Critical issues in trace gas biogeochemistry and global change

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The atmospheric composition of trace gases and aerosols is determined by the emission of compounds from the marine and terrestrial biospheres, anthropogenic sources and their chemistry and deposition processes. Biogenic emissions depend upon physiological processes and climate, and the atmospheric chemistry is governed by climate and feedbacks involving greenhouse gases themselves. Understanding and predicting the biogeochemistry of trace gases in past, present and future climates therefore demands an interdisciplinary approach integrating across physiology, atmospheric chemistry, physics and meteorology. Here, we highlight critical issues raised by recent findings in all of these key areas to provide a framework for better understanding the past and possible future evolution of the atmosphere. Incorporating recent experimental and observational findings, especially the influence of CO₂ on trace gas emissions from marine algae and terrestrial plants, into earth system models remains a major research priority. As we move towards this goal, archives of the concentration and isotopes of N₂O and CH₄ from polar ice cores extending back over 650 000 years will provide a valuable benchmark for evaluating such models. In the Pre-Quaternary, synthesis of theoretical modelling with geochemical and palaeontological evidence is also uncovering the roles played by trace gases in episodes of abrupt climatic warming and ozone depletion. Finally, observations and palaeorecords across a range of timescales allow assessment of the Earth’s climate sensitivity, a metric influencing our ability to decide what constitutes ‘dangerous’ climate change.

Keywords: atmospheric composition; climate change; methane; isoprene; ozone; palaeoclimates

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1. Introduction

The distinguished Victorian scientist John Tyndall FRS (1820–1893) was one of the first to appreciate that trace gas constituents in the atmosphere act as so-called ‘greenhouse gases’ (GHGs), i.e. they inhibit outgoing long-wave radiation from the Earth’s surface escaping back into space. Tyndall launched his pioneering investigations into this field in the mid-nineteenth century with the invention of a new instrument, the ratio spectrophotometer. The ratio spectrophotometer allowed him, for the first time, to reliably undertake quantitative measurements of the capacity of different gases to absorb infrared radiation; previous investigations of this sort were confined to liquids and solids because they were easier to work with. Tyndall’s main results were published in his momentous 1863 work *Heat considered as a mode of motion*, in which he correctly identified that carbon dioxide, water vapour, methane, nitrous oxide and ozone were all effective absorbers of infrared radiation, whereas oxygen, nitrogen and hydrogen were not. He presciently speculated that variations in the atmospheric concentration of this suite of GHGs might account for ‘all of the mutations of climate which the researches [sic] of the geologists’ reveal’. A century and a half later, the unique historical perspective afforded by ice cores confirmed that trace GHGs exhibit considerable natural variations in concentration nearly instep with glacial–interglacial climate cycles reaching back some 650,000 years (Spahni et al. 2005; Wolff & Spahni 2007).

Current concerns regarding ongoing and probable future global environmental change have focused particularly on the exponential rise in the atmospheric carbon dioxide concentration over the past century due to our combustion of fossil fuels and changes in land use, especially deforestation (Prentice et al. 2001). However, it is increasingly clear that collectively, non-CO₂ GHGs are powerful levers of the global climate system (IPCC 2007), and that their concentrations depend directly or indirectly on gaseous emissions from the marine and terrestrial biospheres, as well as anthropogenic sources (Hansen et al. 2000; Hansen & Sato 2004). This realization has stimulated considerable research effort in the last two decades directed towards improving our understanding not only of the biochemical processes involved in the synthesis and emission of trace gases from the terrestrial and marine biospheres, but also their biogeochemical cycling between the land–ocean–atmosphere system, their atmospheric chemistry and their feedbacks on climate (Brasseur et al. 1999).

Credible projections of global warming in the twenty-first century and beyond, as well as the formulation of options for mitigation strategies, demand a deeper scientific understanding of the processes underlying variations in trace gases evident in short-term instrumental (decadal) and long-term polar ice-core (century to millennia) records (IPCC 2007). This realization has given new urgency to investigations into the fundamental nature of trace gas biogeochemistry and climate change. Here, we critically review key issues dealing with exciting new discoveries and advances made in three related areas: physiological processes; atmospheric chemistry; and climatic feedbacks.
2. Physiological and climatic processes governing the synthesis and emissions of selected critical trace gases

(a) Volatile organic compounds

Plants emit a number of volatile organic compounds (VOCs) that have a substantial impact on the chemistry of the atmosphere. Isoprene (2-methyl-1,3-butadiene, C₅H₈) is one of the most reactive biogenic VOCs. With an estimated annual emission from the terrestrial biosphere of approximately 500–750 Tg (Guenther et al. 1995, 2006) comparable with present-day CH₄ release (500–600 Tg yr⁻¹; Prather & Ehhalt 2001), isoprene is a major player in the oxidative chemistry of the troposphere (Fehsenfeld et al. 1992). It is a precursor for the formation of tropospheric ozone, can decrease the hydroxyl radical (OH) concentration, increase the lifetime of CH₄ and, together with other VOCs, it is involved in secondary organic aerosol (SOA) formation. Aerosols influence climate by acting as cloud condensation nuclei (CCN) and by scattering and absorbing solar radiation. Above Northern European boreal forests, VOCs emitted during late spring and early autumn contribute to substantial SOA formation (Tunved et al. 2006), while recent observations over the Amazonian rainforest (Claeys et al. 2004) and the Southern Ocean (Meskhidze & Nenes 2006) suggest that photo-oxidation of isoprene produces considerable quantities of SOAs, with important implications for radiation budgets.

The climatic significance of isoprene emissions from terrestrial vegetation is clear, and improving our understanding of the biochemical, physiological and climatic controls on isoprene emissions in a changing climate is a research priority (Guenther et al. 1995, 2006; Arneth et al. 2006). Of particular interest in this context is the recent observation from a wide variety of global change experiments, including free-air CO₂ enrichment experiments in North America, indicating that plant growth in elevated CO₂ concentrations strongly inhibits isoprene emissions from leaves (Rosenstiel et al. 2003, 2004; Possell et al. 2005; Monson et al. 2007). The metabolic explanation for this response is uncertain, but it may be that isoprene emissions represent a ‘safety valve’ balancing the carbon flow between the cytosol and the chloroplast (Logan et al. 2000; Rosenstiel et al. 2003, 2004). Sharkey (2005) has shown that the biosynthesis of isoprene confers additional thermotolerance on plants, and this may give such plants a competitive advantage under conditions of higher temperatures. Similarly, isoprene biosynthesis confers a degree of additional protection against ozone damage (Loreto & Fares 2007) and this may provide a competitive advantage as tropospheric composition changes in the future (Lerdau 2007).

These observations and suggestions raise the new challenge of incorporating the direct effect of changes in atmospheric composition into global calculations of isoprene emissions from forest canopies in response to future and past climates when the CO₂ concentration was different from present (Possell et al. 2005; Arneth et al. 2006; Monson et al. 2007). This, in addition to indirect effects arising from changes in vegetation distribution and productivity, is of particular significance for explaining glacial–interglacial changes in the atmospheric CH₄ concentration revealed by ice-core records (Valdes et al. 2005; Kaplan et al. 2006; Harder et al. 2007). Global chemistry calculations indicate that the atmospheric CH₄ concentration is sensitive to estimated reductions in VOC emissions from the terrestrial biosphere under simulated last glacial maximum climates (LGM;
Valdes et al. 2005; Kaplan et al. 2006; Harder et al. 2007). These modelled reductions in VOC emissions during the LGM effectively amplify the chemical sink for CH$_4$ under glacial conditions by lowering OH consumption. However, further investigation is needed to better quantify to what extent any isoprene reductions due to a cooler, drier LGM climate and contractions of tropical and temperate forests are offset by the possible stimulatory effect of a low LGM atmospheric CO$_2$ concentration (180–200 ppmv).

Other factors that give rise to uncertainties in VOC emission rates and their impact on the atmosphere include the recent discovery of a strong circadian rhythm in isoprene emission rates from some plant species (Wilkinson et al. 2006), and the suggestion that a significant fraction of the emitted mass of the most reactive VOCs never leaves the forest canopy owing to its rapid reaction with OH (Di Carlo et al. 2004).

Most work on understanding the role of biogenic VOCs on the chemistry–climate system has been process based, from a plant physiological, atmospheric physics or atmospheric chemistry perspective. However, with the development of new satellite-borne observational instruments and new methods of data retrieval, it is now beginning to be possible to ‘see’ emissions of biogenic VOCs on the regional scale, which should ultimately allow the validation of current process-based emission inventory methods. In particular, space-borne column measurements of formaldehyde (HCHO), a high-yield oxidation product of VOCs, provide continuous quantification of net VOC fluxes on spatial scales of tens to hundreds of square kilometres (Palmer et al. 2003, 2007). Unfortunately, as yet their capacity to rigorously evaluate modelled isoprene and other VOC emission fluxes from terrestrial vegetation is still limited, and the resulting uncertainties feed into global calculations of tropospheric ozone, methane concentration and lifetime, and SOA in past, present and future climates (Monson et al. 2007).

(b) Dimethylsulphide

The marine biota is a major source of dimethylsulphide (DMS), producing it from a precursor compound dimethyl sulphoniopropionate (DMSP). Since the surface oceans are supersaturated with respect to DMS, there is net flux of the gas from the sea to the atmosphere where it is oxidized to a variety of products, including sulphate aerosols which interact directly and indirectly with sunlight to form CCN, major determinants of cloud formation and therefore planetary albedo. DMS production by marine phytoplankton is the main source of CCN and is thought to be involved in climate regulation (Charlson et al. 1987). Perturbation simulations with a coupled ocean–atmosphere climate model, that includes models of oceanic ecosystems and the global sulphur cycle, support this proposed DMS–climate link (Gunson et al. 2006). These model experiments have shown that increased/decreased DMS emissions exert a strong negative feedback on climate via higher/lower albedo caused by changes in cloud formation (Gunson et al. 2006). Furthermore, a negative feedback of DMS on climate is seen in the strong correlation between solar radiation dose and DMS concentration over the surface global ocean (Vallina & Simó 2007).

At present, factors controlling DMS emissions from marine phytoplankton are poorly understood (Liss 2007; Watson & Liss 1998), and this situation limits confident predictions of future (or past) DMS fluxes to the atmosphere.
Global-scale modelling studies suggesting a small increase in oceanic DMS production in response to a warm $2\times CO_2$ climate (Bopp et al. 2003; Gabric et al. 2004) depend heavily on a limited database of observed DMS fluxes in the modern ocean (e.g. Kettle et al. 1999). The urgent need to underpin these sorts of calculations with the development and application of process-based models derived from experimental evidence is obvious. Moreover, this class of models may need to account for limited experimental observations that elevated atmospheric CO$_2$ concentrations unexpectedly suppress DMS emissions (Sunda et al. 2002). If this turns out to be a general response in marine phytoplankton, suppression of DMS fluxes in a future high CO$_2$ world could diminish the strength of a negative feedback mechanism that helps lower planetary temperatures.

(c) Methane

Atmospheric methane is a potent GHG; on a per-molecule basis, it is more than 20 times as powerful as CO$_2$. Increases in CH$_4$ emissions cause tropospheric O$_3$ concentrations to rise and lower the oxidizing capacity of the troposphere by consuming OH radicals. Approximately two-thirds of the global emissions are from natural and anthropogenic (mainly rice agriculture) wetlands, and because CH$_4$ release from these systems responds strongly to temperature and moisture, CH$_4$ has the capacity to amplify global warming. Its global concentration is also influenced by biogenic VOC emissions (Monson et al. 2007). Components of the global methane cycle are far from comprehensively understood (Bousquet et al. 2006) and recent findings have called into question both the identity and magnitude of several important source terms. Analyses of observations from the space-borne SCIAMACHY instrument have led to claims of an unexpectedly large tropical source of methane (Frankenberg et al. 2005) and, as yet uncorroborated, experimental evidence suggests that plants may emit methane aerobically (Keppler et al. 2006). Longer-term records also pose significant challenges. The 2000-year-long record of CH$_4$ and $\delta^{13}$C–CH$_4$ from an Antarctic ice core has revealed unexpectedly large changes in the global methane budget during the late pre-industrial period that are difficult to explain from known processes (Ferretti et al. 2005).

Methane emissions from the high northern latitudes are principally from wetlands and the seasonal thawing of permafrost. In the subarctic, detailed studies of mire ecosystems have shown that historical changes in permafrost and vegetation between 1970 and 2000 are associated with increases in CH$_4$ emissions of 20–60% (Christensen et al. 2004). However, determining the overall GHG budget of a subarctic ecosystem requires the difficult-to-achieve ideal of accounting for net land–atmosphere CO$_2$ and CH$_4$ exchanges, in addition to the lateral fluxes of other carbon species like dissolved inorganic and particulate/dissolved organic forms across a heterogeneous landscape. Christensen et al. (2007) take the first step towards quantifying landscape-scale carbon cycle feedbacks on climate for a mosaic catchment of heath, pine and birch forest, lakes and alpine ecosystems in Northern Sweden. According to their analysis, this ecosystem is presently a small net sink for carbon, CO$_2$ uptake in forests offsetting CH$_4$ emissions from mires. But the current balance is delicately poised, with the capacity of forests to sequester CO$_2$ being limited and the high sensitivity of CH$_4$ emissions from mires and melting permafrost to climatic warming (Christensen et al. 2007).
Continued careful long-term monitoring in the high latitudes is therefore required to diagnose possible shifts in GHG fluxes in response to ongoing atmospheric and climatic change. These sorts of careful field campaigns are exemplified by measurements of CH₄ emitted from thaw lakes owing to bacterial decomposition of organic matter previously sequestered in permafrost and released in thaw lakes (Walter et al. 2006, 2007). The magnitude of this previously underappreciated flux is significant and leads to its recognition as a new and important source term in the global CH₄ budget. Walter et al. (2007) calculate that the total annual flux from lakes in the Northern Hemisphere may be as large as 24.4 Tg CH₄ yr⁻¹, and future warming could significantly increase this flux.

3. The atmospheric chemistry of trace gases

Trace gases either influence climate directly by absorbing long-wave radiation emitted from the Earth’s surface and/or indirectly via their involvement in the atmospheric chemistry of GHGs. The significance of the latter interactions is effectively assessed using three-dimensional global atmospheric chemistry models (Prather & Ehhalt 2001), although important questions are raised about the meaning of a ‘lifetime’ of a gas by simplified mathematical linearization of the chemistry used in these models (Prather 2007).

The emissions of biogenic VOCs like isoprene and organohalides by the marine biota are of particular significance in the context of climate–chemistry feedbacks. Organic biogenic halocarbons, like methyl bromide, decompose to release inorganic bromine which influences the contemporary O₃ budget (Yang et al. 2005). Both natural emissions of bromine from the oceans and isoprene from the terrestrial biosphere are sensitive to climate, indicating that chemistry–climate feedbacks with future warming are important to quantify, even if the fluxes in a future ‘greenhouse’ world are uncertain and difficult to estimate. Detailed assessment of future releases of bromine from the oceans on tropospheric O₃ lag those undertaken for biogenic VOCs (Yang et al. 2005; Pyle et al. 2007). However, future changes in atmospheric circulation may increase the concentration of reactive inorganic bromine compounds in the lower stratosphere, with the potential for O₃ destruction (Yang et al. 2005; Pyle et al. 2007).

Sensitivity calculations with scenarios for the projected rise in anthropogenic emissions of VOCs and NOₓ for 2100 suggest increased surface O₃ concentrations and a deteriorating air quality. This arises due to the combined effects of chemistry and a strengthening of Brewer–Dobson circulation substantially increasing the net influx of O₃ from the stratosphere into the troposphere (Pyle et al. 2007). One emerging feature of these calculations is that different scenarios lead to regional differences in O₃ changes over Europe, suggesting that continued O₃ measurements might allow attribution of anthropogenic environmental change. Introducing biogenic isoprene emissions into the calculations complicates the picture further by revealing the sign of significant future changes in surface O₃ depends on the background chemical regime (Pyle et al. 2007).

Aerosols influence climate through their effects on cloud processes and the solar radiation transfer, yet they are one feature of the real world not yet adequately represented in chemistry models. In the marine realm, iodine-containing emissions
from algae can be converted into aerosol particles (O’Dowd et al. 2002) and thus could hold considerable climatic significance, because of the lighter colour of the aerosols relative to the darker ocean (O’Dowd & de Leeuw 2007). Factors controlling primary (i.e. sea spray) and secondary (i.e. oxidative chemistry) marine aerosol production are being elucidated and a key finding is that attention must be given to both physical and chemical processes, like the photolysis of iodinated compounds (O’Dowd & de Leeuw 2007).

4. Trace gases and palaeoclimates

The feedback of GHGs and chemistry on climate, directly and/or indirectly via organic aerosol production, is a major feature of the earth system-governing climate. The nature of this feedback can be assessed directly for the Quaternary by using archives of variations in stable GHGs recovered by analysing ancient samples of air closed-off from the atmosphere in ice (Spahni et al. 2005; Wolff & Spahni 2007). Remarkable new records of N₂O and CH₄ from polar cores extend back over the past 650,000 years and illustrate unequivocally that the current concentrations of both trace gases are unprecedented in recent Earth history. At 1730 ppbv, the current (2005) global CH₄ concentration is three times a typical interglacial value (approx. 400–500 ppbv), while the modern N₂O concentration of 319 ppbv (Jiang et al. 2007) exceeds a typical interglacial value by approximately 100 ppbv. Analyses of the covariation of GHGs and palaeoclimate from the EPICA Dome C record shows methane variations have tracked glacial–interglacial climate change for the last eight glacial cycles (Spahni et al. 2005; Wolff & Spahni 2007). The response of N₂O is more complex but exhibits a periodicity tracking millennial-scale Dansgaard–Oeschger warming events (Flückiger et al. 2004; Spahni et al. 2005; Wolff & Spahni 2007).

Critical constraints on interpreting the historical records of both gases are provided by the isotopic composition of both N₂O (δ¹⁵N) and CH₄ (δ¹³CH₄). In particular, the multiple isotope signals (hydrogen (δD–CH₄), carbon (δ¹³CH₄) and radiogenic ¹⁴CH₄) of gases in ice may provide clues to identify the processes underlying past changes in the tropospheric CH₄ budget (Schaefer et al. 2006; Whiticar & Schaefer 2007).

The role of trace gases in Pre-Quaternary Earth history is more difficult to decipher and is either inferred from earth system modelling (Lamarque et al. 2006) or from the geochemical consequences of massive releases of gases like CH₄ (Dickens et al. 1995) and H₂S (Kump et al. 2005). The Palaeocene–Eocene thermal maximum (PETM, approx. 55 Ma) represents a well-documented brief episode of prominent global warming when global temperatures rose abruptly by more than 5°C in less than 10 kyr (Sluijs et al. 2006) due to a large addition of GHGs to the ocean–atmosphere system. As far as we know, the rate and degree of warming at the PETM is unprecedented in Earth history. The event is marked by a striking large synchronous negative δ¹³C excursion (CIE, more than 2.5‰) in carbonate and organic matter deposited in terrestrial, shallow marine and deep marine environments (Kennett & Stott 1991; Koch et al. 1992; Dickens et al. 1995). The only satisfactory explanation for the prominent CIE in the entire exogenic carbon pool is the sudden addition of a large quantity of
isotopically light carbon (\(^{13}\)C deficient) to the ocean or atmosphere from large reservoirs of organic material, because biological processes preferentially incorporate \(^{12}\)C.

The PETM has attracted considerable interest, not least because it probably involved the release of more than 4500 Gt C, a mass similar to the total amount of carbon stored as fossil fuels (3000–4000 Gt C), and which may be anthropogenically released in the coming centuries (Zachos et al. 2005). It also offers an intriguing analogue for investigating the behaviour of the earth system to the massive input of GHGs. A generalized working scenario involves gradual warming, perhaps driven by CO\(_2\) release from mid-ocean ridge volcanism, which eventually breaches some threshold triggering catastrophic clathrate destabilization, CH\(_4\) release and further warming (Zachos et al. 2005). This, in turn, may have entrained a number of additional carbon cycle feedbacks including the oxidation of terrestrial (Kurtz et al. 2003) and marine (Higgins & Schrag 2006) organic carbon sources that added more carbon to the atmosphere and the accelerated warming.

Characterizing the nature of the source(s) of carbon added to the atmospheric and surface ocean pools is a major issue. A key constraint is the rate of carbon release. Isotopic analysis of individual mixed-layer planktonic foraminifera shell records show a single-step CIE with no transitional values, regardless of location, water depth or depositional facies (Zachos et al. 2007). This suggests that the \(\delta^{13}\)C of atmospheric and surface ocean carbon pools exchanged rapidly within a few 100 000 years. Furthermore, agreement of pelagic and coastal \(\delta^{13}\)C records indicates that the actual magnitude of the CIE has been underestimated from studies of bulk carbon or benthic foraminifera, and may be as large as 4‰ (Zachos et al. 2007). These results place new constraints on the nature and origin of the carbon cycle perturbation (Pagani et al. 2006), and highlight the pressing need to understand better the magnitude of the clathrate CH\(_4\) reservoir in the modern oceans and its sensitivity to climate change (Buffett & Archer 2004).

Volcanic eruptions inject substantial amounts of climate-modifying trace gases and aerosols into the atmosphere sometimes over sustained periods lasting for tens or hundreds of thousands of years at a time (e.g. Thordarson & Self 1996). The potential for gases released by the massive and unusually explosive Siberian flood basalt eruptions at the end of the Permian, 251 Myr ago, to disrupt the chemistry and transport of stratospheric O\(_3\) is only now being considered (Beerling et al. 2007), prompted by palaeobotanical claims for a global mutagenesis event at this time (Visscher et al. 2004). According to model calculations, the extent of damage to the O\(_3\) layer is dependent upon the duration of the eruption, the nature of the underlying geology and high CO\(_2\) Permian atmosphere cooling the stratosphere by 10 K to allow extensive polar stratospheric cloud formation catalysing O\(_3\) destruction (Beerling et al. 2007).

Further back in time in the Archean, the biogenic flux of what is today a trace gas, CH\(_4\), was climatically far more significant before oxygenation of the Earth’s atmosphere some 2.5 Gyr ago (Claire et al. 2006; Catling et al. 2007). An anoxic atmosphere may have allowed the atmospheric CH\(_4\) concentration to have reached 200 to 3000 ppmv. In an anoxic environment, the O\(_3\) layer shielding surface-dwelling life forms from UV radiation is largely absent and this raises the question of how it influenced the colonization of land by early life...
Calculations indicate that contrary to initial expectations, this may not have represented a significant environmental barrier to life colonizing the landmasses of Archean Earth and that a layer of just approximately 2–4 mm of simple minerals would have been sufficient to provide photosynthetic microbes with effective protection against a ‘worse case’ scenario for UV fluxes.

5. Earth’s climate sensitivity and ‘dangerous’ climate change

Model-based predictions of future global warming, and assessments of GHG global warming potentials (Shine et al. 2007), hinge on an estimate of the Earth’s climate sensitivity, defined as the amount of warming resulting from an increase in radiative forcing, usually due to a doubling in CO₂. Climate sensitivity can be calculated from observed past or current climatic warming and the estimated magnitude of the forcing. The current net forcing is 1.6 W m⁻² (range 0.6–2.4 W m⁻²) calculated as the difference between the positive forcing due to the rise in GHGs and the negative forcing arising from the cooling effects of aerosols (IPCC 2007). It implies an estimated climate sensitivity to a doubling of CO₂ of 1.9–6.2 K (Andreae et al. 2005), with aerosols contributing the largest uncertainty in such calculations (Andreae 2007 a). The realization that our current atmosphere loaded with aerosols is offering a degree of ‘climate protection’ from the GHGs implies that the Earth’s real climate sensitivity may lie towards the upper end of the range (Andreae et al. 2005). Better resolving the importance of aerosols is therefore crucial but requires knowledge of the aerosol content of the atmosphere before significant human activity to make a reasonable assessment of the increase subsequently, a quantity difficult to estimate (Andreae 2007 b).

Palaeorecords also offer a means of deriving the Earth’s climate sensitivity for comparison with estimates derived from observations of recent (century to millennia) climate change (e.g. Hergerl et al. 2006). Those derived from the PETM event suggest that it lies towards the higher end of the above range, and higher than those currently found in general circulation models, with estimates from 4°C (Higgins & Schrag 2006) up to 6.8–7.8°C per doubling of atmospheric CO₂ (Pagani et al. 2006). These analyses and those of ice-core records of GHG, sea level change and ice volume over glacial–interglacial cycles (Hansen et al. 2007) indicate that the Earth’s climate could be highly sensitive to global forcings. Current analyses suggest projected increases in globally averaged surface air warming up to 4°C (range 2.4–6.4°C) by the end of the twenty-first century (IPCC 2007). This could far exceed what constitutes dangerous climate change, largely because all the detailed factors governing ice-sheet melting are not yet considered in the models. If ice sheets are vulnerable to catastrophic melting and disintegration, as suggested by the palaeoevidence, then they could entrain a positive high latitude climate feedback by reducing planetary albedo and amplifying future warming (Hansen et al. 2007). Collectively, a high sensitivity of the Earth’s climate system to global forcings, coupled with a positive climate feedback due to ice-sheet melting, and a diminishing degree of climate protection from aerosols point to the urgent need to simultaneously reduce CO₂ emissions and those of non-CO₂ GHGs and black carbon aerosols (Hansen et al. 2000, 2007; Hansen & Sato 2004).

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Both direct and indirect evidence points unequivocally to the fact that many trace gases are now present in the atmosphere in concentrations unprecedented during the last 650,000 years. Many of these gases (e.g. methane) are radiatively active and play an important direct role in the Earth’s climate system, while others (e.g. isoprene) have indirect effects on climate through their role in mediating the oxidant budget of the atmosphere, and because they can oxidize to form radiatively active particles. In addition, it is now clear that the biogeochemistry of some of these gases are affected by climate (in the simplest example, biogenic VOC and anaerobic methane emission rates are both directly influenced by temperature) leading to the possibilities of strong positive feedbacks between the biogeochemical cycles of trace gases and climate. As the Earth enters a period of very rapid anthropogenically produced climate change, with the possibility of dangerous climate change occurring in the next few decades, understanding the biogeochemistry of trace gases and their role in the Earth’s climate system remains a critical research priority.

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