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Cory C. Cleveland
The University of Montana, cory.cleveland@umontana.edu

Joseph B. Yavitt

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Consumption of atmospheric isoprene in soil

Cory C. Cleveland,[1] and Joseph B. Yavitt

Department of Natural Resources, Cornell University, Ithaca, New York

Abstract. Natural vegetation annually emits 503 Tg yr^{-1} of isoprene (2-methyl-1,3 butadiene) to the global atmosphere where it reacts very rapidly with hydroxyl radicals and strongly regulates atmospheric chemistry. Current models of the compound's chemical behavior assume the atmosphere is the only significant sink; however, there is evidence that soil may consume isoprene. Here we show through field and laboratory studies that soil exposed to isoprene at low mixing ratios removed isoprene to concentrations below those commonly observed in forest canopies, and that the removal of isoprene was biologically mediated. On the basis of laboratory studies with soil from several different ecosystems worldwide, we provide a first approximation of a global annual soil sink for isoprene of 20.4 Tg yr^{-1}, suggesting a soil sink should be included in models that attempt to describe the effect of isoprene emission on atmospheric chemical processes.

Introduction

Global emission of isoprene from natural vegetation to the atmosphere is 503 Tg yr^{-1} (1 Tg = 10^{12} g), similar to methane (CH_4) emissions of 500 Tg yr^{-1} (*Tyler*, 1991), and accounting for more than 50% of the total annual emissions of volatile organic carbon (VOC) to the atmosphere (*Guenther et al.*, 1995). Isoprene regulates tropospheric chemistry by photochemically reacting with hydroxyl (OH) radicals, and with nitrogen oxides (NO_x) to produce tropospheric ozone (O_3) and urban photochemical smog (*Trainer et al.*, 1987; *Chameides et al.*, 1988). Therefore, there is considerable interest in knowing all sources and sinks affecting the global budget for atmospheric isoprene.

Until recently, the atmosphere has been considered the only significant sink for isoprene (*Chameides et al.*, 1988; *Brasseur and Chatfield*, 1991). However, because recent studies have demonstrated that soil can be a significant sink for organic atmospheric compounds, it seems possible that isoprene also may be consumed in soil. For example, soil consumes 5-20% of atmospheric CH_4 emissions (*Tyler*, 1991) and may remove ~30% of atmospheric methyl bromide (CH_3Br) emissions (*Shorter et al.*, 1995) annually. Moreover, isoprene is similar to other volatile organic compounds (e.g., monoterpenes) consumed by soil microorganisms (*Trudgill*, 1994). In addition, there is ample room in the current global isoprene budget for a soil sink, as emission estimates vary by 2-fold (*Guenther et al.*, 1995).

In this study, we investigated whether soil might be a sink for atmospheric isoprene, and whether this sink is significant in the global budget for atmospheric isoprene. We investigated soil consumption of isoprene at mixing ratios of <50 to ~500 parts per billion by volume (p.p.b.v.) in both laboratory studies and field experiments. Although higher than ambient levels, these concentrations are 100-1000 times lower than those used in previous studies. Field experiments occurred at a 24-acre temperate northern hardwood forest (McGowen) located near Ithaca, NY. The field study was designed to demonstrate that isoprene uptake occurs *in situ*, and that the sink is strong enough to remove isoprene from the ambient atmosphere. Laboratory experiments were performed with soil obtained from several ecosystems worldwide (Table 1). We expected that soil microorganisms would consume isoprene, and that this phenomenon would vary among soil from different ecosystems.

Methods

Soil collected per site was placed in airtight polyethylene bags, put on ice and returned to Cornell for analysis within 72 hours of collection. We measured isoprene consumption in the laboratory by placing 35-40 g of fresh soil into 0.91 L glass vessels to provide a soil layer of ~0.5 cm. Soil water content was adjusted to 40% (dry weight basis), vessels were sealed, and initial isoprene headspace concentrations were adjusted to 508 p.p.b.v. by injecting 2 ml of a 230 p.p.m. standard. Vessels had a butyl-rubber septum for gas sampling, and we sampled for 12 hours to determine the time course of isoprene consumption in soil. Unless otherwise indicated, soil incubations were performed in duplicates in the dark at 25° C. To verify that biological rather than physical processes consumed isoprene, we carried out studies with soil autoclaved three times for 1 hour at 120°, with sterile, distilled water added to restore the desired soil moisture level. Blanks (no soil) were included in each assay to verify that chemical oxidation/leakage was not responsible for declines in isoprene headspace concentrations.

We measured isoprene flux in the field using 1.4-L nylon static chambers. On each visit, we placed five chambers randomly on the forest floor and packed soil around the outside of each chamber to prevent leakage. An aliquot of isoprene standard was injected into each chamber and mixed thoroughly, and we then collected gas samples in 1-ml glass, gastight syringes every fifteen minutes for an hour. In most cases, initial headspace concentration was ~385 p.p.b. Measurements were made in the same general area on each visit, but we repositioned chambers to avoid previously disturbed locations. Standards were also prepared in the field and sampled at the beginning and end of each experiment to verify that isoprene removal in the chambers was not due to chemical or physical processes. In addition, we measured soil temperature to a depth of 5 cm using a thermistor and soil moisture gravimetrically on each visit. Sampling occurred on five dates in 1996 (June 6, June 12, July 22, September 12,

[1]Now at Environmental, Population, and Organismal Biology, University of Colorado, Boulder.

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Table 1. Characteristics of sites and soil.

Site	#	Vegetation	Soil type	Depth, cm	pH in H2O	Loss on ignition, %	Bulk density, g/cm^3
Tropical moist forest , Barro Colorado	1	mixed deciduous	Oxisol	0-10	6.20	17.92	0.85
Island, Panama, (9°09'N, 79°51'W),	2	mixed deciduous	Alfisol	0-10	5.54	16.59	0.85
Kursar et al., 1995							
Tropical dry forest, Bosque Estatal	3	mixed deciduous	Mollisol	0-5	8.07	18.15	1.3
de Guanica, Puerto Rico, (18°00'N,	4	mixed deciduous	Mollisol	5-10	8.08	16.92	1.3
66°50'W), *Murphy and Lugo*, 1986							
Temperate forest, Monongahela,	5	mixed deciduous	Ultisol	0-10	3.83	17.52	0.67
West Virginia, USA, (39°10'N,	6	mixed deciduous	Ultisol	0-10	3.80	14.55	0.67
79°35'W), *Mattson and Smith*, 1993							
Temperate Forest, McGowen,	7	mixed deciduous	Alfisol	0-5	6.33	8.98	1.20
New York, USA, (42°25'N, 76°28'W),							
This study							
Temperate Forest, Arnot, New York,	8	mixed deciduous	Inceptisol	0-5	4.43	67.93	1.1
(42°15'N, 76°40'W), This study	9	mixed coniferous	Inceptisol	0-5	3.72	35.54	1.1
Temperate forest, Old Forge,	10	mixed deciduous	Spodosol	0-5	3.38	51.73	0.7
New York, USA, (43°35'N, 75°00'W),							
This study							
Temperate forest, Hubbard Brook,	11	mixed deciduous	Spodosol	0-5	3.42	33.19	0.7
New Hampshire, USA, (43°56'N,	12	mixed coniferous	Spodosol	0-5	3.83	15.61	0.7
71°45'W), *Huntington et al.*, 1989							
Cultivated land, Cornell Plantations,	13-16	mixed cultivars	Alfisol	0-5	5.57-6.93	4.74-9.34	1.0-1.2
New York, USA, (42°25'N, 76°28'W),							
This study							
Boreal forest, Nikski, Alaska, USA,	17	mixed coniferous	Spodosol	0-5	4.52	63.17	0.32
(61°00'N, 152°00'W), *Shoji et al.*,	18	mixed coniferous	Spodosol	5-10	4.42	24.32	0.32
1988							

Numbers in column 2 correspond to time courses shown in Figure 1.

and October 1), and gas samples were analyzed within two hours of collection.

Isoprene was measured on a gas chromatograph equipped with a photoionization detector (GC-PID), and a 50 m fused silica column (Megabore SPB-1, 5 mm coating). The carrier gas was highly purified helium (99.99%) further purified with three in-line filter systems to remove any trace contaminants from the carrier stream. The gas samples were injected on-column using splitless injection. Column temperature was 55° C, and the retention time of the isoprene was 4.5 minutes with a carrier gas linear velocity of 18.5 cm s^{-1}. Isoprene concentration was determined by peak area measured with a peak integrator (Shimadzu, model CR 501). The GC-PID had a detection limit of ~5 p.p.b., and repeated measurements rarely varied by more than 5%.

We calibrated the instrument periodically using two standards (846 p.p.b.v. and 106 p.p.b.v.), which were produced by multiple dilution in glass flasks containing pure nitrogen (N_2) by injecting 10 ml of 99.9% liquid isoprene with a 1.0 microliter syringe into a 10.385 L glass vessel equipped with two septum ports. The concentration was adjusted for prevailing temperature and atmospheric pressure according to the ideal gas law.

Results

We verified the consumption of isoprene was biologically mediated: sterile soil consumed <5% of the isoprene added to the headspace after 24 hr, while >95% of the isoprene added to blanks (no soil) remained 24 hr later. In addition, fresh soil consumed isoprene with maximum uptake rates at 25 to 35°C, which is further evidence for biological processes (*Paul and Clark*, 1991). We also isolated a soil bacterium in the genus *Arthrobacter* able to use isoprene as a sole carbon source (*Cleveland*, 1997).

Soil from different ecosystems consumed isoprene under laboratory conditions (Figure 1). Soil displaying high initial isoprene deposition velocities (k) were moist (>35% dry weight) and rich in organic matter (i.e. >15% loss on ignition). Values of k were considerably lower in soil from the tropics and temperate agricultural systems, which were drier and relatively low in organic matter.

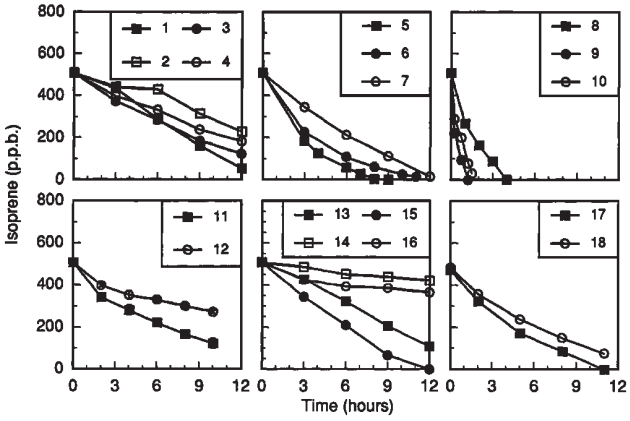

Figure 1. Time course of isoprene consumption in 40 g fresh soil from: 1 BCI (oxisol); 2 BCI (alfisol); 3 Guanica (0-5 cm); 4 Guanica (5-10 cm); 5-6 Monogahela; 7 McGown; 8 Old Forge; 9 Arnot (coniferous); 10 Arnot (deciduous); 11 Hubbard Brook (deciduous); 12 Hubbard Brook (coniferous); 13-16 Plantations; 17 Nikiski (0-5 cm); 18 Nikiski (5-10 cm).

Table 2. Total estimated isoprene consumption in soil worldwide.

Biome type	Area ($\times 10^6$ km^2)	Active season, days	k (min^{-1})	k* ($\times 10^{-5}$ min^{-1} Σ gdw^{-1})	Isoprene flux (g Σkm^{-2} day^{-1})	Total (10^{12} g Σyr^{-1})
Tropical rain forest	17	365	0.000645±0.000118	1.94±0.34	72.7±12.7	0.45±0.078
Temperate deciduous forest	7	270	0.00738±0.00451	25.1±13.7	1197±653	2.26±0.12
Temperate coniferous forest	5	270	0.010138±0.008072	155±143	9579±8837	12.93±11.93
Boreal forest	12	110	0.00203	203	2862	3.77
Tropical seasonal forest	7.5	270	0.000848±0.00031	1.83±0.68	105±39	0.21±0.079
Cultivated land	14	200	0.001071±0.000331	4.62±0.96	265±55	0.74±0.15
Total						20.4±13.5

k is mean of the observed initial isoprene deposition velocities into soil from each ecosystem, and stated errors represent ±1 SE of the mean. Here isoprene flux values are normalized to an average isoprene mixing ratio of 3 p.p.b.

Soil in the field consumed isoprene to concentrations below our detection limit within one hour, while standards prepared and sampled in the field showed no detectable change in isoprene consumption over the course of each experiment; hence, isoprene loss was not due to chemical oxidation with OH in the chambers. Initial deposition velocities in the chambers ranged from -0.0126 ± 0.0034 to -0.0478 ± 0.0017 min^{-1} with consumption rates ranging from 10.08 ± 0.45 to 40.77 ± 1.30 nmol m^{-2} min^{-1} (mean = 23.82 ± 5.09 nmol m^{-2} min^{-1}). In a concurrent study of CH_4 consumption at this site, the diffusive loss rate of a relatively inert CH_3F was -0.0016 min^{-1}, indicating that diffusion alone was not responsible for isoprene loss in the chambers (*Hudgens and Yavitt*, 1997). Flux rates (and *k* values) increased gradually through the summer, with the highest values in late summer (September 12) and lowest values on the final sampling date (October 1) following leaf senescence. The decrease from September to October coincided with an increase in soil moisture from 28% to 45% (dry weight basis) and a decrease in soil temperature from 17.8 to 13.5 °C. Isoprene flux rates did not show a strong correlation with temperature (r = 0.46), but did exhibit a relatively strong negative relationship with soil moisture (r = -0.91). A multiple linear regression showed that soil moisture and temperature together were good predictors of isoprene uptake rate (r^2 = 0.85) in the field.

Discussion

This study provides strong evidence for a biological sink for atmospheric isoprene in soil. Our field studies with static chambers confirm this sink is strong enough to reduce atmospheric isoprene to levels lower than those commonly observed in forest canopies (< 3-10 p.p.b.v.) (*Rasmussen and Khalil*, 1988; *Zimmerman et al.*, 1988; *Baldocchi et al.*, 1995). The apparent seasonal pattern, with a late summer maximum for isoprene consumption, closely resembles the seasonal pattern for emission of VOCs (*Tingey et al.*, 1991; *Goldstein et al.*, 1996). This intriguing correspondence suggests a link between rates of isoprene emission and consumption, as isoprene emission rate is a function of leaf area, which tends to increase through the growing season (*Monson et al.*, 1991). This is noteworthy because the atmosphere may be a less effective sink for isoprene removal in the autumn when atmospheric OH concentrations decrease (*Goldstein et al.*, 1995).

Soil moisture strongly affected isoprene consumption in the field, which agrees with many other studies of microbial oxidation of atmospheric trace gases (*Conrad*, 1996). Soil moisture affects the amount of water available to microorganisms, as well as substrate diffusion, osmotic potential, and O_2 availability (*Conrad*, 1996). In contrast, no clear relationship between temperature and the isoprene flux rate, even though microbial activity in soil does vary with soil temperature (*Paul and Clark*, 1989; *Lloyd and Taylor*, 1994), may reflect the relatively narrow temperature range during the growing season (i.e., 13.5° C to 18° C).

Our laboratory studies confirm that soil from several different ecosystems can consume atmospheric isoprene, and that consumption occurs at different rates in soil from different ecosystems (Figure 1). We put these results into perspective by calculating potential isoprene consumption per biome using the following equation:

$$\text{Consumption (g isoprene yr}^{-1}) = (k^*)\ (c_i)\ (S_a)\ (\text{B.D.})$$
$$(1\times10^{10}\ \text{cm}^2\text{km}^{-2})\ (1440\ \text{min d}^{-1})\ (\text{area})\ (\text{active season}) \quad (1)$$

where: k* is the mean of all initial isoprene deposition velocities determined from laboratory incubations for soil sampled from a specific biome type (see Table 2); c_i is an isoprene mixing ratio of 3 p.p.b.v. (= 0.0000002044 g L^{-1}); S_a is an active soil depth of 3 cm; B.D. is soil bulk density in g/cm^3; area is biome area in km^2); and, active season is growing season length in days.

Accordingly, we estimate soil may consume 20.4 Tg of atmospheric isoprene per year, which is ~5% of the 400 Tg of isoprene emitted annually from the ecosystems we investigated (Table 2). This is very similar in magnitude to the soil sink for atmospheric CH_4 of 5-20% (*Tyler*, 1991).

We suspect our assumptions produce an "upper bound" on the soil sink for isoprene for several reasons. The average mixing ratio of isoprene may be lower than 3 p.p.b.v. in many forest canopies. There have been relatively few studies investigating isoprene concentrations near and below forest canopies, although 3 p.p.b.v. seems reasonable (*Rasmussen and Khalil*, 1988; *Baldocchi et al.*, 1995). We also believe a 3 cm active soil layer is justifiable, even though isoprene consumption may be most vigorous in the top 1 cm of the soil. However, it is notable that soil up to 15 cm deep

consumed isoprene in some ecosystems (Figure 1). Next, we assumed a 24 hour day in our calculations because several studies show that isoprene is detectable in forest canopies even when emission is not occurring (*Rasmussen and Khalil*, 1988; *Zimmerman et al.*, 1988), and because our field and laboratory experiments revealed that isoprene consumption occurs in the dark, However, it is true that isoprene concentrations are highest during daytime when peak production occurs, and consumption may decline at night as isoprene concentrations decrease. Biome classifications, corresponding areas, and active seasons come from an estimate of global isoprene emissions by *Rasmussen and Khalil* (1988). Season length is provided because biogenic isoprene is only produced during the growing season, and because active microbial uptake is diminished in temperate and boreal regions when soil is frozen (*Paul and Clark*, 1991).

Despite potential shortcomings, these assumptions provide a reasonable basis for the first estimate of isoprene consumption in soil on a large scale, and our estimate suggests that the process is a significant component of the global isoprene budget.

Conversely, the much higher k values in our field studies than in the laboratory assays suggests our estimate of isoprene consumption on a global basis may be conservative. A more robust estimate requires an examination of the process at the soil/atmosphere interface in all of the pertinent ecosystems and its seasonal dynamics. Clearly, spatial heterogeneity of microbial communities in landscapes is extremely variable, which makes scaling of biogeochemical processes difficult (*Madsen*, 1996). For example, the k value in soil from an old growth forest site in the Adirondack Mountains in New York was -0.48, or more than two orders of magnitude higher than in any other soil. This site had a thick organic-rich forest floor layer, suggesting isoprene consumption could be more important in sites which have been relatively undisturbed by human activities that alter soil properties. In addition, microbes in soil taken from the field may change rapidly in response to altered environmental and physiological conditions imposed by sampling and laboratory incubation (*Madsen*, 1996). However, in both field and laboratory components of this study, the evidence for a soil sink for isoprene is robust. Therefore, we recommend further studies to increase the accuracy of this estimate, and eventual recognition in models which attempt to describe the effect of isoprene emission on atmospheric chemical processes.

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C.C. Cleveland and J.B. Yavitt, Department of Natural Resources, Cornell University, Ithaca, NY 14853. (e-mail: jby1@cornell.edu)

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