

absorb solar radiation. When steam or  $\text{CO}_2$  are passed through the reactor, the coating material splits the molecules by adsorbing and incorporating oxygen to form a higher oxide. The effluent gas stream then consists of pure  $\text{H}_2$  or  $\text{CO}$ . The temperature in the reactor is then increased, for example, by focusing more mirrors onto the aperture of this reactor. The feed gas stream is cut off, which releases the trapped oxygen and regenerates the active coating. Two reaction chambers are operated in parallel, one for water/ $\text{CO}_2$  splitting and one for reduction.

One of the prototype materials for this kind of reaction is  $\text{Fe}_3\text{O}_4$ . The redox pair in this case is  $\text{FeO}/\text{Fe}_3\text{O}_4$ . In practice, the pure oxide cannot be cycled because the temperature needed to thermally reduce  $\text{Fe}_3\text{O}_4$  is higher than its melting point. However, replacing some of the iron in  $\text{Fe}_3\text{O}_4$  with other metals, such as zinc, manganese, nickel, or cobalt, can lower the reduction temperature while maintaining the spinel structure of these ferrite materials (9–11). Integrating the ferrites into a stabilizing matrix, such as yttrium-stabilized zirconia or cerium oxide (ceria), can also slow down a potential sintering and deactivation of the metal oxide (12).

The second main redox system is based on the redox pair  $\text{CeO}_2\text{--Ce}_2\text{O}_3$ . Ceria has the advantage that the melting point is higher than the temperature required for the thermal reduction step. However, other metals need to

be added to ceria to improve its reactivity and oxygen uptake capacity (13). For both families of materials, the main challenges are the achievement of high oxygen uptake capacities and hydrogen production rates, as well as reduced cost and increased operational lifetime of the redox materials. The coupling of concentrated solar radiation into the process must also be improved, and approaches being investigated include reactors with rotating absorbers and components, fixed and fluidized bed reactors, and the use of heat transfer fluids (7, 14, 15).

The general concept of solar fuel generation was first proven by developing and operating individual components. Subsequently, a miniplant (which could produce about 10 kW of thermal energy) was created and tested in DLR's solar furnace in Cologne, Germany. This technology has recently been scaled up to the size of 100 kW of thermal energy. The reactor, together with all necessary peripherals, was installed in an experimental solar tower at the Plataforma Solar de Almería, Spain. The benefit of using a solar tower arrangement is that only part of the mirrors (heliostats) have to be refocused to vary the temperatures of the two reactors that produce  $\text{H}_2$  and/or  $\text{CO}$ , rather than physically moving the reactors. Several hydrogen production cycles and metal oxide reduction cycles could be successfully investigated, with conversion of steam to  $\text{H}_2$  of up to

30% (16). Continuing developments should enable the solar-driven synthesis of fuels from renewable sources to complement the production of electricity.

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## CLIMATE CHANGE

# The Carbon Dioxide Exchange

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One key to accurately predicting future levels of atmospheric carbon dioxide ( $\text{CO}_2$ ) is understanding how land and atmosphere exchange  $\text{CO}_2$ . Each year, photosynthesizing land plants remove (fix) one in eight molecules of atmospheric  $\text{CO}_2$ , and respiring land plants and soil organisms return a similar number. This exchange determines whether terrestrial ecosystems are a net carbon sink or source. Two papers in this issue contribute to understanding the land-atmosphere exchange by elegantly analyzing rich data sets on  $\text{CO}_2$  fluxes from a global network of monitoring sites. On page 834, Beer *et al.* (1) estimate total annual terrestrial gross primary production (GPP) in an approach

more solidly based on data than previous simple approximations. On page 838, Mahecha *et al.* (2) assess how ecosystem respiration ( $R$ ) is related to temperature over short (week-to-month) and long (annual) time scales, and find a potentially important but difficult-to-interpret relationship.

Beer *et al.* focus on quantifying GPP locally and globally. They use general relationships between GPP and several "drivers," such as temperature, rainfall, and biome type, to characterize and estimate GPP at 352 sites. Then, they use five approaches to extrapolate to global estimates; these include three statistical models, estimating GPP indirectly from data on catchment water flux, and modeling GPP from satellite-based estimates of light interception by vegetation. They make an important advance by better quantifying

Understanding how carbon dioxide cycles between land and atmosphere is key to developing better climate models.

(i) global GPP and the uncertainty surrounding this estimate; (ii) spatial patterns of GPP (how much comes from tropical or boreal forests or from other biomes); and (iii) controls on GPP, such as by rainfall and temperature.

Beer *et al.* note that each of the five approaches includes simplifying assumptions and large uncertainties. They produced estimates of global GPP that vary from  $\approx 105$  to  $\approx 130 \text{ Pg C year}^{-1}$ , with a 95% probability that the value lies between 102 and 135  $\text{Pg C year}^{-1}$ . This is an advance, yet it shows how far we still are from an accurate estimate of global GPP. The 33  $\text{Pg C year}^{-1}$  difference between the low and high values, for instance, is roughly four times the annual  $\text{CO}_2$  emissions from fossil-fuel burning.

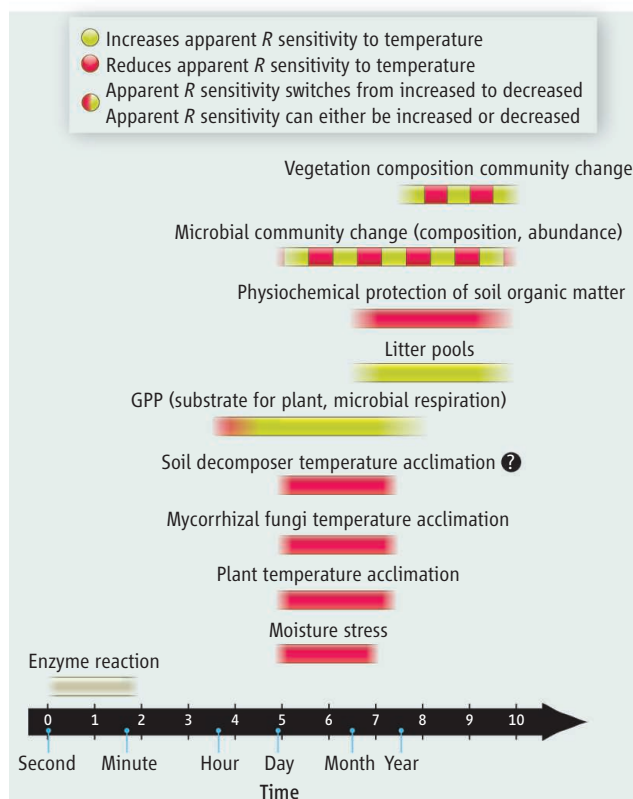
Mahecha *et al.* address the other half of the land-atmosphere  $\text{CO}_2$  flux. Unlike GPP,

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which represents a single process (photosynthesis) involving a single tissue (leaves),  $R$  represents the aggregate  $\text{CO}_2$  flux from the metabolic activities of myriad organisms. The players include plants, their mutualists (mycorrhizal fungi), and decomposers (soil microorganisms). Each has cellular processes that respond almost instantaneously to temperature changes (3, 4). However, the relationship of  $R$  to temperature over longer periods (weeks, months, and seasons) is influenced by many factors, including the availability of chemical substrates, environmental conditions, changes in microbe abundance and community composition, and physiological mechanisms for adjusting to shifting temperatures (2–13) (see the figure).

Mahecha *et al.* used data from 60 sites to characterize how  $R$  depends on temperature over time. They used a dividing line of 3 months to distinguish fast (high-frequency) from slow (low-frequency) processes. They show that high-frequency (week-to-month) processes result in a 40% average proportional increase in  $R$  for every  $10^\circ\text{C}$  increase in temperature, or a “ $Q_{10}$ ” value of 1.4. This value was similar across all sites. In contrast, when assessed conventionally over a year,  $R$  increased by an average of 130% per  $10^\circ\text{C}$  increase, or a  $Q_{10}$  of 2.3 (2). For context, the short-term (near-instantaneous) response reflecting physiological activity within plants and microbes has a  $Q_{10}$  that typically averages between 2 and 3 (3, 4).

Which of Mahecha *et al.*’s estimates better reflects intrinsic responsiveness to temperature—and is thus more relevant to climate modelers trying to predict ecosystem responses to warming? Mahecha *et al.* reasonably argue that the smaller, week-to-month  $Q_{10}$  of 1.4 is most relevant, and that the annual  $Q_{10}$  overestimates the role of temperature as a driver of ecosystem  $R$ . In part, that is because the annual estimate is confounded by environmental and seasonal variations that can increase plant and soil respiration independent of, and in addition to, direct temperature effects (8–10). For example, strong GPP during temperate zone summers provides abundant carbon substrate for both plant and soil microbial respiration, resulting in higher “apparent”



**Complex influences.** Land plant and microbe respiration of  $\text{CO}_2$  into the atmosphere can be increased (yellow) or reduced (red) by a wide range of processes that enhance or limit metabolic processes, operate over varying time scales, and go beyond direct temperature effects on physiology [expanded from (16)]. The numbers on the arrow represent time on a logarithmic scale.

sensitivity to temperature than can be attributed to direct temperature effects on respiration kinetics. They report, moreover, that the week-to-month scale sensitivity is stable across sites varying in mean temperature, whereas annual sensitivity varies markedly from cold to warm ecosystems, reflecting differences in the degree of confounding by environmental drivers.

Why is the “week-to-month”  $Q_{10}$  lower than the  $Q_{10}$  at the instantaneous and annual time scales? Mahecha *et al.* argue that it reflects a direct, “intrinsic” ecosystem functional response to temperature. This explanation is probably true in part, but it is likely that the low week-to-month  $Q_{10}$  of 1.4 also reflects a complex response to an aggregation of factors. For instance, plants (6, 7, 11, 13, 14), their fungal mutualists (15), and perhaps soil microbes (12) exhibit extreme temperature sensitivity that can alter realized  $R$ . As temperatures warm, plants quickly (e.g., in 2 days) dampen their temperature response by “down-shifting” their base respiration, and then “rev up” again in response to cooling. This acclimation results in a lower  $Q_{10}$  over a month than over an hour (6, 11, 13, 14). Further, variation in the types,

abundance, and food supply of soil microbes can also result in a low  $Q_{10}$  at the week-to-month scale.

Regardless of the difficulty of interpreting the processes underlying these numbers, the findings are important. Beer *et al.*’s value for GPP is our best and most broad-based estimate, despite its uncertainty. Mahecha *et al.*’s results are important because they suggest that, at week-to-month scales,  $R$ ’s relationship to temperature converges at a  $Q_{10}$  of 1.4 across many varied ecosystems. Their work also reduces fears that respiration fluxes may increase strongly with temperature, accelerating climate change (4–13). They also add to studies indicating that simple assumptions about respiration-temperature relations can lead to problematic models (4–13). It is not yet clear, however, whether and how their findings can be used in climate models.

What is also not yet clear is how GPP or  $R$  will respond to rising  $\text{CO}_2$  and to changing temperatures or rainfall. Such forecasting will require understanding and mathematically describing how biological processes will respond to novel environmental conditions outside of the current observational universe—a challenging task indeed. Given the urgent need to quantify and predict future land-atmosphere fluxes, however, we need rapid advances in such understanding in the decade ahead.

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