Chapter

Greenhouse Gas Emissions of Agriculture: A Comparative Analysis

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Abstract

Greenhouse gas emissions are accounted by greenhouse gases inventories, which must be produced by common accounting rules, called Guidelines, which are endorsed by the United Nations Framework Convention on Climate Change (UNFCCC). These inventories are fundamental to analyze the impact of agriculture on emissions, and as example of the difficulty and complexity of implementation of the guidelines, a comparative study is made on emissions from Agricultural Soil Management (CRF category 3D source) utilizing biological nitrogen fixation. The analysis carried out for the N_2O emissions under this section of the agrarian sector of Spain, Europe, New Zealand, Canada and the USA, inventories and national communications from Argentina and Brazil permit to observe the wide spectrum of approaches and the importance of the management of the accounting rules to be used mainly if we need that the impact of mitigation policies are captured in a direct way by the inventory. New technologies could introduce changes in the rules and can be utilized for reducing emissions, and examples are also analyzed.

Keywords: inventory of agriculture greenhouse gas emissions, N_2O emissions, biological nitrogen fixation, benchmark of countries, new technologies

1. Introduction

Agriculture is one of the economic sectors that make up the economic structure of a country and, as such economic activity, contributes to generate part of greenhouse gas of the total emissions of each country and, therefore, is an activity co-responsible for climate change.

Emissions of greenhouse gas (GHG) are accounted by greenhouse gases inventories and allow us to characterize both the emitting sources and the amount emitted and must be made respecting common rules designed with high technical qualifications.

This accounting of emissions from the agricultural sector is particularly complex and should be a useful tool for the design of agricultural policies for emissions mitigation from this sector.

To be able to check the difficulty and complexity of application of accounting guidelines and, also, the wide spectrum of options that you can use, a comparative study of the treatment of emissions from a series of inventories or national communications from various countries is made in this chapter.

It is undeniable that knowledge and the correct accounting of emissions we will strongly condition analyses and measures that specifically we design and pretend to implement to achieve lower emissions in this sector. It will enable us and also defines new technologies that may be incorporating gradually and its effect can be captured by each country GHG inventory.

2. Greenhouse inventories and agricultural sector

From the year 2015, national GHG inventories have been developed following the Guidelines of the International Panel of Climate Change (IPCC) 2006 [4]. Until that year, 1996 IPCC Guidelines were used, and the introduction of these new guidelines meant significant changes in the accounting emissions of agricultural sector. In addition to new accounting rules that affect every economic sector, the potential of global warming greenhouse gases also changed, which meant to make updates of all the data series that are measured from the 1990 base year.

Table 1 presents the global warming potential (GWP) of the three major gases that have been used and the new planned reform [1].

In addition to the changes made to the potential of global warming gases, two of which, (CH_4 and N_2O) particularly affect agriculture also changed certain accounting rules which generated significant changes in the volume of emissions in this economic sector. The changes that are made to inventories' rules will affect in proportion to each country's productive structure.

2.1 Emissions from agriculture

Emissions from agriculture activity vary depending on the economic structure of countries and the extent of its territory because agriculture is mainly based on Earth's surface arable in each country. An idea of absolute importance (total emissions) and relative (percentage of agriculture with respect to the total emissions) can be seen in **Table 2** using data on inventories [2] and national communications of different countries [3].

We can see that the developed countries have a much less percentage of agrarian sector emissions (their emissions more importantly tend to belong to the energy sector), and the big countries such as Argentina and Brazil have a large amount of emissions in relative and absolute value. An exception is New Zealand that even being a developed country has a broad agricultural sector.

Gases	Chemical formula	GWP values for 100-year time horizon		
		Second Assessment Report (SAR)	Fourth Assessment Report (AR4)	Fifth Assessment Report (AR5)
Carbon dioxide	CO_2	1	1	1
Methane	CH_4	21	25	28
Nitrous oxide	N_2O	310	298	265

Table 1.
Global warming potential (GWP) values relative to CO_2.

Year/ methodology	Countries	Agriculture emissions Total kt CO_2 eq.	Agriculture emissions/total emissions (%)
2016/AR4	EUR28 + Island	431,000	9.2
2016/AR4	USA	562,600	8.6
2016/AR4	Canada	72,000	10
2016/AR4	New Zealand	38,727	49.2
2016/AR4	Spain	34,405	12.1
2012/SAR	Argentina	119,498	27.8
2010/SAR	Brazil	407,067	32

Table 2.
Agriculture emissions by countries.

3. A comparative analysis of methodologies

In order to show the complexity and diversity of options that can be used, a comparative analysis of the methodologies used will be carried out to evaluate the emissions from agriculture's sector in the inventories and national communications of previous countries.

In a first epigraph, it will use a section of the inventory of emissions from agriculture, the emissions from managed agricultural soils: Agricultural Soil Management by the analysis that the new guidelines have been given to the nitrogen biological fixation (NBF).

We will study methodologies, which not being developed in the United Nations Framework Convention on Climate Change (UNFCCC) guidelines are approved by the inspectors in different reviews carried out inventories and if it be known by other countries could be used.

A detailed analysis is performed, with respect to N_2O emissions under this epigraph of the agrarian sector, of Spain, Europe, New Zealand, Canada and the USA inventories and national communications from Argentina and Brazil to see the broad spectrum of approaches and the importance of management of accounting rules.

We will use, as demonstrative example, legumes' crops because they are widely cultivated throughout the world on a large part of the Earth's surface, and also they have the ability to fix atmospheric nitrogen to facilitate its growth; so it is very important to know the accounting treatment that has been given to these plant species in the IPCC guidelines.

3.1 The treatment of legumes

New 2006 Guidelines introduced a very significant change in the treatment of legumes in GHG's inventories compared to previous 1996 guidelines [4]. This change meant a large reduction in emissions of the main producer countries, and this reduction is not due to an effective policy of mitigation emissions, but it is due to a simple change in accounting criteria, which is based on a technical scientist analysis.

To facilitate understanding of the problem, a brief theoretical nitrogen cycle exposure begins.

We will use the Centro Superior de Investigaciones Científicas (Spain) work, which explains very clearly this topic [5]:

> *"Nitrogen fixation may be purely abiotic or biological. In abiotic fixation, oxides are formed as a result of the combustion of organic compounds, electric shock, etc., which are dragged to the ground by rain, or ammonium by the industrial process Haber-Bosch. Biological nitrogen fixation process are carried out by prokaryotic organisms, N_2 is reduced to ammonium and incorporated into the biosphere."*

"These bacteria from the soil that we could call fixation free, as those of the genus *Azotobacter*, require up to 100 units of glucose equivalents per unit of nitrogen fixed. For this reason, its agricultural significance is low, which increases considerably in the case of the symbiotic fixation, as the established between rhizobia and legumes, where the ratio decreases of 6–12 units of glucose consumed per unit of nitrogen fixed. In this case, moreover, the power source is carbon compounds supplied directly by the plant derived from photosynthesis, while free fixation has to take them from soil, where these carbon compounds (glucose) do not exist in the amount and form necessaries. So in fact, *Azotobacter* provides to the ground a few hundred grams of nitrogen per hectare/year, and on the other hand, this value goes up in the *Rhizobium* association with alfalfa, clover, peas or soybean, until a few hundred kilos. Despite these differences, free fixation alone represents, at global level, rather less than half of the total of N_2 fixed per year [6], because symbiotic fixation, although was more high, is limited to a few plant species, including legumes." Therefore, the N_2 is fixed not only by bacteria in the roots, mostly legumes, but also by the free bacteria (not symbiotic) in the soil.

Data show that 250 Mt. of N_2 are fixed annually for bacteria and about 70 Mt. would be fixed by soil or free bacteria, which would represent 28% of N_2 fixed and about 50% would be fixed for biological fixation.

It is very important to bear in mind this data because it will strongly affect the inventories and the ways of accounting for the whole issue of the fixation of atmospheric N_2 as we will then develop.

On the one hand, it is very common that mitigation measures to tackle climate change are based on the property of legumes to fix atmospheric N_2 by a series of bacteria (genus *Rhizobium* mainly).

Thus, for example, the road map of Spain for the reduction of diffuse emissions proposes, among others, the following course of action [7]: the introduction of legumes in managed grasslands with the aim of reducing the emissions from soils in meadows. The fixation of atmospheric nitrogen produced by legumes outweighs the need for mineral fertilizers.

On the other hand, the United States of America is the only country that counts in their inventory emissions of N_2O due at atmospheric N_2 fixed by the free soil bacteria.

3.2 The measurement of the biological fixation by legumes

With the 1996 IPCC Guidelines [8] to account for emissions of nitrous oxide (N_2O) that occurs naturally in soils: "some agricultural activities bring nitrogen to the soil, increasing the amount of nitrogen (N) available for nitrification and denitrification and, ultimately, the amount of N_2O emitted. Direct emissions of N_2O from agricultural soils due to the application of N and other farming practices should reflect the contributions of anthropogenic (N) resulting from the use of synthetic fertilizers (NSF) and the animal manure applied (AMA), N of fixing varieties (NBF), the incorporation to the soils the crop residues, the nitrogen mineralization of the soil due to the cultivation of organic soils (i.e., histosols) (COS)."

The first conclusion we get is that those 1996 Guidelines address the plantation of legumes as an incorporation of N to the soil and, therefore, the producer of N_2O

emissions. The captured N of the atmosphere as a sink is not considered, but it is a source of emission.

To see how the emission due to the nitrogen biological fixation (NBF) is accounted, it can be seen from the following **Table 3** [9] that shows data of NBF in 2012 from the inventory of 15 European countries.

We can see that because the property of N fixation of legumes Europe-15 have been issued 753,000 tons of nitrogen, which then result in N_2O emissions. Transformed into CO_2 eq., they are equivalent to 4.575 Mt. of CO_2 eq.

3.3 New rules of measurement of biological fixation

As indicated above, from the year 2015, the 1996 IPCC guidelines are no longer used for inventory and entered into force the new 2006 Guidelines currently in the process of improvement.

These Guidelines say: "Biological nitrogen fixation has been removed as a direct source of N_2O because of the lack of evidence of significant emissions arising from the fixation process itself [33]. These authors concluded that the N_2O emissions induced by the growth of legume crops/forages may be estimated solely as a function of the above-ground and below-ground nitrogen inputs from crop/forage residue (the nitrogen residue from forages is only accounted for during pasture renewal). Conversely, the release of N by mineralization of soil organic matter as a result of change of land use or management is now included as an additional source. These are significant adjustments to the methodology previously described in the 1996 IPCC Guidelines."

This change means that they are accounted only for emissions from biological fixation of nitrogen for the purpose of the N_2, which are produced from the crop

Member states 2012	N-fixing crops (Gg N)
Austria	23
Belgium	4
Denmark	42
Finland	0.7
France	224
Germany	78
Greece	0.8
Ireland	0.5
Italy	140
Luxemburg	0.1
The Netherlands	4
Portugal	10
Spain	172
Sweden	35
The United Kingdom	19
EU-15	753

Table 3.
The European Union greenhouse gas inventory 2014.

residue and mineralization and so the inventories will not reflect emissions that are previously counted as biological fixation.

The amounts saved because of this new methodology are significant because they can reduce emissions under this epigraph of the inventory by 50%.

As example, if we analyze successive inventories of Spain since the year 2012–2016, we obtain the following results (**Table 4**). The 1996 IPCC guidelines were used in the year 2012 and, therefore, included the biological fixation of nitrogen emission and also applied the N_2O (SAR = 310) global warming potentials. That year was an emission result of the epigraph of agricultural soils 3D = 18,167 kt of CO_2 eq.

Subsequently, this year 2012, inventories were calculated with the new warming potential of N_2O (AR4 = 298) and began to gradually introduce the 2006 Guidelines, because as we have said is required to recalculate since 1990 with the new parameters. The result has been that the 2012 emissions calculated in the year 2018 and referred to the year 2016 have meant 9245 kt CO_2 eq. for the year 2012.

This has meant that without changing the variables of activity of this section due to the recalculations, the year 2012 emissions were almost lower 50%. The inventory lowered emissions due to a change in accounting criteria, not the implementation of mitigation measures.

Table 4 presents the evolution of Spain emissions for 2012, taking into account the recalculations marked in each annual inventory for the indicated methodological changes.

3.3.1 The cultivation of soybean

Then, we analyze the accounting treatment that different inventories of large producers of legumes make use of nitrogen biological fixation. We utilize, as an example, the crop of soybean, because it is the most widely legume cultivated worldwide and its high impact will allow us to better appreciate the distortions that occur in the accounting treatment of biological fixation. In **Table 5**, we can observe the increase of soybean crop between 2020 and 2016 surfaces mainly in Brazil and Argentina, and as in the United States, it has not changed, but remains as the maximum world producer of this crop.

These data provide us with an idea of the magnitude of the cultivation of these countries, some of which possess more hectares dedicated only to the soybean crop that the entire surface of Spain dedicated to all crops (Spain = 26.6 Million ha in the year 2016).

We can see that with such immense extensions dedicated to the cultivation of this legume, "accounting" treatment that Guidelines gives to the biological fixation will be a great importance for the inventory of emissions of these countries.

We will study two of the major producer countries (Argentina and Brazil) through their national communications and the inventories from the USA and Canada to observe how this phenomenon of biological fixation for the purposes of accounting has been treated.

Emissions of Spain in 2012 in the successive inventories in kt. CO_2				
2012	2013	2014	2015	2016
18,167	16,151	11,872	8823	9245

Table 4.
Spain emissions N_2O activity 3D.

	Soybean crop			
Year	**2000**		**2016**	
Countries	Million ha	Million tonnes	Million ha	Million tonnes
Argentina	8.6	20.1	19.5	58.8
Brazil	13.6	32.8	33.2	96.3
Canada	1.06	2.7	2.2	5.8
USA	29.3	75.1	33.5	117.2

Table 5.
Data from FAOSTAT [10].

3.3.1.1 Argentina

To analyze how this item is addressed in Argentina, in your inventory, we will use data available from the second [11] and the third national communications [12]. These two communications are still made according to the 1996 IPCC guidelines since it closes its data in 2012.

The second national communication of Argentina says "the amount of nitrogen incorporated by NBF increased around 63% between 1990/91 and 2000/01 campaign. This fact was due to the strong increase in soybean production that went from 12 to nearly 20 million tons, making it the main crop of the country. The main increase in the amount of N was due, again, to the great increase of soybean production, the main crop with contribution of the NBF."

The third communication data already indicate a rise of 5.354 Mt. CO_2 eq., that is, an increase of 31% in emissions in those 12 years (**Table 6**).

The data, in **Table 5**, show that soybean crop in Argentina increases until 19.5 Million ha and 58.8 Million tonnes in the year 2016. These data lead us to conclude that emissions from this crop and the NBF would grow strongly by applying the 1996 Guidelines. When they are finally implementing the 2006 Guidelines, the emissions reduction, due to this item, will be very significant.

As it is indicated above, Argentina will reduce its emissions simply by a change in accounting criteria unless it really is because of a mitigation policy.

The data show that the year 2012 Europe-15 saved with the accounting change of the NBF = 4.7 Mt. CO_2 eq. front the 22.5 Mt. CO_2 eq. that will save Argentina. That year 2012, Argentina only accounted 7.04 Mt. CO_2 eq. (much lower than that of the NBF) due to the use of synthetic fertilizers that are usually the most important epigraph in agriculture emissions of developed countries.

We can see that the two large producers of soybean as Brazil (33.2 Mhas.) and the USA with (33.5 Mhas.) in 2016, compared the 17.6 Mhas. of Argentina in 2012, if they counted with this methodology that would have a great impact on their emissions.

Argentina	**Years**	
	2000	**2012**
Surface of soybean (Mhas.)	8.6	17.6
Direct emissions from crops fixing (Mt. of CO_2 eq.)	17.231	22.585

Table 6.
Argentina emissions.

The Argentine Government makes a [13] comparative study to analyze the impact that would have to apply the new accounting standards (1996 Guidelines against the 2006 Guidelines) and also apply the changes of global warming potentials from methane and nitrous oxide with a result of = −58.257 Mt. CO_2 eq. if the new guidelines had been applied in the 2012 inventory (**Table 7**).

3.3.1.2 Brazil

To analyze the accounting treatment of the emissions from this crop in Brazil, third national communication [14] sent to the UNFCCC in April 2016 will be used. In this document, Brazil already uses the IPCC 2006 Guidelines and, therefore, does not consider NBF as a source of N_2O.

They also used a "study of Cardoso et al. (2008) that would demonstrate that don't exist any differences between the emissions of N_2O measured in soils planted with inoculated varieties (in Brazil, soybean is inoculated with the specific bacteria for N_2 fixation) and other varieties not inoculated." The authors of this national communication don't take into account, therefore the NBF, and they use the methodology of the 2006 Guidelines for analyses the N, which is incorporated into the soil by residue. To estimate these emissions of residues, annual productions and the amount of dry matter by crop type were used.

Brazil introduced an innovation by including a new measuring method and it explains their results also using the potential of global temperature that is proposed by the IPCC. To explain its emissions, results using three warming potential in addition to those specified in **Table 1** were used, the potential SAR and the AR5, and a new one is introduced: the global potential temperature (GTP) (**Table 8**). But, for the calculations, do not use the AR4 potential, which should be used according to the rules of implementation of the guidelines for 2006. Therefore, the results would be questionable and are not comparable.

Brazil with much more surface dedicated to the cultivation of soybean (33.2 Mhas. 2016) should produce much higher emissions than Argentina with much less soybean surface (in 2012 with 17.6 Mhas. produced 22.6 Mt. of CO_2 eq.), but the use of 2006 Guidelines that do not account NBF and the use of different potential warming involve that this country has fewer emissions.

The gap would be much better if these divergent rules had been applied to the year 2016, in which both countries doubled their crop surfaces. The conclusion is that accounting rules are very important, because Brazil "save" important

	Emissions from agriculture in Argentina in 2012 according to the different guidelines. Mt. CO_2 eq.			
Category	**IPCC 2006**	**IPCC 1996**	**Absolute difference**	**Difference %**
4A. Livestock	52.900	49.372	3.528	+7%
4.B. Agriculture	35.242	70.130	−34.887	−50%
5.A. Change of land use and forestry	63.616	90.515	−26.898	−30%
			−58.257	

Table 7.
Evaluation guidelines effect.

Gases	Chemical formula	Global temperature potential: GTP/100 years
Carbon dioxide	CO_2	1
Methane	CH_4	4
Nitrous oxide	N_2O	234

Table 8.
Global temperature potential

emissions, using the guidelines for 2006, which would be much greater with the 1996 Guidelines.

Knowing in depth how inventories are produced is, therefore, very important, and thus, we would conclude that the reduction of emissions from the agriculture sector was due to an "effective mitigation policy" when actually is due to a simple change of the accounting rules.

3.3.2 Canada

Let us look at another example, the case of Canada [15–17], which also uses the 2006 Guidelines and it is another large producer of soybeans, although in smaller amounts (5, 8 Mt. in 2016). Canada, in its 2016 inventory, reports the emissions of leguminous crops in residues which are incorporated into the soil (6.5 Mt. CO_2 eq.) [18].

As shown in **Table 9**, another novelty introduced in 2004 Canada's inventory is the appearance of new emissions due to summer fallow (0.43 Mt. CO_2 eq.) and a sink effect (−0.63 Mt. CO_2 eq.) due to the use of practices that do not till the soil, known as conservation agriculture.

These emissions and these sinks have no specific methodology in the 2006 Guidelines and their effects are calculated with methodologies developed by the country. According to the 2016 Canada's inventory, these emissions accounted for 0.22 Mt. CO_2 eq. in the case of the fallow summer and −1.5 Mt. CO_2 eq. as a sink due to conservation agriculture. Canada's inventory reports 20 Mt. CO_2 eq. as direct sources of agricultural soils (N_2O) and, therefore, conservation agriculture has been a significant sink (7,5%).

Agricultural soils (N_2O) Direct sources. Kt. CO_2 eq.	Inventory 2003	Inventory 2004	Inventory 2016
Synthetic nitrogen fertilizers	8816.77	5800	11,000
Manure applied as fertilizers	3280.76	2100	2100
Biological nitrogen fixation	3779.12	—	—
Crop residue decomposition	6154.48	3800	6500
Cultivation of organic soils	61.01	60	60
Grazing animals (pasture, range and paddock manure)	3272.71	4300	210
Mineralization of soil organic carbon	—	—	800
Conservation tillage practices		−630	−1500
Summer fallow		430	220
Irrigation			330

Table 9.
Evolution of Canada's inventories.

They also incorporate emissions from irrigation practices by which we can conclude that a great evolution has suffered the emissions of this section of direct sources of agricultural soils.

3.3.3 The United States of America (USA)

In addition to changes in the measurement of nitrogen biological fixation, the introduction of emissions' new categories, as we saw in Canada, "innovations" will continue to generate and, thus, the inventory of the United States [19], extends the computation of their emissions. This inventory includes in the accounting the nitrogen fixed, by what we have called-fixing bacteria N_2 of the soil, which belong, for example, the genus *Azotobacter* and so-called biological fixation free. The USA in your inventory calls this fixation as asymbiotic fixation and, therefore, reports emissions. (**Figure 1**) shows the scheme how are calculated agricultural soils N_2O emissions' in United States inventory.

The US inventory defines asymbiotic fixation as the fixation of atmospheric N_2 by bacteria living in the soil and that do not have direct relationship with plants. This inventory says that although the nitrogen incorporated by asymbiotic N fixation is not specifically collected by the 2006 Guidelines, it is a

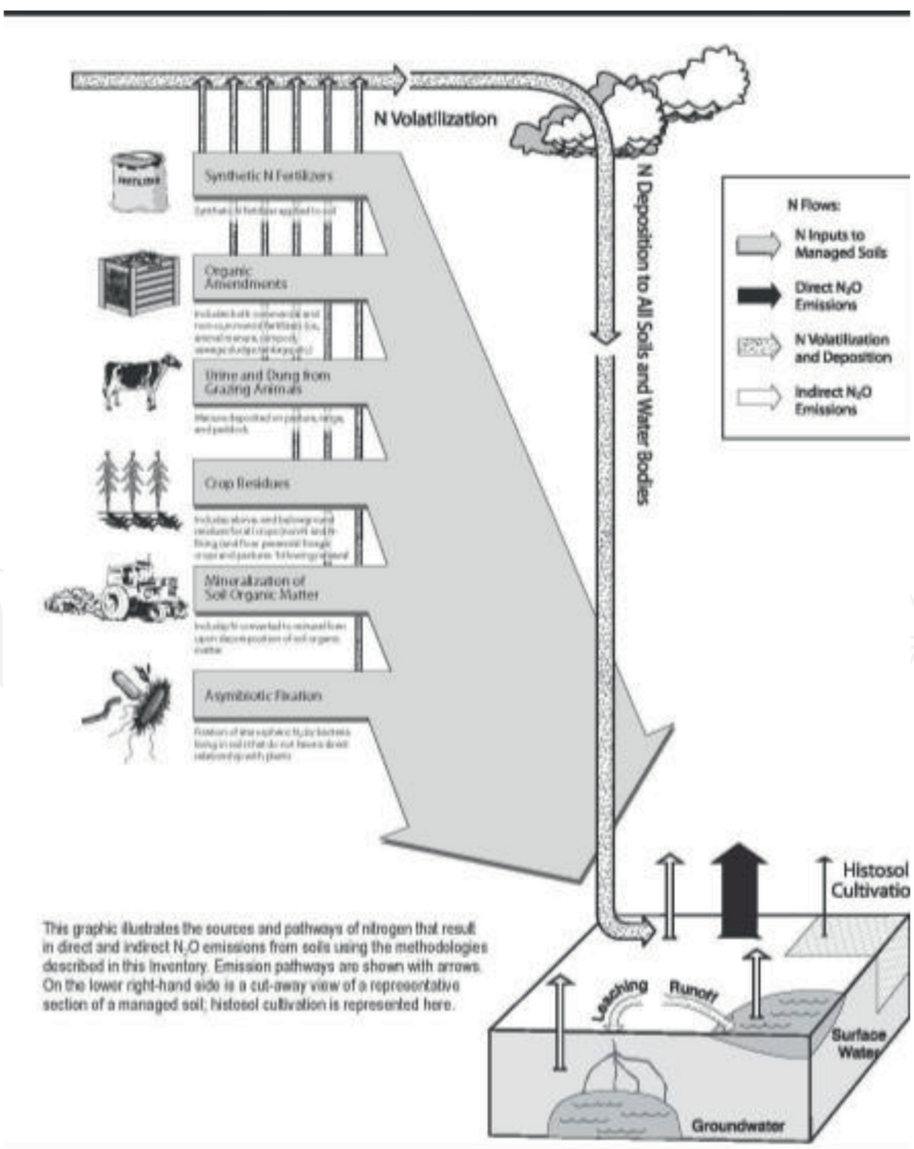

Figure 1.
Asymbiotic fixation [19].

component of the total emissions for managed soils and it should be included. It is calculated by a method of the high level developed to assess the source. To make the calculations, they use a combination of different methods using a specific model called Daycent.

The result for the year 2016 was 95.1 Mt. CO_2 eq., which includes the mineralization and asymbiotic fixation, and we can observe that it is a very significant amount. It is difficult to obtain which data belong to asymbiotic fixation and which are due to mineralization.

But what is striking is that it introduces a concept [20] that does not force the 2006 Guidelines.

We can observe in his inventory data that how meadows and crops emit more due to mineralization and asymbiotic fixation (95.1 Mt. of CO_2 eq.) by the addition of the synthetic fertilizer (64.5 Mt. CO_2 eq.) to the soils.

Only these emissions be over all Canada emissions from agricultural soils (24 Mt. of CO_2 eq.). Compared to Spain' emissions, only this item exceeds the emissions of all Spanish agriculture (34.4 Mt. CO_2 eq. in 2016) (the United States has 405 Mhas. agricultural soils and Spain 26.6 Mhas. in 2016).

We can conclude that the methodology used to measure the nitrogen biological fixation is very relevant for the emissions of a country and consideration of asymbiotic fixation (free or mineral) is an issue to consider. In the case of large agrarian countries, it would have important effects on the emission amount.

4. New technologies

In this section, we will discuss, using New Zealand GHG inventories as example [21, 22], how we can make improvements in GHG inventories and we introduce measurement methodologies of new technologies applied in the agricultural sector.

4.1 The nitrification inhibitors

The application of nitrogen fertilizers to the soil means the occurrence of biological and physicochemical reactions that leads to loss of nitrogen. The use of fertilizers with nitrification inhibitors has become a useful tool to reduce loss and improve the efficiency of the N. The use of nitrogen fertilizers stabilized become widespread and its are added, during the production process, with some substances, such as nitrification inhibitors, which can keep N applied as NH_4^+ for longer.

These products delayed the transformation of ammonia nitrogen (NH_4^+) to nitrate nitrogen (NO_3-) through temporary inhibition of various bacteria *Nitrosomonas* spp., and thus, the nitrogen is released in a progressive and gradual way and, at that same rate, it is assimilated by the crop.

Nitrification inhibitors degrade over time after being applied on the ground, and this degradation is influenced by temperature, moisture, pH and quantity of organic matter. There is already a long list of chemical compounds that have been tested as inhibitors of nitrification in the world (more than 64), but the most studied and used nitrification inhibitors are nitrapyrin, dicyandiamide (DCD) and 3,4-dimethylpyrazol phosphate (DMPP) [23].

In the United States, nitrapyrin is being used in corn, sorghum, wheat, cotton and strawberries (in a manner restricted in these). However, more than 90% is used in corn. Nitrapyrin must be injected and immediately incorporated into the soil due to its volatility and therefore its use is limited in the regions where N is typically injected to the ground. In principle, only it is marketed in the United States.

The dicyandiamide (DCD) has a bacteriostatic effect on bacteria *Nitrosomonas* spp., which only has a depressive effect on those, without killing them (not bactericidal). The disadvantage is that it requires a large amount of DCD for to contribute with between a 10% to 15% of the N-NH_4^+ to the ground. (Applications are approximately 10 kg per hectare, twice a year, in spring and autumn).

It is a very soluble product that easily seeps with rainfall separating the fraction of ammonium. Another disadvantage is that this molecule can be absorbed by the plant, and in some cases, has generated toxicity. Currently, this product is not only used but also is formulated in combination with other molecules.

3,4-dimethylpyrazol phosphate (DMPP), equally to the DCD, has a bacteriostatic effect, not the bactericidal effect (does not kill bacteria but it inhibits its action for a certain period of time), and it is relatively immobile into the soil; so it does not occur losses by leaching. On the other hand, application rates are very low compared to other nitrification inhibitors (+ −1% of the N-NH_4^+). Their application rate is 16 times lower than the rate of application of the DCD. It has a high selectivity, because it effectively inhibits only the action of *Nitrosomonas* bacteria and it degrades completely into the soil without leaving any residue. To retard the passage of ammonium to nitrate, avoiding nitrogen losses by leaching, it also reduces the effect of soil acidification.

Used as an inhibitor of nitrification, 3,4- dimethylpyrazol phosphate is regulated in the European countries and also fertilizers are used with this product in Asia and Latin America. In contrast to the DCD, in which several authors have cited toxic effects, the 3,4-dimethylpyrazol phosphate has not been demonstrated, for the moment, toxic effects on the plants.

The GHG inventory from New Zealand in the year 2012 has incorporated an amendment to the IPCC methodology that consists in introducing the use of inhibitors of the nitrification for mitigation of emissions of N_2O. They developed a methodology for incorporating the inhibitor of nitrification dicyandiamide (DCD) in the agriculture sector. N_2O emissions in the agricultural soils category take into account the use of nitrification inhibitors on dairy farms.

Based on several investigations, they have produced a good management practice that consists of the incorporation of the DCD to pastures and maximize reductions of N_2O emissions. The utilization of DCD has been reflected on the accounting and, so, incorporated in the inventory calculations and they modified parameter FracLEACH [24] and emission factor EF3PR & P [25] that are minor when using nitrification inhibitors. With these new emission factors, significant reductions of N_2O emissions from soils in both direct (nitrate leaching) and indirect (volatilization of N_2O) are achieved.

The emission factors are fixed by the Guidelines, but it is possible to modify the amount with scientific studies and this practice is done in New Zealand.

Table 10, [26] shows the differences between emission factors when DCD is not used (for example in 2012, EF3PR & P = 0.00994 front EF3PR & P = 0.01, that it is the amount fixed in the Guidelines, and FracLEACH = 0.06964 front FracLEACH = 0.07, that it is the amount fixed in the Guidelines) and as such these small differences of the emission factors meant, in total, that in 2102 its “save” 19.6 Mt. CO_2 eq.

Currently, the dicyandiamide (DCD) retired voluntarily in New Zealand’s market due to the concern of customers by the existence of certain residues in dairy products even though it is at a very low level. On this point, the inventory of Agriculture of New Zealand says: “there is no risk in dairy products for humans with low levels of inhibitor used.” However, in the last inventory of 2018, they asserted that sales of this product have been suspended and they have not returned to use this discount since the year 2012.

	2007	2008	2009	2010	2011	2012
Percentage of dairy area applied with inhibitor	3.5	4.5	3.1	2.2	3.0	2.9
Final modified emission factor or parameter, EF3(PRP) (kg N_2O-N/kg N)	0.00992	0.00990	0.00993	0.00995	0.00993	0.00994
Final modified emission factor or parameter, FracLEACH (kg N_2O-N/kg N)	0.06957	0.06944	0.06962	0.06973	0.06963	0.06964
Mitigation (Gg CO_2 eq.)	18.7	25.4	18.3	13.7	19.5	19.6

Note: EF3(PRP) = 0.01 and FracLEACH = 0.07 when inhibitor is not applied. All other emission factors and parameters relating to animal excreta and fertilizer use (FracGASM, FracGASF, EF4 and EF5) remain unchanged when the inhibitor is used as an N_2O mitigation technology.

Table 10.
Emission factors, parameters and mitigation for New Zealand's DCD inhibitor calculations from 2007 to 2012.

Within the existing inhibitors, 3,4-dimethylpyrazol phosphate is the inhibitor which has major advantages over the rest of nitrification inhibitors existing, due to his effectiveness at low concentrations, its stability and movement on the ground. The DMPP is an inhibitor of nitrification considerate under different national regulations of fertilizers, including the Spanish. In particular, the Royal Decree 824/2005 on fertilizer products includes fertilizers with DMPP as suitable for marketing in Spain. Similarly, Portugal has authorized the commercialization of fertilizers with DMPP.

4.2 Urea inhibitors

The New Zealand GHG inventory from agriculture has also developed a methodology for urea inhibitor called urease. Urea is the nitrogen fertilizer most used in the grasslands that are grazed in New Zealand and in addition to be excreted in the urine while the animals are grazing.

Urea inhibitors suspend or delay, during a period of time, the transformation of nitrogen in form of amide that exists in the urea to the ammonium NH_4^+ by the hydrolytic action of the urease enzyme. It reduces the speed at which urea is hydrolyzed in the soil and, therefore, losses of ammonium in the atmosphere by volatilization or nitrate by runoff are reduced or avoided.

The objective is to increase the efficiency of fertilizations with urea and to minimize the environmental impact of their use. For the purpose of the inclusion in the GHG inventory, they change the value of FracGASF [27] parameter when using the urease inhibitor.

Field- and laboratory-based studies [28] have come to the conclusion that using these inhibitors could lower FracGASF = 0.1, which is the amount fixed in the Guidelines, to a new FracGASF = 0.055, when they apply the urea inhibitor at 0.025% rates.

As a result of these practices, we can see in **Table 11** [29] a strong increase in the use of inhibitor every year and this practice has meant that in 2016 will save 20.1 kt CO_2 eq. of emissions.

Year	Percentage of urea applied that included urease inhibitor (urea treated/total urea)	Estimated greenhouse gas mitigation from using urease inhibitor kt. CO_2 eq.
2007	5.0	3.0
2008	5.2	3.0
2009	9.4	4.7
2010	6.9	4.1
2011	5.3	3.5
2012	7.0	4.6
2013	8.6	5.9
2014	20.2	13.6
2015	16.2	13.1
2016	26.5	20.1

Table 11.
Mitigation impact of urease inhibitors on nitrous oxide emissions from volatilization, from 2007 to 2016.

We can conclude that nitrification inhibitors and urea inhibitors are chemical compounds whose use can be a valid methodology to reduce the accumulation of nitrates in the soil and prevent emissions both by leaching and by volatilization of N_2O.

Different studies on mitigation policies propose the use of these practices with fertilizers or urea with inhibitors as, for example, France [30], that in a study of the INRA, proposes this mitigation measure in its roadmap for the agricultural sector. Similarly, the FAO [31], in his study of mitigation of emissions from production livestock, proposes the addiction of these inhibitors to the manure.

The use of inhibitors can be a useful tool to improve the efficiency of N in the soil, and for this reason, the use is being increased. However, this use needs still more securities, in particular, with regard to its possible effect on the food chain and in the environment and more research for the security on these products should be carried out.

Currently, these products accounted for GHG inventories do not appear and, the development of a methodology similar to the made by New Zealand could be used by other countries to reduce emissions. The 2018 USA inventory indicates that it will develop a methodology for use in next inventory due to the use of these products in the country.

4.3 The inoculation of nitrogen-fixing bacteria

The importance of legumes in the agricultural crops and its property of symbiotic fixation open the possibility of extend this property to other plant species of agricultural interest. The consequent descent of the need to use nitrogen fertilizers has made nitrogen biological fixation a subject of intense research over the years.

We will use other works of the Centro Superior de Investigaciones Científicas (Spain) for explaining this topic [32].

> *"NBF is capable of providing between 25 and 84% of the nitrogen required for normal growth and development of the cultivation of soybean. Therefore, nitrogen fixation presents great economic and ecological interest. In fact, and as an example, the high productions of soybeans around the world are due to this process through the application of microbial inoculants."*

One of the new technologies to be applied in the agricultural field that could be used for reducing emissions, in addition to other benefits, is known as biofertilization, which continues influencing mutualistic symbiosis of nitrogen fixation.

Biofertilization is defined as the use of living organisms to improve the growth of plants by two ways or increasing their nutrition making available available the required nutrients or acting on its development by the production of phytohormones. Also we can use biological control and biological remediation when with the inoculation of microorganisms we want to remove pathogens or increase the defensive response of the plants or remove xenobiotics compounds from the environment.

The use of inoculants for legumes is essential if the vegetal species has not been grown in that soil and, therefore, there is no presence of the corresponding *Rhizobium* species. This is the case of soybean in Europe that has to be inoculated with the bacteria *Bradyrhizobium japonicum* or *Sinorhizobium fredii*. This practice is also made in Brazil because most of the farmland comes from deforestation of the jungle and soybeans should be inoculated for their cultivation.

In a soil where is planted a new vegetal specie, if the natural infection's plant with these bacteria isn't possible, the crop efficiency is not superior to 40% potential. With the inoculation, up to 80% can be reached.

For example, in Spain, there are, in our soil, bacteria appropriate for crops how, alfalfa, clover, pea, lentil, chickpea, etc., but are not always effective enough; these are nitrogen fixative, and there are cases in which the inoculation is necessary if we want to obtain satisfactory yields. The same occurs when characteristics of the soil, such as acidity, drought, etc., influence the persistence of *Rhizobium* bacteria.

New knowledge is being developed in this field of biological nitrogen fixation and investigators start to get the extension of the fixing capacity to other non-leguminous plants of interest. So, they are trying to achieve that corn, wheat or rice be infected efficiently by *Rhizobium*, and begin to glimpse the possibility of transferring to these plants the fixing capacity. So its plants will be able to take advantage of the atmospheric N_2 for themselves.

In the short term, the selection of strains and their appropriate genetic manipulation are underway, to prepare the most suitable inoculants and, also, to improve the plant so that there are no limiting factors in the establishment of the corresponding symbiosis.

> *"Researchers point that not everything is optimal in obtaining self-sufficient plants for nitrogen, because although the crops should not be fertilized, it would be less productive. The energy cost involved in fixing becomes up to three times higher than the utilization of nitrate and the plants would grow less, the performance would be lower and may even were reduced the area of cultivation. But this independence of nitrogen fertilization would possibly more profitable crop, more suitable for economically weak areas and environmentally cleaner" [32].*

In short, as we have seen above, the 2006 Guidelines do not consider the contribution of nitrogen by biological fixation, which involves a direct emission of N_2O to the atmosphere and, therefore, this technology should be taken into account.

5. Conclusions

The GHG inventory is a great source of information, not only for its environmental aspect, but also by the possibility of using their data for relevant technical and economic analyses. Other quality is its role for serving us a guidance when preparing mitigation policies.

This comparative study of different inventories show the wide spectrum of approaches and the importance of the management of the accounting rules.

A detailed analysis of the nitrogen biological fixation and, particularly, the cultivation of soybeans, allow us to appreciate the importance of the follow-up to the guidelines that govern the preparation of inventories.

This article also shows significant differences in the volume of emissions due to the use of the 1996 Guidelines front the 2006 Guidelines, and both change the rules and the changes of global warming potentials. Using the emissions from the cultivation of an important legume such as Argentina and Brazil soybeans, we can observe in a practical way the importance of methodological changes in "accounting standards."

The case of the USA includes emissions that would not be bound by these guidelines, such as those due to asymbiotic fixation and the case of Canada incorporates the non-tillage (conservation agriculture) sink effect as the emissions due to fallow and irrigation systems.

On the other hand, examples of introduction of new technologies are exposed that are not included in the Guidelines, which require the development of specific methodologies. The case of the inventory of New Zealand regarding the nitrification inhibitors and urea inhibitor is a relevant example. Nitrogen Biological Fixation should be one of the fields to research in more depth because the specificity of some bacteria to capture atmospheric N_2 could provide large reductions in the use of synthetic nitrogen fertilizers.

Although the guidelines seek to unify criteria, we have exposed the full spectrum of options that have all these inventories to the same heading of emission from agricultural soils. We must bear in mind that correct accounting will condition strongly the analyses and measures that specifically we design and try to implement in the agricultural sector.

The objective should be that the effectiveness of a mitigation policy was validated for the concrete results of the GHG inventory and, of course, that this policy could be applied at the farm level. Deep knowledge of accounting rules is a necessary premise. It is very important that all persons participating in the measurement of emissions (technicians, researchers, public, professional managers of agriculture, etc.) are aware of the use of the same rules.

A country greenhouse gas measurement methodology is a science, not well known among professionals, which requires, in addition to a large sectoral specialization, to be addressed, by large multidisciplinary teams, and should be given in college and, perhaps, the most difficult, to be conducted at the level of agricultural farm in an understandable way. We must bear in mind that farmers will be responsible for putting into practice any measure of mitigation or generation of sinks that intends to.

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