for Xe (28). The difference in chemical shifts for H_2O in this study is 0.11 ppm (fig. S32), which is consistent with the size of an H_2O molecule between that of H_2 and Ar. No difference in chemical shift of the ^{13}C NMR was observed among $H_2O@C_{60}$, $HDO@C_{60}$, and $D_2O@C_{60}$.

Separations of $He@C_{60}$, $H_2@C_{60}$, $Ar@C_{60}$, $Kr@C_{60}$, and $Xe@C_{60}$ from empty C_{60} were usually difficult and possible only when an HPLC equipped with Buckyprep [3-(1-pyrenyl)propylsilyl] or PYE [2-(1-pyrenyl)ethylsilyl] column(s) was used with many time-consuming recycles. In contrast, $H_2O@C_{60}$ was easily separated from empty C_{60} by the single-stage HPLC (Buckyprep, toluene), with retention times of 7.93 and 8.28 min for empty C_{60} and $H_2O@C_{60}$, respectively (fig. S33). It is believed that π-π interaction of the fullerene cage with pyrene moieties attached to the silica gel surface is important for the separation, and the presence of the encapsulated H_2O molecule might influence such interactions. One of the characteristic properties of an H_2O molecule is its high dipole moment, whereas C_{60} with the I_h symmetry does not have the dipole. Thus, we expect that $H_2O@C_{60}$ should be a polar molecule. The density functional theory (DFT) calculations at the M06-2X/6-311G(2d, p) level of theory (29) with basis set superposition error correction during structural optimization showed that the dipole moments of H_2O, C_{60}, and $H_2O@C_{60}$ are 2.02, 0.00, and 2.03 Debye, respectively.

Infrared spectroscopy is a useful method to study the properties of water (30). However, the vibrational frequency analysis of $H_2O@C_{60}$ by the DFT calculations suggested that the symmetric and asymmetric stretching modes of the H_2O molecule inside C_{60} (3810 and 3894 cm^{-1}) should be very weak (15). It was difficult to see spectral features clearly in the observed Fourier transform infrared spectrum (diffuse reflectance spectroscopy, KBr, fig. S34), probably because of the shielding effect of the dipole (30). The observed peaks for $H_2O@C_{60}$ were 1429.3, 1182.4, 576.7, and 526.6 cm^{-1}, which were exactly the same as those of empty C_{60}.

Upon cyclic voltammetry in ODCB with 0.1 M Bu_4NPF_6 as a supporting electrolyte, an irreversible oxidation peak and four quasi-reversible reduction waves were observed (fig. S35), and the redox potentials were determined by differential pulse voltammetry (fig. S36) as +1.32, –1.08, –1.46, –1.91, and –2.38 V versus a ferrocene/ferrocenium couple within the potential window. These values were almost the same as those of empty C_{60} (+1.32, –1.08, –1.47, –1.92, and –2.39 V) under the same conditions. This result indicated that the single molecule of H_2O is electrochemically stable under the hydrophobic environment inside C_{60}.

The $H_2O@C_{60}$ molecule, which can be considered as "wet fullerene" or "polar C_{60}," should allow the study of the intrinsic properties of a single molecule of H_2O, such as ortho and para conversion (31). When this synthetic methodology is expanded to other small molecules into C_{60}, C_{70}, and higher fullerenes, research work on the isolated molecule or the control of physical properties of outer fullerene cages will progress in the near future.

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Climate Trends and Global Crop Production Since 1980

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Efforts to anticipate how climate change will affect future food availability can benefit from understanding the impacts of changes to date. We found that in the cropping regions and growing seasons of most countries, with the important exception of the United States, temperature trends from 1980 to 2008 exceeded one standard deviation of historic year-to-year variability. Models that link yields of the four largest commodity crops to weather indicate that global maize and wheat production declined by 3.8 and 5.5%, respectively, relative to a counterfactual without climate trends. For soybeans and rice, winners and losers largely balanced out. Climate trends were large enough in some countries to offset a significant portion of the increases in average yields that arose from technology, carbon dioxide fertilization, and other factors.

Inflation-adjusted prices for food have shown a downward trend over the last century as increases in supply have outpaced demand. More recently, food prices have increased rapidly,

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and many observers have attributed this in part to weather episodes such as the prolonged drought in Australia or the heat waves and wildfires in Russia. However, efforts to model the effects of climate on prices or food availability, even for individual countries, must consider effects throughout the world, given that agricultural commodities are traded worldwide and that world market prices are determined by global supply and demand (*1*–*3*).

Global average temperatures have risen by roughly 0.13°C per decade since 1950 (*4*), yet the

impact this has had on agriculture is not well understood (5). An even faster pace of roughly 0.2°C per decade of global warming is expected over the next two to three decades, with substantially larger trends likely for cultivated land areas (4). Understanding the impacts of past trends can help us to gauge the importance of near-term climate change for supplies of key food commodities. In addition, identifying the particular crops and regions that have been most affected by recent trends would assist efforts to measure and analyze ongoing efforts to adapt.

We developed a database of yield response models to evaluate the impact of these recent climate trends on major crop yields at the country scale for the period 1980–2008. Publicly available data sets on crop production, crop locations, growing seasons, and monthly temperature (T) and precipitation (P) were combined in a panel analysis of four crops (maize, wheat, rice, and soybeans) for all countries in the world (6). These four crops constitute roughly 75% of the calories that humans directly or indirectly consume (7).

Time series of average growing-season T and P revealed significant positive trends in temperature since 1980 for nearly all major growing regions of maize, wheat, rice, and soybeans (Fig. 1, Fig. 2, and figs. S1 to S4). To put the magnitude of trends in context, we normalized them by the historical standard deviation (σ) of year-to-year fluctuations (i.e., a T trend of 1.0 means that temperatures at the end of the period were 1.0σ higher than at the beginning of the period). A notable exception to the warming pattern is the United States, which accounts for ~40% of global

maize and soybean production and experienced a slight cooling over the period (Fig. 1). Overall, 65% of countries experienced T trends in growing regions of at least 1σ for maize and rice, with the number slightly higher (75%) for wheat and lower (53%) for soybean. Roughly one-fourth of all countries experienced trends of more than 2σ for each crop (Fig. 2). This distribution of trends stands in marked contrast to the 20 years before 1980, for which trends were evenly distributed about zero (Fig. 1). Precipitation trends were more mixed across regions and were significantly smaller relative to historical variability in most places. The number of countries with extreme trends reflected the number expected by chance (Fig. 2), indicating no consistent global shift in growing-season average P.

Translating these climate trends into potential yield impacts required models of yield response. We used regression analysis of historical data to relate past yield outcomes to weather realizations. All of the resulting models include T and P, their squares, country-specific intercepts to account for spatial variations in crop management and soil quality, and country-specific time trends to account for yield growth due to technology gains (6). Because our models are nonlinear, both year-to-year variations in historical weather as well as the average climate are used for the identification of the coefficients (unlike a linear panel, which only uses deviations from the average). However, we do not directly estimate the full set of adaptation possibilities that might occur in the long term under climate change (8). For this reason, we prefer to view these not as predictions of actual im-

pacts, but rather as a useful measure of the pace of climate change in the context of agriculture. The greater the estimated impacts, the faster any adaptation or action to raise yields would have to occur to offset potential losses.

The models exhibited statistically significant sensitivities to T and P that are consistent with process-based crop models and the broader agronomic literature (figs. S6 and S7). Given the hill-shaped yield-temperature function, predicted decreases are larger the warmer a country is to begin with. A 1°C rise tends to lower yields by up to 10% except in high-latitude countries, where rice in particular gains from warming. Precipitation increases yields for nearly all crops and countries, up to a point at which further rainfall becomes harmful. Tests of alternate climate data sets and groupings of countries identified some important differences, but responses for most countries were robust to these model choices (fig. S8).

To estimate yield impacts of climate trends, we used the statistical models to predict annual yields for four scenarios of historical T and P: (i) actual T and actual P for each country for the period 1980–2008, (ii) actual T and detrended P, (iii) detrended T and actual P, and (iv) detrended T and detrended P. Trends in the difference between (iv) and (i) were used to quantify the impact of historical climate trends, whereas (ii) and (iii) were used to determine the relative contribution of T and P to overall impacts.

At the global scale, maize and wheat exhibited negative impacts for several major producers and global net loss of 3.8% and 5.5%, respectively,

Fig. 1. (**A** and **B**) Maps of the 1980–2008 linear trend in temperature (A) and precipitation (B) for the growing season of the predominant crop (among maize, wheat, rice, and soybean) in each 0.5 × 0.5 grid cell. Trends are expressed as the ratio of the total trend for the 29-year period (e.g., °C per 29 years) divided by the historical standard deviation for the period 1960–2000. For clarity, only cells with at least 1% area covered by maize, wheat, rice, or soybean are shown. Temperature trends exceed more than twice the historical standard deviation in many locations, whereas precipitation trends have been smaller.
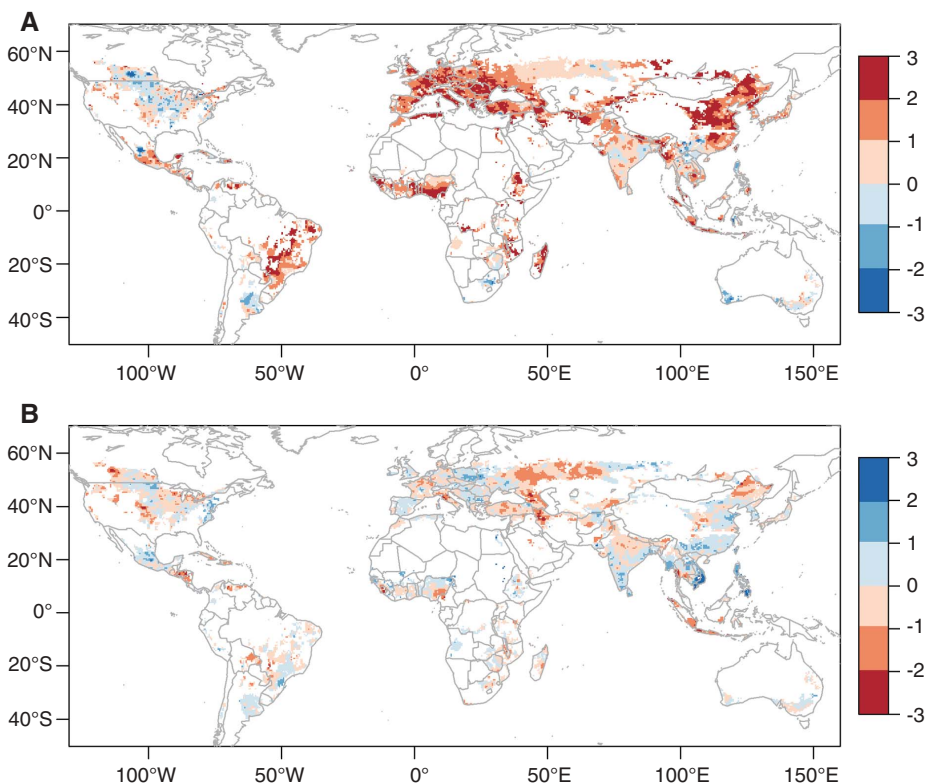
relative to what would have been achieved without the climate trends in 1980–2008 (Fig. 3 and Table 1). In absolute terms, these equal the annual production of maize in Mexico (23 MT) and wheat in France (33 MT), respectively. The net impact on rice and soybean production was insignif-

icant, with gains in some countries balancing losses in others. Among the largest country-specific losses was wheat in Russia (almost 15%), whereas the country with the largest overall share of crop production (United States) showed no effect because of the lack of significant climate trends.

The majority of impacts were driven by trends in T rather than P (Fig. 3). Precipitation is an important driver of interannual variability of yields, and indeed our models often predict a comparable yield change for a 1σ change in P or T (fig. S7). However, the magnitude of recent T trends

Fig. 2. (**A** to **D**) Frequency distributions of country-level growing-season temperature trends (top) and precipitation trends (bottom) for the periods 1960–1980 (left) and 1980–2008 (right) for four major crops, with trends expressed as the total trend for the period (e.g., °C per 29 years), divided by the historical standard deviation for the period 1960–2000. The null distribution (derived from 10,000 runs with simulated random noise) is shown by gray line, reflecting the frequency of different trends expected by chance. The distribution across countries of precipitation trends for both 1960–1980 and 1980–2008, as well as temperature trends for 1960–1980, do not appear different from what would be expected from random variation. In contrast, the temperature distribution for 1980–2008 is shifted relative to the null distribution, with temperature trends often two or more times the historical standard deviation.
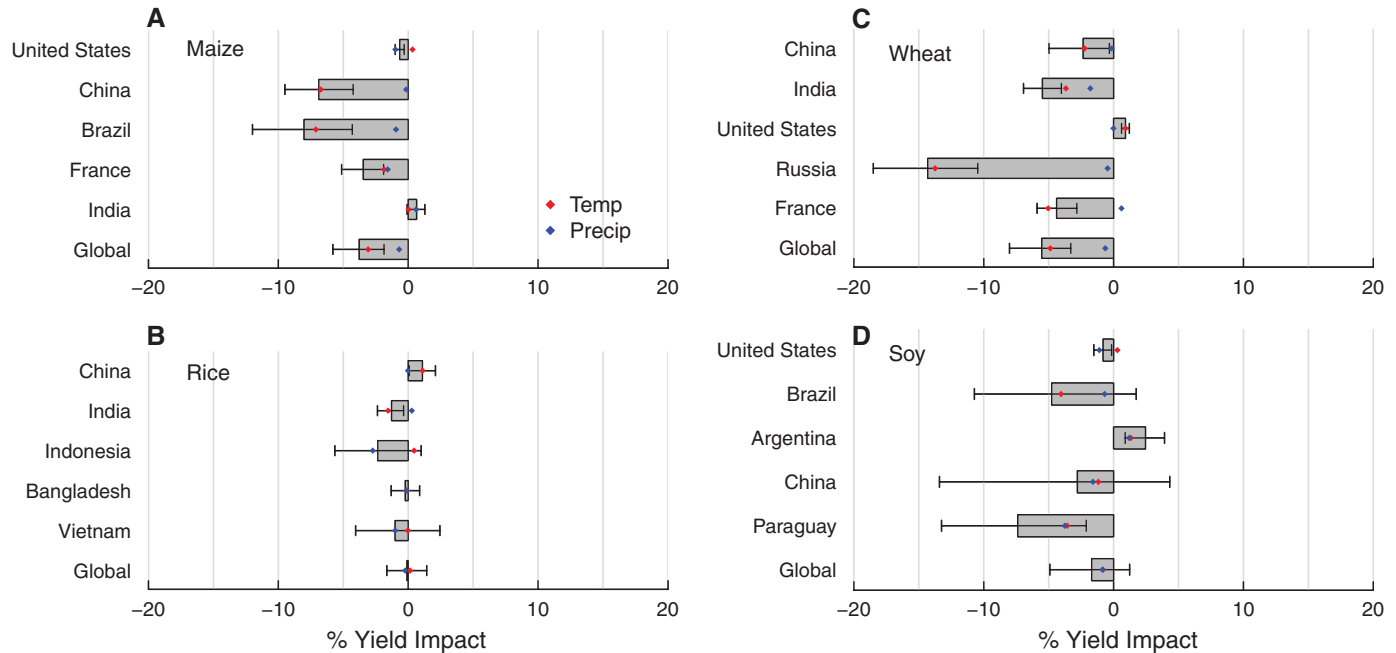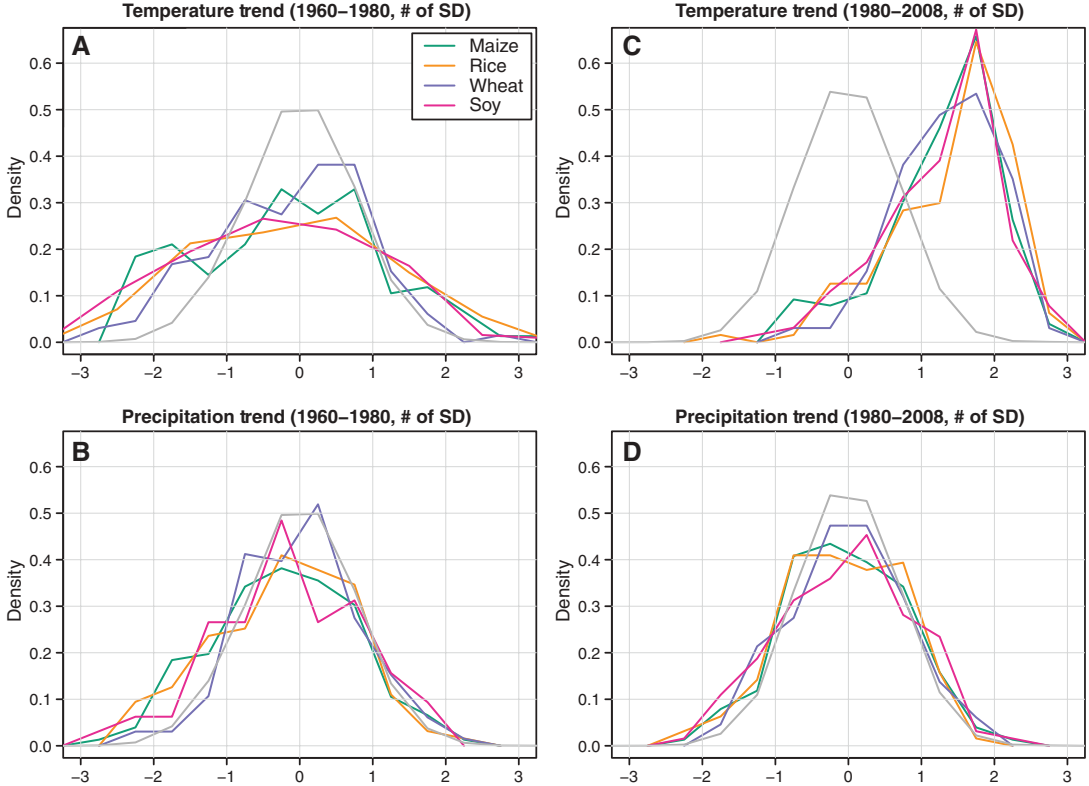

Fig. 3. (**A** to **D**) Estimated net impact of climate trends for 1980–2008 on crop yields for major producers and for global production. Values are expressed as percent of average yield. Gray bars show median estimate; error bars show 5% to 95% confidence interval from bootstrap resampling with 500 replicates. Red and blue dots show median estimate of impact for T trend and P trend, respectively.

(Fig. 2) is larger than those for P in most situations. This finding is consistent with models of future yield impacts of climate change, which indicate that changes in T are more important than changes in P, at least at the national and regional scales (*9, 10*).

Prior studies for individual countries and at the global scale also found that recent trends have depressed maize and wheat yields (*5*). For example, a recent study of wheat yields in France suggests that climate is an important factor contributing to stagnation of yields since 1990 (*11*). Similarly, warming trends in India have a well-understood negative effect on yields and are thought to explain part of the slowdown in recent yield gains (*12, 13*). For rice, the lack of significant impacts is consistent

with a recent study of rice in Asia, which showed that past changes in average T had small effects at large scales, in part because of opposing influence of nighttime and daytime temperatures, and in part because of opposing climate trends in different countries (*14*). The trends reported in the current study are dependent on the time period used, 1980–2008, but adjustments to this time period did not qualitatively affect the results (fig. S9). Separating the effects of maximum and minimum temperature, or different treatments of the time trend, also did not qualitatively alter the conclusions (figs. S10 and S11).

Climate is only one factor likely to shape the future (or past) of food supply. It is therefore important to assess how these impacts of climate

trends compare to other factors over the same time period. As one measure, we divided the climate-induced yield trend by the overall yield trend for 1980–2008 in each country (Fig. 4). We emphasize that this is a simple metric of the importance of climate relative to all other factors, and does not address the overall pace of yield growth, nor does it separately attribute yield growth to the many technological and environmental factors that influence trends. However, it provides a useful measure of the relative importance of climate, with values of −0.1 indicating that 10 years of climate trend is equivalent to a setback of roughly 1 year of technology gains.

The ratio exhibits wide variation across countries because of differences in both the growth rate of average yields and climate impacts (Fig. 4). Cases where negative climate impacts represent a large fraction of overall yield gains include wheat in Russia, Turkey, and Mexico, and maize in China. Rice production in high-latitude regions appears to have benefited from warming, but latitudinal gradients are not apparent for other crops. Although temperate systems tend to be hurt less from a given amount of warming in many model assessments (*15*), in reality these systems often have much lower nonclimatic constraints—for instance, their sensitivity to weather may be increased by high rates of fertilizer use (*9*). Moreover, temperate systems tend to warm more quickly than tropics (*16*), and several high-latitude growing regions have seen substantial warming since 1980 (Fig. 1).

Any model has its limitations, and we recognize a few caveats that are common to statistical models. Our approach may be overly pessimistic because it does not fully incorporate long-term adaptations

Table 1. Median estimates of global impacts of temperature and precipitation trends, 1980–2008, on average yields for four major crops. Estimates of the 47 ppm increase in CO_2 over the time period were derived from data in (*21*). Values in parentheses show 5% to 95% confidence interval estimated by bootstrap resampling over all samples.

Crop	Global production, 1998–2002 average (millions of metric tons)	Global yield impact of temperature trends (%)	Global yield impact of precipitation trends (%)	Subtotal	Global yield impact of CO_2 trends (%)	Total
Maize	607	−3.1 (−4.9, −1.4)	−0.7 (−1.2, 0.2)	−3.8 (−5.8, −1.9)	0.0	−3.8
Rice	591	0.1 (−0.9, 1.2)	−0.2 (−1.0, 0.5)	−0.1 (−1.6, 1.4)	3.0	2.9
Wheat	586	−4.9 (−7.2, −2.8)	−0.6 (−1.3, 0.1)	−5.5 (−8.0, −3.3)	3.0	−2.5
Soybean	168	−0.8 (−3.8, 1.9)	−0.9 (−1.5, −0.2)	−1.7 (−4.9, 1.2)	3.0	1.3

Fig. 4. (**A** to **D**) Estimated net impact of climate trends for 1980–2008 on crop yields by country, divided by the overall yield trend per year for 1980–2008. Values represent the climate effect in the equivalent number of years of overall yield gains. Negative values indicate that the climate trend slowed yield trends, and positive values indicate that the climate trend sped up yield trends, relative to what would have occurred without trends in climate.
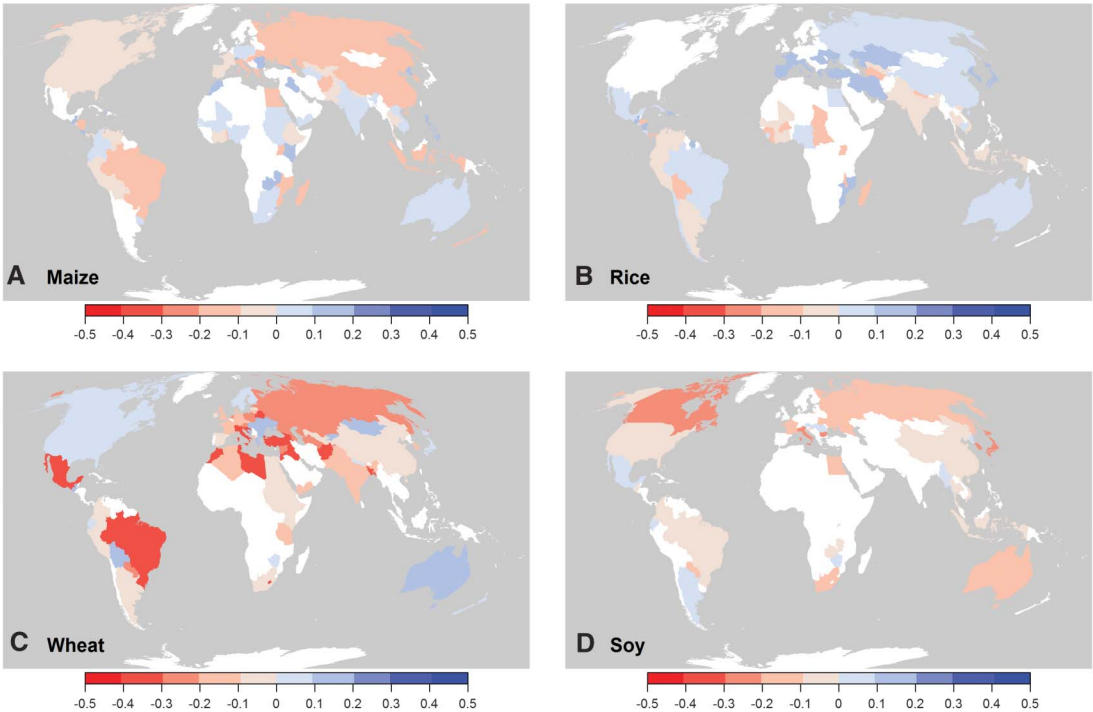
that may occur once farmers adjust their expectations of future climate. Examples of this would include expansion of crop area into cooler regions, switches to new varieties (*17*), or shifts toward earlier planting dates, although there is little evidence that the latter is happening beyond what is expected from historical responses to warm years (*18*). Moreover, the incentives to innovate have been limited in most of our sample period because prices have been low. On the other hand, our estimates may be overly optimistic because data limitations prevent us from explicitly modeling effects of extreme temperature or precipitation events within the growing season, which can have disproportionately large impacts on final yields (*19*). For example, although we captured the decline in growing-season total precipitation for wheat in India, there has also been a trend toward heavy rain events as an increased fraction of total rainfall, which is likely harmful to wheat yields (*20*).

Finally, we note that our study does not estimate the direct effect of elevated CO_2 on crop yields that are captured in the smooth time trends. Atmospheric CO_2 concentrations at Mauna Loa, Hawaii have increased from 339 ppm in 1980 to 386 ppm in 2008 (www.esrl.noaa.gov/gmd/ccgg/trends). Free-air CO_2 enrichment experiments for C_3 crops (i.e., wheat, rice, and soybean) show an average yield increase of 14% in 583 ppm CO_2 relative to 367 ppm CO_2 [i.e., 0.065% increase per ppm (*21*)]. This suggests that the 47 ppm increase since 1980 would have boosted yields by roughly 3%. Impacts of higher CO_2 on maize were likely much smaller because its C_4 photosynthetic pathway is unresponsive to elevated CO_2 (*22*). Thus, the net effects of higher CO_2 and climate change since 1980 have likely been slightly positive for rice and soybean, and negative for wheat and maize (Table 1).

The fact that climate impacts often exceed 10% of the rate of yield change indicates that climate changes are already exerting a considerable drag on yield growth. To further put this in perspective, we have calculated the impact of climate trends on global prices using recent estimates of price elasticities for global supply and demand of calories (*23*). The estimated changes in crop production excluding and including CO_2 fertilization (subtotal and total columns in Table 1, respectively) translate into average commodity price increases of 18.9% and 6.4% when we use the same bootstrap procedure as used in table 3 of (*22*).

Our study considers production of four major commodities at national scales. There are many important questions at subnational scales that our models cannot address, many important foods beyond the four modeled here, and many important factors other than food production that determine food security. Nonetheless, we contend that periodic assessments of how climate trends are affecting global food production can provide some useful insights for scientists and policy makers. This type of analysis should be accompanied by studies that evaluate the true pace and effectiveness of adaptation responses around the world, particularly for wheat and maize. By identifying countries where the pace of climate change and associated yield pressures are especially fast, our study should facilitate these future analyses. Without successful adaptation, and given the persistent rise in demand for maize and wheat, the sizable yield setback from climate change is likely incurring large economic and health costs.

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Sr-Nd-Pb Isotope Evidence for Ice-Sheet Presence on Southern Greenland During the Last Interglacial

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To ascertain the response of the southern Greenland Ice Sheet (GIS) to a boreal summer climate warmer than at present, we explored whether southern Greenland was deglaciated during the Last Interglacial (LIG), using the Sr-Nd-Pb isotope ratios of silt-sized sediment discharged from southern Greenland. Our isotope data indicate that no single southern Greenland geologic terrane was completely deglaciated during the LIG, similar to the Holocene. Differences in sediment sources during the LIG relative to the early Holocene denote, however, greater southern GIS retreat during the LIG. These results allow the evaluation of a suite of GIS models and are consistent with a GIS contribution of 1.6 to 2.2 meters to the ≥4-meter LIG sea-level highstand, requiring a significant sea-level contribution from the Antarctic Ice Sheet.

The response of ice sheets to climate change is the largest source of uncertainty in predicting future sea-level rise (*1*). In the case of the Greenland Ice Sheet (GIS), observations of mass changes are restricted to the past few decades, providing limited context with which to assess present changes and future model predictions (*1*). An alternative approach for assessing the GIS response to climate change is to use the geologic record of the GIS during earlier climate periods that were naturally warmer than the present in the boreal summer (*2*, *3*), the season that affects GIS ablation.

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