

# N<sub>2</sub>O release from agro-biofuel production negates global warming reduction by replacing fossil fuels

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**Abstract.** The relationship, on a global basis, between the amount of N fixed by chemical, biological or atmospheric processes entering the terrestrial biosphere, and the total emission of nitrous oxide (N<sub>2</sub>O), has been re-examined, using known global atmospheric removal rates and concentration growth of N<sub>2</sub>O as a proxy for overall emissions. For both the pre-industrial period and in recent times, after taking into account the large-scale changes in synthetic N fertiliser production, we find an overall conversion factor of 3–5% from newly fixed N to N<sub>2</sub>O-N. We assume the same factor to be valid for biofuel production systems. It is covered only in part by the default conversion factor for “direct” emissions from agricultural crop lands (1%) estimated by IPCC (2006), and the default factors for the “indirect” emissions (following volatilization/deposition and leaching/runoff of N: 0.35–0.45%) cited therein. However, as we show in the paper, when additional emissions included in the IPCC methodology, e.g. those from livestock production, are included, the total may not be inconsistent with that given by our “top-down” method. When the extra N<sub>2</sub>O emission from biofuel production is calculated in “CO<sub>2</sub>-equivalent” global warming terms, and compared with the quasi-cooling effect of “saving” emissions of fossil fuel derived CO<sub>2</sub>, the outcome is that the production of commonly used biofuels, such as biodiesel from rapeseed and bioethanol from corn (maize), depending on N fertilizer uptake efficiency by the plants, can contribute as much or more to global warming by N<sub>2</sub>O emissions than cooling by fossil fuel savings. Crops with less N demand, such as grasses and woody coppice species, have more favourable climate impacts. This analysis only considers the conversion of biomass to biofuel. It does not take

into account the use of fossil fuel on the farms and for fertilizer and pesticide production, but it also neglects the production of useful co-products. Both factors partially compensate each other. This needs to be analyzed in a full life cycle assessment.

## 1 Introduction

N<sub>2</sub>O, a by-product of fixed nitrogen application in agriculture, is a “greenhouse gas” with a 100-yr average global warming potential (GWP) 296 times larger than an equal mass of CO<sub>2</sub> (Prather et al., 2001). As a source for NO<sub>x</sub>, i.e. NO plus NO<sub>2</sub>, N<sub>2</sub>O also plays a major role in stratospheric ozone chemistry (Crutzen, 1970). The increasing use of biofuels to reduce dependence on imported fossil fuels and to achieve “carbon neutrality” will further cause atmospheric N<sub>2</sub>O concentrations to increase, because of N<sub>2</sub>O emissions associated with N-fertilization. Here we propose a global average criterion for the ratio of N to dry matter in the plant material, which indicates to what degree the reduced global warming (“saved CO<sub>2</sub>”) achieved by using biofuels instead of fossil fuel as energy sources is counteracted by release of N<sub>2</sub>O. This study shows that those agricultural crops most commonly used at present for biofuel production and climate protection can readily lead to enhanced greenhouse warming by N<sub>2</sub>O emissions.

## 2 A global factor to describe N<sub>2</sub>O yield from N fertilization

We start this study by deriving the yield of N<sub>2</sub>O from fresh N input, based on data compiled by Prather et al. (2001) and Galloway et al. (2004) with some analysis of our own. Fresh



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fixed N input includes N, which is produced by chemical, biological and atmospheric processes. The pre-industrial, natural N<sub>2</sub>O sink and source at an atmospheric mixing ratio of 270 nmol/mol is calculated to be equal to 10.2 Tg N<sub>2</sub>O-N/yr (Prather et al., 2001), which includes marine emissions. By the start of the present century, at an atmospheric volume mixing ratio of 315 nmol/mol, the stratospheric photochemical sink of N<sub>2</sub>O was about 11.9 Tg N<sub>2</sub>O-N/yr. The total N<sub>2</sub>O source at that time was equal to the photochemical sink (11.9 Tg N<sub>2</sub>O-N/yr) plus the atmospheric growth rate (3.9 Tg N<sub>2</sub>O-N/yr), together totalling 15.8 Tg N<sub>2</sub>O-N/yr (Prather et al., 2001). The anthropogenic N<sub>2</sub>O source is the difference between the total source strength, 15.8 Tg N<sub>2</sub>O-N/yr, and the current natural source, which is equal to the pre-industrial source of 10.2 Tg N<sub>2</sub>O-N/yr minus an uncertain 0–0.9 Tg N<sub>2</sub>O-N, with the latter number taking into account a decreased natural N<sub>2</sub>O source due to 30% global deforestation (Klein Goldewijk, 2001). Thus we derive an anthropogenic N<sub>2</sub>O source of 5.6–6.5 Tg N<sub>2</sub>O-N/yr. To obtain the agricultural contribution, we subtract the estimated industrial source of 0.7–1.3 Tg N<sub>2</sub>O-N/yr (Prather et al., 2001), giving a range of 4.3–5.8 Tg N<sub>2</sub>O-N/yr. This is 3.8–5.1% of the anthropogenic “new” fixed nitrogen input of 114 Tg N/yr for the early 1990s; the input value is derived from the 100 Tg of N fixed by the Haber-Bosch process, plus 24.2 Tg of N fixed due to fossil fuel combustion and 3.5 Tg difference from biological N fixation, BNF, between current and pre-industrial times (Galloway et al., 2004), reduced by the 14 Tg of Haber-Bosch N not used as fertilizer (Smeets et al., 2007). (This total of 114 Tg N is very similar to the sum of the different values for N from fertilizer and BNF given by Smeets et al.: 81+38=119 Tg.) In an earlier study (Mosier et al., 1998) the source of N<sub>2</sub>O from agriculture was estimated to be even larger, 6.3 Tg N<sub>2</sub>O-N, giving an N<sub>2</sub>O yield of 5.5%. In comparison, the N<sub>2</sub>O-N emission estimated by Prather et al. (2001) is 2.9–6.3 Tg N<sub>2</sub>O-N/yr, or 3.4–6.8 Tg N<sub>2</sub>O-N/yr if we also include biomass and biofuel burning (which we consider an agricultural source), leading to N<sub>2</sub>O-N yields of 2.6–5.5% or 3.0–6.0%, respectively.

Because of good knowledge of the chemical processing of N<sub>2</sub>O in the atmosphere and its tropospheric concentrations, obtained from air enclosure in ice cores, its natural sources and sinks are well known and can be calculated with models. Thus, pre-industrial, natural conditions provide additional information on the yield of N<sub>2</sub>O from fixed N input. For that period, the global source and sink of N<sub>2</sub>O was 10.2 Tg N<sub>2</sub>O-N/yr with 6.2–7.2 Tg N<sub>2</sub>O-N/yr coming from the land and coastal zones (Prather et al., 2001), derived from a fresh fixed N input of 141 Tg N/yr (Galloway et al., 2004), giving an N<sub>2</sub>O-N yield of 4.4–5.1%. Both for the pre-Haber-Bosch natural terrestrial emissions and the agricultural emissions in the Haber-Bosch era, we find that the ratio  $y = \text{N}_2\text{O output/fresh fixed N input}$  is 3–5%. This is a parametric relationship, based on the global budgets of N<sub>2</sub>O and fixed N input, and atmospheric concentrations and known lifetime of N<sub>2</sub>O,

and thus is not dependent on detailed knowledge of the terrestrial N cycle. We assume that this global ratio will be the same in agro/biofuel production systems. This is a reasonable assumption, as similar agricultural plants are currently used as feedstocks for biofuel production as those grown in regular agriculture. Some correction is needed for the use of animal manure in biofuel crop production, but this is quite small: Cassman et al. (2002) noted that approximately 11% of total N input to world’s cropland came from animal manures.

A comparison of our “top-down” estimates of N<sub>2</sub>O emissions from inputs of newly fixed N with the “bottom-up” estimates that are made with the IPCC inventory methodology (Mosier et al., 1998; IPCC, 2006) is presented in Appendix A. A key feature of our methodology is that the 114 Tg of 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 N<sub>2</sub>O emissions.

### 3 N<sub>2</sub>O release versus CO<sub>2</sub> saved in biofuels

As a quick indicator to describe the consequence of this “background” N<sub>2</sub>O production we compare its global warming with the cooling due to replacement of fossil fuels by biofuels. Here we will only consider the climatic effects of conversion of biomass to biofuel and not a full life cycle, leaving out for instance the input of fossil fuels for biomass production, on the one hand, and the use of co-products on the other hand.

We assume that the fixed nitrogen which is used to grow the biofuels is used with an average efficiency of 40% (see below) and that this factor determines how much newly fixed N must be supplied to replenish the fields over time. We also obtain the fossil CO<sub>2</sub> emissions avoided from the carbon processed in the harvested biomass to yield the biofuel. With these assumptions, we can compare the climatic gain of fossil fuel-derived CO<sub>2</sub> “savings”, or net avoided fossil CO<sub>2</sub> emissions, with the counteracting effect of enhanced N<sub>2</sub>O release resulting from fixed N input. Our assumptions lead to expressions per unit mass of dry matter harvested in biofuel production to avoid fossil CO<sub>2</sub> emissions, “saved CO<sub>2</sub>”, (*M*), and for “equivalent CO<sub>2</sub>”, (*Meq*), the latter term accounting for the global warming potential (GWP) of the N<sub>2</sub>O emissions. We derive *M* from carbon contained in biomass as the lower heat value per carbon, and consequently the CO<sub>2</sub> emissions per energy unit, are almost identical for the fossil fuels and biofuels discussed here (JRC, 2007):

$$M = r_C * \mu_{\text{CO}_2} / \mu_C * cv \quad (1)$$

$$Meq = r_N * y * \mu_{\text{N}_2\text{O}} / \mu_{\text{N}_2} * \text{GWP}/e \quad (2)$$

In these formulae *r<sub>C</sub>* is in g carbon per g dry matter in the feedstock; *r<sub>N</sub>* is the mass ratio of N to dry matter in g N/kg;

**Table 1.** Relative warming derived from N<sub>2</sub>O production against cooling by “saved fossil CO<sub>2</sub>” by crops as a function of the actual nitrogen content  $r_{N(\text{actual})}$ . Uncertainty ranges presented derive from the uncertainty of the yield factor  $y$  (see text).

Crop	$r_{N(\text{actual})}$ (g N/kg dry matter)	Relative warming (Meq/M) (N-efficiency $e=0.4$ )	Type of fuel produced
Rapeseed	39	1.0–1.7	Bio-diesel
Maize	15	0.9–1.5	Bio-ethanol
Sugar cane	7.3	0.5–0.9	Bio-ethanol

$cv$  is the mass of carbon in the biofuel per mass of carbon in feedstock biomass (maize, rapeseed, sugar cane);  $e$  is a surrogate for the uptake efficiency of the fertilizer by the plants;  $y=0.03$ – $0.05$ , the range of yields of N<sub>2</sub>O–N from fixed N application;  $GWP=296$ ;  $\mu_{CO_2}/\mu_C=44/12$ ,  $\mu_{N_2O}/\mu_{N_2}=44/28$ , where the  $\mu$  terms are the molar weights of N<sub>2</sub>O, N<sub>2</sub>, CO<sub>2</sub>, and C.

Inserting these values in Eqs. (1) and (2) we thus obtain, with expressions in parentheses representing ranges,

$$M=3.667 \cdot cv \cdot r_C \quad (3)$$

$$\text{Meq}=(14 - 23.2)r_N/e \quad (4)$$

$$\text{Meq}/M=(3.8 - 6.3)r_N/(e \cdot cv \cdot r_C) \quad (5)$$

The latter term is the ratio between the climate warming effect of N<sub>2</sub>O emissions and the cooling effect due to the displacement of fossil fuels by biofuels.

These equations are valid for all above-ground harvested plant material, and separately also for the products and residues which are removed from the agricultural fields. If  $\text{Meq} > M$ , there will be net climate warming, the greenhouse warming by increased N<sub>2</sub>O release to the atmosphere then being larger than the quasi-cooling effect from “saved fossil CO<sub>2</sub>”. There will neither be net climate warming nor cooling by biofuel production when  $\text{Meq}=M$ , which occurs for

$$r_N=(0.158 - 0.263) \cdot (e \cdot cv \cdot r_C) \quad (6)$$

Under current agricultural practices, worldwide, the average value for  $e \approx 0.4$  (or 40%) (Cassman et al., 2002; Galloway et al., 2003; Balasubramanian et al., 2004). This value reflects the considerable amounts of N lost to the atmosphere via ammonia volatilization and denitrification (N<sub>2</sub>) and by leaching and runoff to aquatic systems. Fertilizer N use efficiency much higher than this (e.g. Rauh and Berenz, 2007) is certainly possible when fertilizer N is made available according to plant uptake requirements, but this does not reflect the agricultural practice in many countries of the world.

Nonetheless, we recognise the possibility of better efficiencies in future, as has been possible in special circumstances on a research basis. Below we derive values for  $r_N$  based on both  $e=0.4$  and  $e=0.6$ .

The data (and their sources) used to calculate the carbon contents,  $r_C$ , and the conversion efficiency factors,  $cv$ , and the calculations themselves, are given in Appendix B. As  $r_C$  we use 0.61, 0.44 and 0.43 for rapeseed, maize, and sugar cane, respectively. We derive values of  $cv=0.58$  for rapeseed bio-diesel,  $cv=0.37$  for maize bio-ethanol, and  $cv=0.30$  for sugar cane ethanol production.

Consequently, for  $e=0.4$ ,

$r_N=22.3$ – $37.2$  g N/kg dry matter for rapeseed bio-diesel,

$r_N=10.3$ – $17.1$  g N/kg dry matter for maize bio-ethanol

$r_N=8.1$ – $13.6$  g N/kg dry matter for sugar cane bio-ethanol.

Similarly, for  $e=0.6$ ,

$r_N=33.5$ – $55.8$  g N/kg dry matter for rapeseed bio-diesel,

$r_N=15.4$ – $25.7$  g N/kg dry matter for maize bio-ethanol

$r_N=12.2$ – $20.4$  g N/kg dry matter for sugar cane bio-ethanol.

For each of these biofuels, a larger value of  $r_N$  in the plant matter than this range implies that use of the fuel causes a net positive climate forcing.

Note that our analysis only considers the conversion of biomass to biofuels, emphasizing the role of N<sub>2</sub>O emissions. It does not take into account the supply of fossil fuel for fertilizer production, farm machinery and biofuel process facility, which require a considerable fraction of the energy gained (Hill et al., 2006). Furthermore, we assume that biofuel production is based on mineral fertilizer only (substitution of manure for synthetic fertilizer would offset our result by the percentage of synthetic fertilizer that is not used). The energy content gained from by-products will largely be offset from additional energy needed to produce it (Hill et al., 2006), here we also neglect its potential to replace other animal feed crops (and the associated N<sub>2</sub>O emissions). We are aware that integrated processes exist which better connect biofuel production with animal husbandry, but we believe this cannot be taken for granted on a global scale.

## 4 Results and discussion

### 4.1 Nitrogen content in biofuels

Data on  $r_N$  for several agricultural products, in g(N)/kg dry matter (Velthof and Kuikman, 2004; Biewinga and van der Bijl, 1996), are presented in Table 1, together with results on

**Table 2.** Sensitivity analysis, showing the impact on relative warming (Meq/M) resulting from changes to parameters used for Table 1. The calculations depend on assumptions made about the global agricultural practice of biofuel production. In each column, values differ from those presented in Table 1 by one parameter only as indicated in the relevant column heading.

Crop	Increased N-efficiency ( $e=0.6$ )	High share of manure (20%) in fertilizer for biofuels	Efficient use of by-products: Considerable fraction (50%) of N harvested for biofuel production replaces crops that would need N fertilizer
Rapeseed	0.7–1.2	0.8–1.4	0.5–0.9
Maize	0.6–1.0	0.7–1.2	0.4–0.7
Sugar cane	0.4–0.6	0.4–0.7	0.3–0.4

“relative warming”. They show net climate warming, or considerably reduced climate cooling, by fossil fuel “CO<sub>2</sub> savings”, due to N<sub>2</sub>O emissions. The  $r_N$  value for maize is equal to 15 g N/kg dry matter, leading to a relative climate warming of 0.9–1.5 compared to fossil fuel CO<sub>2</sub> savings. The effect of the high nitrogen content of rapeseed is particularly striking; it offsets the advantages of a high carbon content and energy density for biodiesel production. World-wide, rapeseed is the source of >80% of bio-diesel for transportation, and has been particularly promoted for this purpose in Europe. For bio-diesel derived from rapeseed, this analysis indicates that the global warming by N<sub>2</sub>O is on average about 1.0–1.7 times larger than the quasi-cooling effect due to “saved fossil CO<sub>2</sub>” emissions. For sugar cane / ethanol the relative warming is 0.5–0.9, based on a  $r_N$  value of 7.3 g N/kg dry matter (Isa et al., 2005), causing climate cooling with respect to N<sub>2</sub>O (not necessarily for the whole process, as fossil energy input is not considered).

Although there are possibilities for improvements by increasing the efficiency, e.g. for the uptake of N fertilizer by plants (Cassman et al., 2002) – which is much needed in regular agriculture as well – on a globally averaged basis the use of agricultural crops for energy production, with the current nitrogen use efficiencies, can readily be detrimental for climate due to the accompanying N<sub>2</sub>O emissions, as indicated here for the common biofuels: rapeseed / bio-diesel, and maize / ethanol. However, if nitrogen use efficiency can be increased to  $e=0.6$ , then as the calculations above and in Table 2 show, maize / ethanol and rapeseed / biodiesel may be climate-neutral or beneficial. Also the effect of other assumptions on our result (substitute manure; replace other crops) is tested in Table 2.

More favourable conditions for bio-energy production, with much lower nitrogen to dry matter ratios (Tillman et al., 2006), resulting in smaller N<sub>2</sub>O emissions, exist for special “energy plants”, for instance perennial grasses (Christian et al., 2006) such as switch grass (*Panicum virgatum*) and elephant grass (*Miscanthus × giganteus* hybrid), with a  $r_N$  of 7.3 g N/kg dry matter. The production of biofuel from palm oil, with a  $r_N$  of 6.4 g N/kg dry matter

(Wahid et al., 2005), may also have moderately positive effects on climate, viewed solely from the perspective of N<sub>2</sub>O emissions. Other favourable examples are ligno-cellulosic plants, e.g. eucalyptus, poplar and willow.

The importance of N<sub>2</sub>O emissions for climate also follows from the fact that the agricultural contribution of 4.3–5.8 Tg N<sub>2</sub>O-N/yr gives the same climate radiative forcing as that provided by 0.55–0.74 Pg C/yr, that is 8–11% of the greenhouse warming by fossil fuel derived CO<sub>2</sub>. Increased emissions of N<sub>2</sub>O will also lead to enhanced NO<sub>x</sub> concentrations and ozone loss in the stratosphere (Crutzen, 1970). Further, NO is also produced directly in the agricultural N cycle. Adopting the relative yield of NO to N<sub>2</sub>O of 0.8 (Mosier et al., 1998), and the agricultural contribution to the N<sub>2</sub>O growth rate of 4.3–5.8 Tg N<sub>2</sub>O-N/yr, the global NO production from agriculture is equal to 3.4–4.6 Tg N/yr, about 20% of that caused by fossil fuel burning (Prather et al., 2001), affecting tropospheric chemistry in significant ways.

#### 4.2 Potential impact on life cycle analysis

An abridged analysis as presented above, yielding N/C ratios to indicate whether biofuels are GHG-positive or GHG-negative, can not replace a full life cycle assessment. In recent years, a number of such assessments have become available (Adler et al., 2007; Kaltschmitt et al., 2000; von Blotnitz et al., 2006; Farrell et al., 2006; Hill et al., 2006). At this stage, we can not discuss the differences between these respective approaches, which also affect conclusions. But we may look into the release rate of N<sub>2</sub>O-N used, presented as a function of applied fertilizer N. In these life cycle studies, release rates typically are based on the default values estimated by IPCC (2006) for “direct” emissions which were derived from plot-scale measurements (1% of the fertilizer N applied, or, in a previous version, 1.25%). Only a few studies (Adler et al., 2007) also incorporate the corresponding default values for “indirect” emissions also specified by IPCC (totalling less than 0.5% and which, together with the direct emissions, add up to c. 1.5% of fertilizer N), whereas our global analysis indicates a value of 3–5%. Past studies seem to have underestimated the release rates of N<sub>2</sub>O to the

atmosphere, with great potential impact on climate warming. The effect of applying higher N<sub>2</sub>O yields can be assessed using the openly accessible EBAMM model (Farrell et al., 2006).

## 5 Conclusions

As release of N<sub>2</sub>O affects climate and stratospheric ozone chemistry by the production of biofuels, much more research on the sources of N<sub>2</sub>O and the nitrogen cycle is needed. Here we have shown that the yield of N<sub>2</sub>O-N from fixed nitrogen application in agro-biofuel production can be in the range of 3–5%, 3–5 times larger than assumed in current life cycle analyses, with great importance for climate. We have also shown that the replacement of fossil fuels by biofuels may not bring the intended climate cooling due to the accompanying emissions of N<sub>2</sub>O. There are also other factors to consider in connection with the introduction of biofuels. Here we concentrated on the climate effects due only to required N fertilization in biofuel production and we have shown that, depending on N content, the current use of several agricultural crops for energy production, at current total nitrogen use efficiencies, can lead to N<sub>2</sub>O emissions large enough to cause climate warming instead of cooling by “saved fossil CO<sub>2</sub>”. What we have discussed is one important step in a life cycle analysis, i.e. the emissions of N<sub>2</sub>O, which must be considered in addition to the fossil fuel input and co-production of useful chemicals in biofuel production. We have not yet considered the extent to which any loss by volatilisation of part of the fertilizer N may stimulate CO<sub>2</sub> uptake from the atmosphere, following deposition on natural ecosystems; estimates for this effect are very uncertain (de Vries et al., 2006; Magnani et al., 2007; Hyvönen et al., 2007). We conclude that the relatively large emission of N<sub>2</sub>O exacerbates the already huge challenge of getting global warming under control.

## Appendix A

### Comparison between the present and the IPCC method to estimate the global N<sub>2</sub>O yields

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 related N<sub>2</sub>O emissions, and furthermore these emissions may not all happen in the season of application, but involve longer cycling times (which are nonetheless short compared with the lifetime of N<sub>2</sub>O in the environment). These emissions can be conveniently considered in three categories:

- direct emissions from N-fertilized soils;

- “secondary” emissions resulting from the complex transformations of N compounds in the various flows within agricultural systems; and
- indirect emissions (in the IPCC meaning of the phrase) arising from leached N leaving agricultural fields and entering water systems, and from volatilized N deposited onto natural ecosystems.

Examples of the “secondary” emission sources are:

- crop residues ploughed in as fertilizer for a successor crop;
- dung and urine from livestock (both grazing and housed) fed variously on N-fertilized grain crops, feeds containing BNF-N (e.g. soya bean meal, alfalfa, clover-rich pasture and silage in Europe, and tropical grasses with *Azospirillum* associations in Brazil); and
- N mineralized from soil organic matter and root residues following cultivation or grassland renewal.

In contrast, in the IPCC approach, emissions from crop residues and mineralization are included in the “direct” emissions and have the same emission factor (*EF*); separate *EF*s are used for emissions from grazing animals, and the N source here is quantified on the basis of the N excreted, and essentially is treated as a “new” N source, not as fertilizer- or BNF-derived N. The fractions of the N applied to fields that are lost by leaching, runoff and volatilization have additional *EF*s applied to them. The aggregate emissions from agriculture are arrived at by summing all these individual sources. The IPCC’s 1% *EF* for direct N<sub>2</sub>O emissions contains an uncertainty of one-third to 3 times the default value. The default *EF* for emissions from cattle, poultry and pigs is 2% of the N excreted, with a range of 0.7% to 6% – again, from one-third to 3 times the default value. The *EF*s for N derived from N volatilization and re-deposition and N derived from leaching and runoff are 1% (uncertainty range 0.2–5%) and 0.75% (0.05–2.5%), respectively. At default volatilization fractions of 10% (mineral fertilizer) or 20% (animal manure), and default leaching fraction of 30%, indirect emissions amount to 0.35–0.45% of N applied. Each of the source terms in the bottom-up, IPCC method is very uncertain. However, their sum is not inconsistent with the total derived by the top-down methodology.

## Appendix B

### Calculation of cv values

- a) Bio-ethanol production from maize:

Yield=2.66 US gallons per US bushel (mean of values for wet and dry milling processes) (USDA 2002, cited in UK Dept for Transport, 2006)

$$=2.66 \times 3.785 = 10.07 \text{ l ethanol/25.4 kg maize}$$

$$\equiv 7.945 \text{ kg ethanol/25.4 kg maize}$$

$$=0.313 \text{ kg ethanol/kg maize.}$$

C content of ethanol (C<sub>2</sub>H<sub>5</sub>OH, mol. wt. 46) by weight = 24/46 = 522 g/kg.

C content of maize ( $r_C$ )  $\approx 0.44 \text{ g/g} \approx 440 \text{ kg/t}$ .

$$cv = (0.313 \times 522) / 440 = 0.37.$$

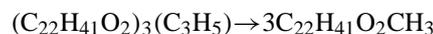
b) Bio-diesel production from rapeseed:

- the average oil yield is 45% (450 kg/t rapeseed) (Elaine Booth, SAC Aberdeen, personal communication)
- the average composition of the oil is adequately represented by the triglyceride of the dominant fatty acid, erucic acid, i.e. (C<sub>22</sub>H<sub>41</sub>O<sub>2</sub>)<sub>3</sub>(C<sub>3</sub>H<sub>5</sub>), mol. wt. 1052, then

C content of the oil by weight = 828/1052 = 0.787 kg/kg.

Thus the C content of the oil = (450 × 0.787) = 354 kg/t rapeseed.

The conversion to bio-diesel involves conversion to the methyl ester:



but the C content of the bio-diesel is almost unchanged from that of the natural oil:

mol. wt. of methyl ester = 352, and  
C content = (276/352) × 450 = 353 kg/t rapeseed.

Oil content of original rapeseed = 45% (450 kg/t), and non-oil components  $\approx 550 \text{ kg/t}$ , of which

- protein is 40% ( $\approx 220 \text{ kg/t}$  original rapeseed), with a C content of 510 g/kg;
- the remainder (60%,  $\approx 330 \text{ kg/t}$  original rapeseed) is dominantly carbohydrate,

(Colin Morgan, SAC Edinburgh, personal communication)

Thus the C content of the protein fraction in the original rapeseed = 220 × 510/1000 = 112 kg/t; and

the C content of the carbohydrate fraction (for which a C content of 440 g/kg can be adopted, as for grains) = 330 × 440/1000 = 145 kg/t.

The overall C content of the original rapeseed ( $r_C = C_{oil} + C_{protein} + C_{CHO}$ ) = 354 + 112 + 145 = 612 kg/t.

$$cv = 353 / 612 = 0.58.$$

c) Bio-ethanol production from sugar cane:

Yield is 86 l dry ethanol (density 0.79 kg/l) per tonne sugar cane harvested at a water content of 72.5%, or 247 kg ethanol per tonne dry sugar cane (Macedo et al., 2004, as cited by JRC, 2007).

C content of ethanol (C<sub>2</sub>H<sub>5</sub>OH, mol. wt. 46) by weight = 24/46 = 522 g/kg.

C content of dry sugar cane is determined by its structural material, cellulose, and its sugar content (polysaccharides: 440 g/kg; saccharose: 420 g/kg), we use  $r_C = 430 \text{ g/kg}$

$$cv = (0.247 \times 522) / 430 = 0.30.$$

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## References

- Adler, P. R., Del Grosso, S. J., and Parton, W. J.: Life-cycle assessment of net greenhouse-gas flux for bioenergy cropping systems, *Ecol. Appl.*, 17, 675–691, 2007.
- Balasubramanian, V., Alves, B., Aulakh, M., Bekunda, M., Cai, Z., Drinkwater, L., Mugendi, D., van Kessel, C., and Oenema O.: Crop, environmental, and management factors affecting nitrogen use efficiency, in: *Agriculture and the Nitrogen Cycle*, edited by: Mosier, A. R., Syers, J. K., and Freney, J., SCOPE 65, 19–33, Island Press, Washington, Covelo, London, 2004.
- Biewinga, E. E. and van der Bijl, G.: Sustainability of energy crops in Europe, Centre for Agriculture and Environment (CLM), Utrecht, The Netherlands, 1–209, 1996.
- Cassman, K. G., Dobermann, A., and Walters, D. T.: Agroecosystems, nitrogen-use efficiency, and nitrogen management, *Ambio*, 31, 132–140, 2002.
- Christian, D. G., Poulton, P. R., Riche, A. B., and Yates, N. E.: The recovery over several seasons of <sup>15</sup>N-labelled fertilizer applied to *Miscanthus x giganteus* ranging from 1 to 3 years old, *Biomass Bioenerg.*, 30, 125–133, 2006.
- Crutzen, P. J.: The influence of nitrogen oxides on the atmospheric ozone content, *Q. J. Roy. Meteor. Soc.*, 96, 320–325, 1970.
- de Vries, W., Reinds, G. J., Gundersen, P., Sterba, H.: The impact of nitrogen deposition on carbon sequestration in European forests and forest soils, *Global Change Biol.*, 12, 1151–1173, 2006.
- Farrell, A. E., Plevin, R. J., Turner, B. T., Jones, A. D., O'Hare, M., and Kammen, D. M.: Ethanol Can Contribute to Energy and Environmental Goals, *Science*, 311, 506–508, 2006.
- Galloway, J. N., Dentener, F. J., Capone, D. G., Boyer, E. W., Howarth, R. W., Seitzinger, S. P., Asher, G. P., Cleveland, C. C., Green, P. A., Holland, E. A., Karl, D. M., Michaels, A. F., Porter, J. H., Townsend, A. R. and Vörösmarty, C. J.: Nitrogen cycles: Past, present, and future, *Biogeochemistry*, 70, 153–226, 2004.

- Galloway, J. N., Aber, J. D., Erisman, J. W., Seitzinger, S. P., Howarth, R. H., Cowling, E. B., and Cosby B. J.: The nitrogen cascade, *Bioscience*, 53, 341–356, 2003.
- Hill, J., Nelson, E., Tilman, D., Polasky, S., and Tiffany, D.: Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels, *Proc. Nat. Acad. Sci.*, 103, 11 206–11 210, 2006.
- Hyvönen, R., Persson, T., Andersson, S., Olsson, B., Ågren, G. I., and Linder, S.: Impact of long-term nitrogen addition on carbon stocks in trees and soils in northern Europe, *Biogeochemistry*, online edition, doi:10.1007/s10533-007-9121-3, 2007.
- IPCC: 2006 IPCC Guidelines for National Greenhouse Gas Inventories, prepared by the National Greenhouse Gas Inventories Programme, edited by: Eggleston, H.S, Buendia, L., Miwa, K., Ngara, T. and Tanabe, K., Volume 4, Chapter 11, N<sub>2</sub>O emissions from managed soils, and CO<sub>2</sub> emissions from lime and urea application, IGES, Hayama, Japan, 2006.
- Isa, D. W., Hofman, G., and van Cleemput, O.: Uptake and balance of fertilizer nitrogen applied to sugarcane, *Field Crop. Res.*, 95, 348–354, 2005.
- JRC: Well-to-Wheels analysis of future automotive fuels and powertrains in the European context. Well-to-Tank report, version 2c, Joint Research Centre, Ispra, Italy, March 2007.
- Kaltschmitt, M., Krewitt, W., Heinz, A., Bachmann, T., Gruber, S., Kappelmann, K.-H., Beerbaum, S., Isermeyer, F., and Seifert, K.: Gesamtwirtschaftliche Bewertung der Energiegewinnung aus Biomasse unter Berücksichtigung externer und makroökonomischer Effekte (Externe Effekte der Biomasse), Final Report (in German), IER, University of Stuttgart, Germany, 2000.
- Klein Goldewijk, C. G. M.: Estimating global land use change over the past 300 years: The HYDE data base, *Global Biogeochem. Cy.*, 15, 415–434, 2001.
- Magnani, F., Mencuccini, M., Borghetti, M., et al.: The human footprint in the carbon cycle of temperate and boreal forests, *Nature*, 447, 848–850, 2007.
- Mosier, A., Kroeze, C., Nevison, C., Oenema, O., Seitzinger, S., and van Cleemput, O.: Closing the global N<sub>2</sub>O budget: nitrous oxide emissions through the agricultural nitrogen cycle, *Nutr. Cycl. Agroecosyst.*, 52, 225–248, 1998.
- Prather, M., Ehhalt, D., et al.: Atmospheric chemistry and greenhouse gases, in: *Climate Change 2001: The Scientific Basis*, edited by: Houghton, J. T., Ding, Y., Griggs, D. J., et al., 239–287, Cambridge University Press, Cambridge, UK, 2001.
- Rauh, S. and Berenz, S.: Interactive comment on “N<sub>2</sub>O release from agro-biofuel production negates global warming reduction by replacing fossil fuels” by: P.J. Crutzen et al., *Atmos. Chem. Phys. Discuss.*, 7, S4616–4619, 2007.
- Smeets, E., Bouwman, A. F., and Stehfest, E.: Interactive comment on “N<sub>2</sub>O release from agro-biofuel production negates global warming reduction by replacing fossil fuels” by P.J. Crutzen et al., *Atmos. Chem. Phys. Discuss.*, 7, S4937–4941, 2007.
- Tillman, D., Hill, J., and Lehman, C.: Carbon-negative biofuels from low-input high-diversity grassland biomass, *Science*, 314, 1598–1600, 2006.
- UK Department for Transport, International resource costs of bio-diesel and bio-ethanol, published 26 January 2006, <http://www.dft.gov.uk/pgr/roads/environment/research/cqvcf/internationalresourcecostsof3833>, 2006.
- Velthof, G. L. and Kuikman, P. J.: Bepierking van lachgasemissie uit gewasresten, Alterra rapport 114.3 (in Dutch), Wageningen, The Netherlands, 2004.
- von Blottnitz, H., Rabl, A., Boiadjev, D., Taylor, T., and Arnold, S.: Damage Costs of Nitrogen Fertilizer in Europe and their Internalization, *J. Environ. Plan. Manage.*, 49, 413–433, 2006.
- Wahid, M. B., Abdullah, S. N. A., and Henson, I. E.: Oil palm – achievements and potential, *Plant Prod. Sci.*, 8, 288–297, 2005.