ing flow of charge back and forth between the NO molecule and the valence electrons in the metal. Thus, the coupling to substrate electronic excitations becomes strong. Further credence for this interpretation is given by other experiments (*12*) showing that vibrational energy can cause ejection of low-energy surface electrons.

Shenvi *et al*. represent the continuum of electronic states by considering the NO molecule in its neutral and ionic states coupled to 40 discrete substrate states, each one having its own potential energy surface. They allow the molecule to jump randomly along its way between these discrete states. This demanding calculation reproduces the relaxation of the molecule seen by the experimentalists.

Further analysis of these results suggests that the molecule is steered during the scattering event into an orientation favorable for electronic coupling. Shenvi *et al*. also make predictions that could be tested experimentally, but more important, their results corroborate the strongly nonadiabatic character of the scattering process. One concern is that these effects might be specific to molecules like NO that have an odd number of electrons. However, similar effects in more typical closed-shell molecules may be more difficult to identify unambiguously.

In contrast, nonadiabatic effects are a minor concern in the dissociative adsorption of H_2 (the formation of two bound H atoms) on the flat copper surface [the close-packed (111) face]. To describe the interaction of the molecule with the surface, Díaz *et al*. must use density functional theory (DFT), but at present, no functionals—which are at the heart of DFT—have been developed that achieve for gas-surface systems a good description of the stable bonding situation as well as the transition state separating reactants and products.

Given this difficulty, the authors made the brave assumption that the real potential energy surface is straddled by the ones obtained from calculations based on two different and widely used functionals. They merged the two results by weighting them with an adjustable parameter. As Díaz *et al*. show, this potential energy surface results in excellent agreement with extensive experimental results that have been obtained for this particular system at the level of individual quantum states. They emphasize that it is crucial to include in the calculation all six nuclear degrees of freedom of the scattering molecule. As a larger number of degrees of freedom comes at high computational cost, they treat the surface atoms as frozen in space.

In some sense, the authors of the two reports work from opposing ends of the general problem of describing molecule-surface interactions. Shenvi *et al*. try to improve ab initio methods by nailing down the error induced by one suspicious approximation. Díaz *et al*. take a pragmatic approach and show that, in principle, a potential energy surface exists that allows calculations to reproduce experiments quantitatively applying adiabatic dynamics and that serves as a target for future, more exact calculations. It remains to be seen to what extent their approach is generalizable, or if canceling errors have led to fortuitous results in this system. In any case, both reports demonstrate that gas-surface dynamics provide a sensitive test for the theories used to calculate molecular structures.

References and Notes

1. As there are many coordinates, the "surface" is really a "hypersurface" in multidimensional space.
2. N. Shenvi, S. Roy, J. C. Tully, *Science* **326**, 829 (2009).
3. C. Díaz *et al., Science* **326**, 832 (2009).
4. S. A. Harich *et al., Nature* **419**, 281 (2002).
5. E. Hasselbrink, B. I. Lundqvist, Eds., *Handbook of Surface Science, Vol. 3, Dynamics* (Elsevier, Amsterdam, 2008).
6. M. Born, R. Oppenheimer, *Ann. Phys.* **389**, 457 (1927).
7. P. W. Anderson, *Phys. Rev. Lett.* **18**, 1049 (1967).
8. E. Müller-Hartmann, T. V. Ramakrishnan, G. Toulouse, *Phys. Rev. B* **3**, 1102 (1971).
9. Modern schemes that seem to calculate the potential energy "on the fly" implicitly make use of this two-step approach.
10. E. Hasselbrink, *Curr. Opin. Solid State Mater. Sci.* **10**, 192 (2007).
11. Y. Huang, C. T. Rettner, D. J. Auerbach, A. M. Wodtke, *Science* **290**, 111 (2000).
12. J. D. White *et al., Nature* **433**, 503 (2005).

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ENVIRONMENTAL SCIENCE

Peatland Response to Global Change

Peatlands can buffer the impact of external perturbations, but can also rapidly shift to a new ecosystem type, with large gains or losses of stored carbon.

Nancy B. Dise

Meter for meter, peatlands store more carbon than any other terrestrial ecosystem. Covering only about 3% of Earth's land area, they hold the equivalent of half of the carbon that is in the atmosphere as CO_2 (*1*, *2*). Waterlogged conditions slow decomposition, and slow rates of subsurface flow allow the partly decayed organic matter to accumulate in place. But the same processes of anaerobic decomposition that allow carbon to accumulate also produce the strong greenhouse gas methane (CH_4). Over the time span of centuries, peatlands exert a net cooling effect on the global radiation balance, because the effect of removing long-lived atmospheric CO_2 ultimately surpasses that of releasing short-lived CH_4 (*3*). However, should peatlands begin to degrade on a large scale, this stored carbon could be released, reducing—or even reversing—their climate cooling effect. How will the carbon balance of peatlands change over coming centuries?

The clearest threat to peatlands today is direct damage by humans: agricultural conversion or drainage (for example for rice, palm oil, or forests) and mining (for horticulture and fuel). Far less obvious, but potentially as damaging, however, are long-term environmental changes such as global warming. Most peatlands are located in the boreal and subarctic Northern Hemisphere, where the climate is warming faster than anywhere else on Earth (*2*). Peatlands are also affected by numerous other environmental factors that are likely to change in the future, including precipitation amount and frequency, atmospheric deposition of reactive nitrogen and sulfur, atmospheric CO_2 levels, extreme weather, and fire. These drivers interact in complex ways, and predicting their net effect will not be possible by simply attempting to combine individual impacts.

Research from a variety of areas and approaches is converging upon the concept of peatlands as complex adaptive systems: self-regulating to some degree, but capable of rapid change and reorganization in response to internal developmental changes or to external forcing (*4*). It has long been known,

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for instance, that the surface of a peatland can rise and fall, sometimes dramatically, in response to rainfall or mild drought, while maintaining a fairly constant water level relative to the surface. This "Mooratmung" ("bog-breathing") is related to the sponge-like nature of *Sphagnum*, which can adsorb water and trap gases. Recent studies have shown that the carbon balance of peatlands can in turn be surprisingly resilient to perturbations, even fairly severe ones. For example, subjecting peat cores (*5*) or a peatland field site (*6*) to a water table drawdown similar to a prolonged drought initially led to a respiration-driven loss of soil carbon. But both carbon loss and subsidence (*6*) lowered the peat surface, decreasing its height above the water table, and effectively shifted the system back toward its starting state. Conversely, a rising water table stimulated growth of *Sphagnum* and other vegetation, which increased carbon accumulation, raised the surface of the peat and, in effect, lowered the local water table (*5*). Thus, an environmental perturbation may trigger an initial gain or loss of carbon, but recovery in the direction of the initial state can moderate the impact.

Shifting states. (Left) Hummock-hollow pattern at Rygmossen, a small raised bog near Uppsala, Sweden. (**Right**) "Ladder" system of ridges and pools, Inverewe Bogs, Scotland. Persistent environmental change, such as a long-term increase in climate wetness, can trigger a shift from one such peatland type to another.

CREDITS: (LEFT) ANDREW BAIRD/UNIVERSITY OF LEEDS. (RIGHT) LISA BELYEA/QUEEN MARY, UNIVERSITY OF LONDON

Subject to a stronger or more persistent environmental change, a peatland may shift from one state to another (see the figure). Analysis of cores from a bog in Sweden showed a succession of three different *Sphagnum* assemblages, each characteristic of progressively wetter conditions, in response to an increase in precipitation over 5000 years (*7*, *8*). Transitions were sudden (years to decades) and accompanied by a major increase in the rate of carbon accumulation. Between transitions, carbon accumulation rates slowly declined, in part [as in (*5*)] because growth of *Sphagnum* raised the surface of the peat in relation to the water table. However, over the past 1000 years, carbon accumulation rates have declined sharply. It appears that the climate has become wet enough for low microsites to flood, creating a ridge- and hollow-patterned peatland with a much-diminished capacity to sequester carbon

The responses to global warming of peatlands and tundra in the vast boreal/subarctic region underlain by permafrost may also follow the pattern of a complex adaptive system. Analysis of peat cores in boreal Canada covering a 150-year period showed that thawing of raised peat underlain by discontinuous permafrost caused the surface to collapse to near the level of the water table (*9*). This collapse induced a rapid vegetation change from species characteristic of dry, cold climates to *Sphagnum* species characteristic of wet depressions, increasing both carbon accumulation and CH_4 emission. Both rates then gradually declined as the ecosystem developed into a continental bog. Given that these bogs characteristically emit low levels of CH_4 and steadily sequester carbon, the authors concluded that in the long-term, conversion from permafrost peatland to lawn and finally to bog in western Canada has a climate cooling effect.

However, warming and drying without surface collapse can result in substantial carbon loss, as shown in the initial years of a long-term field study in Alaskan Arctic tundra (*10*). Overall, whether carbon is gained or lost depends on whether the transition is toward or away from the optimal conditions for carbon accumulation for that ecosystem, and this is mainly determined by the hydrologic response.

Long-term global changes—particularly warming, drought, and elevated nitrogen deposition—are likely to ultimately induce shifts in some existing peat-forming areas to new ecosystems such as grassland or shrubland (*10*, *11*), and the increase in biomass from vascular plants could in part compensate for carbon losses from soil oxidation during the transition. However, even if some net carbon accumulation returns, the gains are short-lived: The key peatland quality of slowly removing and storing carbon for hundreds or thousands of years is lost.

Considering peatlands as complex adaptive systems characterized by quasistable equilibrium states—resilient to change at some level of perturbation but shifting to new states at higher levels of disturbance—provides a meaningful framework for understanding and modeling their response to environmental change. Ignoring the strong feedbacks inherent in peatlands may lead to substantial under- or overestimates of their response to global change. The challenge is to forecast both the future environmental conditions that peatlands will experience and the internal feedbacks and state changes that may be triggered by these conditions. To meet this challenge it is vital to continue and expand long-term monitoring networks to characterize the present, paleoenvironment research to reconstruct the past, and manipulation experiments in the field and laboratory to build our understanding of these unique and valuable ecosystems.

References and Notes

1. J. Limpens *et al.*, *Biogeosciences* **5**, 1475 (2008).
2. S. Solomon *et al.*, Eds., *Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* (Cambridge Univ. Press, Cambridge, 2007).
3. S. Frolking, N. T. Roulet, *Glob. Change Biol.* **13**, 1079 (2007).
4. L. R. Belyea, A. J. Baird, *Ecol. Monogr.* **76**, 299 (2006).
5. S. D. Bridgham *et al.*, *Ecology* **89**, 3041 (2008).
6. M. Strack, J. M. Waddington, *Global Biogeochem. Cycles* **21**, GB1007 (2007).
7. L. Belyea, N. Malmer, *Glob. Change Biol.* **10**, 1043 (2004).
8. G. Svensson, *Boreas* **17**, 89 (1988).
9. M. R. Turetsky *et al.*, *Glob. Change Biol.* **13**, 1922 (2007).
10. W. C. Oechel *et al.*, *Nature* **406**, 978 (2000).
11. H. B. M. Tomassen *et al.*, *J. Ecol.* **91**, 357 (2003).

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