

Plant–Soil Distribution of Potentially Toxic Elements in Response to Elevated Atmospheric CO₂

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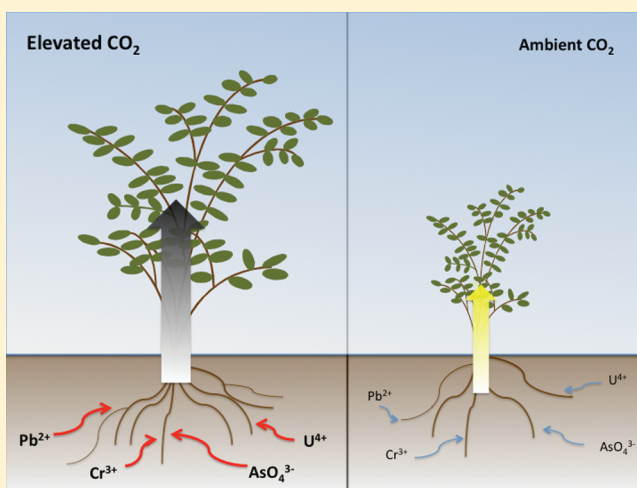
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S Supporting Information

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 CO₂ generally increases plant productivity and alters nutrient element cycling, but whether CO₂ causes similar effects on the cycling of contaminant elements is unknown. Here we show that 11 years of experimental CO₂ 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 CO₂ alters the distribution of contaminant elements in ecosystems, with plant element accumulation and declining soil availability both likely explained by the CO₂ 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 CO₂ generally increases plant productivity, alters nutrient cycling,⁴ and often reduces plant nutrient concentration.^{5,6} However, the effects of elevated CO₂ 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 CO₂ and increases in soil organic matter (SOM) that can control metal availability in soils,^{8–10} but CO₂ effects on contaminant element distribution from soils to plants on a mass basis have not been evaluated. Elevated CO₂ 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 CO₂.¹⁷ Previous work has shown that where elevated CO₂ increases SOM, the concentrations of metals in soil rises.^{8,9} We predict that, in a system where elevated CO₂ 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 CO₂ increases the mobility of contaminants, leading to declines in available contaminant

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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 CO₂ experiment at Kennedy Space Center in July 2007. This was an open-top chamber experiment that increased atmospheric CO₂ ~360 μmol·mol⁻¹ above ambient (*n* = 8 elevated chambers, *n* = 8 ambient chambers). The chambers had been exposed to elevated CO₂ 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 H₂O. 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 HNO₃, and dilution in 0.32 M HNO₃.

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 CO₂ 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

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

element	ambient CO ₂		elevated CO ₂	
	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 CO₂ experiment at Kennedy Space Center, Florida, were collected in 2007 from trees in open-top chambers under ambient atmospheric CO₂ and from trees in chambers exposed to 11 years of elevated (ambient + 360 μmol·mol⁻¹) CO₂. 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.

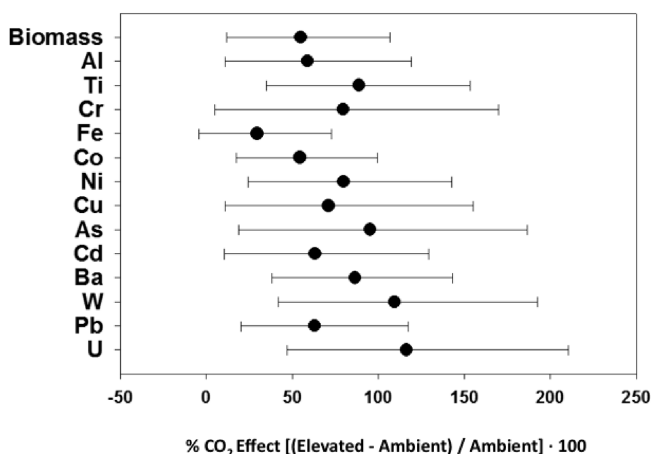


Figure 1. Relative effect of elevated CO₂ [(means from elevated CO₂ plots – means from ambient CO₂ plots)/(means from ambient CO₂ plots) × 100] on contaminant element mass (grams per square meter) in the above- and below-ground plant biomass [(leaf element concentration × leaf mass) + (stem element concentration × 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.

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 CO₂ 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

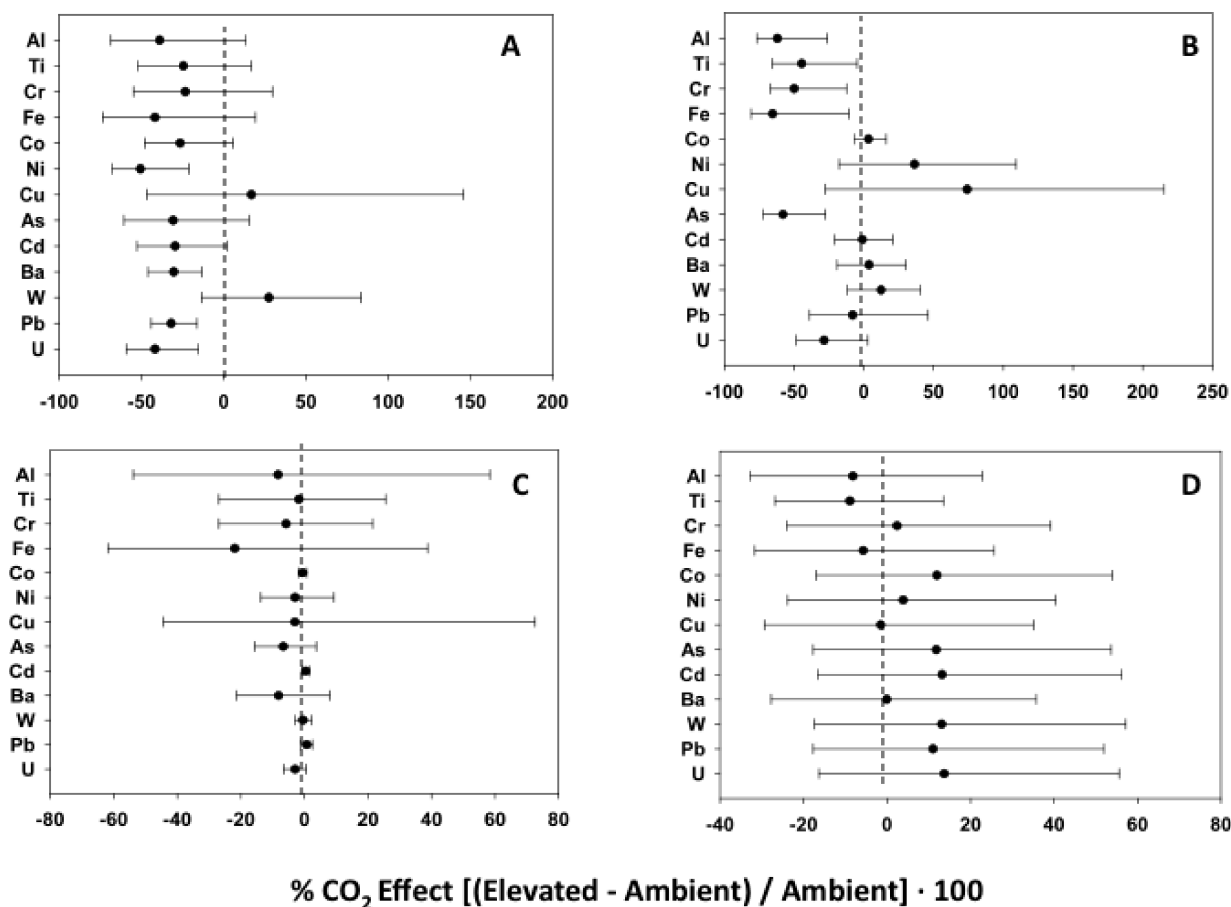


Figure 2. Relative effect of elevated CO_2 [(means from elevated CO_2 plots – means from ambient CO_2 plots) / (means from ambient CO_2 plots) \times 100] on extractable element mass (grams per square meter) in soil of a Florida scrub-oak ecosystem, Kennedy Space Center, FL. Error bars are bootstrapped 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 CO₂ Enrichment^a

element	absolute CO ₂ effects (E – A)					
	whole system mass			change in plant element mass + change in soil-extractable element mass		
	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

^aThe effect of CO₂ on whole-system mass is the effect of CO₂ 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 CO₂ 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 CO₂ in this system, are toxic to organisms involved in decomposition and N mineralization,³ and therefore, elevated CO₂ could also alter key ecosystem processes by altering the mobility of these elements.

Elevated CO₂ 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 CO₂.³² 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 O₃, that can depress productivity.³³

■ ASSOCIATED CONTENT

S Supporting Information. Additional text with analytical details and one table showing the effect of elevated CO₂ on total plant element masses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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