Soil Greenhouse Gas Emissions and Their Mitigation

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Glossary

Carbon sequestration   Carbon storage in soil and plants.

Climate forcing   The difference between solar energy reaching the earth's surface and energy (both light and heat) radiated back to space. A positive forcing warms the biosphere.

Gas flux   The movement of a gas molecule into or out of an ecosystem.

Life cycle assessment   A full accounting of the environmental consequences of a product from creation to disposal.

Mitigation   Reducing the emission of greenhouse gases to alleviate the severity of climate change harm.

Radiative energy   Energy transmitted by electromagnetic waves.

Sources and sinks   Places within the biosphere where carbon, nitrous oxide, and other molecules are either released (source) or stored (sink).

Introduction

Greenhouse gases (GHGs) make up a tiny proportion of today's atmosphere but make life on earth possible. In their absence, the light absorbed by the earth's surface and re-emitted as long-wave radiation (heat) would be immediately lost to space. Instead, a substantial fraction of the 161 W m^{-2} absorbed and reemitted by the earth's surface is temporarily held in the atmosphere, warming the biosphere to an inhabitable temperature. In the absence of GHGs the earth's surface would be frozen with an average surface temperature of -18 °C (Ramanathan, 1988).

It thus stands to reason that changes in atmospheric GHG concentrations will lead to changes in the earth's surface temperature, and, although radiative feedbacks make the story more complex, in general this is in fact the case. As GHG concentrations have increased in the atmosphere, the biosphere has correspondingly warmed (IPCC, 2007). Almost all of the recent increase in global surface temperatures can be attributed to increases in GHG concentrations (IPCC, 2007).

In what way has agriculture played a role in GHG changes? Of the six major radiative sources of climate forcing since 1750 (Figure 1), agriculture has directly influenced five: carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), tropospheric ozone (O_3), and black carbon (IPCC, 2001). These sources are together responsible for approximately 80% of contemporary climate forcing, and agricultural activities affect some GHGs more than others. Overall, agriculture is estimated to directly contribute 10–14% of total global anthropogenic GHG emissions annually (Smith *et al.*, 2007; Barker *et al.*, 2007). This includes N_2O emissions from soil (38% of agriculture's direct contribution) and manure (7%), enteric emissions of CH_4 from ruminant animals (32%), and N_2O and CH_4 from biomass burning (12%).

Not included in this estimate are GHGs from land-cover change due to agricultural expansion; the manufacture of agricultural inputs such as fertilizer and pesticides; or post-harvest activities such as processing, transport, refrigeration, and food management. Land-cover change emits both CO_2 and N_2O to the atmosphere, and in total is responsible for

another 12–17% of global GHG emissions (Barker *et al.*, 2007; van der Werf *et al.*, 2009). The manufacture of nitrogen fertilizers and pesticides together adds another 0.6–1.5% to agriculture's global GHG footprint (calculated from Vermeulen *et al.*, 2012), and postproduction activities add at a minimum another 3% (Vermeulen *et al.*, 2012). Including these sources brings agriculture's GHG footprint to 26–36% of all anthropogenic GHG emissions.

The purpose of this article is to describe the ways that agricultural soils have contributed to the GHG burden of the atmosphere, and – as importantly – to show how future agricultural management might mitigate the GHG build-up and thereby contribute to climate stabilization.

In the pages that follow are descriptions of agricultural sources and sinks of the major GHGs affected by agriculture and potential mitigation strategies related to soil management. Because agriculture is a systems enterprise in that all of its parts are interconnected, mitigation must also be approached from a systems and not just a soils standpoint. The penultimate section presents the case for a life cycle assessment of entire agricultural systems in the context of a Midwest US
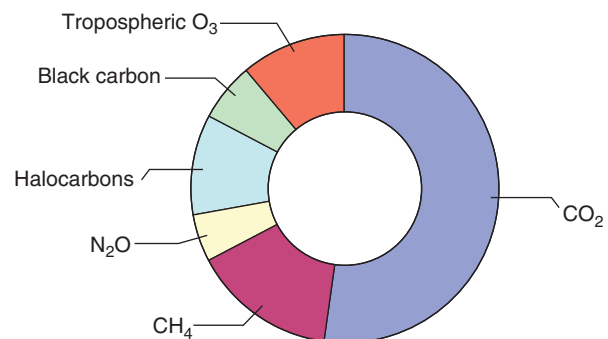
Figure 1   Global sources of atmospheric radiative forcing over the period 1750–2005. Drawn from data in IPCC, 2007. Climate change 2007: The physical science basis. In: Solomon, S., Qin, D., Manning, M., *et al.* (Eds.), Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. New York, NY: Cambridge University Press.

Table 1   Global warming potentials (GWPs) for the major greenhouse gases affected by agriculture

Greenhouse gas[a]	Atmospheric lifetime (years)	GWP		
		20 Years	100 Years	500 Years
Carbon dioxide (CO_2)	Variable	1	1	1
Methane (CH_4)	12	72	25	8
Nitrous oxide (N_2O)	114	289	298	153

[a]Short-lived and heterogeneously distributed gases such as tropospheric ozone and water vapor are too variable to be calculated.

Source: Data extracted from IPCC, 2007. Climate change 2007: The physical science basis. In: Solomon, S., Qin, D., Manning, M., *et al.* (Eds.), Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. New York, NY: Cambridge University Press.

cropping system. Finally, future mitigation is discussed in the context of biofuels and carbon capture and sequestration technologies.

Nitrous Oxide

The significance of N_2O stems not from its atmospheric mass, which is small, but from its high global warming potential (GWP). GWP is a measure of the capacity of a well-mixed gas to trap heat once emitted to the atmosphere (IPCC, 2001). Its value is relative to a reference gas, by convention CO_2, and its magnitude depends on both its efficiency as a GHG and its atmospheric lifetime – long-lived gases will have high GWPs even if their heat trapping efficiency is relatively low. Nitrous oxide has a GWP of approximately 300 over a 100-year time horizon (Table 1), meaning that it traps heat in the atmosphere 300 time more effectively than CO_2. Thus, a kilogram of N_2O emitted to the atmosphere is equivalent to approximately 300 kg of CO_2 emitted at the same time. Conversely, avoiding the emission of 1 kg of N_2O is equivalent to sequestering approximately 300 kg of CO_2.

Sources and Sinks of Nitrous Oxide in Agricultural Soils

Agriculture is responsible for approximately 84% of the global anthropogenic N_2O flux of 8.1 Tg yr^{-1} and approximately 38% of the total global flux (anthropogenic+natural sources) of 17.7 Tg yr^{-1} (**Figure 2(a)**; Mosier *et al.*, 1998a; Robertson, 2004). A small portion (0.5 Tg yr^{-1}) of the N_2O flux is due to biomass burning, primarily in the tropics and subtropics when crop residues are burned and when new land is cleared for row crops and pastures. A larger amount (2.1 Tg yr^{-1}) is associated with microbial activity during animal waste treatment. Nitrification and denitrification, the primary microbial pathways for N_2O production, occur readily in manure and other animal waste products when conditions are right. A still larger source of anthropogenic N_2O is agricultural soils, which emit approximately 4.2 Tg N_2O per year globally or approximately 52% of the total anthropogenic N_2O source. Nitrification and denitrification also occur readily in soils, where their rates are stimulated by the abundant nitrogen that cycles rapidly in virtually all cropped ecosystems.

During nitrification, ammonium (NH_4^+) added as fertilizer or mineralized from soil organic matter, crop residues, or other organic inputs is oxidized by nitrifiers to nitrite

(NO_2^-) and eventually to nitrate (NO_3^-) in a series of reactions that can also produce N_2O.

$$NH_4^+ \longrightarrow NH_2OH \longrightarrow NO_2^- \longrightarrow NO_3^- \qquad [1]$$
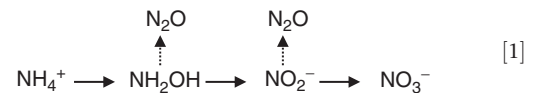
Some N_2O is produced from the chemical decomposition of hydroxylamine (NH_2OH), an intermediate formed during the oxidation of NH_4^+ to NO_2^-. Significantly more N_2O is produced by nitrifiers under low oxygen conditions, when they use NO_2^- as an electron acceptor, a pathway they have in common with denitrifiers (Robertson and Groffman, 2007).

Denitrifiers use NO_3^- and other oxidized forms of nitrogen as an electron acceptor during cellular respiration when oxygen is in limited supply. Nitrous oxide is an intermediate product that can either escape to the atmosphere or be further reduced to N_2 gas by the enzyme N_2O reductase, thereby closing the global nitrogen cycle.

$$2NO_3^- \longrightarrow 2NO_2^- \longrightarrow 2NO \longrightarrow N_2O \longrightarrow N_2 \qquad [2]$$
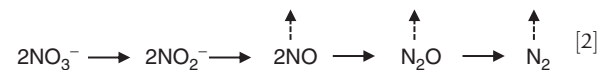
Each transformation step is mediated by a specific inducible enzyme, such that delays in the production of one enzyme can lead to the accumulation and release to the environment of its substrate: N_2O in the case of delays in N_2O reductase formation (Bergsma *et al.*, 2002; Robertson and Groffman, 2007). Theoretically, atmospheric N_2O can also diffuse into cells and be reduced directly to N_2, though in practice this appears to be a negligible global sink for N_2O: rarely are negative soil N_2O fluxes detected.

Soil N_2O fluxes are thus largely controlled by the same environmental factors that control nitrification and denitrification: Soil temperature and moisture as they affect microbial activity in general and the diffusion of oxygen to microsites where nitrification and denitrification occur; soil carbon as it affects the availability of electron donors to heterotrophic denitrifiers as well as the consumption of oxygen in soil microsites; and the availability of soil inorganic nitrogen (NH_4^+ for nitrifiers and NO_3^- for denitrifiers). Soil inorganic nitrogen is derived from the mineralization of soil organic matter and from the addition of synthetic or organic fertilizers and animal manure. Soil structure also plays an important role in N_2O production in that sandy or otherwise poorly structured soils have fewer
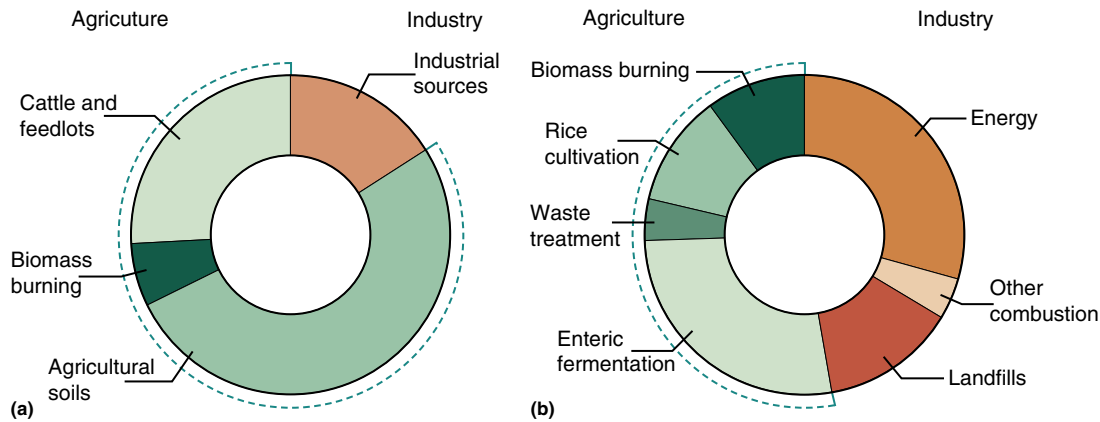
Figure 2   Anthropogenic sources of (a) nitrous oxide and (b) methane. Redrawn from Robertson, G.P., 2004. Abatement of nitrous oxide, methane, and the other non-CO_2 greenhouse gases: The need for a systems approach. In: Field, C.B., Raupach, M.R. (Eds.), The Global Carbon Cycle. Washington, DC: Island Press, pp. 493–506 and based primarily on data in IPCC, 2001. Climate change 2001: The scientific basis. In: Houghton, J.T., Ding, Y., Griggs, D.J., *et al.* (Eds.), Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change. New York, NY: Cambridge University Press.

anaerobic microsites than well-structured or heavier soils with higher clay content.

In upland soils, denitrification occurs primarily within soil aggregates (Sexstone *et al.*, 1985) or within soil organic matter particles (Parkin, 1987) where ample carbon fuels oxygen consumption at rates greater than oxygen can be immediately replaced via diffusion from the bulk soil atmosphere. Diffusion of oxygen is substantially inhibited by the water film that surrounds biologically active soil aggregates and particles. Denitrification also occurs in submerged low-oxygen wetland soils, riparian zones, and stream and lake sediments, and insofar as these habitats receive nitrate leached from cropped soils, agriculture is also a major source of N_2O from these environments (Ostrom *et al.*, 2002; Whitmire and Hamilton, 2005; Beaulieu *et al.*, 2011).

It is not surprising, then, that arable soils, managed to cycle carbon and nitrogen rapidly in order to support high crop productivity, produce large quantities of N_2O particularly in mesic or irrigated environments. That for any given cropping system N_2O fluxes are directly related to nitrogen inputs should also come as no surprise: typically fluxes are highest following fertilization (**Figure 3**) or the incorporation of nitrogen-rich residues such as leguminous cover crops into soil. Production of nitrous oxide during these periods can dominate the annual soil flux. Moreover, the rate of nitrogen fertilizer addition is generally the best predictor of N_2O flux in both cropped and pasture systems: On average, approximately 1% of the nitrogen applied to cropland is emitted as N_2O–N (Bouwman *et al.*, 2002) and this emission factor is the basis for the Intergovernmental Panel on Climate Change (IPCC) GHG inventory estimates of N_2O flux from cropped soils (De Klein *et al.*, 2006). Recent evidence suggests that this value will be high for nitrogen fertilizer levels that exceed crop nitrogen needs (McSwiney and Robertson, 2005; Hoben *et al.*, 2011) – in these cases the excess nitrogen available to nitrifiers and denitrifiers will result in still higher N_2O fluxes.
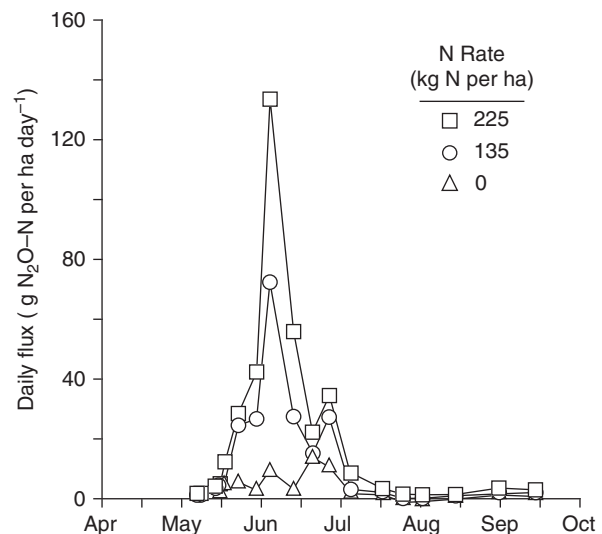
Figure 3   Nitrous oxide (N_2O) flux response to fertilizer addition. Reproduced from Hoben, J.P., Gehl, R.J., Millar, N., Grace, P.R., Robertson, G.P., 2011. Nonlinear nitrous oxide (N_2O) response to nitrogen fertilizer in on-farm corn crops of the US Midwest. Global Change Biology 17, 1140–1152.

Mitigation of Nitrous Oxide in Agricultural Soils

Because there are no significant environmental sinks for N_2O, mitigation is best pursued by avoiding or attenuating known N_2O sources. For agriculture, this means slowing the microbial conversion of inorganic nitrogen (NH_4^+, NO_3^-) to N_2O by altering one or more of the environmental factors that affect the conversion – carbon, oxygen, and soil nitrogen – or by biochemically inhibiting these pathways using soil additives.

Nitrification, for example, can be managed to reduce N_2O production during manure handling by creating an anaerobic environment that suppresses nitrifier metabolism. By storing

manure in anaerobic lagoons, nitrification will be inhibited by the lack of oxygen. Although anaerobic conditions typically promote denitrification, without the nitrate provided by nitrifiers this pathway will be substrate-limited and denitrifiers will produce less N_2O.

In soils, N_2O mitigation is more complex. Nitrification is necessary in order to provide nitrate to plants, and generally occurs very quickly in arable soils (Robertson and Groffman, 2007) whether the source of ammonium is mineralized soil organic matter, manure, or ammonium-based fertilizers such as urea or anhydrous ammonia. In some soils, nitrification can be inhibited with commercial chemical additives such as nitrapyrin and dicyandiamide. These compounds slow ammonium oxidation and thus mitigation is achieved both by reducing nitrifier-derived N_2O and reducing the nitrate supply to denitrifiers. Field experiments suggest that N_2O fluxes can be reduced by inhibitors to 40% in some soils (Akiyama et al., 2010; Halvorson et al., 2010), though very little in others (e.g., Parkin and Hatfield, 2010). In some cases, the reduction may be simply delayed production – nitrification is inhibited, not prevented, such that added ammonium will eventually be nitrified and hence available for N_2O production. But if less fertilizer is applied because plant fertilizer-use efficiency is improved, then the avoided N_2O loss will be permanent. Likewise, theory suggests that urease inhibitors ought also to be effective for reducing N_2O fluxes by slowing the conversion of urea to ammonium, but results of field trials are even more mixed than those for nitrification inhibitors (Akiyama et al., 2010; cf. Halvorson et al., 2010).

A more direct means for N_2O mitigation in agricultural soils is more precise nitrogen fertilizer management (Millar et al., 2010), i.e., reducing the availability of excess inorganic nitrogen to nitrifiers and denitrifiers. Because the best predictor of N_2O fluxes from soils is nitrogen availability, it makes sense that the most effective mitigation strategy is to reduce fertilizer additions to the lowest levels necessary to ensure optimal crop yields. Millar et al. (2010) suggested that N_2O fluxes from agricultural soils could be reduced 50% if farmers adopted more conservative fertilizer practices.

How can fertilizers be used more conservatively? Four factors contribute most importantly to fertilizer-use efficiency: fertilizer rate, placement, timing, and formulation. Rates of fertilizer application vary widely across the globe even for the same crop. In China, rates are exceedingly high (Vitousek et al., 2009) and not much based on expected yields. In North America, nitrogen fertilizer rates are typically based on a yield-goal approach wherein a projected yield is multiplied by a standard factor to provide a recommended nitrogen rate, sometimes debited for nitrogen credits provided by a preceding legume crop, manure application, or soil nitrogen tests. However, even this approach is not very conservative. A more robust Maximum Return to Nitrogen (MRTN) approach (Sawyer et al., 2006) is instead based on nitrogen field trails, fertilizer costs, and commodity prices. Recommended rates for a particular region are based on the asymptotic response of that crop to incremental nitrogen additions. Data from hundreds of field trials are used to identify the nitrogen rate at which the cost of further nitrogen fertilizer additions is not paid for by the economic return of additional yield. Though MRTN is now the university-recommended approach for corn in seven Midwest US states, it is not yet widely adopted (Stuart et al., 2012). Quantitative crop models such as Adapt-N (Melkonian et al., 2007) and Maize-N (Setiyono et al., 2011) can provide even more precise nitrogen recommendations based on still more localized climate and soils information.

Fertilizer placement refers to putting nitrogen fertilizer where it is most likely to be taken up by nearby plants or kept from volatilizing to the atmosphere as ammonia (NH_3). Subsurface banding, for example, can achieve higher fertilizer-use efficiencies, as can nitrogen application calibrated to the spatial distribution of crop nitrogen needs across a field. This spatial pattern of nitrogen needs can be estimated from the spatial patterns of prior crop yields across the field – readily provided by yield monitors on modern grain combines. Or nitrogen needs can be estimated in real time during the growing season using spectral sensors that indicate a growing crop's nitrogen stress based on leaf chlorophyll content (Raun et al., 2002; Gehl and Boring, 2011). The optimal placement of fertilizer nitrogen across a cropped field can substantially reduce nitrogen fertilizer rates without affecting crop yields (e.g., Scharf et al., 2005; Mamo et al., 2003).

The timing of nitrogen fertilizer application can also affect nitrogen fertilizer-use efficiency and, by inference, N_2O fluxes. Adding nitrogen closer to the time of plant nitrogen need will leave less nitrogen available in the soil for N_2O production. This can be achieved by avoiding fall fertilization of spring planted crops, by splitting fertilizer applications into smaller portions added more frequently (e.g., some at planting and the remainder after the plants are growing), or by adding fertilizer to irrigation water.

Fertilizer formulation can also affect N_2O fluxes, though the effects are not consistent among the major fertilizer types such as anhydrous ammonia, urea, manure, or urea ammonium nitrate. For this reason, the IPCC GHG inventory methods make no distinctions among fertilizer types (De Klein et al., 2006), nor do other mitigation protocols (Millar et al., 2010, 2012; CAR, 2012). Slow-release formulations, however, are designed to delay the release of nitrogen to the soil solution by coating fertilizer particles with sulfur, polymers, or other temperature- or moisture-sensitive compounds, and to the extent that they can improve fertilizer-use efficiency – and thereby reduce fertilizer rates for the same yield – they ought to reduce N_2O fluxes. There are currently too few successful N_2O field trials to judge their effectiveness.

Mitigation of N_2O through carbon market cap and trade programs has only recently become available with the 2012 approvals of nitrogen management protocols by the major carbon registries. The American Carbon Registry (ACR), Verified Carbon Standard (VCS), and Climate Action Reserve (CAR) have approved methodologies that allow payments to farmers for reducing N_2O emissions by changing fertilizer practices. In one of ACR's methods, the protocol is based on the application of a complex quantitative N_2O model not thoroughly field tested. In other cases (ACR, CAR, and VCS), the method is based on fertilizer rate reductions by whatever means a farmer chooses to use – by more precisely predicting fertilizer need (e.g., using the MRTN rather than yield-goal fertilizer estimators), or the use of precision application technologies, nitrification inhibitors, slow-release formulations, or other strategies that reduce nitrogen fertilizer use without

affecting crop yield. Avoided N_2O emissions are credited using the relationships between nitrogen fertilizer use and N_2O emission noted above – either linear as for the IPCC methodology (De Klein et al., 2006) or nonlinear as for more recent analyses (Millar et al., 2010). Avoided N_2O, determined as the difference between estimated past emissions during a 5-year baseline period and estimated emissions during the credit period, is multiplied by its GWP (298) to provide a saleable CO_2 credit that can then be traded on carbon markets (Millar et al., 2010).
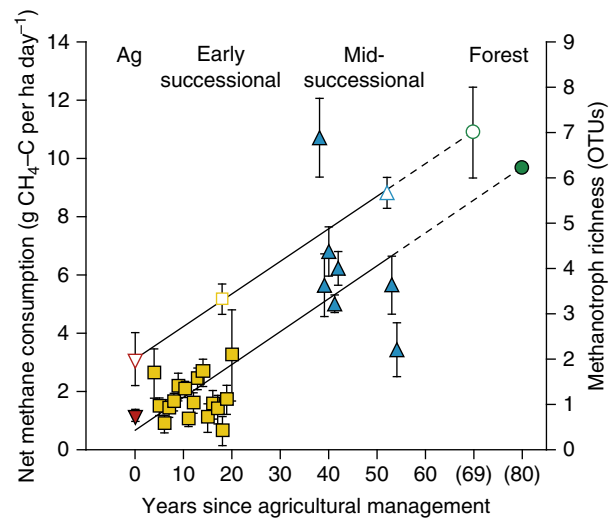
Methane

Globally, agriculture is responsible for approximately 53% of the total anthropogenic CH_4 flux of 344 Tg CH_4 per year (Figure 2(b)), itself approximately 58% of the total global CH_4 flux of 598 Tg CH_4 per year (Mosier et al., 1998b; Sass et al., 1999; IPCC, 2001; Robertson, 2004). Agricultural sources of CH_4 include enteric fermentation by anaerobic bacteria within ruminant animals such as cattle and sheep, which accounts for approximately 52% of agricultural emissions; methanogenesis by anaerobic bacteria in submerged soils during rice cultivation (approximately 19% of agricultural emissions); biomass burning when crop residues are burned or land is cleared for agricultural production (approximately 19% of agricultural emissions); and methanogenesis during the handling and treatment of animal wastes (approximately 10%).

Sources and Sinks of Methane in Agricultural Soils

Biological CH_4 production is the result of methanogenesis carried out by methanogens – a class of microbes that inhabit anaerobic environments such as submerged soils and cow rumens and derive their energy from substrates formed during fermentation or from fermentation derivatives (McGill, 2007). In lowland rice, much of the CH_4 produced depends on the plant itself, which provides both photosynthate to methanogens inhabiting the rhizosphere and a pipeline to the atmosphere. While some CH_4 exits rice sediments via ebullition – bubbles formed on the accumulation of sufficient gas that float to the surface – much also exits through the rice plant itself: some portion of the CH_4 produced near its roots passes from sediments through aerenchyma in the rice stem and out open stomata to the atmosphere.

In well-aerated soils everywhere, CH_4 is not produced but rather consumed. Methane consumption is performed by methanotrophs, a class of microbes with the capacity to oxidize CH_4 to CO_2 for energy. In so doing, methanotrophs provide an important ecosystem service: globally, they remove from the atmosphere approximately 30 Tg CH_4 per year. Although it is not a large sink relative to the total global flux of 598 Tg CH_4 per year, it is nevertheless equivalent to the annual loading rate for CH_4 in the atmosphere; without methanotrophs, the atmosphere would be accumulating CH_4 at approximately twice today's rate. Thus, the fact that land conversion to agriculture reduces CH_4 oxidation by 60–90% in most soils (Mosier et al., 1991; Smith et al., 2000) is significant.

Figure 4 The simultaneous recovery of methanotroph diversity (in operational taxonomic units or OTUs; open symbols) and methane consumption (closed symbols) in ecological succession from row-crop fields (Ag, green) through early (yellow) and mid-successional (blue) fields to mature forest (orange) at a site in southwest Michigan, USA. Reproduced from Levine, U., Teal, T.K., Robertson, G.P., Schmidt, T.M., 2011. Agriculture's impact on microbial diversity and associated fluxes of carbon dioxide and methane. ISME Journal 5, 1683–1691.

Reduced CH_4 oxidation capacity may be related to faster nitrogen cycling in arable soils (Hütsch et al., 1993) – ammonium, either mineralized from crop residues or added as fertilizer, appears to competitively inhibit the enzymes involved in CH_4 oxidation (Gulledge and Schimel, 1998). Agronomic management of the soil environment, such as tillage, appears to have little effect on CH_4 oxidation (Burke et al., 1999; Suwanwaree and Robertson, 2005). Recent results suggest that microbial diversity may also influence the CH_4 oxidation capacity of soils. Levine et al. (2011) found a remarkable positive association between CH_4 oxidation and methanotroph diversity along a 100+-year successional gradient (Figure 4).

Mitigation of Methane Fluxes in Agricultural Soils

Rice management provides a ready means to attenuate CH_4 production in paddy rice fields. High-yielding varieties tend to have substantially lower CH_4 emissions (Corton et al., 2000; van der Gon et al., 2002) owing to more efficient photosynthate use – higher-yielding plants allocate more fixed carbon to biomass and transmit less to methanotrophs in the rhizosphere.

Residue management and drainage also affects CH_4 fluxes in lowland rice. Encouraging the decomposition of residues before flooding through tillage or composting can substantially diminish CH_4 emissions after flooding (Wassmann et al., 1993). Likewise, drainage for several-day periods during the growing season can also markedly reduce seasonal emissions (Lu et al., 2000) due to accelerated organic matter decomposition as soils become aerated during drainage periods.

Recovering the lost oxidation potential of agricultural soils represents another potential mitigation opportunity. To date,

however, no management practices have been identified that can enhance CH_4 oxidation in cropped soils. Only after abandoning cropland to secondary succession (e.g., Robertson et al., 2000) does soil CH_4 oxidation return, although new insights into the role of microbial community composition (Levine et al., 2011) may eventually provide some new management insights as well.

Reactive Nitrogen Oxides

Oxides of nitrogen, most notably nitric oxide (NO), are also emitted from agricultural systems. Because NO oxidizes quickly in the atmosphere to form NO_2 and other compounds, most fluxes of reactive oxidized N are reported collectively as nitrogen oxides (NO_x), the sum of all such forms. NO_x is not itself radiatively active and is therefore not explicitly a GHG. Nevertheless, emitted NO_x leads to the formation of tropospheric ozone (O_3), which is both a GHG (Figure 1) and toxic to crops and humans.

Agriculture is responsible for approximately 25% of the global anthropogenic NO_x flux, which itself represents approximately 80% of the total terrestrial NO_x flux (Galloway et al., 2004). Of the agricultural flux, Galloway et al. (2004) estimated that approximately 30% is derived from agricultural soils, with the remainder from the burning of crop residue (27%) and native vegetation as land is cleared for agriculture (44%). Davidson and Kingerlee (1997) estimated that agricultural soils worldwide are responsible for 5.5 Tg of NO_x–N emissions annually, approximately twice the estimate made by Galloway et al. (2004). Jaeglé et al. (2005) used top-down atmospheric modeling to estimate 2.5–4.5 Tg NO_x–N per year from fertilized agricultural soils.

The role of NO_x in tropospheric photochemistry is substantial: elevated NO_x leads to the oxidation of atmospheric hydrocarbons and carbon monoxide, which leads in turn to O_3 production. Conversely, low NO_x concentrations lead to O_3 consumption (Chameides et al., 1992).

Sources and Sinks of Nitrogen Oxides in Agricultural Soils

Soil-derived NO_x is from NO produced during nitrification and denitrification (Robertson and Groffman, 2007). When hydroxylamine (NH_2OH in eqn [1]) is oxidized to nitrite (NO_2^-) during nitrification, intermediary compounds can result in the formation of NO (as well as N_2O) that then escapes to the atmosphere. In denitrification, NO is formed by the enzyme nitrite reductase (nir) and is either further reduced to nitrous oxide via nitric oxide reductase (nor) or escapes to the atmosphere. Because denitrifier enzymes are induced sequentially, there is often a lag between the production of NO and its subsequent reduction to N_2O in soil, leading to a substantial opportunity for NO escape in environments where denitrification occurs sporadically following wetting events. This is the case in most arable soils, where NO_x fluxes can for short periods equal or exceed N_2O fluxes (e.g., Matson et al., 1998). In general, however, annual global NO_x–N fluxes from cropland soils are approximately half the magnitude of N_2O–N emissions from cropland soils (Stehfest and Bouwman, 2006).

Mitigation of Nitrogen Oxides from Agricultural Soils

Because NO emitted from soils is formed during nitrification and denitrification, NO emissions are affected by the same environmental and management factors discussed earlier for N_2O. These include fertilizer rate, placement, timing, and formulation. There is evidence that some management factors such as no-till may have a different effect for NO than for N_2O (e.g., Liu et al., 2006) but in general effects are consistently similar based on available data.

Carbon Dioxide

By mass, CO_2 is by far the largest source of radiative forcing in the atmosphere, responsible for >50% of the greenhouse warming that has occurred since 1750 (Figure 1). Most of this, of course, is from fossil fuel use, but a substantial portion is from the net release of CO_2 from soils when forests and grasslands are first cleared for agriculture. Before 1900, agricultural expansion in North America, Australia, Southern Africa, and Eastern Europe may have released as much as 100 Pg C from soils (Wilson, 1978), contributing as much as 25% of the increase in atmospheric CO_2 at that time (Paustian et al., 1995). Today, approximately 16% of the global CO_2 flux is from deforestation (Canadell et al., 2007), mostly in South America and Southeast Asia.

In well-established croplands, CO_2 emissions are largely confined to the use of fossil fuel during the manufacture and transport of fertilizers, pesticides, and other agrochemicals, as well as from changes in soil organic carbon (SOC) as affected by various management practices.

Sources and Sinks of Carbon Dioxide in Agricultural Soils

Soil carbon in agricultural lands can represent a net sink or source of CO_2 depending on cropping history and contemporary management. As described in Paustian et al. (1995), soil carbon stores typically decline 40–60% in the first 40–60 years following conversion to agriculture. The decline happens faster in the humid tropics and is even more abrupt in high-organic matter soils such as drained wetlands, but in general soils reach an equilibrium carbon content that is relatively stable for a given soil type and climate. Deviations from equilibrium values indicate CO_2 uptake from or release to the atmosphere, and occur due to management and climate change.

Net carbon storage in soils results from changes in carbon inputs, changes in decomposition rates, or both. Carbon enters soil primarily as plant residues – aboveground leaves, stems, and other tissues as well as belowground roots and their exudates. The rate at which this material decomposes largely determines whether soil carbon will accumulate: If more organic carbon enters the soil pool than can be readily oxidized by microbes and invertebrates, soil carbon stores will increase and the soil will become a net sink of CO_2. If biomass that enters the soil is readily decomposed, then there will be no net change in carbon stores. If decomposers oxidize soil organic matter faster than it is replaced by new biomass, then carbon stores will decline.

Decomposition is affected both by the quality of organic matter – the degree to which its chemical constituents are

readily metabolized by soil organisms – and the soil microclimate. Biomass with a high carbon:nitrogen ratio such as senesced leaves and stems and biomass with a high lignin content such as corn stalks and wood will decompose relatively slowly. Biomass with low carbon:nitrogen and lignin content such as legume leaves and stems will decompose rapidly.

Likewise, tillage accelerates decomposition by breaking apart soil aggregates that would otherwise delay decomposition of the carbon they contain by restricting the supply of oxygen to microbes within the aggregates (Sexstone et al., 1985). Exposing this otherwise protected carbon to air leads to its rapid oxidation (Six et al., 2000; Grandy and Robertson, 2007). Plowing also leads to higher soil surface temperatures as residue that would normally shade the soil from direct insolation is instead buried, further accelerating decomposition. Thus, management that affects the quantity and quality of organic matter inputs or the microenvironment where decomposition occurs can have profound effects on soil CO_2 emissions. In the absence of erosion, any change in organic soil carbon from year to year represents a net annual flux of soil CO_2.

Erosion presents a special case. Although erosion removes carbon from a particular location, it usually deposits carbon elsewhere in the landscape rather than oxidize it directly to CO_2. Often these locations are in toe-slope positions where the added soil can serve to bury existing carbon and thereby slow its decomposition, or particles can be washed into waterways or surface waters where they can accumulate in anaerobic sediments. Perversely, erosion can result in a carbon sink as decomposition slows in areas of deposition and carbon is replaced on the eroded sites (Harden et al., 2008). Quine and van Oost (2007) estimated a sink capacity of approximately 26% for eroded soil.

Energy inputs and soil amendments can also represent sources of agricultural CO_2. Fossil fuel, usually diesel, is used to power equipment used for tilling, planting, and harvesting and for applying fertilizers, herbicides, and other inputs, and this fuel is emitted as CO_2 on use. Likewise, the fossil fuel used to manufacture herbicides and synthetic fertilizers represents a CO_2 cost of agriculture. As will be seen in the Section Synthesis: System-Wide Global Warming Impact, these costs are small but significant. The CO_2 cost of atrazine, for example, is 2.3 kg CO_2 per kg of active ingredient (750 g l^{-1}) (Gelfand et al., 2013) and the CO_2 cost of nitrogen fertilizer manufacture – which uses CH_4 as a feedstock in addition to using fossil fuel to meet its temperature and pressure requirements – is 4.5 kg CO_2 per kg of N applied (Schlesinger, 1999).

Agricultural lime is another special case. Lime, as crushed limestone ($CaCO_3$) and dolomite ($CaMg (CO_3)_2$), is commonly applied to agricultural land to counteract the acidity caused by nitrogen fertilizers and the removal of base cations in harvested biomass. The carbonate (CO_3^{-2}) in lime weathers to CO_2 or bicarbonate (HCO_3^{-}) depending on the strength of the weathering agent (Hamilton et al., 2007). If the weathering agent is nitric acid, produced by nitrifying bacteria, then the carbon in lime is dissolved and released to the atmosphere directly, as in the equation:

$$CaCO_3 + 2HNO_3 \rightarrow Ca^{2+} + 2NO_3^{-} + H_2O + CO_2 \qquad [3]$$
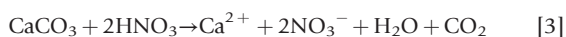
If, however, the weathering agent is the weaker carbonic acid, produced by the dissolution of CO_2 from root and microbial respiration in soil solution, then the lime is transformed to bicarbonate, as in the equation:

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^{-} \qquad [4]$$
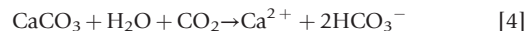
Interestingly, the latter reaction consumes an additional mole of CO_2 from the atmosphere for every mole of $CaCO_3$ dissolved. Thus, lime dissolved by strong acid becomes a source of CO_2 whereas lime dissolved by weak acid becomes a CO_2 sink. Current evidence suggests that more lime is dissolved by carbonic than by nitric acid (West and McBride, 2005; Oh and Raymond, 2006; Hamilton et al., 2007), resulting in sequestration equivalent to approximately 33% of the lime's carbon content. This is counterbalanced, however, by emissions from fossil fuel use during the mining and transport of lime (West and Marland, 2002), which is more than sufficient to offset its sequestration potential. Agricultural lime use may thus be largely neutral with respect to CO_2.

The growth of perennial vegetation represents a sink for CO_2 as carbon is captured in growing biomass both above and belowground. And because perennial crops are rarely tilled, CO_2 is also sequestered as SOC, which, because of persistent roots, can build soil carbon at even faster rates than can annual crops managed with no-till practices. For example, successional vegetation on abandoned farmland and perennial grasses planted as part of set-aside programs such as the US Department of Agriculture's Conservation Reserve Program (CRP) can sequester soil carbon at rates twice those of no-till annual crops (Robertson et al., 2000; Gelfand et al., 2011). However, replanting practices can have a major impact on the persistence of this stored carbon. Syswerda et al. (2011), for example, found that a large portion of the soil carbon stored by a 12-year-old hybrid poplar plantation was lost during harvest and reestablishment, due apparently to warmer and moister soils during early reestablishment that stimulated decomposition rates. Likewise, converting perennial cropland back to annual cropping – for example, the return of CRP lands to corn-soybean production – can release large amounts of CO_2 (and N_2O) even when conversion involves no-till management (Zenone et al., 2011; Gelfand et al., 2011), but especially when the soil is plowed (Grandy and Robertson, 2006; Ruan and Robertson, 2013).

Mitigation of Soil Carbon Dioxide Fluxes in Agricultural Soils

Mitigation of soil CO_2 fluxes generally involves increasing SOC stores. This can be accomplished by increasing the inputs of biomass carbon to soil, by reducing soil decomposition rates or both (CAST, 2011). Crops that produce abundant residue will sequester more soil carbon than those that do not; corn, for example, will produce 2–3 times more biomass than soybean and, if not harvested, corn residue will contribute more than soybean to building or maintaining SOC. Thus, continuous corn rotations will build soil carbon faster than corn–soybean rotations. Likewise, cover crops can help to build soil carbon by increasing the quantity or biochemical complexity of residue carbon inputs (Syswerda et al., 2011).

The reduction of soil decomposition rates is generally accomplished through tillage management. No-till practices are one of the most widespread and effective ways to sequester soil carbon in most soils. Other forms of conservation tillage – strip tillage and shallow tillage, for example – can provide some of the benefit of no-till, but not as much (CAST, 2011).

However, no-till is not effective at storing soil carbon in all soils, and some have suggested that increased storage in the surface layers of many soils may be offset by lost carbon deeper in the profile (Baker et al., 2007). Others (Kravchenko and Robertson, 2011) have pointed out that a failure to detect whole-profile carbon change with no-till is a consequence of low statistical power rather than the absence of effects, and the fact that most no-till soils show an increased surface soil carbon content is ample evidence for no-till carbon gain. No studies to date have shown statistically significant carbon declines below the A horizon of no-till soils.

Evidence to date suggests that all cropping system soils – unless continuously amended by exogenous inputs such as manure, biochar, or sewage sludge – will equilibrate at some soil carbon content less than that in the native ecosystem that existed before cultivation (Six et al., 2002; Stewart et al., 2007). Quantitative models suggest that this will occur within 60–100 years of management in most temperate region soils.

Evidence also suggests that carbon thus stored is at significant risk of re-release (CAST, 2011). Grandy and Robertson (2006), for example, showed that a substantial fraction of the soil carbon stored in a native never-plowed soil was released after a single plowing, which immediately destabilized soil aggregates to the same degree as in an adjacent field that had been plowed for > 100 years. Permanent no-till is by far the preferred mitigation approach (Grandy et al., 2006); although occasional light tillage may permit the persistence of some stored carbon, there is too little evidence to date to judge its effectiveness.

Synthesis: System-Wide Global Warming Impact

The balance of all GHG sources and sinks in a given cropping system for a particular year is termed the net GHG balance or net global warming impact (GWI). The GWI is calculated by summing all GHG fluxes (whether positive or negative) after first converting each to a CO_2-equivalent (CO_2e) basis. For N_2O and CH_4, this is performed by multiplying each by its respective 100 year GWP (Table 1; 298 for N_2O and 25 for CH_4). For N_2O (g CO_2e per ha day^{-1}) the equation is:

$$CO_2e\,(N_2O) = \frac{x_1 \text{ g } N_2O-N}{ha \times day} \times \frac{44 \text{ g } N_2O}{28 \text{ g } N_2O-N}$$

$$\times \frac{365 \text{ days}}{1 \text{ year}} \times \frac{1 \text{ ha}}{10^4 \text{ m}^2} \times \frac{298 \text{ g } CO_2}{1 \text{ g } N_2O} \quad [5]$$

where x_1 is the average daily N_2O emission rate (g N per ha day^{-1}). For CH_4 the equation is similar but the mole ratio 44:28 for N_2O:N becomes 16:12 for CH_4:C and the GWP term for CH_4 (25) substitutes for N_2O's (298).

The energy used for field operations must also be determined, usually by standard tables to calculate annual diesel use, which is then converted into CO_2e.

$$CO_2e\,(diesel) = \frac{x_1 \text{ l } C_{16}H_{34}}{ha \times year} \times \frac{832 \text{ g } C_{16}H_{34}}{1 \text{ l } C_{16}H_{34}}$$

$$\times \frac{192 \text{ g C}}{226 \text{ g } C_{16}H_{34}} \times \frac{44 \text{ g } CO_2}{12 \text{ g C}}$$

$$\times \frac{1 \text{ ha}}{10^4 \text{ m}^2} \quad [6]$$

where x_1 is the average annual diesel use for the field. Likewise, the CO_2e costs of other agronomic inputs such as fertilizer and pesticides must be calculated on the basis of actual use and their embedded CO_2e costs (e.g., Gelfand et al., 2013).

Annual SOC change is calculated as:

$$CO_2e\,(SOC) \text{ g } CO_2 \times m^{-2} \text{ yr}^{-1} = \frac{(x_1 - x_2) \text{ kg C}}{m^2 \times x_3 \text{ year}}$$

$$\times \frac{44 \text{ kg } CO_2}{12 \text{ kg C}} \times \frac{10^3 \text{ g } CO_2}{1 \text{ kg } CO_2} \quad [7]$$

where x_1 is the current soil carbon content of the target system (in kg C per m^2), x_2 is the original soil carbon content, and x_3 is the period of carbon accumulation (the difference in years between current and original).

Once calculated, the overall balance for a given system can be tallied as in Table 2, which shows results of a GWI analysis

Table 2   Global warming impacts (GWIs) for four cropping systems and a field abandoned from agriculture and undergoing ecological succession[a]

| Cropping System	Soil C	N_2O	CH_4	Farming input							Net GWI
				N	P	K	Lime	Fuel	Seeds	Pesticides	
				(g CO_2e per m^2 yr^{-1})							
C–S–W conventional	0 (31)	34 (6)	−0.8 (0.1)	32.7	0.4	1	3	13	7	7	98 (31)
C–S–W no-till	−122 (31)	35 (4)	−0.8 (0.1)	32.7	0.3	1	4	9	7	16	−18 (31)
Alfalfa	−122 (92)	33 (3)	−1.0 (0.1)	0	0.3	4	14	11	6	3	−52 (92)
Hybrid poplar	61 (153)	17 (3)	−0.8 (0.0)	3.3	0	0	0	1	0	2	84 (153)
Successional	−397 (31)	11 (1)	−1.1 (0.1)	0	0	0	0	0	0	0	−383 (31)

[a]GWIs are based on annual greenhouse gas emissions of cropping systems of the Kellogg Biological Station Long-term Ecological Research site in southwest Michigan, USA for the period 1989–2009. Values are means±SE ($n=4$–6 replicate blocks). C–S–W=corn–soybean–wheat rotation.
Source: Reproduced from Gelfand, I., Sahajpal, R., Zhang, X., et al., 2013. Sustainable bioenergy production from marginal lands in the US Midwest. Nature 493, 514–517.

for five different cropping systems in Southwest Michigan, USA (Gelfand et al., 2013). Here, for example, one can see that for a conventionally managed corn–soybean–wheat rotation the greatest GHG cost over a 20 year period was from N_2O emissions at 34 g CO_2e per m^2 yr^{-1}, followed closely by nitrogen fertilizer manufacture (33 g CO_2e per m^2 yr^{-1}). The cost of fuel, seeds, and pesticides summed to 27 g CO_2e per m^2 yr^{-1}, for a total cost of 98 g CO_2e per m^2 yr^{-1}. The no-till system, otherwise identical but for tillage, in contrast had a net cost of −20 g CO_2e per m^2 yr^{-1} – indicating net mitigation – on account of substantial soil carbon sequestration. Figure 5 provides a graphical illustration of the net balances: in the top part of the figure is the net GWI for each system broken out by component. The bottom graph shows clearly those systems that are net GHG sources versus net GHG mitigators.

Such a comparison has at least two purposes. First, one can identify the practices within each system that contribute the greatest GHG burden (or conversely, the least) and target mitigation efforts toward those practices with the greatest payout. Second, one can use such comparisons as a basis for crediting systems on a GHG market. If the conventional system is considered business as usual, the conversion of this system to another ought to generate carbon credits as the difference between business as usual and the alternative system. Converting to no-till, for example, would generate 118 g CO_2e credits per year on average, whereas retiring the land to successional vegetation would generate 481 CO_2e credits (see
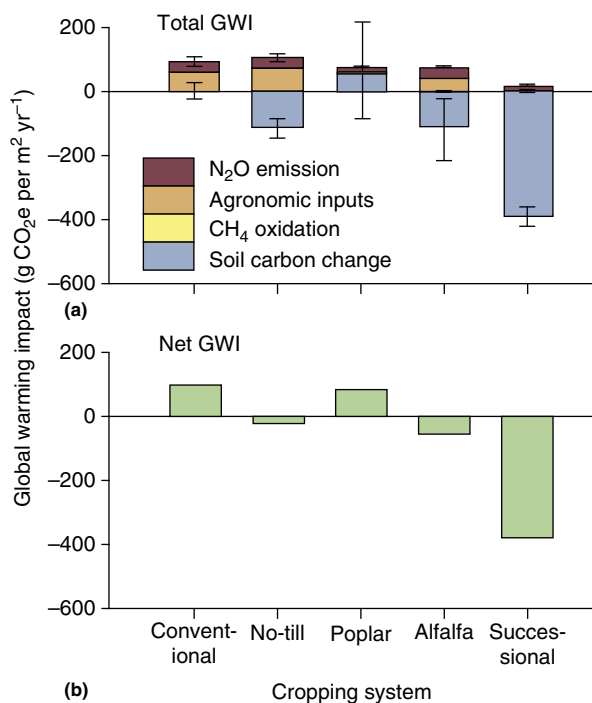
Figure 5 (a) Total and (b) net GWI for four cropping systems and a field abandoned from agriculture and undergoing ecological succession at the W.K. Kellogg Biological Station Long-term Ecological Research site in southwest Michigan, USA for a 20-year period ending in 2009. Conventional and no-till systems are corn-soybean-wheat rotations. Reproduced from Gelfand, I., Sahajpal, R., Zhang, X., et al., 2013. Sustainable bioenergy production from marginal lands in the US Midwest. Nature 493, 514–517.

Table 2). If the products of these systems were used to generate biofuels, then the respective fossil fuel offset credits could be added in as well (Gelfand et al., 2013) – assuming management changes do not create indirect carbon costs by displacing lost food production to lands newly converted to agriculture elsewhere (Searchinger et al., 2008). This also assumes that net soil carbon gains are permanent.

Not yet included in these analyses is the GWI of changes in NO_x fluxes. This is because of spatial variability in the regional conversion of NO_x to tropospheric ozone and the complexity of ozone's subsequent effect on radiative forcing. The short lifetime of ozone in the atmosphere (hours to days) precludes the calculation of a meaningful GWP for ozone (IPCC, 2007).

This type of systems approach is crucial for fully evaluating the total GHG effects of different agricultural practices. Otherwise it is difficult to know, for example, that the additional herbicides needed for no-till offset the fuel savings or carbon sequestration relative to conventional practices (Table 2). These sorts of trade-offs must be evaluated at the systems level.

Future Mitigation Potentials via Soil Management: Cropping Systems and Biofuels

Our current understanding of agriculture's impact on the atmosphere's GHG burden reveals many opportunities for mitigation, almost none of which have been implemented to date. Designing effective mitigation practices for soil management requires a systems approach because some practices are incompatible with one another and others involve trade offs. The CO_2e costs of each consequence must be evaluated, in turn, to show that no-till management does, indeed, provide a net GWI benefit, i.e., net mitigation (see Figure 5).

The design of future climate-benefiting systems can be best informed by existing whole-system studies (e.g., Robertson et al., 2000; Robertson and Grace, 2004; Mosier et al., 2005, 2006; Adviento-Borbe et al., 2007; Piva et al., 2012; Sainju et al., 2012; Ma et al., 2013). A number of mitigation practices can be implemented to significantly reduce GHG emissions from agricultural soils. Among those most important across most types of annual cropping systems are:

- more precise fertilizer nitrogen management to reduce N_2O emissions;
- permanent no-till management to maximize soil carbon gain and reduce fuel use;
- irrigation management to minimize the need for electricity and fuel to pump water;
- leguminous cover crops to maximize soil carbon gain and reduce the need for synthetic nitrogen fertilizers; and
- diverse rotations that include perennial crops such as alfalfa and high-biomass crops such as corn to build soil carbon and reduce the need for pesticides.

Many of these practices can be combined such that it is possible to not just reduce cropping system GHG costs to nil but to make the system net negative, thereby providing a valuable ecosystem service beyond the farm boundary.

An additional, emerging mitigation opportunity is cellulosic biofuels (Perlack *et al.*, 2005; Robertson *et al.*, 2008). Biofuels made from cellulosic feedstocks – crop residues and purpose-grown lignocellulose biomass – can offset fossil fuel use and thereby provide a climate benefit substantially greater than that of the cropping system itself (NRC, 2009; Gelfand *et al.*, 2013).

The environmental hazards of grain-based biofuels are well known (Crutzen *et al.*, 2008; Donner and Kucharik, 2008; Landis *et al.*, 2008; Robertson *et al.*, 2011) and can be largely avoided by the use of perennial feedstocks that require little soil disturbance after planting but for harvest and perhaps fertilizer applications. Perennial cellulosic feedstocks use little fossil fuel to plant and maintain, require few inputs, and have a correspondingly high energy return on investment (Farrell *et al.*, 2006), which can translate into high climate benefit.

However, the climate benefits of biofuels are conditional. First, the CO_2 captured and used to offset fossil fuel use must be greater than the CO_2e costs of establishment (Fargione *et al.*, 2008), which can create a so-called carbon debt that can take decades to a century or more to repay (Gelfand *et al.*, 2011). Almost all of this debt is related to soil processes. Second, the establishment of a new biofuel crop must not result in the creation of new cropland elsewhere to replace food production that was displaced by the new biofuel crop (Searchinger *et al.*, 2008). Indirect land use change with its associated soil- and vegetation-related GHG costs can discount a substantial fraction of the local crop's CO_2e benefit (Plevin and Kammen, 2013). And third, the CO_2e benefit of the new crop must be discounted by the expected CO_2e benefit of the existing ecosystem (Searchinger *et al.*, 2009). For example, a growing forest sequesters substantial carbon in its soil and biomass. To achieve a climate benefit, the carbon capture of a replacement crop must exceed both the current and future expected rate of carbon capture by the forest vegetation and soil (Field *et al.*, 2008). Soil carbon storage and fluxes of N_2O and CH_4 play a large role in the GHG balance of biofuel cropping systems.

Worth noting overall is that although soil GHG emissions from agriculture can be substantial, and are the single greatest contributors to the GHG footprint of agriculture, emissions can be managed. Purposeful changes to cropping practices and careful consideration of their GHG impacts can substantially reduce and even reverse their climate impacts.

Acknowledgments

> *See also*: Climate Change: Agricultural Mitigation. Energy and Greenhouse Gases Footprint of Food Processing. Soil: Carbon Sequestration in Agricultural Systems. Soil: Nutrient Cycling. Soil Fertility and Plant Nutrition

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