Research

The role of N$_2$O derived from crop-based biofuels, and from agriculture in general, in Earth’s climate

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In earlier work, we compared the amount of newly fixed nitrogen (N, as synthetic fertilizer and biologically fixed N) entering agricultural systems globally to the total emission of nitrous oxide (N$_2$O). We obtained an N$_2$O emission factor (EF) of 3–5%, and applied it to biofuel production. For ‘first-generation’ biofuels, e.g. biodiesel from rapeseed and bioethanol from corn (maize), that require N fertilizer, N$_2$O from biofuel production could cause (depending on N uptake efficiency) as much or more global warming as that avoided by replacement of fossil fuel by the biofuel. Our subsequent calculations in a follow-up paper, using published life cycle analysis (LCA) models, led to broadly similar conclusions. The N$_2$O EF applies to agricultural crops in general, not just to biofuel crops, and has made possible a top-down estimate of global emissions from agriculture. Independent modelling by another group using bottom-up IPCC inventory methodology has shown good agreement at the global scale with our top-down estimate. Work by Davidson showed that the rate of accumulation of N$_2$O in the atmosphere in the late nineteenth and twentieth centuries was greater than that predicted from agricultural inputs limited to fertilizer N and biologically fixed N (Davidson, E. A. 2009 Nat. Geosci. 2, 659–662.). However, by also including soil organic N mineralized following land-use change and NO$_x$ deposited from the atmosphere in our estimates of the reactive N entering the agricultural cycle, we have now obtained a good fit between the observed atmospheric N$_2$O concentrations from 1860 to 2000 and those calculated on the basis of a 4 per cent EF for the reactive N.

**Keywords:** nitrous oxide; biofuels; reactive N; agriculture; N$_2$O emission factor; life cycle analysis

1. INTRODUCTION

Data from ice-core analysis show that for thousands of years, atmospheric N$_2$O mixing ratios (i.e. the concentrations in dry air) were close to 270 ppbv [1]. In more recent times, however, a 20 per cent increase has occurred. The increase began around AD 1850 and the concentration now exceeds 320 ppbv. Since the 1960s, the annual increase has been about 0.7 ppbv [2]. The Intergovernmental Panel on Climate Change (IPCC) Third Assessment Report [3] concluded that the primary driver of this increase was enhanced by microbial production of N$_2$O in expanding and fertilized agricultural lands. This production requires nitrogen (N) in a reactive form, N$_r$ [4], as substrate—virtually any form other than dinitrogen, N$_2$. Reactive N is introduced into the natural terrestrial environment primarily by biological N fixation, together with a smaller contribution as NO$_x$ formed by lightning. Galloway et al. [5] estimated this input in 1860, at the beginning of the industrial age, at ca 140 Tg (million metric tonnes) per year of N. Within the past few decades, human activities have roughly doubled this supply, mainly through synthetic fixation of N by the Haber–Bosch process [6], and also through industrial processes and as a by-product of fossil fuel combustion.

The main microbial reactions involved in the production of N$_2$O are nitrification (oxidation of ammonium to nitrite) and denitrification (reduction of nitrate, via N$_2$O, to N$_2$). Nitrification is essentially an aerobic
Table 1. Reactive N inputs to the biosphere and atmosphere, atmospheric N$_2$O mixing ratios and associated N$_2$O emission factors in 1860 and 2000 (after Crutzen et al. [10]).

<table>
<thead>
<tr>
<th>source/process</th>
<th>annual rate/EF</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1860 (atmospheric mixing ratio = 270 ppbv)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[A] total N$_2$O source</td>
<td>10.2 Tg N$_2$O-N yr$^{-1}$</td>
<td>[11]</td>
</tr>
<tr>
<td>[B] land and coastal zone source</td>
<td>6.2–7.2 Tg N$_2$O-N yr$^{-1}$</td>
<td>[11]</td>
</tr>
<tr>
<td>[C] input of new reactive N</td>
<td>141 Tg N yr$^{-1}$</td>
<td>[5]</td>
</tr>
<tr>
<td>[D] N$_2$O emission factor (i.e. [B]/[C])</td>
<td>4.4–5.1%</td>
<td></td>
</tr>
<tr>
<td>2000 (atmospheric mixing ratio = 315 ppbv)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[E] atmospheric increase</td>
<td>3.9 Tg N$_2$O-N yr$^{-1}$</td>
<td>[11]</td>
</tr>
<tr>
<td>[F] photochemical loss (stratosphere)</td>
<td>11.9 Tg N$_2$O-N yr$^{-1}$</td>
<td>[11]</td>
</tr>
<tr>
<td>[G] total N$_2$O source (= [E] + [F])</td>
<td>15.8 Tg N$_2$O-N yr$^{-1}$</td>
<td>[11]</td>
</tr>
<tr>
<td>[H] decrease in natural source</td>
<td>0–0.9 Tg N$_2$O-N yr$^{-1}$</td>
<td>[12]</td>
</tr>
<tr>
<td>[I] total anthropogenic source (i.e. [G] – [A] + [H])</td>
<td>5.6–6.5 Tg N$_2$O-N yr$^{-1}$</td>
<td>[11]</td>
</tr>
<tr>
<td>[J] non-biological anthropogenic source</td>
<td>0.7–1.3 Tg N$_2$O-N yr$^{-1}$</td>
<td>[11]</td>
</tr>
<tr>
<td>[L] new terrestrial anthropogenic N input</td>
<td>114 Tg N yr$^{-1}$</td>
<td>[5,13]</td>
</tr>
<tr>
<td>[M] N$_2$O emission factor for new N (i.e. [K]/[L])</td>
<td>3.8–5.1%</td>
<td></td>
</tr>
</tbody>
</table>

process and denitrification an anaerobic process. The main source of emissions is N-fertilized agricultural land—both directly from the soil surface and also from the considerable portion of the N additions to the land that is lost to the environment through runoff, leaching of nitrate and ammonia volatilization and subsequently nitrified and denitrified [7,8].

Two general methods used to estimate soil N$_2$O emissions can be broadly considered as either (i) bottom-up approaches based on estimates of emission rates from land and waters or (ii) top-down approaches based on changes in the atmospheric concentration of N$_2$O and estimates of sink size. Here, we describe how we used a global top-down approach to calculate the fraction of all newly fixed N entering terrestrial systems that is converted to N$_2$O, and how we applied the outcome to determine the extent to which a reduction of global warming by the use of crop-based liquid biofuels instead of fossil fuels would be offset by the associated N$_2$O emissions. We also examine the impact of more complete life cycle analyses (LCAs) on our initial conclusions, the implications of generalizing the results derived for biofuel crops to agriculture in general, and the extent to which the global N$_2$O emission factor (EF) obtained by our approach can be reconciled with those derived by Davidson [9] and the IPCC [7,8].

2. BIOFUELS AND GLOBAL WARMING

We [10] used the data in table 1 to calculate the global EFs for N$_2$O for the newly fixed N entering terrestrial and coastal ecosystems in 1860 when there had not yet been a major perturbation resulting from human activities, and also for 2000 when the annual quantity of new reactive N had more or less doubled. The results showed very similar ranges for the EFs: 4.4–5.1% for 1860 and 3.8–5.1% for the year 2000 (table 1).

We adopted a conservative lower limit of 3 per cent for the EF in 2000, rather than the calculated value of 3.8 per cent, and rounded the upper limit down to 5 per cent. We applied these values to the fertilizer N input for the production of maize and sugarcane for bioethanol and rapeseed oil for biodiesel—together

with the global average N-use efficiency (NUE) by crops of 40 per cent [5,14,15]—and found that for rapeseed and maize, the global warming impact of the resulting N$_2$O emissions matched or even exceeded the corresponding ‘cooling’ achieved by the reduction in CO$_2$ emissions resulting from the replacement of fossil fuels by the biofuels, as shown in figure 1. There are substantial differences in NUE between regions and farming systems, and figure 1 also shows the pro-rata reduction in calculated global warming by the biofuels if the NUE is set at 60 per cent.

Although figure 1 indicates net cooling for sugarcane bioethanol, in contrast with rapeseed- and maize-based fuels, the overall balance may not be quite so favourable. Lisboa et al. [16] report that the mean EF for direct N$_2$O emissions from sugarcane fields, based on published data, is about 3.9 per cent, even with the exclusion of very high emissions from sites with unusual soil conditions. If one were to include the inevitable associated indirect emissions, the total EF for this dataset would be of the order of the 5 per cent used to model the upper end of the relative warming range shown in figure 1, and thus any global cooling achieved by the use of sugarcane ethanol would be very dependent on
the NUE of the crop. Smeets et al. [17] also concluded that N₂O emissions can have an important impact on the overall greenhouse gas (GHG) balance of biofuels. This conclusion was reached even though their analysis included only some aspects of N₂O emissions and did not account for locations, such as those discussed by Lisboa et al. [16] or Weier [18], where N₂O emissions from sugarcane fields were large.

Our original study [10] only took into consideration the N₂O emissions associated with the biofuel crop production, thus ignoring the additional GHG emissions associated with fertilizer production, transport and energy use on the farm and in the biofuel refinery. Conversely, no account was taken of the energy savings associated with the biofuel coproducts that can replace grain and soya bean meal as animal feed. However, in subsequent work [19], we introduced the global N₂O EF range of 3–5% into three existing LCA models that included GHG emissions from the various stages of crop production and fuel refining: two for maize in the USA and one for wheat in the UK. The EBAMM model [20] includes GHG emissions from fertilizer manufacture, crop production, transport of feedstock to the refinery and production, distribution and use of the biofuel; the EF for N₂O is set at 1.5 per cent of fertilizer N input. The model also takes account of coproducts that can replace other sources of animal feed. The BESS model [21] also analyses GHG emissions for maize bioethanol production, including those associated with crop production, the refinery and cattle on feedlots that use the coproduct animal feed produced. The total N₂O emissions used in the model are ca 1.8 per cent of fertilizer N input. The Bioethanol GHG Calculator (BGGC) [22,23] calculates the emissions associated with the whole production train for bioethanol from wheat in the UK, and as in EBAMM, the EF for N₂O is set at 1.5 per cent of fertilizer N input. The insertion of the higher EFs for N₂O (3 and 5%) changed the GHG balance significantly for all three models; for EBAMM and BGGC, the predicted net outcomes in terms of relative warming/cooling were broadly similar to those predicted by the original method of Crutzen et al. [10], although the BESS model showed a greater GHG saving (figure 2).

Based on the EBAMM analyses, net GHG emissions from the average US Corn Belt maize-ethanol production do not fulfil the requirement in the US Energy Independence and Security Act [24] for a 20 per cent reduction compared with emissions from fossil fuels for renewable fuel production, whereas in all cases tested BESS estimates indicate that maize ethanol decreases net GHG emissions by more than the EISA minimum requirement. In the European Union, the current requirement for GHG savings using biofuels is that total GHG emissions must be at least 35 per cent below fossil fuel emissions [25], and the calculations with BGGC show that wheat-based bioethanol just fails to comply at an N₂O EF of 1.5 per cent, and the GHG balance becomes even more unfavourable at the higher EFs (figure 2).

Recent LCA calculations for bioethanol production from locally grown wheat in Sweden, using actual N₂O emission data for two farms on mineral soils, show a similar picture, with only a 50 per cent chance of emissions reductions meeting the EU minimum requirement [26]. Of the arable land in Sweden, 9 per cent is on organic soils, where stored N is released by mineralization, causing emissions of the order of 10 kg N₂O-N ha⁻¹ yr⁻¹ when cultivated for cereal crops [27]; 28 per cent of the organic soils in Sweden are used in this way [28]. There is no regulation controlling which soil type can be used for biofuel production. Taking the emissions from organic soils into account increases the regional average emission by almost 1 kg N₂O-N ha⁻¹ yr⁻¹, making biofuel production from arable crops impossible under the EU’s 35 per cent GHG savings rule [26].

The global warming implications of biofuel production extend beyond those resulting from making full allowance for N₂O emissions. The additional demand for grains, oilseeds and sugars brought about by increased biofuel production is expected to indirectly bring about the conversion of land currently under forest or other natural ecosystems into agriculture, with the concomitant release into the atmosphere of carbon stored in trees and soil. This land is not necessarily in the EU or the USA, but may be anywhere in the developing world. The increase in global warming engendered by the carbon release from this so-called indirect land-use change will cancel out any benefit derived from the biofuel for decades or even centuries to come [29,30]. Using linked economic and terrestrial biogeochemistry models, Melillo et al. [31] predicted that indirect land use will be responsible for substantially more carbon loss than direct land use; however, because of predicted increases in fertilizer use, N₂O emissions will become more important than carbon losses themselves in terms of warming potential. Erisman et al. [32] analysed the current knowledge of fertilizer N use and global biofuel production and...
concluded that criteria for sustainable biofuel production should include the disturbance of the N cycle for biomass options that require additional fertilizer inputs.

3. N₂O EMISSIONS FROM GLOBAL AGRICULTURE

The top-down approach [10] for estimating the impact of newly fixed N on N₂O emissions was developed in the context of biofuel crop production, but applies equally to agriculture in general. The basis of our methodology is that the newly fixed N entering agricultural systems (synthetic fertilizer N and N from biological nitrogen fixation (BNF)) is regarded as the source of all agriculture-related N₂O emissions, including: direct emissions from N fertilizer added to soils and N mineralized from crop residues following cultivation or grassland renewal; emissions from dung and urine from livestock (both grazing and housed) fed variously on N-fertilized grain crops and on feeds containing BNF-N; and indirect emissions from leached N leaving agricultural fields and entering water systems, and from volatilized N deposited onto natural ecosystems.

In contrast, in the IPCC approach [8], emissions from crop residues and mineralization are included in the direct emissions and are assigned the same EF—a default value of 1 per cent; separate EFs are used for emissions from grazing animals (2%), and the N source here is quantified on the basis of the N excreted, and essentially treated as an additional N source, not as fertilizer- or BNF-derived N. Indirect emissions from N lost by leaching, runoff or volatilization are estimated at 0.3–0.4% of the N applied to the land. Summing the individual sources gives the total emission from agriculture. Each of the source terms in the bottom-up IPCC method is very uncertain. However, their sum is consistent with the total derived by the top-down methodology, as shown by Del Grosso et al. [33], who calculated that approximately 5.8 Tg of N as N₂O is currently emitted annually from agricultural systems at the global scale. This is close to the middle of the range (4.2–7.0 Tg N₂O-N yr⁻¹) given by our top-down approach [10]. Del Grosso et al. concluded that ‘the convergence of top-down and bottom-up approaches increases confidence in emissions estimates because the methods are based on different assumptions, and this convergence suggests that we have at least a rudimentary understanding of the factors that control emissions at large spatial and temporal scales’.

In a similar way, Corazza et al. [34] apply atmospheric measurements and inverse modelling and conclude that there is ‘good agreement with the bottom-up emission inventories reported to the United Nations Framework Convention on Climate Change’ at least for Northwestern and Eastern Europe, where a sufficiently dense measurement network is available.

Davidson [9] reported that, although the calculation of a global EF of 4 ± 1% [10] fits the atmospheric concentration data well for 1860 and the 1990s, it underestimates the emissions that must have taken place in the late nineteenth and early twentieth centuries. He argued that other sources of N₂O were important in that period, in particular, the previously plant-unavailable N released from old soil organic matter following land-use change to agriculture (white triangles). Bottom curve (inverted triangles) includes all these sources except mineralized N. Black and white squares indicate the increase for EFs of 3 and 5%, respectively. Note: values for synthetic fertilizer N, N from BNF and NO₃-N, and also net contribution to atmospheric concentration change from N₂O release from biomass burning, fossil fuel combustion and nylon production, and decrease in forest soils, all taken from the electronic supplementary material in the study of Davidson [9]. N mineralization based on an estimate of soil C release from land-use change, 1850–1990, of 35 Pg [36]; corresponding N release would have been ca 3 Pg, or an average of 21 Tg yr⁻¹. Mineralization-N included in graph set at 10 Tg yr⁻¹ 1860–1890, 15 Tg yr⁻¹ 1890–1910 and 20 Tg yr⁻¹ 1910–1990.
As a contribution to the European Nitrogen Assessment, Butterbach-Bahl et al. [37] recently analysed the multitude of effects related to N specifically for Europe. Because of data availability, they focused on European Union member countries. Applying approaches as cited above, as well as referring to other relevant literature, they also concluded that the overall emissions of N$_2$O seem to be well understood, even if use of IPCC default EFs may lead to underestimation (owing to implicit negligence of the full N cycle, but also because indirect emissions from soil seem to be at least a factor of two higher than suggested by IPCC). Their paper also attempted to look at additional climate effects, such as carbon sequestration facilitated by N inputs, ozone formation owing to atmospheric NO$_x$ and cooling effects owing to aerosol formation. For the European situation, the conclusion was that the carbon sink and aerosol formation, as a consequence of NO$_x$ and NH$_3$ emissions, possibly outweigh their cooling effects the global warming caused by N$_2$O emissions. At this stage quantification of the agricultural effects (NO$_x$ predominantly derives from combustion), and an extension beyond Europe, are not possible.

4. CONCLUSIONS

By extending our original definition of ‘newly fixed N’ entering the terrestrial N cycle beyond fertilizer N and BNF-N to include the N mineralized as a result of land-use change and N deposited as NO$_x$, the observed upward trend in the atmospheric concentration of N$_2$O over the 140 years between 1860 and 2000 is very closely matched when an overall EF of 4 per cent (i.e. the average of the 3–5% range) is applied.

Agriculture (and the creation of new arable land for its expansion) is the activity mainly responsible for the additional N$_2$O emissions over the past century and a half. Its expansion in recent years to meet the demand for biofuels has resulted in additional emissions; on the basis of the likely EFs associated with first-generation biofuel crops, these crops can exacerbate, rather than alleviate, global warming. It is thus important to avoid biofuel production based on crops with a high N demand and use those that can be grown with little or no fertilizer N requirement: the so-called ‘second-generation’ biofuel crops such as willow and Miscanthus.

For all biofuels, a complete LCA, including the effect of fossil carbon used in biofuel production as well as the N$_2$O emission, and the energy equivalent of by-products, is needed to get the full picture, but the application of existing LCA has to date given broadly similar outcomes to our earlier conclusion based simply on the global N$_2$O EF.

REFERENCES


