SUPPORTING INFORMATION

Methylmercury content in soil and litter from the Amazonian rainforest and potential fate during forest fires

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Supplemental Text

Text S1. Methylmercury analyses

Mercury speciation analysis method leading to precise and accurate methylmercury concentration [MeHg] measurement has been developed, validated, discussed, and applied to various environmental matrices in detail elsewhere (Clémens et al., 2011; Feng et al., 2016; Monperrus et al., 2008; Rodríguez Martin-Doimeadios et al., 2003). It is divided in four steps: 1) microwave assisted extraction (MAE); 2) double isotopic dilution; 3) derivatization of the species; and 4) analyses in the Gas Chromatography Inductive Coupled Plasma Mass Spectrometer (GC-ICP-MS). MAE assisted extraction was carried out in CEM Pyrex vessels and with a CEM MW system (Discover SP-D, CEM Corporation) coupled to an autosampler Explorer 4872 96 (USA). Sample preparation consisted of weighting c.a. 250 mg of each sample or certificate material, adding 3 or 5 mL HNO₃ 6 mol L^{-1} (according to the total Hg in the sample) and putting the vessels in the MAE. MW program consisted of heating the system up to 75 °C and maintaining it at this temperature for 5 minutes with magnetic agitation. SRM IAEA-405 and IAEA-336 were also digested to evaluate the accuracy and precision of the method (both total Hg and MeHg for IAEA 405, only total Hg for IAEA 336). Detailed results are given in Table S2. Sample spiking following preparation consisted of adding 5 mL deionized water plus 5 mL acetate buffer in 22 mL glass tubes. Two isotopic enriched standards were used for the quantification: Methylmercury (0.25 ng mL⁻¹~96% ²⁰¹MeHg solution) and inorganic mercury (25 ng mL⁻¹~92 % ¹⁹⁹iHg solution). Proper aliquots of the MW extracts were added and weighted in the tubes as proper amounts of each spike. Sample pH was adjusted to 3.9 with HCl or NaOH. Hg species were derivatized with sodium tetraethylborate (NaBEt₄) and then extracted with isooctane in a mechanical shaker for 20 minutes. GC-ICP-MS analyses were performed Trace Ultra GC equipped with a Triplus RSH autosampler coupled to an ICP-MS XSeries II (Thermo Scientific, with USA) as detailed in previous works (Clémens et al., 2011; Monperrus et al., 2008). All samples were analyzed in triplicate (i.e. triplicate GC-ICPMS injections).

Supplemental Tables

Sub-area	Litter mass ^(a)	Mass that Ass ^(a) Wood mass ^(b) remained af burning		CC ^(c)
	$({\rm kg} {\rm m}^{-2})$	$({\rm kg} {\rm m}^{-2})$	$({\rm kg} {\rm m}^{-2})$	(%)
CJ1	1.15	4.55	0.88	84.5
CJ3	2.83	2.23	0.09	98.11
CJ4	4.21	4.64	0.19	97.9
CJ5	7.69	1.31	0	100.0
CJ6	9.58	7.30	0	100.0
CJ8	1.07	2.27	1.11	66.6
CJ9	0.73	0.88	0.29	81.7
CJ11	2.64	3.87	0.60	90.8
CJ12	2.20	2.62	0.42	91.3
Average	3.57	3.30	0.40	90
SD	3.10	2.01	0.40	11

Table S1. Data used for combustion completeness (CC) at each 4 m² experimental burning sub-areas in Candeias do Jamari.

(a) Litter includes material with diameter (D) < 5 cm

(b) Wood includes material with $5 \le D \le 10$ cm

(c) In each area, CC (%) was calculated as [(Litter + wood mass) - (Mass that remained after burning)*100]/(Litter + wood mass).

Table S2. Obtained and certified values of methylmercury [MeHg], total mercury species ($[THg_{sp}]=[MeHg]+[iHg]$ and total Hg concentration [THg] (ng g⁻¹) in SRM IAEA-336 and IAEA-405. Values in parentheses correspond to the standard deviation.

SRM	[THg _{sp}]obtained	[THg]certified	[MeHg]obtained	[MeHg]certified
IAEA-336	178.2 (4.5)	200 (40)	4.70 (0.03)	-
IAEA-405	773 (4)	810 (40)	5.51 (0.18)	(5.49 (1.06)

IAEA-336 is not certified for [MeHg]

Sub-area	[MeHg]	[TH _{sp}]	[THg] ^(a)	THg _{sp} Recovery (%)	
CJ1	0.19	25.8	39.6	65	
CJ3	0.15	30.5	49.8	61	
CJ4	0.15	16.2	24.5	66	
CJ5	0.16	25.7	36.8	70	
CJ6	0.21	25.7	30.7	84	
CJ8	0.19	21.4	25.2	85	
CJ9	0.13	24.9	32.9	76	
CJ11	0.11	21.9	28.3	78	
CJ12	0.16	24.7	34.7	71	
Average	0.16	24	34	73	
SD	0.03	4	8	8	

Table S3. Concentration (ng g⁻¹) of methylmercury [MeHg], total mercury species ([THg_{sp}]=[MeHg]+[iHg]), total Hg [THg], and THg_{sp} recovery (%) ([THg_{sp}]*100/[THg]) in litter samples.

(a) [THg] determined by TDAAS

Table S4. Concentration (ng g⁻¹) of methylmercury [MeHg], total mercury species $([THg_{sp}]=[MeHg]+[iHg])$, total Hg [THg], and THg_{sp} recovery (%) ([THg_{sp}]*100/[THg]) in ash samples.

Sub-area	[MeHg]	[TH _{sp}]	[THg] ^(a)	THg _{sp} Recovery (%)	
CII	0.11	10.4	23.9	43	
CJ3	0.09	6.6	11.8	56	
CJ4	0.08	14.6	30.7	48	
CJ5	0.14	15.1	28.8	52	
CJ6	0.13	11.9	27.5	43	
CJ8	0.18	16.5	21.8	76	
CJ9	0.10	6.5	11.7	56	
CJ11	0.04	4.6	16.5	30	
CJ12	0.10	14.6	30.3	48	
Average	0.11	11	23	50	
SD	0.04	4	8	12	

(a) [THg] determined by TDAAS

Sub-area	[MeHg]	[THg _{sp}]	[THg] ^(a)	THg _{sp} Recovery (%)
		Before burn	ing	
CII	0.02	50.2	127.5	12
CJI	0.83	59.3	137.5	43
CJ3	0.6/	51.3	135.1	38
CJ4	1.20	88.4	171.8	51
CJ5	1.03	59.5	141.4	42
CJ6	1.00	73.9	138.4	53
CJ8	1.08	80.7	145.9	55
CJ9	1.00	92.0	153.6	60
CJ11	NA	NA	145.9	NA
CJ12	1.23	80.6	166.4	48
Average	1.0	73	148	49
SD	0.2	15	13	7
		After Burni	ing	
CJ1	0.54	47.4	122.2	39
CJ3	0.59	61.4	114.5	54
CJ4	0.60	84.3	166.7	51
CJ5	0.66	67.0	131.3	51
CJ6	0.60	68.7	124.7	55
CJ8	0.88	79.5	160.2	50
CJ9	0.75	58.9	115.0	51
CJ11	NA	NA	113.2	NA
CJ12	$1.18^{(b)}$	77.8 ^(b)	154.1	50 ^(b)
Average	0.7	67	134	50
SD	0.1	13	21	5

Table S5. Concentration (ng g⁻¹) of methylmercury [MeHg], total mercury species ($[THg_{sp}]=[MeHg]+[iHg]$), total Hg [THg], and THg_{sp} recovery (%) ($[THg_{sp}]\times100/[THg]$) in soil (0-1 cm) samples before and after burning

(a) [THg] determined by TDAAS. (b) [MeHg] in CJ12 AB not included in the average calculation because it was considered as an outlier (Grubbs' test for outliers, P < 0.05). NA: not analyzed.

Table S6. Pearson's correlation coefficient (r, in black) and corresponding *P* value (in red) between total biomass (kg m⁻²), combustion completeness (CC, %), OM lost from vegetation (%), THg lost from vegetation (%), MeHg lost from vegetation (%), OM lost from 0-1 cm soil (%), THg lost from 0-1 cm soil (%).

	Total	CC	OM	THg	MeHg	OM lost	THg lost	MeHg lost
	Biomass		lostVeg	lostVeg	lostVeg	0-1cm	0-1cm	0-1cm
Total Biomass		0.062	0.438	0.180	0.639	0.192	0.540	0.150
CC	0.642		0.139	0.915	0.267	0.353	0.857	0.303
OM lostVeg	-0.297	-0.534		0.464	0.561	0.189	0.703	0.433
THg lostVeg	-0.490	-0.041	0.281		0.674	0.623	0.048	0.075
MeHg lostVeg	0.182	0.415	-0.225	0.164		0.392	0.727	0.358
OM lost-0-1cm	-0.479	-0.352	0.482	0.191	0.326		0.906	0.979
THg lost 0-1cm	-0.237	0.070	0.148	0.670	-0.136	-0.046		0.480
MeHg lost 0-1cm	0.604	0.456	-0.356	-0.708	0.412	0.013	-0.323	

Supplemental figure



Figure S1. Localization of the twelve 2×2 m sub-areas in which combustion consumption was estimated inside the prescribed fire experiment at Candeias do Jamari. The numbered areas are those in which soil, litter and ash were sampled (CJ1 to CJ12).

References

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