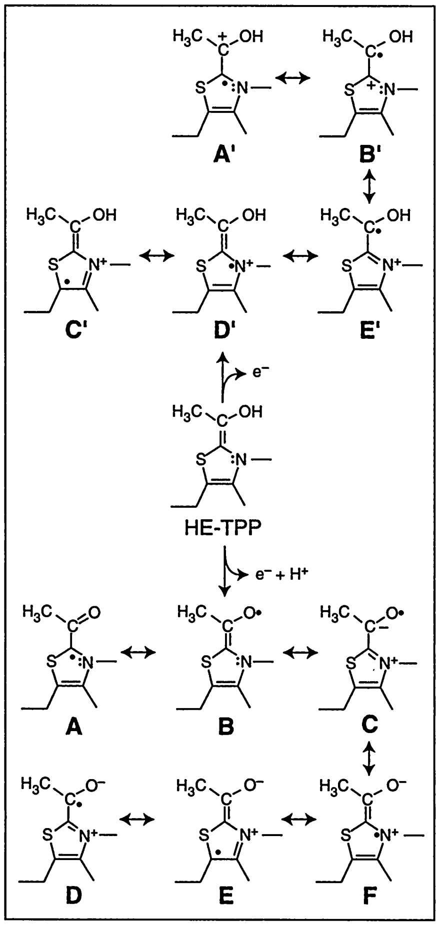

Principal resonance form for cation and neutral HE-TPP radicals. One-electron oxidation of HE-TPP gives a cation radical in which both the positive charge and the unpaired electron are highly delocalized. The delocalization is represented by the principal resonance forms **A′** to **E′** (**top**). One-electron oxidation coupled with loss of a proton gives a neutral radical, with the resonance forms **A** to **F** (**bottom**). It is not known whether the radical in PFOR is the cation or neutral radical.

the cationic charge and the unpaired electron are delocalized (see structures **A′** to **E′** in the second figure). Removal of one electron and one proton from HE-TPP leads to a neutral radical, in which only the unpaired electron is delocalized (see structures **A** to **F** in the second figure).

We do not know which protonation level pertains to the radical in PFOR. In radicals in which the unpaired electron is delocalized, the resonance forms generally do not contribute equally to the structure, and one or a few are dominant. The puckered ring observed by Chabrière *et al.* rules out resonance forms with two double bonds in the ring (**E′**, **C**, and **D** in the second figure) as dominant forms and relegates them to minor status. Further clues come from the fact that incorporation of ^{13}C or deuterium into the exocyclic carbons of the radical leads to very modest perturbations of the EPR signal (*4–6*). If the unpaired electron were localized on the exocyclic carbons, dramatic changes in the signal would have been expected (*12*).

Therefore, the unpaired electron is likely to be largely confined to the ring. The resonance forms **A′**, **C′**, and **D′** for the radical cation or **A**, **E**, and **F** for the neutral radical may be the principal forms. These groups differ mainly by the presence of the proton in the cation radical. Detailed EPR analysis in H_2O and D_2O, with ^{13}C labeling at positions in the thiazole ring and with deuterium labeling in the methyl and methylene carbons, by available methods (*13*) will answer the remaining questions about the electronic structure.

Chabrière *et al.* suggest structures for the HE-TPP radical that include tautomeric forms resulting from labilization of protons from the methyl group of TPP. These unprecedented tautomeric isomerizations would lead to deuterium incorporation into the methyl group whenever the enzymatic reaction is conducted in D_2O. Analysis of TPP recovered from such experiments will provide an essential future test for their hypothesis.

Because CoA is required for the second electron transfer in PFOR, it is likely that CoA itself donates the second electron to the iron-sulfur centers in PFOR (*4*) and is transformed transiently into a thiyl radical, which undergoes radical coupling with the HE-TPP radical to form acetyl CoA and TPP. CoA may therefore be added to the list of coenzymes that participate as radicals in enzymatic reactions.

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PERSPECTIVES: GLOBAL CHANGE

Sharing the Garden

Christopher B. Field

Human activities have profound impacts on our planet, from the extinction of once-abundant species, to changes in the composition of the atmosphere, to the strong likelihood of effects on climate. There is no doubt that these human impacts are large, but it can be difficult to say how large in a way that is accurate, meaningful, and easy to explain.

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Among the most useful measures proposed to date is the fraction of Earth's total plant growth or net primary production (NPP) that is appropriated by humans. NPP is the energy transferred from plants to other levels in the food chain. It provides support for nearly all of Earth's heterotrophs (organisms that require preformed organic compounds for food), including humans. In an influential 1986 paper, Vitousek *et al.* (*1*) estimated that human appropriation of NPP was 32% of the land total with a conservative definition and 40% using the most reasonable definition of human appropriation. This is a huge fraction. If we already control two-fifths of the land's productive capacity, then the prospects for future increases are strongly constrained, especially if there is to be anything left for other species.

Since 1986, research in global ecology has increased dramatically, with improved data sets, simulation models, and analytical techniques. On page 2549 of this issue, Rojstaczer *et al.* (*2*) use some of the new products to revisit human appropriation of land NPP. Their mean value of 32%, using the conservative definition of (*1*), is the same as the comparable value from the 1986 study (*1*). Partly, this reflects the insight and judgment of the authors of that study. Partly, it is luck, as upward revisions of some appropriations nearly balance downward revisions in others.

The new numbers are based on a huge body of information, but the estimate for the core quantity—human appropriation of land NPP—is still uncertain. The magnitude of the uncertainty depends on how the data are analyzed. With a simple approach that does not take into account the spatial dimension of the data, the 95% confidence limits around the mean are huge (*2*). This simplified approach increases the uncertainty but also highlights opportunities for profound improvements in the future. The key will be progress on four issues.

First, it is important to define human appropriation of NPP to capture the full suite of human impacts. Vitousek *et al.* (*1*) explored three options, including both land and ocean NPP. Their low option is based on the NPP directly consumed, fed to animals, or used in cooking and building. With this definition, humans appropriate only about 4% of land NPP. The intermediate or conservative option of Vitousek *et al.*, the sole definition considered by Rojstaczer *et al.* (*2*), is a comprehensive account of the NPP co-opted by humans, in the sense that its use by humans makes it unavailable to a natural community. It includes total plant growth in agriculture, managed pastures, and plantation forestry, as well as part of the NPP of unmanaged pastures and forests, based on the fraction of the area actively used by humans. Vitousek *et al.* (*1*) also considered a high option (their 40%), based on potential NPP in the absence of humans.

Each of these definitions quantifies different aspects of human appropriation. But all of them underestimate the total human involvement with NPP because consequences of changes in climate and the composition of the atmosphere, as well as biological invasions, have effects on NPP in geographic regions where the products are not diverted to human uses (*3*).

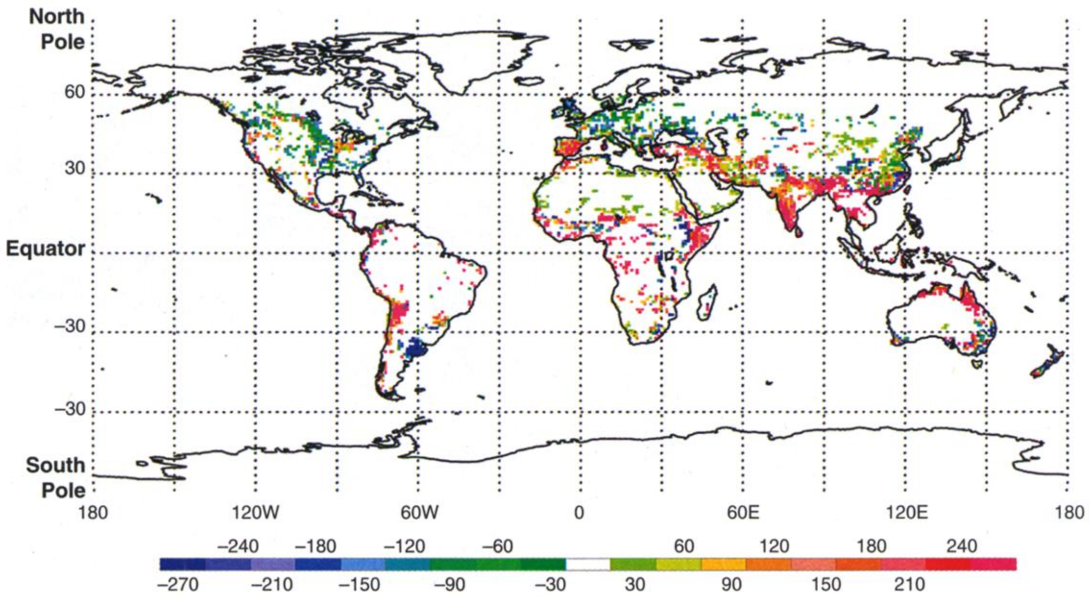
Second, spatially explicit analysis is critical for extracting maximum information from the data. In the calculations to date, human appropriation is quantified as an average rate multiplied by the total area affected. Perhaps the clearest message from the past decade of global studies is the pervasive importance of spatial and temporal heterogeneity. Human activities are also spatially heterogeneous, and improper averaging can therefore lead to large errors. Most ecological, demographic, and geographic studies that provide the raw data for a calculation of human appropriation of NPP are now spatially explicit. Adding this sophistication to the integrated estimate of human appropriation will engage the potential of satellite data and spatial statistics.

Third, global analyses need a systematic approach to quality control when extracting results from published papers. The uncertainty analysis in Rojstaczer *et al.* (*2*) is based on the assumption that every published estimate, independent of methods and publication date, should carry equal weight. In an emerging field like global ecology, initial estimates are typically crude, with experience and analysis leading to gradual winnowing and improvement. Any approach that ignores progress will exaggerate uncertainty.

Fourth, appropriation of NPP is one of many human impacts on Earth. Without considering interactions among these, as well as individual effects, it is difficult to assess overall importance. For example, changes in climate and the composition of the atmosphere may cause large changes in NPP. These will alter human appropriation of NPP both directly, by changing the NPP of human-dominated areas, and indirectly, through decisions about farming, grazing, and forestry. Furthermore, human appropriation of NPP could modulate other ecosystem services (*4*), from freshwater availability to biodiversity (*5*). The critical aspect of human appropriation of NPP is not its absolute level, but the point at which it fundamentally reshapes Earth's ecosystems and their prospects for sustainability.

Humans have always relied on NPP for food, fuel, and fiber. As human population and technology have expanded, so has our ability to appropriate the fruits of natural processes, including NPP. Although we manage ecosystems extensively, we do not generally manage them in a way that augments natural potential. In most parts of the world, human activities, and agriculture in particular, have resulted in decreases in NPP from the levels that likely existed prior to human management (see the figure). In human-modified regions where NPP exceeds that of the pristine vegetation, subsidies of nutrients and often water and pesticides are also high.

Humans appropriate a large fraction of land NPP, probably more than any other species in Earth history. We do not yet know the maximum limit for a sustainable future or whether it has already been passed. We do know, however, that insuring a sustainable future entails sharing NPP with a great host of other species.



Change in net primary production (NPP) from land cover conversions. Hot colors and positive numbers indicate that modification led to decreased NPP. Cool colors and negative numbers indicate higher NPP in the human-altered ecosystem. Land cover conversions have decreased global NPP by about 5%. NPP values are given in grams of C per square meter per year.

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