tween euxinic and ferruginous conditions would have favored the early evolution and ecological expansion of a variety of anoxygenic photosynthetic metabolisms in pelagic environments. Expressions of biological oxygen production (such as those seen in the upper Mount McRae and Brockman BIF) would then have varied with the extent to which episodic or sustained pulses of reductants from the Earth's interior would have buffered photosynthetic oxygen, contributing to the protracted nature of Earth surface oxygenation during the Archean and Proterozoic (26).

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Improved Attribution of Climate Forcing to Emissions

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Evaluating multicomponent climate change mitigation strategies requires knowledge of the diverse direct and indirect effects of emissions. Methane, ozone, and aerosols are linked through atmospheric chemistry so that emissions of a single pollutant can affect several species. We calculated atmospheric composition changes, historical radiative forcing, and forcing per unit of emission due to aerosol and tropospheric ozone precursor emissions in a coupled composition-climate model. We found that gas-aerosol interactions substantially alter the relative importance of the various emissions. In particular, methane emissions have a larger impact than that used in current carbon-trading schemes or in the Kyoto Protocol. Thus, assessments of multigas mitigation policies, as well as any separate efforts to mitigate warming from short-lived pollutants, should include gas-aerosol interactions.

Multicomponent climate change mitigation strategies are likely to be much more cost effective than carbon dioxide (CO_2)–only strategies (1, 2) but require quantification of the relative impact of different emissions that affect climate. Because globally and annually averaged radiative forcing (RF) is generally a good predictor of global mean surface temperature change, a scale related to RF is a logical choice for comparing emissions. The most widely used, and that adopted in the Kyoto Protocol, is the global warming potential (GWP), defined as the integrated global mean RF out to a chosen time of an emission pulse of 1 kg of a compound relative to that for 1 kg of CO_2. GWPs are thus based on radiative impact and atmospheric residence time and can include both the direct radiative effect of emitted species and radiative effects from indirect chemical responses. Previous studies, including the Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report (AR4), provide estimates of RF and GWPs of short-lived gas emissions (3–5). However, except for the indirect effect of NO_x emissions on nitrate aerosol, gas-aerosol interactions were not included. These interactions occur primarily through ozone precursors altering the availability of oxidants, influencing aerosol formation rates, and through sulfate-nitrate competition for ammonium.

We used the composition-climate model Goddard Institute for Space Studies (GISS) Model for Physical Understanding of Composition-Climate Interactions and Impacts (G-PUCCINI) (6) to calculate the response to removal of all anthropogenic methane, carbon monoxide (CO) plus volatile organic compounds (VOCs), NO_x, SO_2, and ammonia emissions. This model couples gas-phase, sulfate (7), and nitrate (8) aerosol chemistry within the GISS ModelE general circulation model (GCM). Anthropogenic emissions are from a 2000 inventory (9). We calculated both the "abundance-based" RF owing to the net atmospheric composition response by species when all emissions are changed simultaneously and the "emissions-based" forcing attributable to the responses of all species to emissions of a single pollutant (Fig. 1). The sum of the forcings that take place via response of a particular species in the emissions-based analysis (each represented by a different color in Fig. 1) is approximately equal to the forcing due to that species in the abundance-based analysis. Likewise, the sums of all emissions-based and all abundance-based forcings are similar. Hence, the two viewpoints provide different but compatible pictures of how emissions and composition changes influence RF.

Emissions of NO_x, CO, and methane have substantial impacts on aerosols by altering the abundance of oxidants, especially hydroxyl, which convert SO_2 into sulfate. Global burdens of hydroxyl and sulfate change by 18% and 13% for increased NO_x, by –13% and –9% for CO, and by –26% and –11% for methane (sulfate forcing closely follows the sulfate burden change). Coupling in the other direction is very weak because reactions of gas-phase species upon aerosol surfaces have only a small effect on the global burden of the radiatively active species ozone and methane (e.g., anthropogenic SO_2 emissions enhance the removal of NO_x through reactions on particulate

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surfaces, causing ozone to decrease, but the RF is only –0.004 W/m^2). Increased SO_2 leads to substantially reduced nitrate aerosol, however, owing to greater ammonium sulfate formation at the expense of ammonium nitrate (10, 11). We group CO and VOCs together for RF because they play similar roles in atmospheric chemistry, but the effects of historical CO emissions are ~3 to 7 times as great.

Methane emissions provide the second-largest contribution to historical warming after carbon dioxide. Including direct and indirect chemical effects and only the direct radiative effects of aerosols, NO_x emissions are the most powerful cooling agents (Fig. 1). However, adding in aerosol indirect effects (AIE) on clouds, which are highly uncertain (12), could make SO_2 emissions the stronger contributor to negative historical forcing. Atmospheric responses to individual species emissions changes are largely additive, with increases of 15% or less in the response of methane, ozone, sulfate,

and hydroxyl when all pollutants are changed simultaneously, compared with the summed response to individual changes. Nitrate shows a greater discrepancy (~0.04 W/m^2), but the difference is well within uncertainty (0.10 W/m^2) (see Fig. 1 caption).

We present the results of several calculations of 100-year GWPs, the most commonly used time horizon, first reporting values without including indirect chemical responses of aerosols or CO_2 (as in the AR4, although the indirect responses of CO_2 are only 0.04 W/m^2 for CO and 0.02 W/m^2 for methane), then adding in the radiative effects resulting from the aerosol response to oxidant changes (Fig. 2). Reference CO_2 forcing is taken from the AR4, whereas the RF for all other gases and the direct radiative effects of aerosols are calculated within the GISS GCM for current conditions using the model's radiative transfer calculation and simulated composition response to 1-year pulse emissions. We also computed GWP, including a

rough estimate of AIE, assuming they augment the sulfate aerosol direct radiative effects calculated here by 150%, taking the uncertainty range as 75 to 225% (13). Uncertainties in GWP are otherwise based on the RF uncertainties from AR4 (as in Fig. 1). We report GWPs for CO alone, because GWPs for different VOCs vary by an order of magnitude (14).

Our value for the 100-year GWP of methane when including only the responses of methane, ozone, and stratospheric water vapor is almost identical to the comparable AR4 value. The GWP is substantially larger when the direct radiative effects of the aerosol responses are included, however. It becomes larger still, including aerosol-cloud interactions, although uncertainties increase as well. Although results are not statistically different at the 95% confidence level, the best estimate is nonetheless substantially larger when gas-aerosol interactions are included. The 100-yr GWP for CO was 1.9 in AR4, with a 1.0 to 3.0 range based on the third IPCC assessment and subsequent results (3, 14). As with methane, our GWP is similar to those in previous work when aerosol responses are neglected but is substantially larger when these responses are included. GWPs become extremely difficult to define for shorter-lived species because they depend strongly on the location and time (season and day) of the emission pulse (15). Estimates of 100-year GWPs for global surface NO_x emissions report values of roughly –10 to –30, including the indirect responses of methane and ozone only (16, 17), in very rough accord with our results, but differences in the imposed emissions changes preclude a rigorous comparison.

Although our calculations are more complete than previous studies, additional processes should be included as they become better understood. These include mixing between aerosol types (18), formation of secondary organic aerosols, which are sensitive to both organic aerosol emissions and oxidant levels (19), and interactions between pollutants and ecosystems. The latter includes suppression of CO_2 uptake by increased surface ozone concentrations (20), aerosols enhancing the ratio of diffuse to direct radiation reaching the biosphere leading to increased CO_2 uptake (21) (at least for some plant types when aerosol loading is not so large as to dramatically reduce total surface irradiance), and the effects of nitrogen and sulfur deposition on ecosystems. These effects may be important but are highly uncertain at present. Ecosystem-chemistry interactions add both positive and negative forcing terms to the GWP of NO_x (NO_x leads to increased ozone, causing increased CO_2, but also leads to increased aerosol, causing decreased CO_2), adding to an already complex set of multiple, sometimes opposing, forcings (Fig. 1). For CO and methane, however, increased emissions lead to increased CO_2 from both the ozone-ecosystem interactions and the aerosol-ecosystem interactions, so would simply increase their positive GWPs still further.
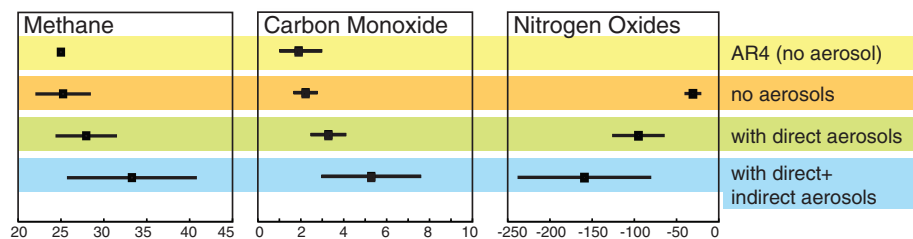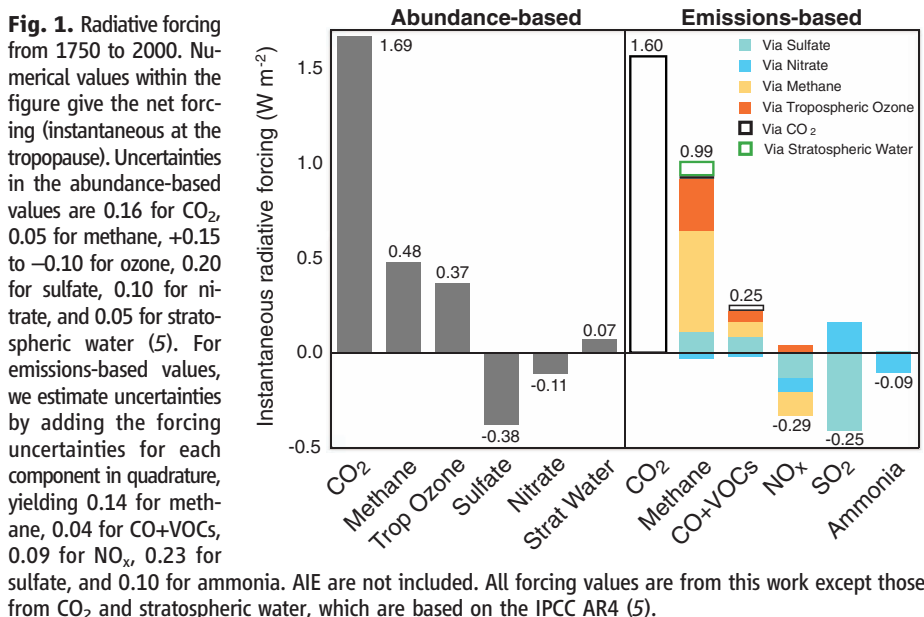
Fig. 1. Radiative forcing from 1750 to 2000. Numerical values within the figure give the net forcing (instantaneous at the tropopause). Uncertainties in the abundance-based values are 0.16 for CO_2, 0.05 for methane, +0.15 to −0.10 for ozone, 0.20 for sulfate, 0.10 for nitrate, and 0.05 for stratospheric water (5). For emissions-based values, we estimate uncertainties by adding the forcing uncertainties for each component in quadrature, yielding 0.14 for methane, 0.04 for CO+VOCs, 0.09 for NO_x, 0.23 for sulfate, and 0.10 for ammonia. AIE are not included. All forcing values are from this work except those from CO_2 and stratospheric water, which are based on the IPCC AR4 (5).

Fig. 2. The 100-year GWPs for methane, CO, and NO_x (per Tg N) as given in the AR4 and in this study when including no aerosol response, the direct radiative effect of aerosol responses, and the direct+indirect radiative effects of aerosol responses. The AR4 did not report uncertainties for methane or CO and gave no mean estimate for NO_x. The range for the GWP of CO is from the third IPCC assessment and encompasses values reported up through the AR4. Our calculations for the shorter 20-year GWP, including aerosol responses, yield values of 79 and 105 for methane, 11 and 19 for CO, and −335 and −560 for NO_x, including direct and direct+indirect radiative effects of aerosols in each case. The 100-yr GWPs for SO_2 (per Tg SO_2) and ammonia would be −22 and −19, respectively, including direct aerosol radiative effects only, and −76 and −15 adding indirect aerosol radiative effects. GWPs for very short-lived NO_x, SO_2, and ammonia will vary widely by emission location and timing, and hence global values are of limited use.

Hence, the uncertainty in quantifying these processes implies only that the larger estimates of CO and methane GWPs presented here may still be too low.

Although we focus on global mean results, the effects of oxidant changes on sulfate are stronger in areas with high SO_2 emissions that are more oxidant-limited. This is in accord with previous results showing a strong sulfate response over high-emission regions in Asia to perturbations in North American emissions attributable to NO_x emissions changes followed by long-range ozone transport (22). The global sulfate response to oxidant changes can be large, because much of the industrialized Northern Hemisphere is oxidant-limited, especially during winter (23), but the oxidant-aerosol interactions may show greater sensitivity to emission trends in peak emission regions. Consistent with this, the ratio of the sulfate to hydroxyl burden changes is greater in response to NO_x and CO emissions, generally colocated with SO_2 emissions, than for methane. Our previous results showed a small global mean net impact of all ozone precursors on sulfate forcing despite large regional forcings (24). Although that study used different emissions (a future scenario), those results seem reasonably consistent because the sum of the sulfate responses to all historical ozone precursors in this work is only 0.06 W/m^2.

Our results indicate that NO_x emissions cause a substantial net cooling at all time scales. In contrast, CO emissions cause warming. The 100-year GWP for methane is ~10% greater (~20 to 40%, including AIE) than earlier estimates (5) that neglected interactions between oxidants and aerosols. GWPs for methane and CO would likely be further increased by including ecosystem responses. Decreased emissions of SO_2 warm climate, but including the sulfate-nitrate interaction makes the climate impact less severe than might otherwise have been thought.

There are many limitations to the GWP concept (25). It includes only physical properties, and its definition is equivalent to an unrealistic economic scenario of no discounting through the selected time horizon followed by discounting to zero value thereafter. The 100-year time horizon conventionally chosen strongly reduces the influence of species that are short-lived relative to CO_2. Additionally, GWPs assume that integrated global mean RF is a useful indicator of climate change. Although this is generally reasonable at the global scale, GWP does not take into account the rate of change, and it neglects that the surface temperature response to regionally distributed forcings depends on the location of the RF (26) and that precipitation and circulation responses may be even more sensitive to RF location (27). Along with their dependence on emission timing and location, this makes GWPs particularly ill-suited to very short-lived species such as NO_x, SO_2, or ammonia, although they are more reasonable for longer-lived CO. Inclusion of short-lived species in agreements

alongside long-lived greenhouse gases is thus problematic (28, 29). Hence, emissions of short-lived species have traditionally been, and will likely continue to be, primarily regulated by local- to regional-scale policies targeting air quality. Should policies aim to mitigate climate change by separately targeting short-lived species emissions, however, they should consider effects across gas-phase and aerosol species. Furthermore, assessment of policies affecting particular sectors that emit both long- and short-lived species should include the overall impact rather than simply the impact of long-lived gases.

Despite their limitations, GWPs are widely used for comparison among long-lived gases, forming the basis for worldwide political agreements on climate and carbon trading. Because the latter was a $126 billion/year market in 2008 (30), even small differences in GWPs can have large economic consequences. Our results suggest that gas-aerosol interactions play an important role in methane's GWP, and hence our larger value would allow better optimization of climate change mitigation policies. Methane's GWP may also change with time as air quality regulations alter the background state of tropospheric chemistry. Finally, our results demonstrate that improving our knowledge of aerosol-climate interactions is important not only for better understanding the aerosol contribution to past and future climate change, but even for correctly evaluating the effects of long-lived greenhouse gas emissions from methane-oxidant-aerosol interactions.

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Control of Iron Homeostasis by an Iron-Regulated Ubiquitin Ligase

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Eukaryotic cells require iron for survival and have developed regulatory mechanisms for maintaining appropriate intracellular iron concentrations. The degradation of iron regulatory protein 2 (IRP2) in iron-replete cells is a key event in this pathway, but the E3 ubiquitin ligase responsible for its proteolysis has remained elusive. We found that a SKP1-CUL1-FBXL5 ubiquitin ligase protein complex associates with and promotes the iron-dependent ubiquitination and degradation of IRP2. The F-box substrate adaptor protein FBXL5 was degraded upon iron and oxygen depletion in a process that required an iron-binding hemerythrin-like domain in its N terminus. Thus, iron homeostasis is regulated by a proteolytic pathway that couples IRP2 degradation to intracellular iron levels through the stability and activity of FBXL5.

Iron regulatory proteins 1 and 2 (IRP1 and IRP2) function as RNA-binding proteins during iron-limiting conditions in order to regulate the translation and stability of mRNAs encoding proteins required for iron homeostasis

(1, 2). In iron-replete cells, IRP RNA binding is reduced because of the assembly of a 4Fe-4S cluster in IRP1 (3) and the proteasomal degradation of IRP2 (4–7). Despite the importance of IRP2 in iron metabolism, the ubiquitin ligase