Environmental Science & Technology

ARTICLE

pubs.acs.org/est

Plant−Soil Distribution of Potentially Toxic Elements in Response to Elevated Atmospheric CO_2

Benjamin D. Duval,[*,†,▲] Paul Dijkstra,[†] Susan M. Natali,[‡] J. Patrick Megonigal,[§] Michael E. Ketterer,[∥] Bert G. Drake,[§] Manuel T. Lerdau,[⊥] Gwyneth Gordon,[▽] Ariel D. Anbar,[▽] and Bruce A. Hungate[†]

[†]Department of Biological Sciences and Merriam-Powell Center for Environmental Research and [∥]Department of Chemistry and Biochemistry, Northern Arizona University, Flagstaff, Arizona 86011, United States

[‡]Department of Biology, University of Florida, Gainesville, Florida 32611, United States

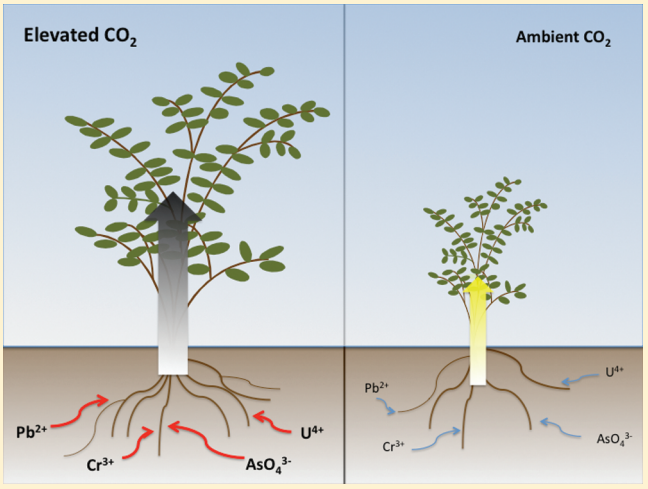
[§]Smithsonian Environmental Research Center, Edgewater, Maryland 21037, United States

[⊥]Department of Environmental Sciences, University of Virginia, Charlottesville, Virginia 22904, United States

[▽]School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287, United States

Supporting Information

ABSTRACT: The distribution of contaminant elements within ecosystems is an environmental concern because of these elements' potential toxicity to animals and plants and their ability to hinder microbial ecosystem services. As with nutrients, contaminants are cycled within and through ecosystems. Elevated atmospheric CO_2 generally increases plant productivity and alters nutrient element cycling, but whether CO_2 causes similar effects on the cycling of contaminant elements is unknown. Here we show that 11 years of experimental CO_2 enrichment in a sandy soil with low organic matter content causes plants to accumulate contaminants in plant biomass, with declines in the extractable contaminant element pools in surface soils. These results indicate that CO_2 alters the distribution of contaminant elements in ecosystems, with plant element accumulation and declining soil availability both likely explained by the CO_2 stimulation of plant biomass. Our results highlight the interdependence of element cycles and the importance of taking a broad view of the periodic table when the effects of global environmental change on ecosystem biogeochemistry are considered.



INTRODUCTION

Potentially toxic elements can be harmful to both animals and plants, depress the decomposition rates of plant litter, and hinder soil microbial ecosystem services.[1−3] Elevated atmospheric CO_2 generally increases plant productivity, alters nutrient cycling,[4] and often reduces plant nutrient concentration.[5,6] However, the effects of elevated CO_2 on the concentration and mobility of micronutrients, nonessential elements, and contaminants are not well understood. Because contaminant elements are not essential and sometimes actively avoided by organisms,[7] changes in their biogeochemical cycles may differ from those of biologically necessary elements.

Several studies have demonstrated significant changes in contaminant stoichiometry in plants exposed to elevated CO_2 and increases in soil organic matter (SOM) that can control metal availability in soils,[8−10] but CO_2 effects on contaminant element distribution from soils to plants on a mass basis have not been evaluated. Elevated CO_2 usually enhances tree growth,[11,12] which can cause plants to mine soil for nutrients if they are nutrient-stressed, enhance root exudate production, and potentially acidify soils.[13−16] The allocation of labile C to the rhizosphere can also be increased under elevated CO_2.[17] Previous work has shown that where elevated CO_2 increases SOM, the concentrations of metals in soil rises.[8,9] We predict that, in a system where elevated CO_2 leads to a decrease in SOM through organic matter mineralization via microbial activity,[18] uptake of contaminants from soil could increase, and toxin mass could accumulate in plant biomass, irrespective of changes in toxin concentration in plants. We hypothesize that in such a system increased plant growth under elevated CO_2 increases the mobility of contaminants, leading to declines in available contaminant

Received: July 4, 2010
Accepted: February 14, 2011
Revised: February 11, 2011

mass in mineral soil due to increased SOM mineralization and higher plant uptake of these elements.

MATERIALS AND METHODS

Soil and oak samples were collected from the Smithsonian Environmental Research Center's elevated CO_2 experiment at Kennedy Space Center in July 2007. This was an open-top chamber experiment that increased atmospheric CO_2 ~360 μmol·mol^{-1} above ambient (n = 8 elevated chambers, n = 8 ambient chambers). The chambers had been exposed to elevated CO_2 for over 11 years at the time of sampling. Soils were Paola sands, Arenic Haplahumods, and Spodic Quartzipsamments, which are uniformly fine sands. *Quercus* spp. constituted >90% of the plant biomass. See ref 19 for a more detailed site description.

Soils were collected from 0 to 10 cm (A horizon), 10−30 cm (E horizon), 30−100 cm (E2 horizon), and Bh horizon (variable depth between 100 and 250 cm deep). We collected oak leaves (*Quercus myrtifolia*) from five different trees per plot. Stems (branches originating from the main trunk not directly attached to leaves) were collected as part of a destructive harvest at the Florida site in July 2007.

Soils were sieved with 2 mm mesh and dried at 105 °C. Roots and coarse particulate organic matter (CPOM) were hand-separated from soil cores. We cleaned sand from roots by sonication in 15 mL acid-washed centrifuge tubes and filtration with ultrapure H_2O. The filtered water was reintroduced to the root samples and evaporated off by drying samples at 70 °C. All samples were extracted or digested in trace-metal free reagents, and blank samples of each extraction (n = 3 after every 10 samples) were analyzed to confirm there was no contamination from reagents.

Concentrations of soluble Al, Ti, Cr, Fe, Co, Ni, Cu, As, Cd, Ba, W, Pb, and U in soil were determined from ammonium oxalate extractions of ~1.0 g of soil.[20] Element concentrations in oak leaves, wood, roots, and CPOM were determined by ashing of samples (~500 mg) at 600 °C, digestion with concentrated HF and HNO_3, and dilution in 0.32 M HNO_3.

Concentrations of elements other than Hg were determined on a Thermo X-Series quadrupole ICP-MS at the Keck Isotope Biogeochemistry Laboratory (Arizona State University, Tempe, AZ). Hg was analyzed on samples collected in 2006 following digestion with EPA protocol 3050, on a Thermo-Finnegan Element 2 multiple-collector ICP-MS at SUNY—Stony Brook, Stony Brook, NY (see Supporting Information for analytical details). Element concentrations were expressed in units of mass of element per gram of plant tissue or soil.

Soil element mass (grams of element per square meter of ground area) was determined by multiplying element concentrations by bulk density (A horizon = 0.83 g·cm^{-3}, E = 1.01 g·cm^{-3}, E2 = 1.15 g·cm^{-3}, and Bh = 1.41 g·cm^{-3}) and the depth of each layer.[21] We did not measure the effect of elevated CO_2 on bulk density or layer depth but assumed no or negligible effects because of the soil's uniformly sandy characteristic.[22]

We calculated contaminant mass in above-ground oak biomass in units of grams of element per square meter of ground area as (leaf element concentration × leaf mass) + (stem concentration × stem and trunk mass). We summed contaminant mass in above-ground oak biomass with contaminant mass in roots to determine the total biomass contaminant pool. Since only a subset of roots were cleaned in the manner described above, root mass was corrected for any adhering soil particles by use of the carbon content of roots.[23]

We used one-way analyses of variance (ANOVAs) to test for differences in toxic element concentration and content in soils and oaks between CO_2 treatments. We estimated 90% confidence intervals using bootstrapping with replacement (sample size = 8, with 1000 iterations). Analyses were performed with R and with the ResampleStat add-in for Microsoft Excel.[24] All tests

Table 1. Concentration of Potentially Toxic Elements in *Quercus myrtifolia*[a]

	ambient CO_2		elevated CO_2	
element	mean	SE	mean	SE
Al	50.216	17.246	39.334	12.236
Ti	5.756	1.202	4.165	1.223
Cr	7.874	4.003	4.865	3.653
Fe	88.259	23.356	67.321	19.008
Co	0.104	0.034	0.109	0.044
Ni	1.282	0.296	1.287	0.292
Cu	15.881	3.773	15.261	3.805
As	0.628	0.337	0.295	0.110
Cd	1.586	1.323	0.197	0.114
Ba	45.666	15.421	30.306	10.556
W	0.887	0.350	0.198	0.136
Hg[b,c]	17.716	2.083	15.938	3.047
Pb	7.384	5.946	0.890	0.531
U[b]	3.104	0.889	1.933	0.448

[a] Leaves from the Smithsonian Environmental Research Center's Elevated CO_2 experiment at Kennedy Space Center, Florida, were collected in 2007 from trees in open-top chambers under ambient atmospheric CO_2 and from trees in chambers exposed to 11 years of elevated (ambient + 360 μmol · mol) CO_2. Values are micrograms of element per gram of leaf dry mass except where noted. [b] Nanograms of element per gram of leaf dry mass. [c] Hg was analyzed from 2006 samples.

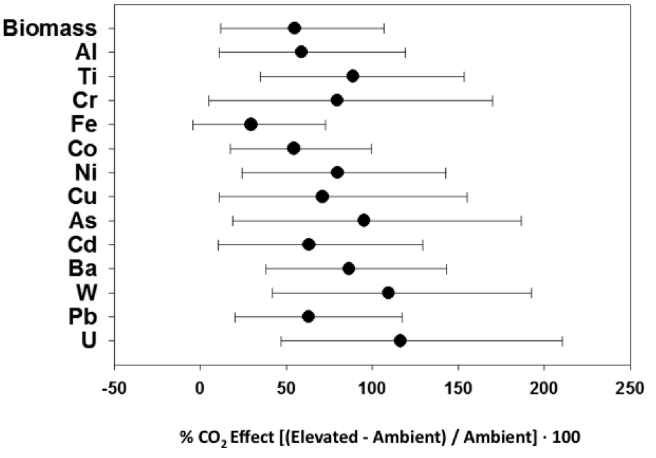


Figure 1. Relative effect of elevated CO_2 [(means from elevated CO_2 plots − means from ambient CO_2 plots)/(means from ambient CO_2 plots) × 100] on contaminant element mass (grams per square meter) in the above- and below-ground plant biomass [(leaf element concentration × leaf mass) + (stem element concentration × stem mass) + root element mass to 1 m depth] of a Florida scrub-oak ecosystem, SERC experiment, Kennedy Space Center, FL. Error bars are bootstrapped 90% confidence levels.

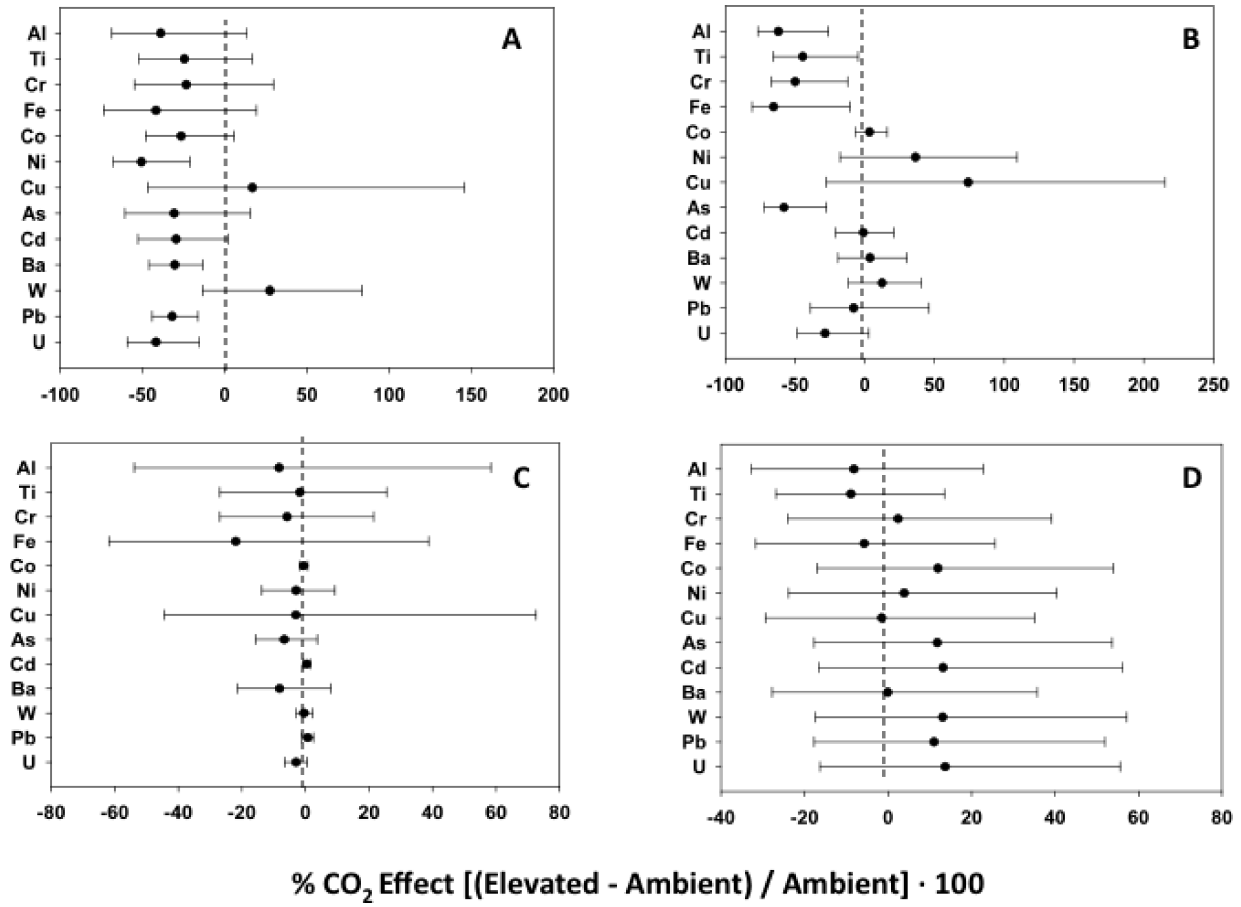


Figure 2. Relative effect of elevated CO_2 [(means from elevated CO_2 plots − means from ambient CO_2 plots)/(means from ambient CO_2 plots) × 100] on extractable element mass (grams per square meter) in soil of a Florida scrub-oak ecosystem, Kennedy Space Center, FL. Error bars are bootstrapped 90% confidence levels. (A) A horizon soil (0−10 cm), (B) E horizon soil (10−30 cm), (C) E2 horizon soil (30−100 cm), and (D) spodic (Bh) horizon soil (variable depth between 100 and 250 cm deep).

were two-tailed, and data were tested for heteroscedasticity with the Flinger−Killeen test; comparisons that did not meet variance assumptions were tested with the Mann−Whitney U test.[25]

To account for multiple comparisons, we used the false discovery rate (FDR) test. That test is less conservative than a *P*-value adjustment such as the Bonferroni correction and determines the probability that a significant test is a false positive (rejection of the null hypothesis of no difference). All FDRs suggested less than one false positive, justifying the use of multiple ANOVAs.[26]

RESULTS AND DISCUSSION

Oak leaves tended to have lower contaminant concentrations under elevated CO_2 for every element we measured, with the exception of Co and Ni (Table 1). However, the variability of these concentrations was high, and the only significant CO_2 effect was for U ($F_{1,\ 14} = 3.17$, $P < 0.10$).

Elevated CO_2 increased above-ground biomass ($F_{1,\ 14} = 10.44$, $P = 0.006$; ref 11) but not below-ground biomass. Elevated CO_2 significantly increased total plant element content for Al, Ti, Co, Ni, As, Cd, Ba, W and U (Figure 1; *F* statistics and *P* values are presented in Table S1, Supporting Information).

The effects of elevated CO_2 on the availability of contaminants in soils depended on horizon. In the A horizon, elevated CO_2 reduced extractable Ba ($F_{1,14} = 6.10$, $P = 0.022$), Pb ($F_{1,14} = 5.97$, $P = 0.028$), U ($F_{1,14} = 4.71$, $P = 0.048$), and Ni (Mann−Whitney U test, $W = 50.0$, $P = 0.065$) (Figure 2A). In the E horizon, elevated CO_2 reduced extractable Al ($F_{1,14} = 3.72$, $P = 0.074$), Cr ($F_{1,14} = 3.05$, $P = 0.10$), and As ($F_{1,14} = 3.82$, $P = 0.071$) (Figure 2B). Elevated CO_2 had no significant effect on extractable element mass in the deeper horizons sampled (E2 and Bh; Figure 2C,D).

Elevated CO_2 stimulation of plant growth in our experiment drives the increased contaminant content in biomass (Figure 1) and the decline in soil available pools (Figure 2). For Al, Fe, Cr, Cu, and As, the increased element content in plant biomass was comparable to the decline in extractable element availability (Table 2), indicating that increased element content of plant biomass was sufficient to explain the decline in extractable element content of soil. For Ti, Co, Ni, Zn, Cd, Ba, W, Pb, and U, increased element mass in plants was more than sufficient to account for the decline of extractable element content of soil. In short, the CO_2 stimulation of plant growth and reduction of SOM caused element accumulation in plant biomass that matched the decline in extractable element mass in soil, but in a system where CO_2 causes an increase in SOM, such a rise in plant biomass may well not be accompanied by an increase in the plant pools of elements. On a whole ecosystem basis (all elements, plants + soil), there was a positive accumulation of Cd under elevated CO_2, but CO_2 caused neither accumulation nor loss of any other element measured (Table 2).

Table 2. Change in Whole-System Element Mass and Distribution of Elements between Plants and Soil-Extractable Pools after 11 Years of Experimental CO_2 Enrichment[a]

	absolute CO_2 effects (E − A)					
	whole system mass			change in plant element mass + change in soil-extractable element mass		
element	mean	lower CL	upper CL	mean	lower CL	upper CL
Al	13.076	−117.817	150.997	−3.285	−45.481	36.219
Ti	−6.784	−39.311	26.714	0.552	0.231	0.930
Cr	0.019	−0.139	0.179	0.011	−0.014	0.039
Fe	0.009	−7.865	4.313	−2.824	−6.343	0.515
Co	0.003	−0.015	0.020	0.010	0.003	0.017
Ni	−0.027	−0.158	0.102	0.031	0.009	0.058
Cu	−0.013	−0.163	0.143	0.544	−0.308	1.379
As	−0.001	−0.026	0.025	0.005	−0.002	0.128
Cd	0.004	0.001	0.007	0.003	0.001	0.006
Ba	−0.342	−0.980	0.303	0.177	0.078	0.296
W	−0.079	−0.214	0.058	0.008	0.003	0.014
Pb	0.029	−0.780	0.736	0.442	0.153	0.755
U	0.004	−0.010	0.017	0.003	0.001	0.006

[a] The effect of CO_2 on whole-system mass is the effect of CO_2 on the total content of elements measured in the system, expressed as an absolute difference (elevated − ambient, in units of grams of element per square meter of ground area). Change in plant biomass + change in soil-extractable mass (in units of grams of element per square meter of ground area) is the increment in elements in plant biomass (elevated − ambient) plus the increment in extractable element availability (elevated − ambient); thus, positive values indicate that the increase in plant element content was greater than the decline in soil-extractable pools. Values are means and bootstrapped 90% confidence limits.

Our results demonstrate that elevated CO_2 significantly affects contaminant element cycling. Uptake of these elements could have implications for plant nutritional quality, herbivore toxin exposure, and bioaccumulation of toxins in the food chain.[27] Furthermore, toxin leaching through soils is a serious concern if those elements enter groundwater. The elements Cd and Pb, which we show are mobilized under elevated CO_2 in this system, are toxic to organisms involved in decomposition and N mineralization,[3] and therefore, elevated CO_2 could also alter key ecosystem processes by altering the mobility of these elements.

Elevated CO_2 often increases root growth and changes the soil microbial community,[28,29] and these effects can drive microsite soil acidification and possibly element mobilization.[30] Furthermore, element availability in surface soils could increase with enhanced rates of soil organic matter mineralization[18,31] and increased soil−water content from reduced evapotranspiration under elevated CO_2.[32] Our work suggests that plant productivity drives contaminant uptake (as SOM dynamics have been suggested to affect contaminant patterns in soils),[8] indicating that contaminant cycling may also be sensitive to other global changes, like N deposition, that can enhance plant growth, or increased atmospheric O_3, that can depress productivity.[33]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Additional text with analytical details and one table showing the effect of elevated CO_2 on total plant element masses. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: bdduval@illinois.edu.

Present Addresses

▲Global Change Solutions and Institute for Genomic Biology, University of Illinois at Urbana−Champaign, Urbana, IL 61801.

■ ACKNOWLEDGMENT

We thank Hans Anderson, Tom Powell, and David Johnson for maintenance of the Florida experiment. This work was supported by NSF Grant DEB-0445324, a NSF-IGERT fellowship awarded to B.D.D., and funds provided by Science Foundation Arizona to B.D.D.

■ REFERENCES

(1) Patra, M.; Bhowmik, N.; Bandopadhyay, B.; Sharma, A. Comparison of mercury, lead and arsenic with respect to genotoxic effects on plant systems and the development of genetic tolerance. *Environ. Exp. Bot.* **2004**, *52*, 199–223.

(2) Strojan, C. L. Forest leaf litter decomposition in the vicinity of a zinc smelter. *Oecologia* **1978**, *32*, 203–212.

(3) Giller, K. E.; Witter, E.; McGrath, S. P. Heavy metals and soil microbes. *Soil Biol. Biochem.* **2009**, *41*, 2031–2037.

(4) Johnson, D. W.; Hungate, B. A.; Dijkstra, P.; Hymus, G. J.; Hinkle, C. R.; Stiling, P.; Drake, B. G. The effects of elevated CO_2 on nutrient distribution in a fire-adapted scrub oak forest. *Ecol. Appl.* **2003**, *13*, 1388–1399.

(5) Cotrufo, M. F.; Ineson, P.; Scott, A. Elevated CO_2 reduces the nitrogen concentration of plant tissues. *Global Change Biol.* **1998**, *4*, 43–54.

(6) Manderscheid, R.; Bender, J.; Jiger, H. J.; Weigel, H. J. Effects of season long CO_2 enrichment on cereals. II. Nutrient concentrations and grain quality. *Agric. Ecosys. Environ.* **1995**, *54*, 175–185.

(7) Bellenger, J. P.; Wichard, T.; Kustka, A. B.; Kraepiel, A. M. L. Uptake of molybdenum and vanadium by a nitrogen-fixing soil bacterium using siderophores. *Nat. Geosci.* **2008**, *1*, 243–246.

(8) Natali, S. M.; Sanudo-Wilhelmy, S. A.; Lerdau, M. T. Plant and soil mediation of elevated CO_2 impacts on trace metals. *Ecosystems* **2009**, *12*, 715–727.

(9) Natali, S. M.; Sañudo-Wilhelmy, S. A.; Norby, R. J.; Zhang, H.; Finzi, A. C.; Lerdau, M. T. Increased mercury in forest soils under elevated carbon dioxide. *Oecologia* **2008**, *158*, 343–354.

(10) Millhollen, A. G.; Obrist, D.; Gustin, M. S. Mercury accumulation in grass and forb species as a function of atmospheric carbon dioxide concentrations and mercury exposures in air and soil. *Chemosphere* **2006**, *65*, 889–897.

(11) Seiler, T. J.; Rasse, D. P.; Li, J.; Dijkstra, P.; Anderson, H. P.; Johnson, D. P.; Powell, T. L.; Hungate, B. A.; Hinkle, C. R.; Drake, B. G. Disturbance, rainfall and contrasting species responses mediated aboveground biomass response to 11 years of CO_2 enrichment in a Florida scrub-oak ecosystem. *Global Change Biol.* **2009**, *15*, 356–367.

(12) Norby, R. J.; DeLucia, E. H.; Gielen, B.; Calfapietra, C.; Giardina, C. P.; King, J. S.; Ledford, J.; McCarthy, H. R.; Moore, D. J. P.; Ceulemans, R.; et al. Forest response to elevated CO_2 is conserved across a broad range of productivity. *Proc. Natl. Acad. Sci. U.S. A.* **2005**, *102*, 18052–18056.

(13) Brady, N. C.; Weil, R. R. *The nature and properties of soils*; Prentice Hall: Upper Saddle River, NJ, 2002.

(14) Lambers, H.; Raven, J. A.; Shaver, G. R.; Smith, S. E. Plant nutrient acquisition strategies change with soil age. *TREE* **2008**, *23*, 95–103.

(15) Houlton, B. Z.; Wang, Y. P.; Vitousek, P. M.; Field, C. B. A unifying framework for dinitrogen fixation in the terrestrial biosphere. *Nature* **2008**, *454*, 327–334.

(16) Oh, N.-H.; Richter, D. D. Soil acidification induced by elevated atmospheric CO_2. *Global Change Biol.* **2004**, *10*, 1936–1946.

(17) Cheng, W.; Johnson, D. W. Elevated CO_2, rhizosphere processes, and soil organic matter decomposition. *Plant Soil* **1998**, *202*, 167–174.

(18) Langley, J. A.; McKinley, D. C.; Wolf, A. A.; Hungate, B. A.; Drake, B. G.; Megonigal, J. P. Priming depletes soil carbon and releases nitrogen in a scrub-oak ecosystem exposed to elevated CO_2. *Soil Biol. Biochem.* **2009**, *41*, 54–60.

(19) Hymus, G. J.; Pontailler, J.-Y.; Li, J.; Stiling, P.; Hinkle, C. R.; Drake, B. G. Seasonal variability in the effect of elevated CO_2 on ecosystem leaf area index in a scrub-oak ecosystem. *Global Change Biol.* **2002**, *8*, 931–940.

(20) Liu, D.; Clark, J. D.; Crutchfield, J. D.; Sims, J. L.. Effect of pH of ammonium oxalate extracting solutions on prediction of plant available molybdenum in soil. *Commun. Soil Sci. Plant Anal.* **1996**, *27*, 2511–2541.

(21) Johnson, D. Personal communication, 2007.

(22) United States Department of Agriculture. https://soilseries.sc.egov.usda.gov/OSD_Docs/O/ORSINO.html.

(23) Janzen, H. H.; Entz, T.; Ellert, B. H. Correction mathematically for soil adhering to root samples. *Soil Biol. Biochem.* **2002**, *34*, 1965–1968.

(24) R Development Core Team. *R: A language and environment for statistical computing*; R Foundation for Statistical Computing, Vienna, Austria, 2007.

(25) Crawley, M. J. *The R Book*; John Wiley & Sons: West Sussex, England, 2007.

(26) Storey, J. D. The positive false discovery rate: a Bayesian interpretation and the q-value. *Ann. Stat.* **2003**, *31*, 2013–2035.

(27) Stiling, P.; Rossi, A. M.; Hungate, B. A.; Dijkstra, P.; Hinkle, C. R.; Knot, W. M., III; Drake, B. Decreased leaf-miner abundance in elevated CO_2: Reduced leaf quality and increased parasitoid attack. *Ecol. Appl.* **1999**, *9*, 240–244.

(28) Carney, K. M.; Hungate, B. A.; Drake, B. G.; Megonigal, J. P. Altered soil microbial community at elevated CO_2 leads to loss of soil carbon. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 4990–4995.

(29) Stover, D. B.; Day, F. P.; Butnor, J. R.; Drake, B. G. Effect of elevated CO_2 on coarse-root biomass in Florida scrub detected by ground-penetrating radar. *Ecology* **2007**, *88*, 1328–1334.

(30) Andresen, L. C.; Michelsen, A.; Jonasson, S.; Schmidt, I. K.; Mikkelsen, T. N.; Ambus, P.; Beier, C. Plant nutrient mobilization in temperate heathland responds to elevated CO_2, temperature and drought. *Plant Soil* **2010**, *328*, 381–396.

(31) Liu, J. X.; Zhang, D. Q.; Zhou, G. Y.; Faivre-Vuillin, B.; Deng, Q.; Wang, C. L. CO_2 enrichment increases nutrient leaching from model forest ecosystems in subtropical China. *Biogeosciences* **2008**, *5*, 1783–1795.

(32) Hungate, B. A.; Reichstein, M.; Dijkstra, P.; Johnson, D.; Hymus, G. J.; Tenhunen, J. D.; Hinkle, C. R.; Drake, B. G. Evapotranspiration and soil water content in a scrub-oak woodland under carbon dioxide enrichment. *Global Change Biol.* **2002**, *8*, 289–298.

(33) Reich, P. B. Quantifying plant response to ozone: a unifying theory. *Tree Phys.* **1987**, *3*, 63–91.