Gaseous mercury emissions from soil following forest loss and land use changes: Field experiments in the United States and Brazil

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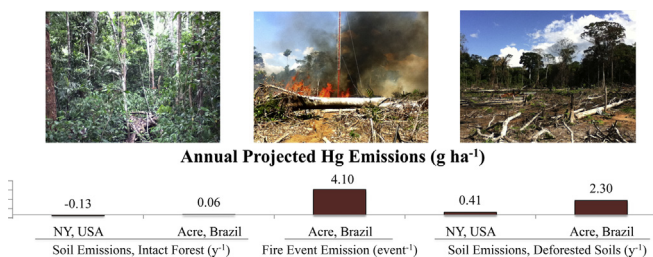[d] Department of Epidemiology, Harvard School of Public Health, 677 Huntington Avenue, Boston, MA 02115, USA
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HIGHLIGHTS

- We examined the effect of deforestation on gaseous mercury emission from soil.
- Soils in intact forest soils were a net sink of gaseous mercury.
- After canopy loss, all soils were a strong source of gaseous mercury.
- Evidence shows elevated mercury emissions from soil continue more than 2 months.
- Deforested soils are estimated to contribute an additional 50% of the mercury emitted by fires.

GRAPHICAL ABSTRACT

Annual Projected Hg Emissions (g ha^{-1})

-0.13	0.06	4.10	0.41	2.30
NY, USA	Acre, Brazil	Acre, Brazil	NY, USA	Acre, Brazil
Soil Emissions, Intact Forest (y^{-1})		Fire Event Emission (event^{-1})	Soil Emissions, Deforested Soils (y^{-1})	

ARTICLE INFO

ABSTRACT

Forest ecosystems are a sink of atmospheric mercury, trapping the metal in the canopy, and storing it in the forest floor after litter fall. Fire liberates a portion of this mercury; however, little is known about the long-term release of mercury post deforestation. We conducted two large-scale experiments to study this phenomenon. In upstate New York, gaseous mercury emissions from soil were monitored continually using a Teflon dynamic surface flux chamber for two-weeks before and after cutting of the canopy on the edge of a deciduous forest. In Brazil, gaseous mercury emissions from soil were monitored in an intact Ombrophilous Open forest and an adjacent field site both before and after the field site was cleared by burning. In the intact forest, gaseous mercury emissions from soil averaged -0.73 ± 1.84 ng m^{-2} h^{-1} (24-h monitoring) at the New York site, and 0.33 ± 0.09 ng m^{-2} h^{-1} (daytime-only) at the Brazil site. After deforestation, gaseous mercury emissions from soil averaged 9.13 ± 2.08 ng m^{-2} h^{-1} in New York and 21.2 ± 0.35 ng m^{-2} h^{-1} at the Brazil site prior to burning. Gaseous mercury emissions averaged 74.9 ± 0.73 ng m^{-2} h^{-1} after burning of the cut forest in Brazil. Extrapolating our data, measured over several weeks to months, to a full year period, deforested soil is estimated to release an additional 2.30 g ha^{-1} yr^{-1} of gaseous mercury to the atmosphere in the Brazilian experiment and 0.41 g ha^{-1} yr^{-1} in the New York experiment. In Brazil, this represents an additional 50% of the mercury load released during the fire itself.

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1. Introduction

Gaseous mercury emissions from soil and water contribute significantly to the overall load of mercury in the atmosphere. Thus, developing good estimates of the load released from these sources is critical to addressing uncertainties in our understanding of the global mercury cycle (Lindberg et al., 2007). Mercury is known to be emitted during forest fires (Friedli et al., 2001; Veiga et al., 1994), and numerous studies have reported the emission of the metal during biomass burning (Friedli et al., 2003; Sigler et al., 2003; Turetsky et al., 2006), including a companion study at the same site in Acre, Brazil (Melendez-Perez et al., 2014). However, less is known about the effect that forest fires and other forms of deforestation have on the release of gaseous mercury from soil in the local environment following the deforestation event.

Elevated mercury emissions from soils are associated with several factors, including temperature (Carpi and Lindberg, 1998; Siegel and Siegel, 1988), sunlight (Carpi and Lindberg, 1997), or more specifically ultraviolet (UV) light (Bahlmann et al., 2006; Moore and Carpi, 2005), rainfall (Lindberg et al., 1999; Song and Van Heyst, 2005), and soil chemistry (Mauclair et al., 2008). Many of these variables would be expected to change significantly following large scale deforestation. Lacerda et al. and Almeida et al. hypothesized that lower soil mercury concentrations in pasture sites compared to field sites could be in part due to losses from soil independent of the burn event (Almeida et al., 2005; Lacerda et al., 2004). The potential for deforested soils to emit elevated levels of gaseous mercury was later confirmed by Magarelli and Fostier in the Negro River basin of Amazônia (Magarelli and Fostier, 2005). Using a surface flux chamber, Magarelli and Fostier found higher emissions of gaseous mercury from soils in deforested areas (2.75 ± 2.07 ng m^{-2} h^{-1}) compared to forested areas (0.034 ± 0.61 ng m^{-2} h^{-1}). Choi and Holsen have further shown that soil gaseous mercury flux during the leaf-off period within a deciduous forest experienced higher peaks than during the leaf-on periods (Choi and Holsen, 2009).

The current work builds on these previous studies in that it quantifies gaseous mercury emissions from soil before and after deforestation at two very different locations and environments: one in the state of New York in the United States, and one in the state of Acre in Brazil.

2. Methodology

2.1. Field sites

Two sites were examined. The first is located at 41° 23′ 50.35″ N, 74° 01′ 17.45″ W within the Black Rock Research Forest in Cornwall, New York, in the United States. The forest in this region is a typical northeast deciduous forest, and soil in the area is classified as a Swartswood gravelly loam in the Hollis class series (USDA, May 7, 2011). The regional climate is continental/microthermal with significant seasonal differences in temperature and radiation. The climate falls in the Dfa class on the Köppen classification system, and precipitation is equally distributed throughout the year with an annual average of 1240 mm. The specific monitoring site was at the edge of a deciduous forest, and covered directly with *Berberis vulgaris* and *Berberis thunbergil* (European and Japanese Barberry) 3–5 m high and at least 10 years in age. The forest in this area consists of over 1550 managed hectares, with dominant tree species consisting of *Quercus rubra* (red oak), *Acer saccharum* (sugar maple), *Carya* sect. *Carya* (hickory) and *Betula lenta* (black birch). The site is located adjacent to a Mercury Deposition Monitoring Network site (NY 99). No direct waterborne or airborne source of mercury exists within an 8 km radius of the site. The upper 5 cm of

soil was collected and sent to the Cornell University Nutrient Analysis Laboratory (Ithaca, NY) for characterization. The soil had a pH in water of 5.0 and an organic matter content of 11.9%. Soil was air dried at room temperature, sieved, homogenized and analyzed in replicate in our laboratory with a Milestone™ DMA 80 Direct Mercury Analyzer. NIST Standard Reference Materials 1547 (peach leaves) and 1547 (San Joaquin soil) were used for instrument calibration and validation. The average concentration of mercury in the soil was 123 ± 11 ng g^{-1}. Two side-by-side 1 m^2 plots were monitored underneath the canopy for 7 days; the Barberry was then carefully removed by cutting so as not to disturb the soil on day 8, and monitoring continued after the cutting event for an additional week.

The second site is located at 10° 1′ 43″ S, 67° 40′ 49″ W at an EMBRAPA (Brazilian Agricultural Research Corporation) experimental field station 14 km from Rio Branco, Acre, Brazil in southwest Amazonia. The forest in this region is characterized as Ombrophilous Open Forest and the soil is defined as typic dystrophic Argisoil within the Brazilian soil taxonomy system (Salimon et al., 2009; Santos et al., 2006). The regional climate is equatorial, hot and humid, type Am in the Köppen classification, with a dry season of approximately four months from June to September; and the average precipitation is between 1600 and 2700 mm per year. The forest in the area was mature, with a canopy of 30–40 m, and was typical for the region, with vegetation consisting of *Carapa guianensis Aubl.* (andiroba), *Tetragastris altissima (Aubl.) Swart.* (breuvermelho/haiawaballi), *Theobroma cacao* L. (cocoa), *Trichilia spec.* (Cajuerinho), *Quararibea guianensis* Aubl. (Envirasapotinha), *Metrodorea flavida* K. Krause (Pirarara), *Hevea brasiliensis* Muell. Arg. (Pará rubber tree/Seringueira), and other typical species. No direct waterborne or airborne source of mercury exists within a 10 km radius of the site. Sampling was done at a number of plots in Brazil to represent various field conditions. Soil was sampled at two depths, 0–2 cm, and 2–5 cm, and analyzed in replicate for mercury concentrations in our Brazilian laboratory with a Milestone™ DMA 80 Direct Mercury Analyzer (Melendez-Perez et al., 2014). Soil mercury concentrations are presented in Table 2 in the results section.

During early July 2011, a 150×150 m^2 (2.25 ha) area was prepared by cutting all trees and vegetation which were then allowed to dry on site for 2+ months. Detailed data regarding Hg concentrations in cut plant and leaf tissue is provided elsewhere (Melendez-Perez et al., 2014). Gaseous mercury emissions from soil in Brazil were studied at a number of plots, each 1 m^2, to mimic different conditions. The Forest plot was located in an area of intact forest that was approximately 20 m from the cut area and represented background forest soil fluxes. Three Field plots within the cut forest were monitored. The Field Litter plot was studied as found, with dry leaf litter intact and covering the soil. Given that we expected the leaf litter to burn off with the fire, we also removed the surface litter from two replicate Field Soil plots to mimic conditions after the fire cleared the site and get a better sense of pre-post fire impacts. Replicate plots were monitored to measure spatial variability and the effect of soil Hg concentrations on surface flux. All three Field plots were co-located within a single 6.25 m^2 area in the cut site. After burning, all three Field plots were monitored as found. As expected, litter on the Field Litter plot had been burned and appeared as ash. Both Field Soil plots had minimum ash on them after burning. Gaseous mercury emission was also monitored at a Pasture plot – an area that had been cleared by slash and burn deforestation some 10 years prior to our research and was now used for grazing. The purpose of this plot was to gauge the long-term effect of deforestation on soil mercury and gaseous mercury emissions.

On September 29, 2011, the cut area was cleared by burning the cut trees and dried vegetation on the site. Soil fluxes from the Field plots were studied for 2 days prior to burning over a 9-h sampling

period from 8:46 AM to 5:33 PM on September 25, and over a 5.5 h sampling period from 9:16 AM to 2:43 PM on September 26, 2011 (see Supplementary Information for additional details). Gaseous mercury emissions from soil were also studied at the Field plots after the burn event over a 3-h period from 10:43 AM to 1:58 PM on September 30. Field plot soil fluxes were also monitored approximately 2 months later, over a 3.5 h period from 11:54 AM to 3:30 PM on November 25, and over a 1.5 h period from 10:16 AM to 11:42 AM on November 26, 2011. Flux values were sorted into one of four light intensity categories for comparison purposes as described in Table 2. While we had planned to have more robust and continuous sampling in Brazil as we did at our New York site, working in the Amazon jungle presented a number of challenges that limited sampling opportunities. To assure team safety, the site could only be accessed during daylight hours and our equipment setup in Brazil did not accommodate automated nighttime sampling as it did in New York. Multiple research teams measuring fire intensity, carbon emissions, biomass mercury emissions, and other variables had to share the limited transportation and electrical resources at the site and this limited sampling events. Thus our sampling regimen represented the most robust possible under the conditions at the site.

2.2. Mercury flux measurements

Gaseous mercury flux measurements were made using a semi-spherical Teflon Dynamic Flux Chamber (DFC) of our own design (Carpi et al., 2007). To allow for maximum penetration of all wavelengths of light, the chamber was made from Teflon with a wall thickness of 0.19 mm, a 24.2 cm internal diameter and an internal volume of ~2.4 L (Welch Fluorocarbon, Dover, NH). In order to prevent this thin-walled chamber from collapsing, it was reinforced by an internal Teflon skeleton created by taking a thicker version of a chamber (1.4 mm wall thickness) with the same dimensions and cutting the walls so that only 8 thin crossing bridges remained (0.5 cm in width evenly spaced around the perimeter and intersecting at the top). The chamber had a 0.635 cm diameter outlet port on the top center, and eight 0.55 cm diameter inlet ports evenly distributed 3 cm above its base.

Gaseous mercury fluxes were estimated by measuring Hg° concentrations at the inlet and outlet of the chamber and then using the steady state flux calculation:

$$F = \left[(C_o - C_i)\left(A^{-1}\right) \right] Q \tag{1}$$

where C_o and C_i are Hg vapor concentrations in ng m^{-3} at the outlet and inlet of the chamber, respectively, Q is the flushing flow rate in m^3 h^{-1}, A is the surface area in m^2 of the base of the chamber, and F is the steady state flux in ng m^{-2} h^{-1} (Zhang et al., 2002). Measurements using the chamber are typically described as flux (F) as they can represent either emission from the soil surface (positive F when $C_o > C_i$) or deposition to the soil surface (negative F when $C_o < C_i$)

At the New York field site, mercury concentrations at the inlet and outlet of the chamber were measured with a Tekran Automated Dual Sampling (TADS) system and a Tekran Mercury Vapor Analyzer Model 2537A unit which has a detection limit of 0.5 ng m^{-3} at an integration time of 5 min (Lindberg and Meyers, 2001; Lindberg and Price, 1999). Flow through the chamber was held 1.5 L min^{-1} via a mass flow controller within the Tekran sampler. Each individual flux reported is in fact the mean of two inlet–outlet paired measurements made with two different gold traps in the Tekran system, thus representing an average flux over a 20 min period.

The Tekran 2537A used in this study underwent calibration with an internal Hg source on a daily basis, and these calibrations remained consistent during the sampling period with the 95% confidence interval of all calibration measurements equaling approximately 1.5% of the mean calibration value. Calibrations against an external Hg source were made prior to and immediately after field measurements and confirmed that the calibrations were valid; the difference in calibrations made with the external and internal sources equaled less than 2.4% of the mean calibration and was not significant at the 95% confidence level.

In Brazil, chamber mercury concentrations were recorded with a RA-915+ Portable Mercury Vapor Analyzer which has a detection limit of 0.5 ng m^{-3} with 1-min sampling integration (OhioLumex, Twinsburg, OH). The RA-915+ was set to record mercury concentrations at a rate of one measurement per second, and showed good reproducibility. The RA-915+ was connected to a closed tubing system that allowed us to monitor chamber inlet and outlet concentrations successively by manually switching a valve system between inlet and outlet tubes. Chamber flow has been shown to affect mercury flux from soil (Lindberg et al., 2002). While the RA-915+ normally operates at a flow rate of 5 L min^{-1}, our tubing system reduced the Lumex flow to 1.47 L min^{-1} as recorded with a mass flow meter used on site, resulting in comparable flushing flow rates in both systems. Reported fluxes were calculated by monitoring inlets and outlets successively for a minimum period of 60 s and a maximum of 5 min. Performance of the RA-915+ was compared to a Tekran 2537A over a period of several days and observed mercury concentrations were normalized between the two instruments.

Before flux measurement at different field sites or under different field conditions, chamber blanks were measured by placing the chamber on a clean Teflon sheet and measuring flux for a minimum of two successive 20-min periods. Chamber blanks averaged 0.19 ± 0.94 ng m^{-2} h^{-1} over the entire period at the New York site. In Brazil, chamber blanks averaged 0.35 ± 0.26 ng m^{-2} h^{-1} in the intact forest, and 1.1 ± 0.17 ng m^{-2} h^{-1} at the field plots. While the Brazil site exhibited slightly higher average chamber blanks, this may be associated with high radiation. Soil fluxes reported here are corrected by subtracting out the blank fluxes from individual measurements.

2.3. Temperature, light, and field conditions

Surface soil temperature was measured using a 675 nm laser infrared thermometer (Fisher Scientific©, Pittsburg, PA). At the New York site, ambient light was measured with a LI200X Pyranometer (Campbell Scientific), which measures photosynthetically active radiation (PAR) reported as total flux per hour in MJ m^{-2}. In Brazil, the experimental design called for measuring light with the same meter type. However, a breakdown in the system while in the Amazon made this impossible and thus we used a LiCor Li250 with a PAR multiwavelength receptor that allows instantaneous measurements of light in μmol m^{-2}. Interconversion of the two units requires a measurement of photon flux as a function of wavelength; unfortunately we were unable to gather this data at the Amazon field site. As such, light levels at each location were categorized as very low, low, high, and very high to allow relative comparisons between the two sites (Table 1). The wavelength profile of incident radiation does vary with latitude, and this is especially true for the UV component of the light profile – a segment of the spectrum with particular relevance to the emission of gaseous mercury from soil (Bahlmann et al., 2006; Moore and Carpi, 2005). Thus categorizing light levels as described gives a measure of the response of gaseous mercury flux to light intensity at a specific site, and allows some comparison between sites at low light levels. However, the

Table 1
Categorization of light levels for the two sampling locations.

	New York site (MJ m^{-2} h^{-1})	Brazil site (μmol m^{-2})
Very low light	0–40	0–100
Low light	41–559	101–599
High light	560–1700	600–1500
Very high light	>1700	>1500

comparison of absolute values of gaseous mercury flux between sites at high light levels should be done with reservation.

3. Results

3.1. New York site

Two side-by-side chambers at the New York site (0.5 m apart) showed good agreement in gaseous mercury fluxes both before and after the canopy cutting event at 7 AM eastern standard time on August 12, 2010 (Fig. 1). During the period when the site was measured with its canopy intact, gaseous mercury flux showed a diel cycle with depositional flux to the soil surface dominating in the evening hours, blank corrected average evening depositional flux equaled -2.33 ± 0.25 ng m^{-2} h^{-1}, and emissions reached a maximum at midday. Additional information regarding flux measurement duration and sample size is provided in the Supplementary Information document provided with this manuscript. Peak mercury flux in the pre-cutting period occurred on August 7, 2010 at 10:00 AM and equaled 8.34 ng m^{-2} h^{-1}. For the entire pre-cut period, gaseous mercury flux averaged -1.54 ± 0.23 ng m^{-2} h^{-1}. Mercury flux continued to show a diel cycle in the post-canopy removal period, with evening fluxes averaging 1.40 ± 1.58 ng m^{-2} h^{-1}. Daytime flux increased immediately after canopy clearing. For the entire post-clearing period, mercury flux averaged 9.13 ± 2.08 ng m^{-2} h^{-1} and was significantly elevated over the pre-clearing average.

Rain is known to affect gaseous mercury emissions from soil (Gustin and Stamenkovic, 2005; Xin et al., 2007). Two significant rain events occurred during our sampling: 4.2 mm of rain fell on August 6 causing us to delay the start of our forest monitoring to August 7, and 9.3 mm of rain fell on August 16 forcing us to interrupt the post-cut period of monitoring. These events did indeed
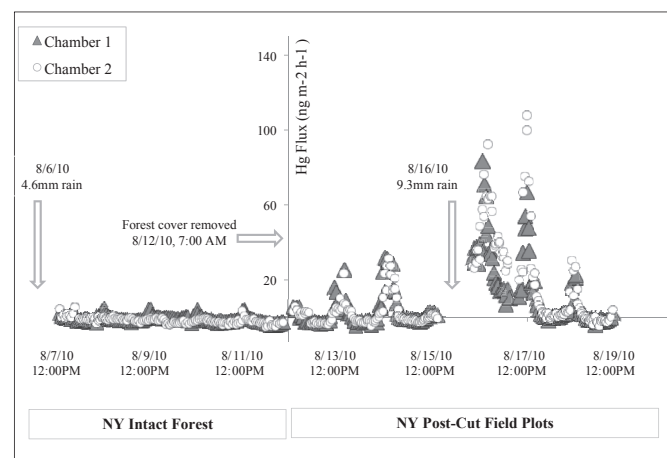
affect soil mercury flux. During the first 24-h of the pre-cut period immediately following the August 6 rain, emissions averaged -0.19 ± 0.8 ng m^{-2} h^{-1} and reached a maximum of 8.3 ng m^{-2} h^{-1}. During the final 24-h of the pre-cut period on August 11, more than 5 days after the rainfall, emissions averaged -2.22 ± 0.7 ng m^{-2} h^{-1} significantly lower than the August 6 average, and they only reached a maximum of 3.6 ng m^{-2} h^{-1} despite similar meteorological conditions. During the post-cut period on August 15, the last day prior to the August 16 rain, gaseous mercury emissions averaged 6.53 ± 4.1 ng m^{-2} h^{-1} and reached a maximum of 31.4 ng m^{-2} h^{-1}. During the first 24-h following the August 16 rain event, gaseous mercury emissions averaged 30.2 ± 6.7 ng m^{-2} h^{-1} and reached a maximum of 82.9 ng m^{-2} h^{-1}, significant elevated over fluxes under dry conditions. However, gaseous mercury emissions from soil during the post-cut period under wet and dry conditions were significantly elevated over all pre-cut fluxes, clearly demonstrating the effect of forest removal. Additionally, the difference between mercury fluxes from wet versus dry soils was greater in the post-cut period than the pre-cut period, suggesting that removal of the forest cover may work in tandem with soil moisture to magnify the affect on gaseous mercury emissions from soil.

Mercury flux values were categorized by light intensity, and mean values were calculated to facilitate comparison between pre- and post-canopy cut fluxes. Independent t-tests and 95% confidence intervals were used to assess significant differences in mean flux values between the light categories described in Table 1. Pre- and post-cut 'very low light' flux values occurred during the evening to predawn hours of 7:00 PM to 6:00 AM. Pre-cut 'low light' flux values were obtained during the daylight hours of 7:00 AM to 6:00 PM; no 'high' or 'very high' light values were obtained pre-cut due to the intact canopy. Post-cut light data ranged from 'low', to 'high' and 'very high' during the same daylight hours. Mean mercury flux values for all pre-cut data showed overall net deposition under both light conditions and with both chambers (Fig. 2).

Mean post-cut mercury flux values increased concomitantly with increasing light levels and did not differ by chamber (Fig. 2). Mercury flux averages in both 'high' and 'very high' light categories differed significantly from 'low' and 'very low' light at the 95% confidence interval in the post-cut data. Further, fluxes under 'very low' light conditions (which occurred during the evening) were significantly higher after the site was deforested despite similar light conditions (Fig. 2).
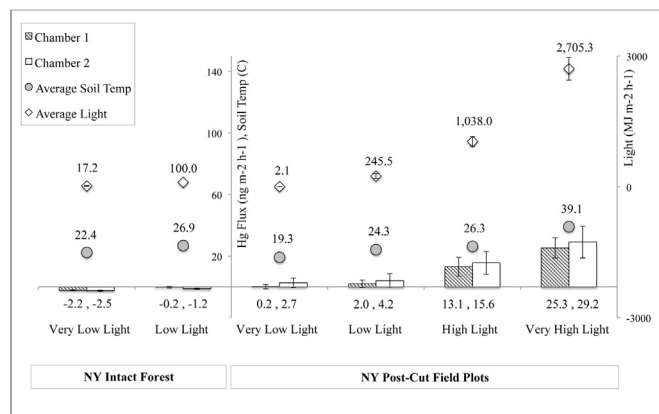

Fig. 1. Gaseous mercury fluxes (ng m^{-2} h^{-1}) from two side-by-side plots in upstate New York both before and after canopy cutting on 8/12/10 at 7:00 AM (indicated by placement of vertical axis). 4.2 mm of rain fell on 8/6/10 and 9.3 mm fell on 8/16/10 as indicated on graph.

Fig. 2. Mean gaseous mercury fluxes (ng m^{-2} h^{-1}) $\pm$ 95% confidence intervals grouped by light level from two side-by-side plots in upstate New York both in the intact forest and after canopy cutting on 8/12/10 at 7:00 AM (indicated by placement of vertical axis). Post-cut mercury fluxes are elevated over intact forest fluxes even under similar light conditions.

3.2. Brazilian Amazon site

Surface soil mercury concentrations were determined using a Milestone DMA analyzer. Soil mercury concentrations at the Forest and Field Soil 1 plots were not statistically different at the 95% confidence level (Table 2). Mercury concentration in soil at plot Field Soil 2 was elevated over the other two plots, which helps explain generally higher gaseous mercury emissions at this site. The Pasture plot showed significantly lower mercury concentrations than all other monitored plots.

Gaseous mercury fluxes from intact forest soils in Brazil were measured in an area of forest 10 m from the edge of the field site. Mercury flux values were obtained on two days prior to the burning of the field site nearby, during a seven hour sampling period from 10:36 AM to 5:49 PM local time on September 24, and during a 1.5 h sampling period from 3:04 PM to 4:51 PM on September 26, 2011. While gaseous mercury fluxes from forest soil were monitored over a relatively short time interval, these measurements were made during peak sunlight hours during full sunlight days, and thus represent a conservative estimate of mercury fluxes during expected maximum periods. Blank-corrected mean mercury flux from the Forest plot on September 24 was -0.24 ± 0.09 ng m^{-2} h^{-1} and 3.16 ± 0.30 ng m^{-2} h^{-1} on September 26 (Fig. 3), these measurements are commensurate with forest soil fluxes reported in other studies (Carpi and Lindberg, 1998; Xiao et al., 1991). Mean mercury fluxes in the forest differed between the two days, but this was likely due to a small difference in light intensity between the periods. Due to the heavy forest canopy, sunlight at the soil surface in the intact forest never exceeds low-light levels. However, time-weighted mean light levels were 16.01 μmol m^{-2} on September 24 and 24.95 μmol m^{-2} on September 26. Time-weighted mean forest flux for the two day period averaged 0.33 ± 0.09 ng m^{-2} h^{-1}.

Mean gaseous mercury fluxes at all Field plots and under all light conditions were significantly higher than mean gaseous mercury fluxes at the Forest plot when tested at the 95% confidence level (Fig. 3). Gaseous mercury fluxes from field soil appeared to be related to light intensity at all field sites. Gaseous mercury fluxes from the Field Litter plot were lower than both Field Soil plots at both 'low' and 'high' light, likely due to the affect of the litter in suppressing emissions from soil. Gaseous mercury emissions from the Field Soil 2 plot were consistently higher than the Field Soil 1 or Field Litter plots and this may have been related to the higher concentration of soil mercury measured at this site compared to the others (Table 2). Post-burn field data was collected one day after the burn event on September 30, 2011, and again approximately two months after the event on November 25 and 26, 2011 to study the longer-term effects of deforestation on soil mercury flux and fluxes from these two periods are averaged in Fig. 4. Mercury fluxes were correlated with light intensity in the post-burn field data (Fig. 4). Post-burn mercury fluxes were significantly higher than pre-burn mercury fluxes at all field sites for every light category observed.

When gaseous soil mercury fluxes measured in September 2011 were compared to those collected two months later, in November, to examine temporal effects, mean November post-burn mercury fluxes at low light (the only light category for which data overlapped in both periods) remained significantly higher than prior to burning with the mean difference between the two equaling 13.52 ± 0.59 ng m^{-2} h^{-1}.
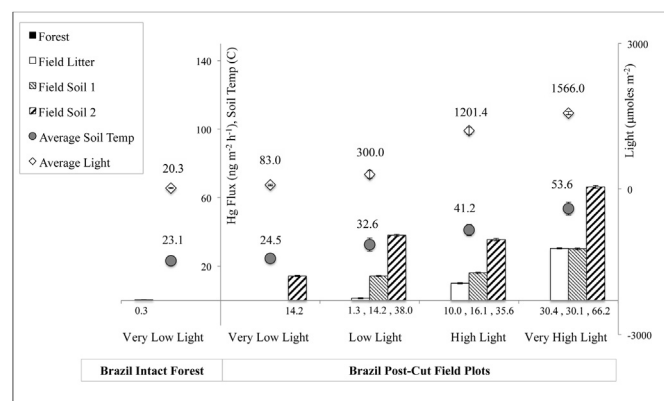

Fig. 3. Mean gaseous mercury fluxes from soil (ng m^{-2} h^{-1}) $\pm$ 95% confidence intervals, mean soil temperature, and mean light levels at one forest site and three field sites in Acre, Brazil, one with leaf litter untouched (Field Litter) and two with leaf litter removed (Field Soil 1 and 2) as measured on September 25 and 26, 2011 before the fire event. Fluxes are categorized by light condition for comparison, not all light conditions were captured for all sites. Very low light conditions at the forest site were due to canopy cover as these measurements took place during full sunlight conditions.

November post-burn data were also statistically higher than September post-burn data under low light with the difference between the two equaling 4.76 ± 1.31 ng m^{-2} h^{-1}.

Gaseous mercury flux from soil was also measured at an additional site in Brazil that had undergone slash and burn deforestation approximately 10 years prior to our visit and had been in service as a cow pasture during the ensuing decade. Mean mercury flux measured over a 1.5 h period from 10:51 AM to 12:14 PM at the Brazil Pasture plot was 2.22 ± 0.22 ng m^{-2} h^{-1} with a mean light value of 1672 μmol m^{2}. Fluxes were measured both over grass, and over a grass-free area and mean grass fluxes averaged 3.29 ± 0.30 ng m^{-2} h^{-1} compared to the grass-free soil area which averaged 0.93 ± 0.28 ng m^{-2} h^{-1}. Despite the very high light conditions that existed at the pasture site, soil mercury fluxes were significantly lower than our post-burn field site fluxes under all lights conditions; and they were significantly lower than pre-burn
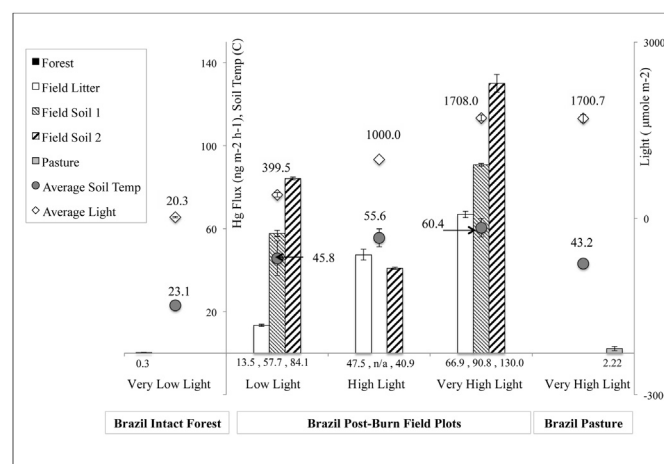

Fig. 4. Mean gaseous mercury fluxes from soil (ng m^{-2} h^{-1}) $\pm$ 95% confidence intervals, mean soil temperature, and mean light levels at the forest site and field sites in Acre, Brazil, but measured on September 30 and November 25–26, 2011 after the fire event. Fluxes are categorized by light condition for comparison, not all light conditions were captured for all sites. Post-burn mercury fluxes were significantly higher than pre-burn fluxes at all sites under every light category. Mean mercury fluxes presented for the Pasture site, which was deforested some 10+ years prior to our sampling, were significantly lower than recently deforested sites.

Table 2
Mean soil mercury concentrations (ng/g) $\pm$ 95% CI at four monitored plots in Brazil.

Depth	Forest	Field Soil 1	Field Soil 2	Pasture
0–2 cm	95.2 ± 1.7	95.8 ± 0.8	106.3 ± 2.1	62.6 ± 1.2
2–5 cm	107.2 ± 1.4	118.6 ± 2.1	111.0 ± 0.8	74.0 ± 1.5

field site fluxes under both high and very high light conditions. These results are consistent with the statistically lower concentrations of mercury in soil found at this site.

4. Discussion

In both studies, removal of the forest cover significantly affected gaseous mercury flux from soil. This effect was largely attributed to the increased light levels associated with removal of the canopy and, in some cases, litter removal. However, gaseous mercury flux from deforested field soil at both the New York and Brazil site were elevated over intact forest soils even when light levels were comparable. In the Brazil study, mercury fluxes were higher following the burn event than prior to burning under all matched light levels. This may be due to the additional removal of leaf litter from the soil surface during the burn.

Increased gaseous mercury emissions were not a transient effect. Higher soil fluxes were noted for the duration of the week-long monitoring period in New York, and elevated soil fluxes were measured in November in Brazil, two months following the burn event. However, gaseous mercury fluxes from soil at the Brazil Pasture plot, deforested some ten years before our study, were significantly lower than the recently deforested field site, though they remained elevated over mercury emissions from the forested soils. Further, the concentration of mercury in soil at the Pasture site was significantly lower than at the Forest plot or either Field Soil plot likely due to the loss of mercury from the soil matrix following deforestation. The loss of mercury from deforested soils is consistent with previous research in this ecosystem (Almeida et al., 2005; Comte et al., 2013).

Despite very different field conditions at the New York and Brazil sites, the effect of forest removal on gaseous mercury flux from soil was comparable, highlighting the effect of deforestation on this transport pathway. Soils in forested areas serve as a net sink of atmospheric mercury as they did in New York (average daytime flux in the intact forest equaled -0.73 ± 1.84) or just a very small source of atmospheric mercury as they did in Brazil (average daytime flux in the intact forest equaled 0.33 ± 0.09 ng m^{-2} h^{-1}). However, following the removal of the forest these same soils serve as a significant source of gaseous mercury to the atmosphere. Average peak daytime fluxes following removal of the canopy in New York were 25.3 and 29.2 ng m^{-2} h^{-1} at two side-by-side sites, and post-cut (pre-burn) peak daytime emissions in Brazil were 30.4, 30.1, and 66.2 ng m^{-2} h^{-1} at three side-by-side sites. Clearing of the site by fire in Brazil resulted in even higher peak daytime fluxes.

The average and maximum gaseous mercury emission levels we found were significantly higher than those presented in an earlier study (Magarelli and Fostier, 2005). This may be due to a different chamber design; we used a UV-transparent Teflon chamber (Carpi et al., 2007) whereas this earlier study used a polycarbonate chamber. And it may be influenced by the timing of sample collection, in the previous study mercury emissions could not be sampled until approximately one year following the deforestation event.

In an effort to compare gaseous mercury emissions from soil following the fire to those released during the actual fire event, we calculated annual values for gaseous mercury emissions from our deforested soils. To do this, mercury emissions from soil were integrated over a 24-h period in both cloudy and full sunlight conditions to yield a total daily flux value (F_D in ng m^{-2} day^{-1}) under cloudy (F_{D-C}) and full sun (F_{D-S}) conditions. By calculating daily flux for these two conditions and under day- and nighttime conditions, our calculations take into consideration changes in flux due to both radiation and soil temperature. Annual
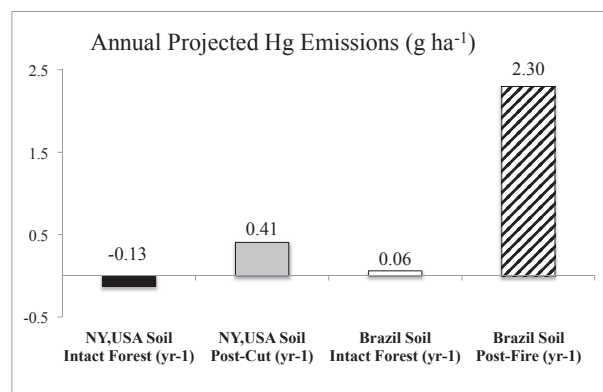

Fig. 5. Projected annual gaseous mercury emissions from soil (g ha^{-1} yr^{-1}) before and after canopy removal at a New York deciduous forest site (bar 1 and 2); and from an intact Ombrophilous Open forest and slash and burned field plot in Brazil (bar 3 and 4). Annual emissions were estimated by integrating daily emission values from short-term monitoring in this study for both cloud-covered and full sun conditions and then weighting these by the number of days expected under cloudy and full sun conditions at each site. Emissions were assumed to occur year round in Brazil given the data we collected in this study for elevated emissions in both September and November. In New York, emissions were conservatively estimated to occur only for 6 months, as low light, temperatures, and snow cover in winter were expected to suppress soil emissions. Post forest cover removal both sites showed significantly elevated mercury emissions.

meteorological conditions were obtained from WeatherSpark (WeatherSpark, 2013a, 2013b) for both the U.S. and Brazilian sites, and median cloud cover data allowed us to estimate the number of days during the year when one would expect primarily full sun conditions (D_S in days) and the number of days that one would expect primarily cloud covered conditions (D_C in days). Soil mercury emissions were assumed to occur year-round in Brazil given the proximity to the equator, and this was corroborated by our findings of high emissions in both September and November. Due to seasonal changes in light, temperature, and snow cover at the New York site, emissions were conservatively assumed to occur only during a 6-month period, and D_S, D_C represent the number of sunny and cloudy days, respectively, during the average April–September period. Annual flux per hectare (F_{An}) was then calculated using equation (2) (full calculations are provided in supplementary information Table SI-5):

$$F_{An} = \left(\left(F_{D-S} * D_S \right) + \left(F_{D-C} * D_C \right) \right) * 10,000 \text{ m}^2\text{ha}^{-1} \qquad (2)$$

Gaseous mercury emissions from deforested soils represent a significant source of atmospheric mercury. At the emission rates we recorded, we calculate that the total release of mercury per day from soils after clearing by fire in Brazil would be 933.8 ng m^{-2} day^{-1} under full sun conditions, and 303.3 ng m^{-2} day^{-1} under cloudy conditions. This would result in an annual flux of mercury from a one hectare plot of approximately 2.30 g ha^{-1} yr^{-1} (Fig. 5). In a companion study of mercury emissions from the fire event itself, Melendez-Perez et al. estimated that thermal desorption accounted for the emission of 4.1 ± 1.4 g ha^{-1} yr^{-1} of mercury from this site (Melendez-Perez et al., 2014). Thus emissions from soils following deforestation represent an additional 50% increase in the mercury load released during the fire in the first year alone, and may come to exceed emissions from the fire itself in ensuing years based on our analysis of soil mercury concentrations. In the top 1 cm of soil at the intact forest and newly cut field site, mercury concentrations were not significantly different from one another (95 ± 2 ng g^{-1} and 92 ± 4 ng g^{-1}, respectively). After burning, soil mercury concentrations at the field site were 80 ± 7 ng g^{-1}, significantly lower than

before the fire. However, mercury concentrations at the pasture site we studied, deforested some 10 years prior to our study, were significantly lower still at 62.6 ± 1.2 ng g^{-1}, suggesting that the total emissions from the soil after burning may exceed the release of mercury during the fire itself.

Hansen et al. have used high resolution satellites images to estimate global forest cover loss from tropical, subtropical, temperate and boreal biomes for the years 2000–2012 (Hansen et al., 2013). Applying our annualized average mercury emission rate at the Brazil site to the tropical and subtropical data provided by Hansen et al. we arrive at an estimate of mercury emissions from tropical and subtropical soils due to deforestation of 324.7 Mg during the 2000–2012 period. Applying our annualized average mercury emission rate at the New York site to temperate regions, we estimate an additional contribution from deforestation of 11.2 Mg of mercury from these ecosystems. This suggests that deforested soils may contribute approximately 28 Mg of gaseous mercury to the atmosphere per year. This contribution is small compared to the 675 Mg that Friedli et al. estimate from biomass burning (Friedli et al., 2009). However, in our side-by-side study in Brazil our results indicate that mercury emissions from soil following deforestation may contribute an additional 50% of the mercury lost during the fire itself. Thus, soil mercury emissions following forest loss may be a significant source of atmospheric mercury and further research is needed to more accurately estimate losses from deforested ecosystems.

Acknowledgments

Appendix A. Supplementary informationcs

Supplementary information related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2014.08.004.

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