

Increased mercury in forest soils under elevated carbon dioxide

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Abstract Fossil fuel combustion is the primary anthropogenic source of both CO₂ and Hg to the atmosphere. On a global scale, most Hg that enters ecosystems is derived from atmospheric Hg that deposits onto the land surface. Increasing concentrations of atmospheric CO₂ may affect Hg deposition to terrestrial systems and storage in soils through CO₂-mediated changes in plant and soil properties. We show, using free-air CO₂ enrichment (FACE) experiments, that soil Hg concentrations are almost 30% greater

under elevated atmospheric CO₂ in two temperate forests. There were no direct CO₂ effects, however, on litterfall, throughfall or stemflow Hg inputs. Soil Hg was positively correlated with percent soil organic matter (SOM), suggesting that CO₂-mediated changes in SOM have influenced soil Hg concentrations. Through its impacts on SOM, elevated atmospheric CO₂ may increase the Hg storage capacity of soils and modulate the movement of Hg through the biosphere. Such effects of rising CO₂, ones that transcend the typically studied effects on C and nutrient cycling, are an important next phase for research on global environmental change.

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Introduction

Hg is a persistent contaminant in terrestrial and freshwater systems, where it may enter into food webs, affecting wildlife and human health (US EPA 1997a). Since the onset of the industrial revolution, anthropogenic Hg deposition has increased by 3–5 times pre-industrial rates (Lamborg et al. 2002). Particulate and gaseous Hg emitted via coal combustion and other industrial activities (such as waste incineration, manufacturing and smelting) can be deposited locally or remain in the atmosphere for a year or more (US EPA 1997b), making Hg important as a local, regional and global contaminant. Vegetation plays a critical role in the transfer of atmospheric Hg to the biosphere—Hg from the atmosphere is deposited onto leaf surfaces or taken up by stomata and subsequently transferred to soils in litterfall and throughfall (Rea et al. 1996; St Louis et al. 2001).

Deposition of Hg under forest canopies can be 3–4 times greater than deposition to bare soils (Grigal 2003; St Louis et al. 2001) and almost all the Hg in forest canopies is derived from the atmosphere (Ericksen et al. 2003). Because of the critical role of vegetation in the transfer of Hg from air to surface, processes that affect plant structure and function can significantly alter Hg inputs to soils. Soil-bound Hg is leached only to a very minor degree, but mobilization to aquatic systems of total and methylated Hg can take place in discharge zones.

One important factor that is affecting terrestrial ecosystem structure and function is the rise in atmospheric CO₂ concentrations. CO₂ concentrations are increasing at an unprecedented rate, primarily due to anthropogenic combustion of fossil fuels (IPCC 2007). Because of the strong biological component that governs Hg cycling, CO₂-induced changes in plant and soil properties may affect both the fluxes and storage of Hg in terrestrial systems. Although some of the effects of elevated CO₂ on plants and soils have been well-studied, the impacts on Hg cycling are less known. For example, while it is known that CO₂ enrichment may affect soil acidity and organic matter (Andrews and Schlesinger 2001; Jastrow et al. 2005; Oh and Richter 2004) and that these soil properties can affect Hg adsorption (Schuster 1991; Yin et al. 1996), it is still unclear how increasing atmospheric CO₂ may affect Hg in soils. Elevated CO₂ may also affect Hg inputs to soils through changes in leaf litter biomass—an increase in litterfall biomass with CO₂ enrichment (Finzi et al. 2001; Norby et al. 2001) may increase Hg uptake and deposition to the forest floor. CO₂-mediated changes in leaf area and leaf tissue chemistry (Lichter et al. 2000) may also affect Hg deposition in litterfall, throughfall and stemflow.

Understanding the factors that may alter the cycling of Hg through soils is critical because soil Hg represents a major portion of the total Hg pool; surface soils store an estimated 95% of the 200,000 t Hg mobilized since the 1890s (EPMAP 2004). As such, terrestrial systems, and forests in particular, have been recognized as major components in the cycling of Hg between the atmosphere and biosphere (Lindberg et al. 1998). Interestingly, Hg concentrations in most forest soils tend to be low; it is the large volume of forest soils globally that leads to this large amount of storage (Fitzgerald and Lamborg 2003). As Hg leaves soils through leaching it can enter vadose and ground water flow paths and move into aquatic systems, where it becomes an important contaminant through methylation and biomagnification processes (Schroeder and Munthe 1998). A challenge facing the scientific community is to understand how rising global CO₂ concentrations may affect this large Hg pool.

To study the potential effects of increased atmospheric CO₂ on Hg cycling in forests we examined plants and soils

from two free-air CO₂ enrichment (FACE) experiments—a loblolly pine (*Pinus taeda* L.) forest in North Carolina (Duke) and a sweetgum (*Liquidambar styraciflua* L.) plantation in Tennessee (Oak Ridge National Laboratory; ORNL)—which have been exposed to CO₂ enrichment (ambient + 200 p.p.m.v.) since 1996 and 1998, respectively. In 2005 we sampled leaves and litter from the dominant canopy tree at Duke FACE, loblolly pine, and the dominant canopy tree at ORNL FACE, sweetgum. *L. styraciflua* was also sampled at Duke where it is a common understory tree. In 2007 we focused sampling on Hg deposition at ORNL in litterfall, stemflow and throughfall. CO₂ effects on plants and certain ecosystem processes at these sites have been well documented (e.g., Andrews and Schlesinger 2001; Finzi et al. 2001; Norby and Iversen 2006; Norby et al. 2001), but the effects of elevated CO₂ on Hg have not been examined.

Materials and methods

Site description

Duke forest FACE site

Duke FACE is a mixed evergreen-deciduous temperate forest dominated by loblolly pine (*Pinus taeda*), located in the Blackwood Division of Duke Forest in Orange County, North Carolina (35°58'N, 79°05'W). The stand of loblolly pine, which was planted in 1983 at a spacing of 2.0 m × 2.4 m, is located on low-fertility, acidic Hapludalf soils. The sub-canopy and understory are diverse, containing more than 50 species, but dominated by sweetgum (*Liquidambar styraciflua*). The FACE experiment, which began in August 1996, comprises three 30-m-diameter ambient-CO₂ rings (~382 μmol mol⁻¹) and three 30-m-diameter elevated-CO₂ rings (~582 μmol mol⁻¹). CO₂ concentrations in the elevated-CO₂ rings are concentrations projected for the mid to end century. The CO₂ treatment is applied to the rings (i.e., experimental plots) via a series of vertical pipes located around the perimeter of each ring. The pipes, which extend from the forest floor to the canopy, are equipped with regulated blowers that deliver a controlled amount of CO₂-fumigated air to maintain ambient or elevated levels of CO₂ into the rings (Hendrey et al. 1999). An experimental N-fertilization treatment (NH₄⁺NO₃⁻ at a rate of 11.2 g N m⁻² year⁻¹) was added to one half of each ring in April 2005. The experimental rings are arranged in a complete block design to account for topographic variation and potential fertility gradients. Descriptions of the site, experimental design and FACE technology have been well documented (Finzi et al. 2001; Hendrey et al. 1999).

Oak Ridge FACE site

The deciduous forest site (ORNL) is a sweetgum (*L. styraciflua*) plantation located in the Oak Ridge National Environmental Research Park in Roane County, Tennessee (35°54'N, 84°20'W). The soil at the site, classified as Aquic Hapludult, has a silty clay loam texture, is moderately well drained and is slightly acidic. The stand was planted with 1-year-old sweetgum seedlings in 1988 at a spacing of 1.2 m × 2.3 m. The FACE apparatus is assembled in four of the five 25-m-diameter experimental rings. There are three ambient (~393 μmol mol⁻¹) rings and two enriched (~549 μmol mol⁻¹) rings. CO₂ enrichment began in 1998 and continues during the growing season through the present time. The site description and experimental design are well documented in Norby et al. (2001).

Field sampling

Soils

Soil samples were collected at ORNL from 25 to 28 July 2005 and at Duke from 8 to 11 August 2005. A core sampler was used to collect two 2.5-cm (diameter) by 20-cm soil cores per ring (ORNL) or N treatment within a ring (Duke) at each site (34 cores total). Acid-washed butyrate plastic core liners were used to maintain an intact core during extraction. We used cores from the N-fertilized sectors of the Duke FACE rings to increase our sub-sampling size. Cores were divided into 5-cm depth increments and pooled within rings (within N treatment of each ring at Duke). In all of our analyses, “ring” is the unit of replication for CO₂ treatment, so pooling of cores within a ring has no consequence in testing for CO₂ or depth effects.

We obtained pre-treatment soil samples (i.e., samples collected prior to initiation of FACE in 1996 at Duke and 1998 at ORNL) from archives at each site. Pre-treatment samples consisted of 16–18 pooled randomly sampled cores per ring (0–7.5 and 7.5–15 cm) at Duke, and from two to six randomly collected cores per ring (0–5 and 0–15 cm) at ORNL. Archived soils were stored in a sealed container at room temperature; ambient-CO₂ and elevated-CO₂ soil samples from each site were stored under identical conditions.

Leaves

Fully expanded outer crown canopy leaves were collected at ORNL from 25 to 28 July 2005 and at Duke from 8 to 11 August 2005. Green leaves were sampled from three canopy heights—low (10–12 m), mid (12–14 m) and upper (14–16 m)—from *L. styraciflua* at ORNL and Duke (lower and mid canopies only, pooled for analysis) and from

P. taeda at Duke (all canopy heights). The canopy at ORNL was accessed using a stationary hydraulic lift located near the center of each ring. At Duke the canopy was accessed by a central walk-up tower and by a mobile hydraulic lift. Both 0-year (originated in 2005) and 1-year (originated in 2004) needles were sampled from *P. taeda*. For each canopy height three replicate samples were collected. For all leaves, a sample consisted of approximately 5 leaves/20 needles from an individual tree.

In October 2005, freshly fallen leaf litter was collected from the forest floor at ORNL (15–20 leaves per ring). Senescent leaves at Duke were collected from three to five trees per species per ring via the central walk-up tower (*P. taeda*) or by gently shaking trees (*L. styraciflua*) and collecting leaves as they fell to the forest floor. Visual observation suggested that falling leaves came from branches distributed throughout the canopy, but this effect was not quantified.

In 2007, leaves were collected from ORNL throughout the growing season on the following dates: 9 June, 5 July, 5 August, 3 September, and 11 November (senescent leaves). Because the lifts in several of the rings were not in operation during the collection periods, green leaves were collected from three to five trees at a height of approximately 8–10 m using a pole pruner, and senescent leaves were collected by shaking from three to five trees in each plot. Leaves were collected as they fell, prior to them reaching the forest floor. All leaves were collected using particle-free gloves into double-bagged polyethylene bags.

Leaf litter biomass was determined from litter basket collections (Finzi et al. 2001; Norby et al. 2001). At Duke, litterfall was collected into twelve 0.16-m² baskets per plot. Litterfall was collected once per month between January and August and twice per month between September and December. At ORNL, leaf litter was collected into seven randomly placed 0.19-m² baskets per plot, and collected weekly to monthly. Further details of litter collection methods can be found in Finzi et al. (2001) and Norby et al. (2001).

Litter Hg deposition was calculated as the product of litter Hg concentration and litterfall biomass. Duke leaf litter comprised *P. taeda* plus a number of broadleaf species. We use litter Hg concentrations from *L. styraciflua*, the most common broadleaf tree at Duke FACE, to represent broadleaf litter Hg concentrations. Duke leaf litter concentrations presented in the text are a weighted average of these two species, based on percent leaf litter biomass of pines and broadleaf trees and the relative dominance of each species.

Throughfall

Six bulk throughfall collectors for Hg analysis were placed in each of the five experimental rings at ORNL in 2007.

Collectors were placed in the field on 9 June, and collections were made on the following dates: 4 July, 22 July, 5 August, 3 September, and 14 September.

Throughfall collectors consisted of 100-mm-inner diameter (i.d.) borosilicate glass funnels set at 1.5 m above the forest floor and attached to a darkened borosilicate collection bottles via 0.5 m Teflon tubing (3/16-inch i.d.). A loop was formed in the tubing to create an airlock over the sample container. To preserve samples in the field, 5 ml of 10% HCl was added to each bottle. Two bulk samplers, of like design, were set up outside of the experimental rings in an open area to determine rainfall Hg inputs.

Three dissolved organic C (DOC) throughfall collectors were placed in each ring, following the same collection schedule as for the Hg collectors. Collectors consisted of a 72-mm-i.d. glass funnel placed directly into a 250-ml borosilicate bottle (with 2.5 ml of 10% HCl) and housed in PVC piping covered with fiberglass screening.

Stemflow

Three stemflow collectors were placed in each of the five experimental rings at ORNL FACE on 22 July 2007. Stemflow, which is the flow of precipitation water that runs down tree branches and trunks, was collected on 5 August, 3 September and 14 September. Stemflow collector design was based on Kolka et al. (1999). Each collector consisted of 9.6 mm i.d. Teflon tubing slit lengthwise to create a “gutter”, snugly wrapped around each tree and connected to borosilicate collection vesicles. The stemflow collectors were designed to capture an unbiased sample of stemflow but not total stemflow.

Hg quality assurance/quality control

All sample handling and analysis was conducted using rigorously tested cleaning and analytical procedures (EPA method 1669). All reagents, water and equipment were routinely analyzed. Clean-room quality polyvinyl gloves and clean hands/dirty hands techniques were used for handling Hg samples and equipment. For aqueous samples, one field blank was collected for every ten samples, and every tenth field sample was split into two bottles for duplicate analysis.

Sample analysis

Soils and leaves

After removal of roots, soils were passed through a 2-mm screen and air-dried. Leaves were dried at 60°C in a Fisher Isotemp oven and homogenized using a ball mill (using acid-washed polypropylene tubes and glass grinding balls). Soils for Hg analysis were digested using repeated addi-

tions of concentrated HNO₃ and H₂O₂ with heating (EPA method 3050B). Green and senescent leaves from 2005 were digested using repeated additions of HNO₃, followed by H₂O₂ and HCl (EPA method 200.3).

Hg and other metals (Al, Fe, Mn) in 2005 leaf and soil samples were analyzed using a Thermo-Finnegan Element2 inductively coupled plasma mass spectrometer, with apple leaf (NIST 1515) and San Joaquin soils (NIST 2709) as digestion standards and river water (NIST 1643d) as an instrumental standard. Digestion recoveries for Hg in NIST 1515 were 98% [coefficient of variation (CV) = 3.2%] and in NIST 2709 were 90% (CV = 5.5%). Instrument detection limits for Hg were 5 ng l⁻¹; method detection limits for Hg were 0.06 µg l⁻¹ (soils) and 0.02 µg l⁻¹ (leaves). Samples were run in duplicate and averaged.

Green and senescent leaves from 2007 were analyzed using a Milestone direct mercury analyzer 80 (Milestone, Monroe, Conn.; EPA method 7473). NIST 1515 and 2709 were used to confirm instrument calibration. Mean percent recovery on NIST 1515 was 100% (CV = 1.4%) and the method detection limit was 2.4 µg kg⁻¹. Samples were run in duplicate and averaged, and every tenth sample was run in triplicate. Standards were analyzed after every tenth sample.

Percent soil organic matter (SOM) was determined by the method of percent loss on ignition (8-h combustion at 400°C). Soil pH was determined in a 1:1 ratio of soil (grams) to water (milliliters).

Throughfall and stemflow

Throughfall, rainwater and stemflow samples for total Hg analysis were analyzed by cold vapour atomic fluorescence spectrometry at Studio Geochimica (Seattle, Wash.) using modified EPA method 1631. NIST 1641d was used as a standard reference material with an average percent recovery of 99% (CV = 7.5%). Every tenth sample was run in duplicate for quality control. Average method detection limit was 0.06 ng l⁻¹.

Throughfall samples for DOC determination were filtered through a 0.45-µm filter and analyzed at the University of Georgia Stable Isotope/Soil Biology Laboratory using a Shimadzu TOC-5000A total organic C analyzer.

Estimated Hg inputs

Hg inputs to forest soils in the United States (US) were calculated based on an estimated US Hg deposition rate of 87 Mg year⁻¹ (US EPA 1997b). While we used an average estimate, variation in geography, topography and vegetation cover can be expected to create heterogeneity in Hg deposition across the US. The total land area of the US is nearly 931 million ha and total forested land is 303 million

ha, or approximately 30% of total US land area (Lubowski et al. 2006). The flux of Hg to forested areas is estimated to be 4 times non-forested areas (Grigal 2003). Using these values, we calculated deposition to US forests of 57 Mg year^{-1} and inputs to non-forested soils of 30 Mg year^{-1} .

Statistical analyses

ORNL 2005 and pre-treatment soil data were analyzed with a mixed linear model ANOVA (SAS 9.0) using a partly nested design with CO_2 as the main plot factor, soil depth as the within-plot factor, and ring (random) as the experimental unit for CO_2 . Duke 2005 soil samples were analyzed using a partly nested design with CO_2 as the main plot factor, and N treatment and soil depth as within-plot factors. The blocked design structure of Duke FACE was removed from our statistical model because there was no block effect on soil Hg concentration ($P = 0.98$). We included samples from the N-addition sector in our soil analysis to increase our sub-sample size (and improve estimation of the mean). There was no effect of N fertilization on Hg concentrations in soils ($P = 0.33$) nor was there a $\text{CO}_2 \times \text{N}$ interaction effect ($P = 0.56$), and removal of the N-fertilized soils from our analysis did not change our statistical results. We, therefore, limit our results and discussion to CO_2 effects on soil Hg.

Multiple regression analysis was used and Pearson correlation coefficients calculated to estimate the relationship between soil Hg and SOM, pH, Al, Mn, and Fe. Based on this analysis, we used the two main drivers of soil Hg concentration—SOM and pH—as covariates in an analysis of covariance (ANCOVA). R^2 -values reported in the text have been adjusted for df .

ORNL 2005 leaf data were analyzed using a partly-nested design with CO_2 as the main plot factor, canopy height as the within-plot factor, and ring (random) as the experimental unit for CO_2 . We analyzed Duke *P. taeda* and *L. styraciflua* in separate ANOVAs so that we could include age and canopy structure into our *P. taeda* model. Duke *L. styraciflua* leaf samples were analyzed using a partly nested design with CO_2 as the main plot factor nested in block (random). The ANOVA on Duke *P. taeda* needles had two additional within-plot factors—needle age and canopy height. Litterfall Hg deposition (both sites) was analyzed using a single-factor ANOVA, with ring or block (random) as the unit of replication for CO_2 .

2007 ORNL samples were analyzed using a repeated measures ANOVA to test for CO_2 effects on Hg concentrations in leaves, throughfall volume, DOC and Hg concentrations in throughfall, throughfall Hg and DOC deposition and stemflow Hg concentrations. Mauchley's W -test statistic was used to test for sphericity, and when conditions of

sphericity were not met, df of the F -statistic were adjusted using the ε estimator (Huynh and Feldt 1976). A single-factor ANOVA was used to test for CO_2 effects on the summed litterfall and throughfall deposition for the 2007 sampling period. A regression model was fit by the method of ordinary least squares and Pearson correlation coefficients calculated to estimate the correlation between rainfall and throughfall volumes, and Hg and DOC throughfall deposition.

For the ANOVAs and ANCOVA with unequal treatment sample sizes, df were estimated using Satterthwaite's approximation (Satterthwaite 1946). Because of the constraints on sample size of the FACE experiments and resulting low statistical power (Filion et al. 2000), we used a probability level of 0.1 for the ANOVAs and ANCOVA, as in other FACE studies (e.g., Jastrow et al. 2005). All data were log-transformed when necessary to meet the assumptions of the statistical tests. Errors presented in the text and tables are 1 SEM.

Results

Soil Hg

There were significantly greater soil Hg concentrations in the elevated- CO_2 rings at both Duke and ORNL FACE after 9 and 7 years of CO_2 enrichment, respectively. Hg concentrations were 20% greater at Duke and 34% greater at ORNL in the top 20 cm of soils from elevated- CO_2 plots compared to ambient plots (Fig. 1). This CO_2 effect occurred across soil depths from surface to 20 cm (no $\text{CO}_2 \times \text{depth}$ interaction effect). There were no pre-FACE treatment differences in soil Hg concentrations at either site ($P > 0.10$); observed differences in soil Hg occurred after

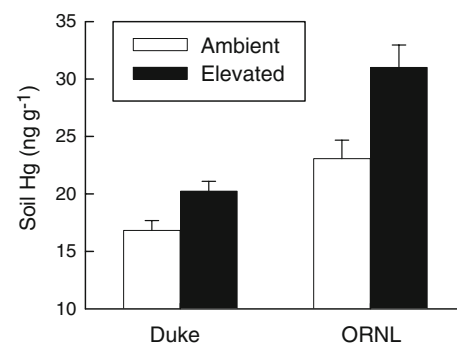


Fig. 1 Soil Hg concentrations in the top 20 cm of soils at Duke and Oak Ridge National Laboratory (ORNL) free-air CO_2 enrichment (FACE) experiments. Points represent least squares means (\pm SE). Statistical significance of main and interactive effects: CO_2 —Duke, $F = 7.97$, $P = 0.05$; ORNL, $F = 9.87$, $P = 0.05$; depth—Duke, $F = 25.75$, $P < 0.01$; ORNL, $F = 5.95$, $P = 0.02$; $\text{CO}_2 \times \text{depth}$ —Duke, $F = 0.62$, $P = 0.61$; ORNL, $F = 1.33$, $P = 0.32$

CO₂ treatment was initiated and were not due to pre-existing soil concentrations.

One possible cause of the observed changes in soil Hg concentrations may be CO₂-mediated effects on the Hg-trapping efficiency of these soils. Soil Hg adsorption is affected by soil properties, such as percent SOM, that may be altered by elevated CO₂. At both Duke and ORNL, there was a significant positive linear relationship between Hg and percent SOM (Fig. 2a), and there was a significant negative linear relationship between Hg and pH at Duke (Fig. 2b). There was not a significant soil Hg–pH relationship at ORNL. However, SOM and pH explained 76% of the variation in soil Hg across sites and CO₂ treatments; therefore, changes in percent SOM and pH at Duke and ORNL under elevated CO₂ (Table 1) even when not statistically significant in and of themselves, may be affecting soil Hg concentrations.

To test the hypothesis that CO₂-mediated effects on soil properties are driving changes in soil Hg concentrations, we used percent SOM and pH as covariates in our statistical model. This covariance test removes the variation in soil Hg that is correlated with SOM and pH. When SOM and pH were included as covariates at Duke, there were no differences in adjusted Hg concentrations between CO₂ treatments (ANCOVA: $F = 1.52$, $P = 0.29$), suggesting that CO₂ effects on Duke soil Hg are mediated by SOM and pH. However, SOM alone as a covariate provided similar results ($F = 1.53$, $P = 0.28$). While pH does account for some of the variation in soil Hg at Duke, it appears that SOM is the main driver of CO₂ effects on soil Hg. At ORNL, we used SOM alone as a covariate since there was no detected pH–soil Hg relationship. The effect of elevated CO₂ on SOM-adjusted soil Hg was still significant ($F = 16.32$, $P = 0.09$), suggesting (in agreement with the low R^2 -values for the soil Hg–SOM relationship) that there are other CO₂ effects, independent of SOM, influencing Hg cycling at ORNL.

Fig. 2 Relationship between soil Hg concentrations (0–20 cm) and **a** percent soil organic matter (SOM) and **b** pH at Duke and ORNL. Points represent 5-cm depth increments within each ring. Statistical significance and R^2 -values: **a** SOM—Duke, $R^2 = 0.81$, $P < 0.01$; ORNL, $R^2 = 0.34$, $P < 0.01$; **b** pH—Duke, $R^2 = 0.33$, $P < 0.01$; ORNL, $R^2 = 0.01$, $P = 0.63$; pH and SOM across sites, $R^2 = 0.76$, $P < 0.01$

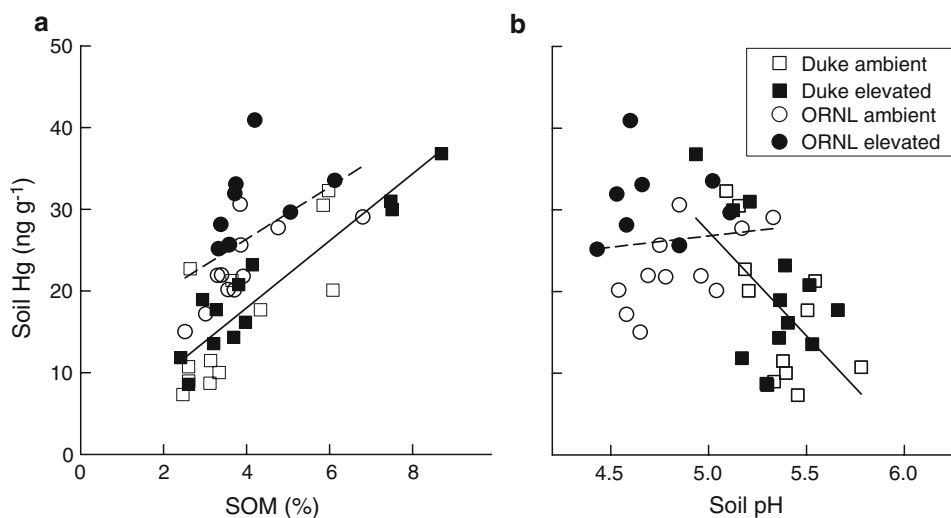


Table 1 Mean (\pm SE) percent soil organic matter (SOM) and soil pH in elevated- and ambient-CO₂ rings at Oak Ridge National Laboratory (ORNL) and Duke free-air CO₂ enrichment (FACE) experiments. Means for each site are followed by P -values and F -statistic: P (F)

	SOM (%)	pH
Duke ambient ^a	4.0 \pm 0.4	5.36 \pm 0.04
Duke elevated ^a	4.5 \pm 0.1	5.33 \pm 0.10
CO ₂ effect: $F_{1,4}$	0.02 (16.54)	0.69 (0.18)
ORNL ambient	3.9 \pm 0.5	4.85 \pm 0.18
ORNL elevated	4.1 \pm 0.4	4.72 \pm 0.08
CO ₂ effect: $F_{1,3}$	0.45 (0.74)	0.43 (0.84)

Significant effects ($P < 0.10$) are in **bold**

^a Ambient and elevated refer to CO₂ concentrations

Green leaf Hg concentrations

L. styraciflua and *P. taeda* green leaf Hg concentrations in 2005 were lower, but not significantly different, under elevated-CO₂ treatment relative to ambient at both Duke and ORNL FACE (Fig. 3a). *P. taeda* foliar Hg concentrations were significantly lower in 0-year than in 1-year needles, but there was not a significant needle age \times CO₂ interaction (Fig. 3a).

In 2007 we collected *L. styraciflua* leaves at ORNL throughout the growing season. There was a significant increase in foliar Hg with time but no significant difference between CO₂ treatments nor a significant time \times CO₂ interaction. Hg concentrations in the elevated-CO₂ plots were slightly lower than in the ambient plots across all measurement periods (Fig. 3b).

There were no detected effects of canopy height on *L. styraciflua* leaves at ORNL in 2005 ($P > 0.10$). At Duke there was a significant CO₂ \times canopy height effect on *P. taeda* foliar Hg concentrations (Fig. 4). Foliar Hg

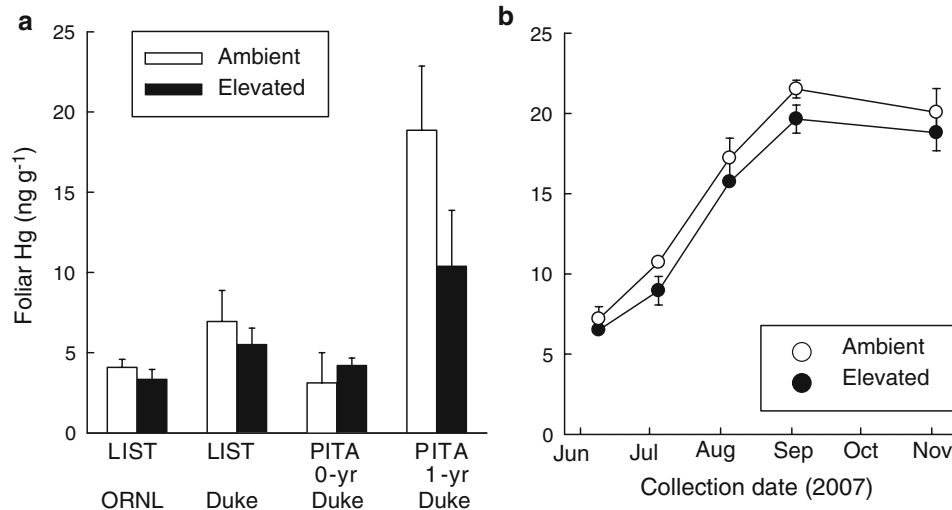


Fig. 3 **a** Least squares mean (±SE) Hg concentrations in 2005 green leaves from *Liquidambar styraciflua* (LIST) at ORNL and Duke, and 0-year (yr) and 1-year *Pinus taeda* (PITA) needles at Duke averaged across canopy heights. **b** Hg concentrations in *L. styraciflua* green and senescent (last sampling date) leaves collected throughout the 2007 growing season at ORNL. Statistical significance: CO₂ effects on a

2005 Duke *L. styraciflua*, $F = 0.43$, $P = 0.55$; ORNL *L. styraciflua*, $F = 0.45$, $P = 0.55$; Duke *P. taeda*, $F = 7.84$, $P = 0.11$. Duke *P. taeda* age effect, $F = 32.14$, $P < 0.01$; age × CO₂, $F = 0.61$, $P = 0.44$. **b** 2007 ORNL *L. styraciflua* CO₂ effect, $F = 1.65$, $P = 0.29$; time, $F = 180.97$, $P < 0.01$; time × CO₂, $F = 0.26$, $P = 0.90$

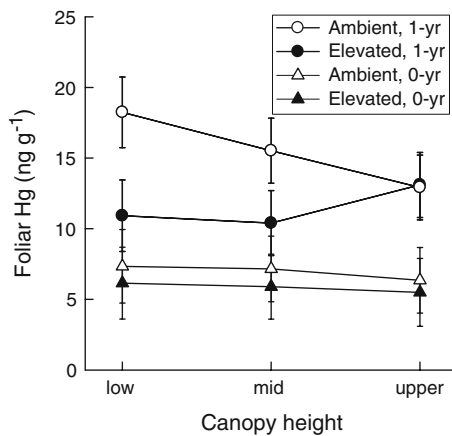


Fig. 4 CO₂ × canopy height interaction effect on Hg concentrations in *P. taeda* 1-year and 0-year needles across low (10–12 m), mid (12–14 m) and upper (14–16 m) canopy heights. Points represent least squares means (±SE). Statistical significance: CO₂ × canopy, $F = 2.70$, $P = 0.07$

concentrations were lower under elevated CO₂ relative to ambient CO₂ in the lower and mid canopy for 1-year needles but not in the upper canopy. There were no canopy height effects on 0-year needles (Fig. 4).

Litterfall Hg concentrations and deposition

At both Duke and ORNL, concentrations of Hg in 2005 litterfall were lower (non-significant at ORNL) in the elevated-CO₂ rings than in ambient rings (Table 2). Litterfall biomass (2005) was significantly greater under elevated CO₂ at both sites, but there was no significant effect of

elevated CO₂ on total litterfall Hg deposition at either site (Table 2). Litterfall Hg deposition was greater at Duke than at ORNL (Table 2) because leaf litter Hg concentrations in the most common tree at Duke, *P. taeda*, were greater by a factor of 8 than concentrations in the predominant species at ORNL, *L. styraciflua* (data not shown). This difference in Hg concentration may be due, in part, to differences in leaf life span between these two species; *P. taeda* needle longevity is 18 months while *L. styraciflua* leaf longevity is less than 6 months.

We collected litterfall at ORNL in 2007 and found similar results to 2005. Litterfall biomass was significantly greater under elevated CO₂ than ambient CO₂, but there was no CO₂ effect on litterfall Hg deposition because Hg concentrations in senescent leaves were (non-significantly) lower with CO₂ enrichment (Table 2). Litterfall Hg concentrations at ORNL were 5 times greater in 2007 compared to 2005 values. This may be due to differences in rainfall between the 2 years (rainfall during the 2007 sampling period was 25% less than during the same time period in 2005; Riggs et al. 2007) and differences in sampling methods and collection dates. In October 2005 we collected freshly fallen leaves off the forest floor, while in November 2007 we collected senescent leaves from the canopy by shaking individual trees.

Throughfall and stemflow

Throughfall and rainfall amounts at ORNL from June up to and including September 2007 were significantly correlated (Fig. 5a), with an average canopy interception of 10%

Table 2 Mean (\pm SE) annual litterfall (LF) biomass, LF Hg concentrations and annual LF Hg deposition at Duke (2005) and ORNL (2005 and 2007); throughfall (TF) amount, TF Hg deposition, and TF dissolved organic C (DOC) deposition at ORNL during the 2007 sampling period (9 June–14 September 2007). Means for each site/year are followed by *P*-values and *F*-statistic: *P* (*F*)

	LF biomass (g m ⁻² year ⁻¹)	LF Hg concentration (ng g ⁻¹)	LF Hg deposition (μ g m ⁻² year ⁻¹)	TF amount (mm)	TF Hg deposition (μ g m ⁻²)	TF DOC deposition (g m ⁻²)
2005						
Duke ambient ^a	611.7 \pm 48.2	23.9 \pm 1.0	14.6 \pm 1.4			
Duke elevated ^a	783.6 \pm 61.4	20.2 \pm 0.7	15.9 \pm 1.8			
CO ₂ effect: <i>F</i> _{1,4}	0.01 (77.85)	0.09 (9.27)	0.42 (1.04)			
ORNL ambient	497.6 \pm 16.0	5.0 \pm 0.9	2.5 \pm 0.5			
ORNL elevated	554.7 \pm 15.5	2.6 \pm 0.9	1.4 \pm 0.5			
CO ₂ effect: <i>F</i> _{1,3}	0.09 (5.89)	0.16 (3.37)	0.25 (2.08)			
2007						
ORNL ambient	447.7 \pm 4.2	20.1 \pm 1.5	9.0 \pm 0.6	21.6 \pm 0.3	3.9 \pm 0.1	0.86 \pm 0.04
ORNL elevated	479.4 \pm 0.6	18.8 \pm 1.1	9.0 \pm 0.6	21.7 \pm 0.3	4.0 \pm 0.1	0.78 \pm 0.05
CO ₂ effect: <i>F</i> _{1,3}	0.01 (3.74)	0.59 (0.37)	0.97 (0.01)	0.97 (0.01)	0.84 (0.05)	0.28 (1.76)

Significant effects (*P* < 0.10) are in *bold*

^a Ambient and elevated refer to CO₂ concentrations

across sampling periods. Throughfall volume varied across sampling dates but was not affected by CO₂ treatment in any sampling period or summed across the sampling season (Fig. 5a; Table 2).

There was a significant effect of sampling date on both throughfall Hg concentrations (Fig. 6a) and throughfall Hg deposition (Fig. 6b) but neither variable was affected by CO₂ treatment. There was no CO₂ effect on throughfall Hg deposition summed across the 2007 collection period (Table 2).

There was a significant effect of sampling time and CO₂ treatment on DOC concentrations in throughfall, with lower DOC concentrations in the elevated-CO₂ rings during all but one sampling period (Fig. 6c). DOC throughfall deposition varied across sampling periods but was not significantly affected by CO₂ treatment (Fig. 6d; Table 2). CO₂ \times sampling date was not significant for any of the throughfall variables (*P* > 0.10). Average DOC concentrations in throughfall (4.8 \pm 0.4 mg L⁻¹) were slightly more than 2.5 times concentrations in rainwater (1.8 \pm 0.2 mg L⁻¹).

There was a positive linear correlation between throughfall Hg deposition and DOC deposition. The strength of this correlation markedly increased with removal of data from the final collection period, when DOC inputs were high relative to Hg inputs (Fig. 5b), likely due to changes in leaf chemistry with senescence.

Stemflow Hg concentrations differed among sampling periods (*F* = 5.08, *P* = 0.07), but again there was no detected CO₂ effect (*F* = 1.12, *P* = 0.37). Across all sampling periods and both CO₂ treatments, Hg concentrations in stemflow (54.27 \pm 3.17 ng l⁻¹) were 3 times greater than concentrations in throughfall (18.37 \pm 1.18 ng l⁻¹) and 5.5

times greater than the concentration in rainwater (9.75 \pm 0.58 ng l⁻¹). While we did not measure total stemflow amount, based on previous studies (Kolka et al. 1999) we expect stemflow inputs to this stand to be about 2–3% of open precipitation, which was 240 mm during the 2007 sampling period (Riggs et al. 2007). Estimated stemflow Hg deposition would therefore be about 0.25–0.39 μ g m⁻² per sampling season or 10% of throughfall Hg deposition.

Discussion

CO₂ effects on soil Hg

The observed CO₂ effect on soil Hg concentrations—which were 20% greater with CO₂ enrichment at Duke and 34% greater at ORNL (Fig. 1)—was likely driven by increased soil retention rather than increased litter, throughfall or stemflow Hg deposition. Our soil pH and SOM data support the hypothesis that CO₂-mediated changes in these two factors—changes that have been found in other elevated-CO₂ experiments (Andrews and Schlesinger 2001; Jastrow et al. 2005; Oh and Richter 2004)—underlie this higher retention. Our hypothesis regarding the Hg-trapping efficiency of soils under high CO₂ is consistent with previous studies of the impact of SOM and pH on soil Hg adsorption (Schuster 1991; Yin et al. 1996). For example, maximum Hg adsorption in soils has been shown to occur at low pH (range of 3–5) when SOM is present (Schuster 1991; Yin et al. 1996); SOM is thus a key determinant of Hg soil-binding capacity (Schuster 1991; Yin et al. 1996). In addition, soil pH affects the physical fractionation of

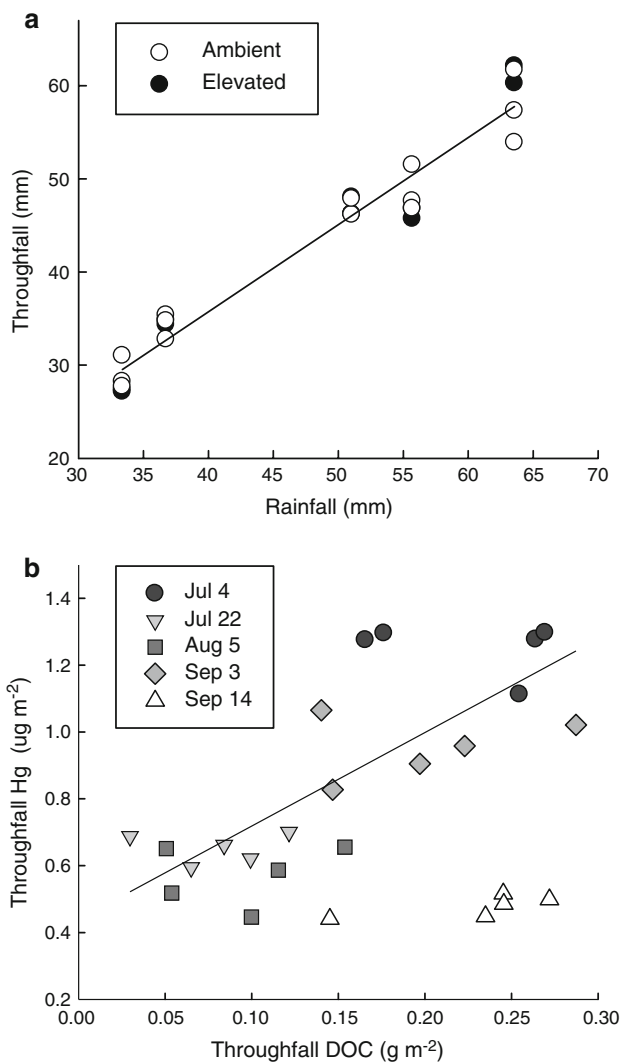


Fig. 5 **a** Relationship between rainfall and throughfall volume at ORNL FACE from June up to and including September 2007 ($R^2 = 0.97$, $P < 0.01$). Symbols represent throughfall in each experimental ring and rainfall (from Riggs et al. 2007) during each of the five collection periods. Statistical significance of treatment effects on throughfall: CO_2 , $F = 0.01$, $P = 0.97$; sampling date, $F = 11.80$, $P < 0.01$. **b** Relationship between dissolved organic C (DOC) and Hg throughfall deposition. Regression line does not include final sampling period (3–14 September; $R^2 = 0.60$, $P < 0.01$). Dates in the legend are collection dates and symbols represent deposition per ring during each collection period. The first collection began on 9 June 2007

SOM (dissolved versus adsorbed), which ultimately determines the fate of soil Hg (Schuster 1991; Yin et al. 1996). We found that soil Hg concentrations were significantly correlated with SOM at both sites, and with pH at Duke and across sites (Fig. 2). The results of our ANCOVA, particularly at Duke, further support the hypothesis that CO_2 -mediated changes in SOM are driving changes in soil Hg concentrations. In addition to CO_2 -mediated changes in SOM quantity, SOM quality may also be an important driver of soil Hg retention. Future research efforts should

focus on CO_2 -mediated changes in soil dynamics (e.g., changes in humic substances) on Hg retention in soils.

While the soils used in this study are from relatively uncontaminated forests, we expect increasing atmospheric CO_2 to affect soil Hg at a range of concentrations and soil types due to the strong relationship between CO_2 and SOM and the relationship between SOM and Hg (Grigal 2003; Schuster 1991). Changes on a global scale that can affect soil Hg, even at low Hg levels, will have a large overall effect on global Hg fluxes and pools. For example, in the US, the estimated amount of Hg stored in the forest floor is 1,350 Mg (Grigal 2003) and the deposition rate to forests is approximately 57 Mg year^{-1} (details of this deposition estimate can be found in the “Materials and methods”). The average increase in Hg storage under elevated CO_2 found in this study (27% over 8 years, or $3.4\% \text{ year}^{-1}$) suggests that greater Hg storage in forests under elevated CO_2 is the same order of magnitude as the annual Hg deposition of 57 Mg to these forests and thus may have strong impacts on the dynamics of Hg in terrestrial ecosystems.

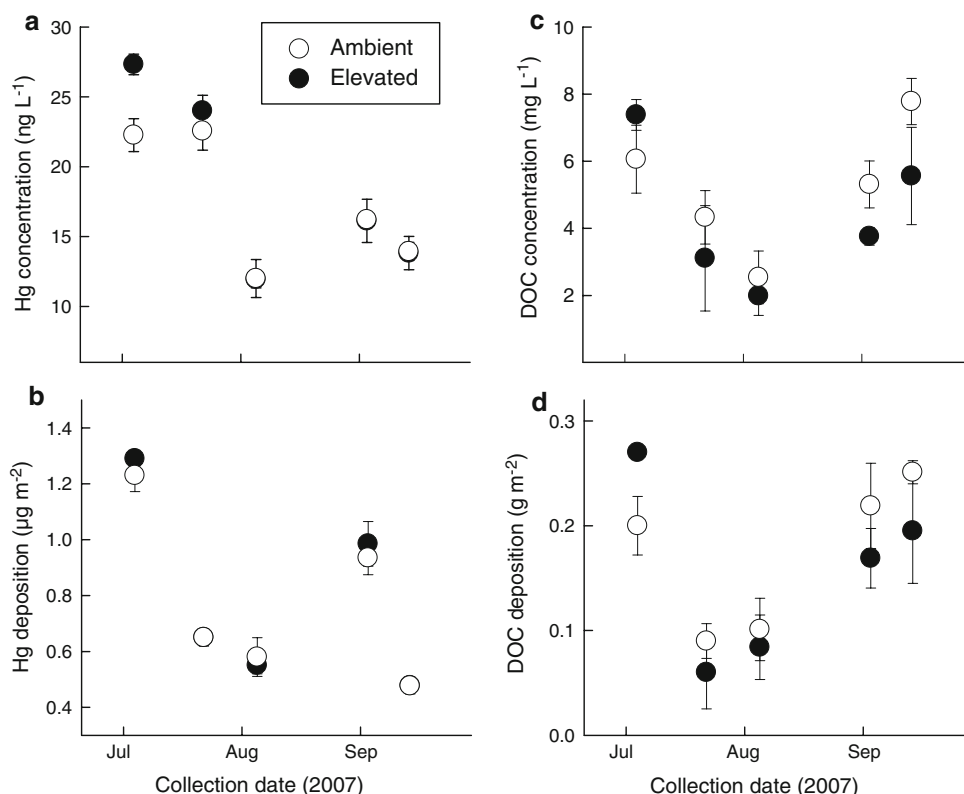
While these results are congruent with the retention hypothesis, other soil factors that may be affected by atmospheric CO_2 concentrations could also be at play. For example, in addition to the above-described pH and SOM impacts, Hg retention can vary with incident solar radiation, soil temperature, and soil moisture (Carpi and Lindberg 1998; Gustin and Stamenkovic 2005). The CO_2 enrichment treatment itself is unlikely to be a source of added Hg to soils in the elevated- CO_2 rings because green leaf, litter and throughfall Hg concentrations in these rings were all lower or similar to concentrations in the ambient- CO_2 rings.

CO_2 effects on leaf and litter Hg concentrations

There was a trend of decreased leaf and litter Hg concentrations in the elevated- CO_2 rings in both species and sites. This decrease may have been caused by growth dilution effects (i.e., increased carbohydrate accumulation/leaf density; Loladze 2002). If leaf density changes are an important driver of foliar Hg concentrations, we would expect to see concentration differences in the upper canopy because changes in leaf density with CO_2 enrichment are generally more pronounced in upper canopy leaves (Norby and Iversen 2006). However, there were no canopy effects on foliar Hg concentrations in *L. styraciflua* at ORNL and none in the upper canopy in *P. taeda* (Fig. 4), suggesting the growth dilution hypothesis does not fit the data.

One potential source of Hg to canopy leaves is volatile emissions from soils. Elevated CO_2 may alter soil Hg fluxes through a CO_2 -mediated decrease in forest floor light levels or increased adsorption of soil Hg to SOM, both of which have been shown to lower volatile Hg fluxes (Carpi and Lindberg 1998; Gabriel and Williamson 2004; Gustin and

Fig. 6 Effect of sampling date and CO₂ concentrations on throughfall **a** Hg concentrations, **b** Hg deposition, **c** DOC concentrations and **d** DOC deposition. Sampling began on 9 June 2007 and samples were collected on the following dates [rainfall during collection periods (Riggs et al. 2007) in parentheses (mm)]: 4 July (51.0), 22 July (33.4), 5 August (55.7), 3 September (63.6), 14 September (36.7). Statistical significance: **a** Hg concentrations—date, $F = 136.41$, $P < 0.01$; CO₂, $F = 0.12$, $P = 0.75$; **b** Hg deposition—date, $F = 88.68$, $P < 0.01$; CO₂, $F = 0.16$, $P = 0.71$; **c** DOC concentrations—date, $F = 7.59$, $P < 0.01$; CO₂, $F = 13.49$, $P = 0.03$; **d** DOC deposition—date, $F = 10.33$, $P < 0.01$; CO₂, $F = 1.76$, $P = 0.28$



Stamenkovic 2005). If soil Hg emissions were an important source of Hg to leaves in these forests then we would expect Hg concentrations in the lower canopy to reflect this source. Hg concentrations in *P. taeda* lower-canopy leaves were higher relative to the upper canopy in the ambient- but not in the elevated-CO₂ plots (Fig. 4), suggesting that soil fluxes may be greater under ambient CO₂ conditions than elevated CO₂ at Duke FACE. At ORNL, however, we found no canopy effect on foliar Hg concentrations.

Decreased stomatal conductance with CO₂ enrichment has also been shown to affect foliar Hg uptake (Millhollen et al. 2006); however, the detected patterns of foliar Hg concentrations in these forests were not congruent with CO₂-mediated changes in conductance (Ellsworth 1999; Wullschlegel et al. 2002). Beyond CO₂ effects, our leaf concentration data support several other Hg studies, which report greater foliar Hg concentrations in evergreen versus broadleaf deciduous trees (Rasmussen et al. 1991; Fig. 3a), increased Hg during the growing season (Rasmussen 1995; Rea et al. 2002; Fig. 3b), and increased Hg concentrations with needle age (Fleck et al. 1999; Rasmussen 1995; Figs. 3a, 4).

CO₂ effects on Hg deposition

The forest canopy provides a means of capturing atmospheric Hg and depositing it to soils, primarily through

litterfall. While there was an increase in litterfall biomass under elevated CO₂, there was no change in litterfall Hg deposition because litter Hg concentrations decreased with CO₂ enrichment (Table 2). Potential changes in leaf area index (LAI; leaf area per unit ground area) with increased CO₂ may be a more important factor affecting the uptake of Hg by the forest canopy than changes in biomass. However, at ORNL, elevated CO₂ has had no effect on LAI (Norby et al. 2001, 2003) and reported effects at Duke have been small and variable (DeLucia et al. 2002; Lichter et al. 2000).

While litterfall Hg deposition may represent the greatest flux of Hg to forest soils (Lichter et al. 2000; St Louis et al. 2001), throughfall Hg deposition also is an important source of soil Hg (Iverfeldt 1991; Munthe et al. 1995; Rea et al. 2001, 2002). Throughfall, which is the flow of precipitation water through the forest canopy, can be affected by canopy architecture, leaf area and rainfall intensity (Lovett et al. 1996; Whelan and Anderson 1996). Lichter et al. (2000) found that elevated CO₂ increased throughfall volume and caused a significant increase in DOC throughfall deposition, attributed to increased soluble C in foliage grown in elevated CO₂. Because of the strong relationship between Hg and DOC (Kolka et al. 1999), we hypothesized that throughfall Hg may also increase with elevated CO₂. As in Kolka et al. (1999) we found a significant relationship between throughfall DOC and throughfall Hg (Fig. 5b).

While there was a significant CO₂ effect on DOC throughfall concentrations, concentrations were lower with CO₂ enrichment during most sampling periods (Fig. 6c). There was no effect of elevated CO₂ on throughfall DOC or Hg deposition throughout the 2007 sampling period at ORNL FACE (Fig. 6b, d). Stemflow Hg deposition also was not affected by elevated CO₂.

Our litter, throughfall and stemflow deposition data allow us to reject the hypothesis that higher soil Hg concentrations in elevated-CO₂ soils were driven by increased deposition. These data support the hypothesis that CO₂-mediated changes in soil properties are increasing the Hg storage capacity of forest soils. Future research efforts should focus on soil processes (i.e., root dynamics, SOM and Hg) under elevated CO₂ to gain a better understanding of potential changes in soil Hg cycling with increasing CO₂. One challenge of conducting research at large-scale multi-user facilities such as the FACE sites is the restrictions on sample size. The fact that a CO₂ effect on soil Hg was detected, in spite of this limitation, suggests that the observed response is robust, but future studies at other FACE sites would strengthen these conclusions.

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