Kudzu (*Pueraria montana*) invasion doubles emissions of nitric oxide and increases ozone pollution

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The nitrogen-fixing legume kudzu (Pueraria montana) is a widespread invasive plant in the southeastern United States with physiological traits that may lead to important impacts on ecosystems and the atmosphere. Its spread has the potential to raise ozone levels in the region by increasing nitric oxide (NO) emissions from soils as a consequence of increasing nitrogen (N) inputs and cycling in soils. We studied the effects of kudzu invasions on soils and trace N gas emissions at three sites in Madison County, Georgia in 2007 and used the results to model the effects of kudzu invasion on regional air guality. We found that rates of net N mineralization increased by up to 1,000%, and net nitrification increased by up to 500% in invaded soils in Georgia. Nitric oxide emissions from invaded soils were more than 100% higher (2.81 vs. 1.24 ng NO-N $cm^{-2} h^{-1}$). We used the GEOS-Chem chemical transport model to evaluate the potential impact of kudzu invasion on regional atmospheric chemistry and air quality. In an extreme scenario, extensive kudzu invasion leads directly to an increase in the number of high ozone events (above 70 ppb) of up to 7 days each summer in some areas, up from 10 to 20 days in a control scenario with no kudzu invasion. These results establish a quantitative link between a biological invasion and ozone formation and suggest that in this extreme scenario, kudzu invasion can overcome some of the air quality benefits of legislative control.

invasive species | nitrogen fixation | nitrous oxide | tropospheric ozone | biogeochemical processes

A lthough many effects of exotic invasive species on community, ecosystem, and biogeochemical processes are well documented (1–3), impacts of plant invasions on the chemical and radiative balance of the atmosphere have received less attention (4). This lack of attention is surprising because invasive species often possess metabolic capabilities that differentiate them from the communities they are invading (e.g., refs. 1–5), and metabolism lies at the heart of exchange of materials between plants and the atmosphere.

There are numerous examples of how the species-specific physiology of plants can determine or strongly influence a number of ecosystem properties, including fire regime, water availability, nutrient cycling, and atmospheric chemistry (1-4, 6). In the area of atmospheric chemistry, the central role that speciesspecific physiology can play in controlling fluxes of both volatile organic compounds (VOCs) and nitric oxide (NO) deserves particular attention. Volatile organic compounds and NO_x [NO and nitrogen dioxide (NO2)] are the two key precursors to the formation of tropospheric ozone, which is often regarded as the most important air pollutant in terms of its impacts on human health and agriculture (7). Biogenic emissions of the VOC isoprene (C_5H_8) are strongly controlled by species identity (8–10), whereas a key group of species-legumes and other N-fixing plants-are linked to substantial increases in NO fluxes from soils (4, 11, 12). Because species identity is so important to the emissions of N oxides and isoprene, a shift in plant community composition such as occurs during a successful plant invasion can result in large shifts in an ecosystem's capacity to produce and emit these reactive compounds.

Kudzu (Pueraria montana, formerly lobata) is an invasive leguminous vine native to Asia. Promotion of the vine as a forage crop and soil stabilization agent during the early 20th century helped it become firmly established across the southeastern part of the United States (5). Like many other legumes, kudzu develops symbiotic associations in its roots with bacteria capable of transforming atmospheric N₂ into biologically available ammonium (NH_4^+) (5). When symbiotically fixed nitrogen is released to the soil from decomposing tissues or leaked from roots, it becomes available to other plants and microbes. Because of these additions of fixed nitrogen to soils, invasions by N-fixing plants tend to cause the overall rate of microbially mediated N transformations in the invaded ecosystem to increase, including rates of nitrification [the oxidation of NH_4^+ to nitrate (NO_3)] and denitrification (the reduction of NO_3 to N_2) (2, 4, 11, 12). When rates of these N transformations increase, gaseous emissions of NO and the powerful greenhouse gas nitrous oxide (N₂O), which are by-products of nitrification and denitrification, tend to increase as well (13).

Estimations based on kudzu's N fixation rates in its native range suggest that it may fix up to 235 kg N ha⁻¹ yr⁻¹ in the United States (5). These fixation rates are an order of magnitude greater than both the N fixation rates in the invasive tree *Morella* (formerly *Myrica*) faya in Hawaii (20 kg N ha⁻¹ yr⁻¹) and the rates of atmospheric deposition of nitrogen species in the eastern United States (7–13 kg N ha⁻¹ yr⁻¹) (2, 5, 14). With a current distribution of more than 3 million ha and an expansion rate of 50,000 ha yr⁻¹, kudzu coverage in the southeastern United States exceeds that of cultivated soybean, making it the dominant Nfixing plant in the region (5, 15).

Kudzu invasion is most severe in the southeastern United States. In this region, atmospheric NO_x concentrations generally limit the formation of tropospheric ozone, and soil emissions of NO are an important determinant of ozone concentrations (16–19). The high rates of N-fixation by kudzu imply large local soil emissions of NO, suggesting, in turn, that the rapid expansion of kudzu has the potential to be an important source of tropospheric ozone production. Kudzu is also a strong emitter of isoprene (C_5H_8), a photochemically reactive hydrocarbon involved with tropospheric ozone production, and thus actually produces all of the precursors necessary for the production of tropospheric ozone (20–22). However, because the strong biogenic isoprene emissions

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from a variety of tree species have made ozone production in the Southeast NO_x -limited rather than VOC-limited (22, 23), isoprene emissions from kudzu are not expected to have much effect on the regional dynamics of ozone production.

Results

To understand the potential regional impacts of kudzu invasion on ecosystems and air quality, we combined field measurements of N pools, N cycling rates, soil NO fluxes, and soil N₂O fluxes from paired invaded and uninvaded plots in Madison County, Georgia with a sensitivity analysis using the GEOS-Chem global chemical transport model (*SI Materials and Methods*). Nitric oxide fluxes were 127% higher in invaded plots in midsummer (P = 0.032; Fig. 1). The measured NO emissions varied from 2.19 to 3.70 ng NO-N cm⁻² h⁻¹ in invaded plots, compared with a much narrower range of 1.21–1.26 ng NO-N cm⁻² h⁻¹ in uninvaded plots. Emissions of N₂O from invaded plots were 158% higher on average, but the difference was not quite significant (Fig. 1; P =0.107). Soil moisture, which can have substantial effects on trace N gas fluxes (24), did not differ between invaded and uninvaded plots in July (P = 0.43) or September (P = 0.48, two-tailed tests).

Laboratory assays of soil cores taken from within each plot demonstrated a clear and consistent association between kudzu invasion and increased N cycling rates in both midsummer and early autumn, when a second set of soil samples were taken. We found large increases in net N mineralization rates under kudzu, with as much as an order of magnitude difference between invaded and uninvaded plots in both July (P = 0.003) and September (P = 0.007; Fig. 2). Net rates of nitrification, which is typically the primary source of NO production in well-drained soils (24), were 110–532% higher in soils invaded by kudzu across the two sampling times (July: P = 0.012; September: P =0.031; Fig. 2). There were no differences in our measurements of denitrification enzyme activity, microbial biomass, total carbon, or total N in soils during either season.

Soil inorganic N pools can provide insight into N availability in relation to plant demand, even though they are not always reliable

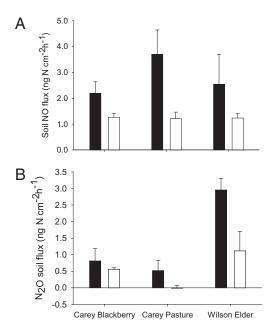


Fig. 1. Bar plots showing mean (\pm SEM) nitrogen trace gas emissions from soils supporting kudzu (black bars) and native vegetation (white bars) at each of three Georgia sites in July 2007. (*A*) NO emissions were larger across soils invaded by kudzu (*P* = 0.032). (*B*) Soil N₂O emissions were not quite significantly different (*P* = 0.107).

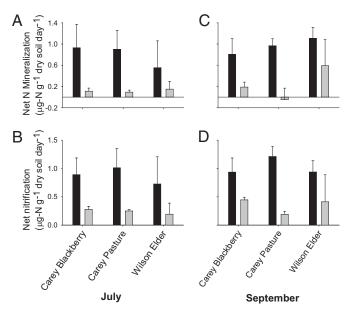


Fig. 2. Bar plots of mean (\pm SEM) net N mineralization and net nitrification from laboratory assays of soils supporting kudzu (black bars) and native vegetation (gray bars) at each of three Georgia sites in July and September 2007. Net N mineralization rates were higher in invaded sites in July (*A*) and September (*C*; *P* = 0.044 for both months); net nitrification rates were also higher in both July (*B*) and September (*D*; *P* = 0.025 for both months).

indicators of changes in N cycling rates (25). Soil pools of inorganic N were also higher in invaded sites, although by a smaller factor than the N cycling rates (Fig. 3). On average, invaded sites had 69% more NH_4^+ (P = 0.028) and 220% more NO_3^- (P =0.0025) in July. In September, invaded plots had an average of 10% more NH_4^+ (P = 0.0085) and 550% more NO_3^- (P = 0.02).

For the sensitivity analysis using GEOS-Chem, we focused on the A1B scenario for 2050 during the summer season (June-

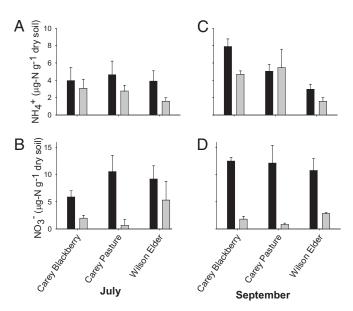


Fig. 3. Bar plots of mean (\pm SEM) inorganic N pools from soils supporting kudzu (black bars) and native vegetation (gray bars) at each of three Georgia sites in July and September 2007. Soil pools of NH₄⁺ were not quite significantly different in July (*A*; *P* = 0.095) and September (*C*; *P* = 0.061). Pools of NO₃⁻ were higher in both July (*B*; *P* = 0.05) and September (*D*; *P* = 0.019).

August) when ozone levels are highest, and we assumed an extreme case in which kudzu covers all nonagricultural, nonurban soils. In this scenario, kudzu produces a 28% increase in soil NO emissions and a subsequent spike in ozone concentrations, relative to the scenario in which kudzu is not included. In the areas most vulnerable to the increase in NO fluxes (parts of Mississippi, Arkansas, and Tennessee), the frequency of high ozone episodes (defined as the number of days for which the daily maximum 8-h ozone levels exceed 70 ppb) increases by up to 7 days during the 3-month period (Fig. 4). In the control scenario lacking the kudzu effect, these same areas experience 10–20 days of high ozone episodes (Fig. S1).

Discussion

Many studies have found that invasions by N-fixing plants increase nitrogen cycling, and a few have connected N-fixers to trace N gas emissions, but none have quantified a link between plant invasion and a reduction in air quality. Additionally, although kudzu has long been one of the most important invasive terrestrial plants in the eastern United States, the effects of this N-fixing plant on ecosystems and the atmosphere have remained unexamined. Our results show that kudzu is responsible for a clear increase in NO emissions and nitrogen cycling in soils.

The observed increase in NO emissions from soils invaded by kudzu occurs against a background of decreasing NO emissions nationally; NO_x emissions in the United States decreased by 33% between 1990 and 2007 as a consequence of reductions in emissions from highway vehicles and stationary fuel combustion (26). However, efforts to reduce ozone concentrations in the southeastern United States through restrictions on VOC and NO_x emissions under the Clean Air Act and its amendments have not always been as successful as hoped (27). Increases in NO emissions are of particular interest for the southeastern United States, because ozone formation in the region is generally NO_x limited. In the warm summer months, large biogenic emissions of VOCs (notably isoprene) in the Southeast create a high VOC/NO_x ratio in the atmosphere, and under these conditions ozone production is very sensitive to perturbations in NO_x (22, 23). The observed doubling of NO emissions under kudzu in Georgia suggests that kudzu invasion could increase regional ozone concentrations as the plant continues to spread throughout its current range.

Under the A1B scenario, NO_x emissions from fossil fuel combustion in the United States decline by 40% between 2000 and

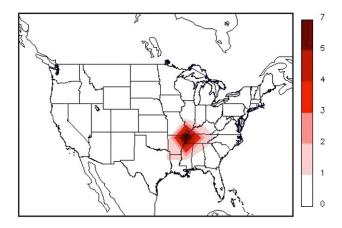


Fig. 4. Calculated change in the number of days with daily maxima 8-h ozone exceeding 70 ppb during the summer (June–August) due to the 28% increase in soil NO_x emissions accompanying kudzu invasion of all non-agricultural, nonurban soils in a nine-state region. Results are from the GEOS-Chem model for 2050's climate conditions.

2050. This change in United States anthropogenic NO_x emissions is partially offset by an 8% increase in soil NO_x emissions in the southeastern United States due to higher surface temperatures in the A1B climate. Against the future reductions in anthropogenic NO_x emissions, the GEOS-Chem results demonstrate that our extreme scenario of extensive invasion by kudzu increases the frequency of pollution events by up to 7 days in areas that would otherwise experience only 10-20 pollution events each summer. The warm temperatures that spawn high ozone events also increase NO fluxes from invaded soils in the GEOS-Chem simulation, so that the relative impact of kudzu invasion is greatest during the weather conditions that promote the worst pollution episodes. Kudzu invasion causes ozone concentrations to increase by up to 2 ppb during these high temperature events (Fig. S2). The increase in the frequency of high ozone events of over 35% over large parts of the southeastern United States substantially offsets the projected ozone reductions from reductions in fossil fuelderived NO that are assumed under the A1B scenario for 2050. Large increases in kudzu cover may need to be considered when estimating biogenic emissions of NOx and establishing strategies for protecting ozone air quality.

These results are based on limited field measurements and include extreme assumptions about increases in kudzu cover, and, as such, they probably represent an upper limit of the potential impact of kudzu invasion on ozone air quality. Longerterm examinations of trace gas emissions across a wider geographical range of kudzu invasion will be needed for a more precise estimation of its impacts on regional air quality. However, our results clearly demonstrate the ability of a plant invasion to reduce the benefits of pollution control efforts. Although biogenic impacts on atmospheric chemistry are now routinely considered in regional air quality assessments (23), the atmospheric impacts of plant invasions have received only limited attention and may represent both an unrecognized cost of invasions and perhaps an obstacle to meeting future air quality standards (4).

Although only supported at P = 0.107, the possibility of a doubling in N₂O emissions warrants further investigation. The impact kudzu may have on N₂O emissions opens the possibility that large-scale efforts to control kudzu may be able to take advantage of carbon-credit schemes to help offset the costs of control and removal (28). In addition, the observed increases in net nitrogen mineralization and net nitrification due to kudzu may lead to environmental problems, such as soil acidification, aluminum mobilization, and increased rates of NO₃⁻ leaching to aquatic ecosystems (29).

The unusual physiological combination of moderate to high emissions of isoprene and a high N-fixation capacity able to double soil NO fluxes in Georgia makes kudzu a unique source of the key precursors to tropospheric ozone in the United States; it may be as close to a "polluting plant" as one can find. In addition, kudzu's vine growth form and its ability to fix nitrogena combination of traits common among tropical plants but largely absent from vines commonly found in the United States are likely to allow it to increase its rate of spread and to expand northward as atmospheric CO₂ concentrations and winter temperatures increase in coming decades. Vines in general have shown larger and more sustained growth responses to increased CO_2 than trees have (30), and the growth responses of N-fixers such as soybean have shown little acclimation to elevated CO_2 (31). Currently, winter temperatures seem to define the northern boundary of kudzu's distribution, possibly as a result of freezinginduced embolisms (32). As it is released from these limits on its growth and spreads, kudzu invasion is expected to extend northward by hundreds of kilometers (33); an observed trebling in the number of populations on Long Island, NY, and the recent discoveries that kudzu is established as far north as Maine and Ontario may represent early evidence of that expansion (33, 34).

As kudzu expands into these new areas, its ability to increase emissions of both NO_x and isoprene could impose a significant perturbation to the local ozone air quality. Understanding how kudzu's unusual physiology will interact with the new environment it encounters in the ecosystems of the northeast will be essential to understanding its potential impact on soils, communities, and the atmosphere.

Kudzu's impact on the atmosphere will be most important in areas that are distant from urban centers, and particularly in landscapes where little fertilizer is added to soils, such as the forested areas of southern Appalachia. Our model results suggest that as kudzu spreads further into these and other areas, the accompanying increase in NO emissions may increase ozone concentrations and the frequency of high ozone events. Future analyses of the economic and environmental impacts of invasive species should take the effects of these species on air quality into account.

Materials and Methods

We measured the impacts of kudzu invasion on microbially mediated nitrogen transformations and emission of NO and N₂O from invaded and uninvaded soils at three sites in Madison County, Georgia in July 2007. We used a paired (invaded and uninvaded) plot design, which is common in investigations of impacts of invasions on soil processes in the field and which controls for potentially confounding factors such as soil type, slope, and land-use history (e.g., refs. 35–37). We worked to reduce the effects of potential confounding factors in the field by locating each pair of invaded and uninvaded plots within 30 m of one another and made sure that each plot pair shares similar land use histories, slopes, aspects, and soils (*SI Materials and Methods*). We made dynamic chamber-based measurements of NO fluxes using a portable chemiluminscent NO_x analyzer (Unisearch model LMA-3D) from four rings within each plot, for a total of eight rings per site (38). We made measurements of N₂O fluxes from the same rings using the static chamber method.

After gas measurements, we took soil cores from alongside each chamber and returned to the laboratory for analysis of inorganic N pools, net nitrification, and net N mineralization using KCI extractions and laboratory incubations (39). Soils were also analyzed in the lab for moisture content, microbial biomass, and denitrification enzyme activity (40–42). We analyzed

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the soil and gas variables using split-plot ANOVA, including site and kudzu invasion as whole and within-plot factors, respectively. We used one-tail tests unless otherwise indicated, and transformed data to meet the assumptions of ANOVA when necessary.

To investigate the potential effects of kudzu invasion on regional ozone levels, we used the global chemical transport model GEOS-Chem, driven by meteorological data fields from the National Aeronautics and Space Administration/Goddard Institute for Space Studies general circulation model following the Intergovernmental Panel on Climate Change A1B scenario for 2050 (43, 44). The A1B scenario describes a future world with rapid economic growth and balanced energy generation from both fossil and alternative fuels. Relative to other scenarios, the A1B scenario represents a middle path in which CO2 levels reach 522 ppm by 2050. We calculated soil NO_x emissions on the basis of Davidson et al.'s estimates of emissions from the southeastern United States, which included annual emissions of 523 g NO-N ha⁻¹ yr⁻¹ from nonagricultural soils (18). Using a simplified approach to scaling up in which we assume no diel or temperature effects on NO emissions during a 260-day growing season (45), we calculated that the mixed-vegetation uninvaded soils at our sites emit 761 g NO-N ha⁻¹ yr⁻¹. In contrast, kudzu-invaded soils emit 1750 g NO-N ha⁻¹ yr⁻¹. We scaled the relative impact of kudzu invasion on soil emissions to the Davidson et al. estimate for uninvaded soils.

Although the Environmental Protection Agency (EPA) has set 75 ppb as the threshold for compliance with the National Ambient Air Quality Standards, the model's coarse horizontal resolution precludes it from capturing detailed local ozone maxima. We therefore use 70 ppb as the threshold that defines a high ozone episode, an approximation that has proven efficient for identifying ozone episodes in this region (46). Additionally, the EPA's plan to adopt a new compliance threshold between 60 and 70 ppb makes our 70-ppb threshold a conservative one (47).

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