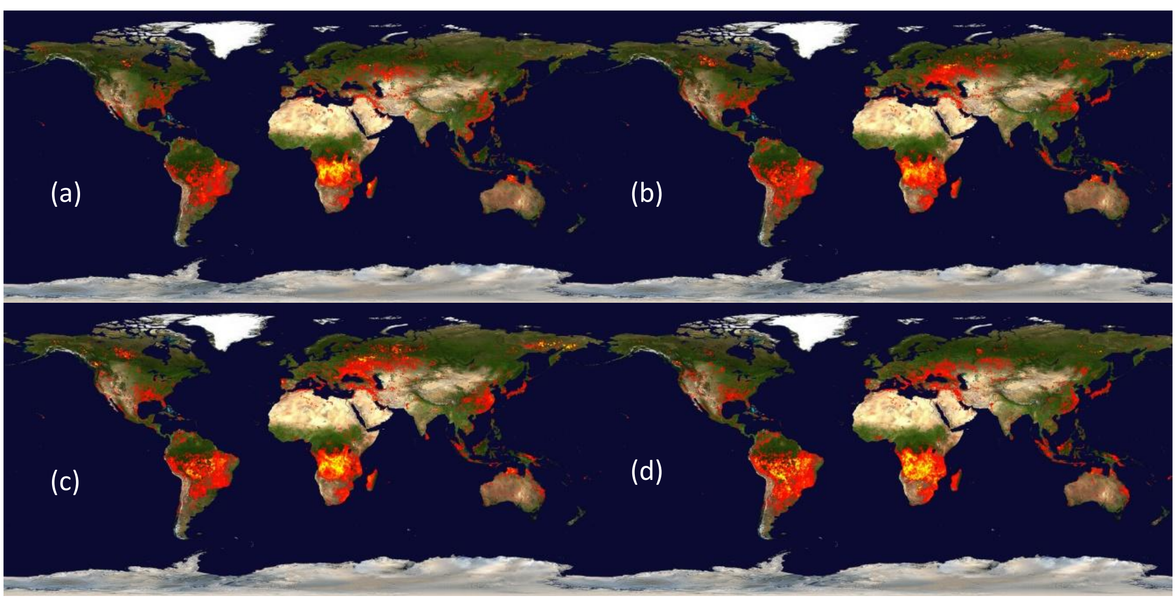
Additionally, the salinity of five pyrene solutions with double the filter mass and half the volume were measured with a refractometer in order to assess if salinity could have affected pyrene's solubility in solution. A measurement of 0 ppt was received in triplicate for all five samples, concluding that the salting out effect of pyrene would be minimal in our set-up.

A series of blank filters were placed on a high volume air sampler at the Graduate School of Oceanography, Narragansett, Rhode Island at a rate of 1.35 m^3min^{-1} (47.5 CFM) for 10, 20, 30, 60, and 120 minutes to test if the carbon blank would decrease inversely as air volume filtered increased. The associated carbon blank was constant for all air volumes, suggesting that the carbon detected by the thermal methods was not due to contamination but rather the filter matrix.

In separate work, corn pollen was analyzed by both CTO-375 and the pyrene fluorescence loss technique to assess its possible interference on the BC measurements. No BC was detected on the pollen using the pyrene fluorescence loss method; however approximately 66% of the pollen remained after the CTO-375 treatment.

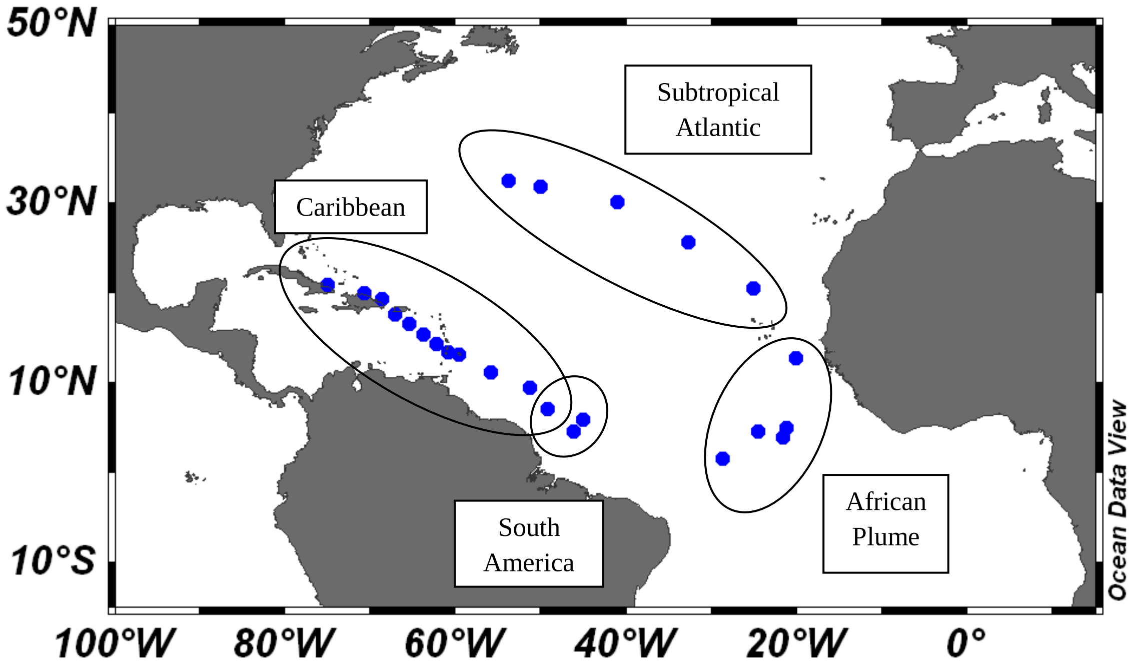
Methodological quality control for the CTO-375 and pyrene fluorescence loss method was also assessed and compared using the NIST standard reference materials 1941b (marine sediment). BC mass fractions for were within the expected range of 0.7 ± 0.1% for the CTO-375 method and 1.6% for the pyrene fluorescence loss (Hammes et al., 2007; Flores-Cervantes et al., 2009).

SI Tables and Figures



SI Fig. 1. Global fire maps generated from the MODIS Terra and Aqua satellites for (a) June 30-July 9 2010, (b) July 20-27, 2010, (c) July 30-August 8, 2010, and (d) August 18-28,

2010. Both (a) and (b) co-occurred during the Caribbean and South America region sampling, (c) occurred during the African plume region sampling, and (d) for the subtropical Atlantic region sampling. The color indicates the number of detected wildfires from red (low) to yellow (high). Credits: Jacques Descloitres, Louis Giglio, and Reto Stokli.



SI Fig. 2. Filter samples grouped by region, as defined by wind direction and locality to land. Note that the Amazon and African Plume regions were below the inter-tropical convergence zone at the time of sampling.

Sample	Start Date (2010)	Minutes Sampled	Latitude	Longitude	Volume (m^3)
QFF-1	6-Jul	721.2	20.983	-74.988	408
QFF-2	7-Jul	725.4	20.021	-70.654	308
QFF-3	7-Jul	684.0	19.285	-68.575	97
QFF-4	8-Jul	736.6	17.615	-67.033	104
QFF-5	8-Jul	707.3	16.550	-65.483	100
QFF-6	9-Jul	740.6	15.416	-63.783	315
QFF-7	9-Jul	708.4	14.338	-62.223	301
QFF-8	10-Jul	691.2	13.453	-60.817	294
QFF-9	14-Jul	2822.6	7.079	-49.156	1199
QFF-10	16-Jul	2455.0	5.906	-45.011	1043
QFF-11	20-Jul	2884.1	11.179	-55.835	1225
QFF-12	22-Jul	1419.6	13.100	-59.650	603
QFF-13	23-Jul	2793.7	9.483	-51.266	3758
QFF-14	27-Jul	3286.7	4.600	-46.200	4421
QFF-15	30-Jul	3983.4	1.580	-28.767	5358
QFF-16	3-Aug	3353.1	3.961	-21.667	4510
QFF-17	6-Aug	4532.0	4.977	-21.215	6096
QFF-18	10-Aug	2234.8	4.554	-24.496	3006
QFF-19	15-Aug	2209.0	12.813	-20.066	2971
QFF-20	21-Aug	2682.2	20.521	-25.118	3608
QFF-21	23-Aug	2718.1	25.717	-32.768	3656
QFF-22	25-Aug	2863.3	30.167	-41.027	3851
QFF-23	27-Aug	2846.1	31.871	-50.100	3828
QFF-24	29-Aug	943.2	32.516	-53.764	1269

SI Table 1. Date, location, and volume of air sampled for each filter.

QFF	CTO-375	PFL	TOT	OT-21	Region
1	0.00	0.62	0.32	0.00	Caribbean
2	1.17	1.12	0.00	0.08	Caribbean
3	0.64	3.56	0.00	0.52	Caribbean
4	3.37	2.86	0.00	0.72	Caribbean
5	1.71	2.98	0.00	0.00	Caribbean
6	1.02	0.95	0.00	0.16	Caribbean
7	0.00	0.99	0.00	0.08	Caribbean
8	1.39	0.00	0.00	0.00	Caribbean
9	0.02	0.19	0.00	0.14	Caribbean/South America
10	0.35	0.42	0.00	0.53	South America
11	0.04	0.06	0.00	0.18	Caribbean
12	0.83	0.53	0.00	0.14	Caribbean
13	0.02	0.25	0.00	0.23	Caribbean
14	0.09	0.33	0.06	0.19	South America
15	0.04	0.33	0.00	0.20	African Plume
16	0.01	0.47	0.03	0.83	African Plume
17	0.08	0.21	0.03	0.92	African Plume
18	0.03	0.91	0.03	1.33	African Plume
19	0.19	0.74	0.01	0.73	African Plume
20	0.03	0.36	0.00	0.30	Subtropical Atlantic
21	0.02	0.40	0.00	0.33	Subtropical Atlantic
22	0.03	0.00	0.18	0.09	Subtropical Atlantic
23	0.03	0.09	0.00	0.13	Subtropical Atlantic
24	0.30	0.56	0.14	0.00	Subtropical Atlantic

SI Table 2: Black carbon concentration (µg m^{-3}) per individual filter for each method.

Sample	TOC[a] ug m^{-3}	TOC[b] ug m-3	δ^{13}C-TOC	δ^{13}C-BC
1	0.4	0.9	-22	2
2	2.1	2.3	-32	-91
3	3.1	3.9	-27	-64
4	3.8	6.1	-27	-39
5	5.8	5.2	-34	-41
6	1.1	0.4	-33	-42
7	1.2	0.8	-9	-17
8	1.9	1.6	-26	-36
9	0.4	0.4	-24	-16
10	0.5	0.9	-26	-35
11	1.0	0.4	22	-23
12	0.8	0.7	-28	-40
13	0.3	0.4	-27	-6
14	0.2	0.2	-32	-34
15	0.1	0.2	-26	-18
16	0.7	1.1	-19	-26
17	1.3	1.6	-19	-16
18	1.5	1.9	-20	-2
19	0.7	0.9	-22	-24
20	0.2	0.4	-23	-13
21	0.3	0.4	-24	3
22	0.2	0.1	-25	-27
23	0.2	0.2	-17	-17
24	0.2	0.4	-25	-21

SI Table 3: Total organic carbon concentrations as measured by the CTO-375 (TOC[a]) and TOT (TOC[b]) methods and the δ^{13}C values for the total organic carbon and black carbon determined for each filter by the CTO-375 method after blank correction.

Regional Average	CTO/PFL	BC/TOC-IRMS	BC/TOC-TOT
Caribbean	1.2	0.45	0.16
South America	0.6	0.45	0.40
African Plume	0.3	0.13	0.73
Subtropical Atlantic	0.2	0.36	0.67
1650 diesel particulate matter	3.1	0.62	

SI Table 4: Regional average of soot-like black carbon (CTO-375) to the broader black carbon spectrum (PFL) ratio and the ratio of black carbon in the total organic carbon determined by the CTO-375 method and TOT.

SI References

Accardi-Dey, A., and Gschwend, P. M.: Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments, Environ Sci Technol, 36, 21-29, Doi 10.1021/Es010953c, 2002.

Flores-Cervantes, D. X., Reddy, C. M., and Gschwend, P. M.: Inferring Black Carbon Concentrations in Particulate Organic Matter by Observing Pyrene Fluorescence Losses, Environ Sci Technol, 43, 4864-4870, Doi 10.1021/Es900043c, 2009.

Hammes, K., Schmidt, M. W. I., Smernik, R. J., Currie, L. A., Ball, W. P., Nguyen, T. H., Louchouarn, P., Houel, S., Gustafsson, O., Elmquist, M., Cornelissen, G., Skjemstad, J. O., Masiello, C. A., Song, J., Peng, P., Mitra, S., Dunn, J. C., Hatcher, P. G., Hockaday, W. C., Smith, D. M., Hartkopf-Froeder, C., Boehmer, A., Luer, B., Huebert, B. J., Amelung, W., Brodowski, S., Huang, L., Zhang, W., Gschwend, P. M., Flores-Cervantes, D. X., Largeau, C., Rouzaud, J. N., Rumpel, C., Guggenberger, G., Kaiser, K., Rodionov, A., Gonzalez-Vila, F. J., Gonzalez-Perez, J. A., de la Rosa, J. M., Manning, D. A. C., Lopez-Capel, E., and Ding, L.: Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere, Global Biogeochem Cy, 21, Artn Gb3016 Doi 10.1029/2006gb002914, 2007.