

Using LCA to Identify Options for Greenhouse Gas Emission Reductions in Australian Wheat Farming

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ABSTRACT

Agriculture can be a contributor to a nation's total greenhouse gas emissions. Nitrapyrin (2-chloro-6-trichloromethylpyridine) is a nitrification inhibitor used globally to improve the efficacy of applied ammoniacal nitrogen fertilizers. By stabilizing nitrogen in the ammoniacal form, it results in more of the applied nitrogen available to plants thereby reducing N_2O and nitrate emissions from the farm. We used LCA to determine if the potential benefit from the use of nitrapyrin exceeded the burdens to create and transport it, and to discover additional opportunities to reduce emissions from high rainfall zone wheat farming in Australia. Use of nitrapyrin could reduce global warming potential (GWP) by 20% and marine eutrophication by 16%, with burdens created by its supply of only 0.5% and 0.01%, respectively. Production of nitric acid for urea ammonium nitrate fertilizer impacts GWP as much or more than the field emissions. Reducing emissions from nitric acid production may provide a similar (15%), independent and additive, benefit in GWP.

Keywords: nitrapyrin, greenhouse gas emissions, nitric acid, wheat, high rainfall zone

1. Introduction

Climate change, driven by emissions of “greenhouse gases” (GHG) such as CO_2 , CH_4 and N_2O , is a critical global issue, but was particularly of concern in Australia. About 93% of electricity in Australia is generated from fossil resources, primarily coal (International Energy Agency, 2012), which generates greenhouse gas emissions and is a challenge to change over the short term. There was great interest and research on various approaches to help Australia meet targets for GHG reduction set out by the Kyoto protocol; one of them was to increase use of nitrification inhibitors to reduce nitrous oxide (N_2O) emissions from agriculture (Dalal *et al.*, 2003; Bhatia *et al.*, 2010).

Nitrapyrin (2-chloro-6-trichloromethylpyridine) is a nitrification inhibitor produced in Pittsburg, California, by Dow AgroSciences, a business unit of The Dow Chemical Company (Dow), and is used globally in agriculture as a way to improve the efficiency and efficacy of applied fertilizers (Dow, 2012). Nitrification is a natural biological process that converts ammonia (from fertilizers) in soils to nitrate. The nitrate form of nitrogen is highly susceptible to losses from the soil root zone as N_2O emissions to air and nitrate emissions to ground and surface waters. The pathways of emissions are shown in Figure 1; nitrapyrin inhibits the nitrification process and thus reduces these emissions (Wolt, 2000; Chen *et al.*, 2010). Reduction in N_2O emissions from fertilizer by use of nitrapyrin has been demonstrated in many studies (Wolt, 2004; Akiyama, Yan and Yagi, 2010).

The goal of our work was to determine if the potential benefit from the use of nitrapyrin exceeded the burdens to create and transport it, to understand other potential impacts, and to discover additional opportunities to reduce GHG emissions from wheat farming. Life Cycle Assessment (LCA) is a useful methodology for examining the total environmental impact of a product or service. LCA takes a holistic view, examining environmental impacts over the complete “cradle to grave” product life cycle. Results from LCA address the complete environmental impacts of a product, and are hence more meaningful than those obtained for a single process or step in the life cycle. A life cycle perspective helps to ensure that environmental burdens are not unintentionally transferred from one life cycle stage to another and helps to prevent unintended environmental consequences.

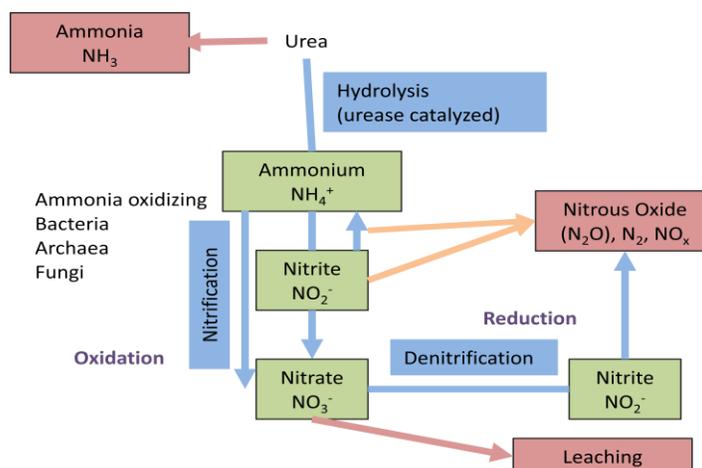


Figure 1. Routes to key emissions from use of fertilizers (re-drawn from a 2012 presentation by Chen and Suter)

Two studies were particularly useful in understanding the inputs to and emissions from wheat farming in Australia. Chen *et al.* (2010) reports the impact of use of nitrification chemicals on nitrogen speciation and emissions from laboratory experiments. It provided a basis for the unit ratio of nitrapyrin to applied N, applied N rate, and for the impact of nitrapyrin on N₂O emissions. Biswas *et al.* (2010) had extensive data and analysis of inputs and emissions from HRZ (high rainfall zone) wheat in rotation farming. Although there was no nitrogen fertilizer used due to the rotation with sheep farming, the other inputs were quite relevant to this project. The report also included field data for N₂O emissions. HRZ farming is distinct from wheat farming in, for example, Western Australia, which has been the subject of previous publications related to LCAs (Biswas *et al.*, 2008; Biswas *et al.*, 2010).

2. Methods

LCA is framed by ISO standards 14040 and 14044 (ISO, 2006a; ISO, 2006b), which provide comprehensive guidelines for conducting an LCA study. Good insights on the uses and limitations of LCA are described in many publications (EU-JRC, 2010; Curran, 2006; Curran, 2012). Previous use of LCA at Dow is also described in publications (DiMuro *et al.*, 2014; Helling and Russell, 2006; Helling *et al.*, 2012).

SimaPro 7.3.3 from Pré Consultants was the life cycle assessment software used in this study. Dow and other data were used directly to create process models in SimaPro. The primary sources of information for nitrapyrin production were Dow technical experts and Dow manufacturing databases. Dow confidential statements of formulation were used for the composition of the delivered product (also referred to by the tradename “eN-trench™”). Ecoinvent v2.2, was used within SimaPro to model utility process operations, transportation, packaging, and other material inputs. For materials produced or operations conducted in Australia, such as fertilizers, a version of the Ecoinvent data based adapted for Australian conditions (primarily for the sources of heat and power) was used (v 2012.5) (Life Cycle Strategies, 2012). Life cycle impact assessment (LCIA) was performed using valuation systems available in Ecoinvent, primarily selected from ReCiPe (Hischier *et al.*, 2009; Goedkoop *et al.*, 2010), using “midpoint” metrics and with no normalization to a target or weighting of different impact categories. The reported results include the impact categories of global warming potential (GWP), cumulative energy demand, water withdrawals, acidification potential (AP), freshwater and marine eutrophication potential (EP), photochemical oxidant creation potential (POCP) (smog), and ozone depletion potential (ODP).

The function of nitrapyrin is to reduce losses of fertilizer nitrogen by nitrification pathways, thereby preventing losses of the nitrogen fertilizer in the crop. Nitrapyrin is marketed and sold on the basis of a treated hectare, so the functional unit was one hectare of high rainfall zone (HRZ) wheat farming in Australia, with and without applied nitrapyrin. Calculation of potential impacts per ton of wheat production was done as part of the sensitivity analysis.

This was a cradle-to-grave study, so the boundaries extended upstream to materials in the earth and continues to materials returned to the earth (air, water, or soil). The primary chemical reaction in the process is the chlorination of alpha-picoline to make 6-chloro-2-trichloromethylpyrine (“α-6-tet”), the active ingredient in nitrapyrin.

rin. A high-level view of the overall system is shown in Figure 2. The figure shows the flow of the primary mass of the product; there are mass and energy inputs to each of these blocks and potentially emissions and by-products from each block. In the figure, TG stands for “technical grade” and AU is the country code for Australia. Capital equipment was excluded from the study, except for farm equipment, for which data were available in Biswas *et al.* (2010). Transportation was included for all significant mass flows or any transport over long distances. TG production, formulation, and packaging are all done in multi-product plants, for which the consumption of utilities and emissions (which are tracked in Dow per facility) were allocated equally by mass to all the production. Raw material consumption was known in detail specifically for each material; no material inputs were excluded, although minor inputs totaling <1% of the formulated products were lumped together as “chemicals, organic”.

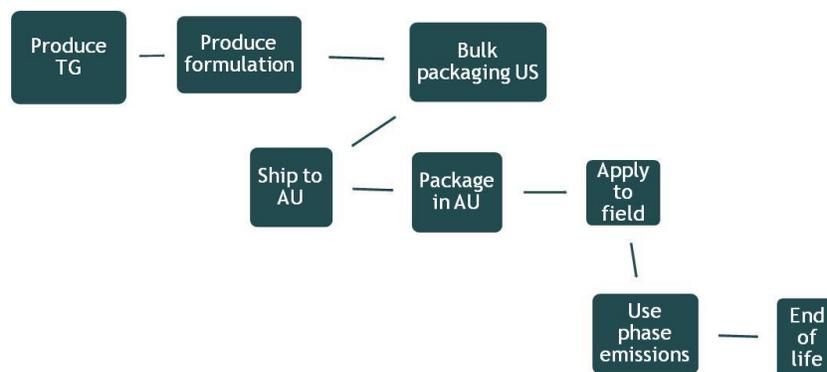


Figure 2. High-level process map for supply and use of nitrapyrin

The data sources and assumptions related to the direct emissions from applied chemicals were important for this project. Direct fossil CO₂ emissions from use of farm chemicals came from two sources: Urea and nitrapyrin, with urea being more significant by a factor of about 50. We assumed that all of the CO in the applied urea was converted to CO₂, as per IPCC guidelines, and also that all of the carbon in the applied nitrapyrin was released as CO₂ (this is expected to be a conservative estimate). N₂O emissions for the no-nitrapyrin case were taken from IPCC (2006) models applied to wheat, with the key inputs (besides the urea-ammonium nitrate (UAN) molecular weight, elemental composition, and application rate) being:

- Nitrogen fraction of crop residues, 0.0064
- Crop dry matter fraction, 0.85
- Mass ratio of residues to crop, 2.3, which was assumed to all be left on the field

The resulting N₂O emissions from fertilizer use and crop residues are 3.95 kg/ha. N₂O emissions were also calculated from the other nitrogen containing components in the formulation, and were less than 0.1% of those from the urea.

There is a range in the reported benefit of using nitrapyrin, as it depends on soil moisture, temperature and other factors (Dalal, *et al.*, 2003). Wolt (2004) found an average reduction in field GHG emissions (N₂O and CH₄) of 51% in fourteen studies covering a range of crops, locations and applied fertilizer type; Chen *et al.* (2010) found a reduction in N₂O emissions of 65-98% in laboratory work covering a wide range of soil temperature and moisture levels. We believe Chen’s work to be of high quality, more recent, and particularly relevant for Australia. To be conservative, we selected the 65% minimum reduction in N₂O emissions from this work.

3. Results

Results for the selected impact categories are shown in Figure 3 for the cradle-to-grave life cycle of one hectare of high rainfall zone wheat production, with (the bar on the right of each set) and without use of nitrapyrin. For all the impact categories, the results have been normalized by the maximum value of the two, which is for

the hectare treated with nitrapyrin for all impacts except GWP and marine eutrophication. The specific maximum values for each impact category are (per hectare):

- Climate change (GWP): 3,100 kg CO₂ eq
- Cumulative energy demand: 18,100 MJ
- Water withdrawals (ReCiPe): 17.8 m³
- Terrestrial acidification (acidification potential, or AP): 9.53 kg SO₂ eq
- Freshwater eutrophication (eutrophication potential, or EP_F): 0.373 kg P eq
- Marine eutrophication (eutrophication potential, or EP_m): 55.2 kg N eq
- Photochemical oxidant formation (photo oxidant creation potential, or POCP): 5.39 kg NMVOC (non-methane volatile organic carbon)
- Ozone depletion (ozone depletion potential, ODP): 4.6E-05 kg CFC-11 eq

There are three primary observations from the figure:

- For most impact categories there is no significant difference between the with and without nitrapyrin cases
- Use of nitrapyrin clearly reduced GWP and marine (nitrogen-based) eutrophication
- Use of nitrapyrin may increase ozone depletion potential.

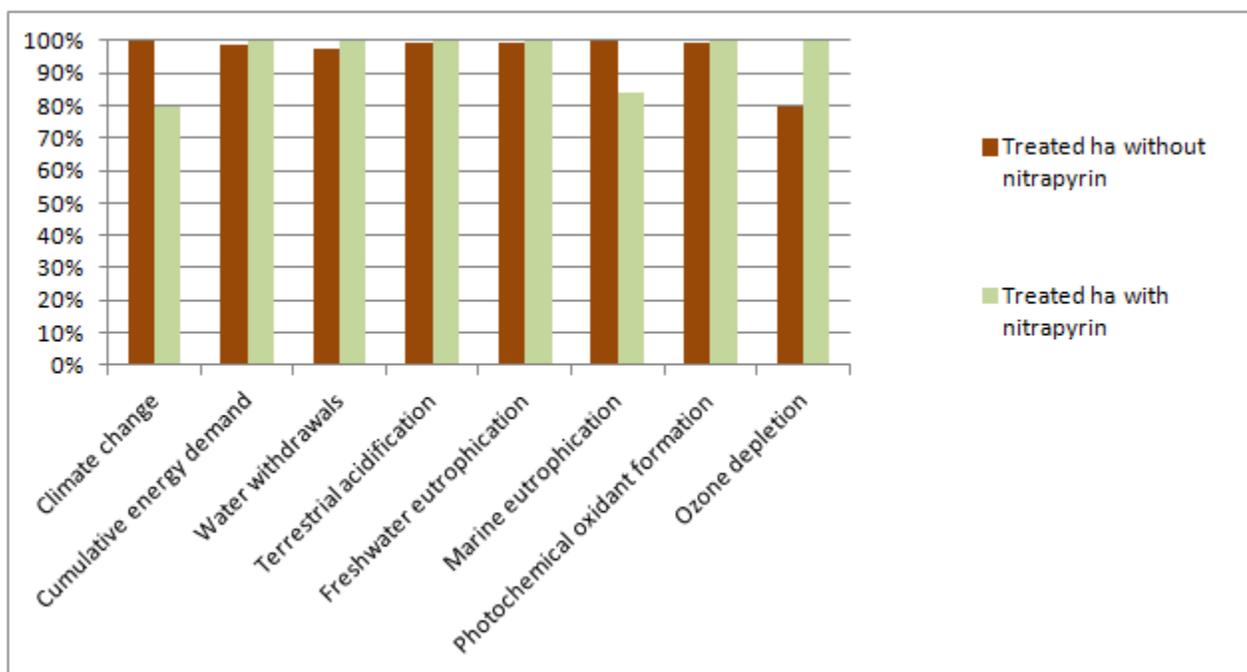


Figure 3. Comparison of potential impacts per hectare of HRZ wheat farming in Australia

The contributions of the different inputs to the full list of metrics considered are shown in Figure 4. For most metrics, the largest contributors are UAN production and single super phosphate production. Direct field emissions are significant for GWP and EP_m. Production of alachlor (a surrogate model for the use of clethodim on-farm) is the largest contributor to ODP. Production of nitrapyrin is a significant contributor only to ODP.

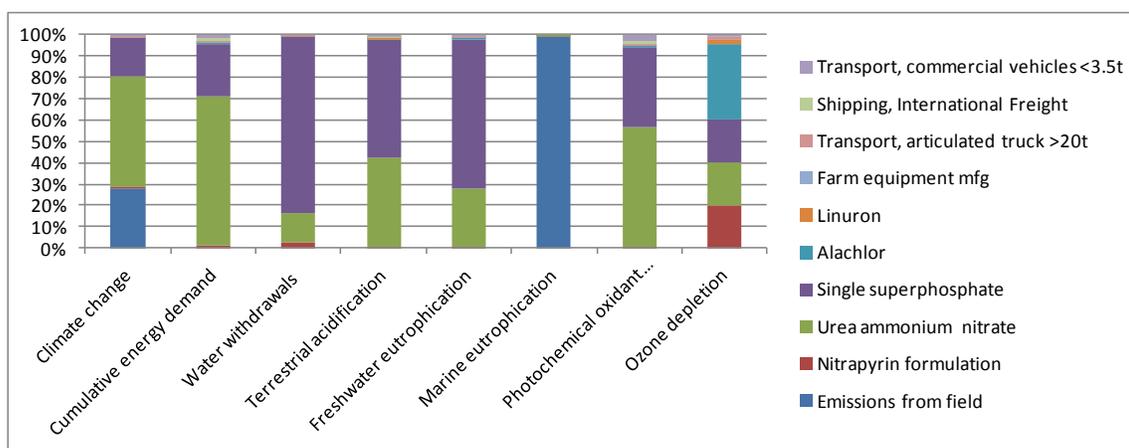


Figure 4. Contributions to potential impacts per treated HRZ hectare

4. Discussion

Use of nitrapyrin, which reduced modeled field emissions of N₂O by 65%, resulted in a GWP reduction of about 20%. The GWP of a treated hectare is 2470 kg CO₂eq/ha, which is 630 kg/ha less than the value for the hectare without nitrapyrin, 3100 kg CO₂eq/ha. About 22% of the GWP comes from field emissions of N₂O and only 0.5% comes from the nitrapyrin (11 kg CO₂eq/ha). The GWP benefit of nitrapyrin (648 kg CO₂eq/ha) is almost 60 times the GWP burden from manufacturing it. The largest contributor to GWP is the production of the UAN fertilizer, which contributes 52% of the GWP. The upstream burden of UAN production is more than twice as large as the impact from the N₂O emitted in the use of the product. There is also a significant contribution of 18% from phosphate fertilizer production and 6.5% from field emissions of CO₂ due to decomposition of the urea in the UAN. The production burden of UAN is still larger than the sum of the N₂O and CO₂ impacts from the use of the product in HRZ wheat farming. CO₂ emissions in UAN production are related to energy use, but N₂O is also a production reaction by-product, for which the emissions can be controlled by using different vent gas treatment technologies. The US EPA has compiled an excellent overview of the state of the art for N₂O abatement from nitric acid production (US EPA, 2010). Appendix C of the EPA report includes data on N₂O emissions (lb/ton) before and after implementation of technology changes at 45 plants in developing geographies. The average emissions of N₂O from the improved plants were 1.3 kg/MT, an 85% reduction from the emissions in the model for nitric acid production in the Australasian LCI dataset (which was unchanged from the European Ecoinvent value); the best technology could be 97% lower. We adapted the Australasian LCI model for nitric acid production by changing only N₂O emissions, neglecting any other inputs required to achieve this performance. Use of more current N₂O emissions technology in nitric acid production could lower the GWP of HRZ wheat farming by 16%, assuming that current nitric acid production in Australia is similar to that described in Ecoinvent. No other potential impacts were changed. This GWP impact is similar to that from using nitrapyrin, but is completely additive: using both more current nitric acid processes and nitrapyrin could combine to reduce GWP by 38%.

The decrease in marine eutrophication (N-load) by 16% with the use of nitrapyrin as shown in Figure 3 was directly due to the impact from the work by Wolt (2004), with the burdens created by supply of nitrapyrin being only 0.01% of the total. Although marine eutrophication is a significant issue for US agriculture, it may not be a significant issue for Australian agriculture (Geosciences Australia, 2013). The relevance of the reduction in marine eutrophication by use of nitrapyrin will depend on the region where it is used.

Figure 3 also showed increased ozone depletion potential with use of nitrapyrin in HRZ wheat farming. This is due estimated CCl₄ emissions from the chlorine production process at the plant of K2 PURE SOLUTIONS NOCAL LP in Pittsburg, California. This is a new facility (not owned or operated by Dow) and will need to publically report CCl₄ emissions, but data are not yet available for this facility (US EPA, 2012). When these data are available, it will be possible to determine if this potentially higher burden for nitrapyrin is real or not. The major contribution to ODP, production of alachlor, also has a high degree of uncertainty. ODP calculations are sensitive to small emissions of materials with high characterization factors. The use of alachlor as a surrogate

for clethodim herbicide based on its structural similarity is reasonable for potential impacts such as GWP or cumulative energy demand, but is likely less so for ODP. The differences in ODP are likely not significant.

During the course of this project, there were also field studies in Managatang, Victoria, to measure the impact on yield of otherwise identically treated areas of wheat production, with and without use of nitrapyrin. A representative comparison using 2.5 L of eNtrench, 50 kg diammonium phosphate (DAP) and 40 L of urea ammonia nitrate increased the yield of wheat from 2.90 to 3.16 MT/ha, or about 9%. The quality of the wheat was similar for both treatments (11.7% protein without nitrapyrin; 11.8% protein with nitrapyrin). The yields, fertilizer inputs, and corresponding emissions were used to create models on a “per MT” basis. For most impact categories there was a small decrease between the cases with and without nitrapyrin, due to the 9% improvement in yield, although differences of this magnitude in LCA are often not considered significant. Use of nitrapyrin reduced GWP 29% and marine (nitrogen-based) eutrophication by 23%. Due to the lower input of fertilizer in the results per MT wheat in Managatang, many of the potential impacts were smaller in magnitude than those per typical treated hectare. This is demonstrated for GWP which was 3,100 kg CO₂eq/ha for the untreated typical hectare compared to 390 CO₂eq/ha for the reported field trial. Fertilizer production contributed 43% and field emissions contributed 44% of the GWP for the field trial without eNtrench; for the typical hectare these were 55% and 41%, respectively. Later field trials in Australia have shown that typically 5-7% increase in yield can be seen when nitrapyrin is used and all other factors are conducive to maximize the yield impact.

5. Conclusion

The potential benefits with respect to global warming potential (GWP) and marine eutrophication through the use of nitrapyrin in high rainfall zone (HRZ) wheat farming in Australia far exceed the burdens of these potential impacts created by its supply. Use of nitrapyrin could reduce global warming potential (GWP) by 20% and marine eutrophication by 16%, with burdens created by its supply of only 0.5% and 0.01%, respectively. There is no significant difference in the broad range of other potential impacts considered between a farmed hectare with and without use of nitrapyrin, with the possible exception of the ozone depletion potential. Production of nitric acid for urea ammonium nitrate fertilizer impacts GWP as much or more than the emissions from the field on its use. Reducing emissions from nitric acid production may provide a similar benefit in GWP as the use of nitrapyrin, and the potential benefits are independent and additive.

6. Acknowledgements

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