Agriculture, Ecosystems and Environment 252 (2018) 69–73

Contents lists available at ScienceDirect

Agriculture, Ecosystems and Environment

journal homepage: www.elsevier.com/locate/agee

Opinion paper

A re-evaluation of the agronomic effectiveness of the nitrification inhibitors DCD and DMPP and the urease inhibitor NBPT

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ARTICLE INFO

Keywords:
Enhanced efficiency fertilisers
Nitrogen use efficiency
Nitrous oxide

ABSTRACT

Increasing evidence is emerging that enhanced efficiency nitrogen (N) fertilisers (EENFs) can lower nitrous oxide (N_2O) emissions from soils, but five recently published meta-analyses reported marginal benefits to agronomic efficiency (biomass or grain yields) when assessed against conventional N fertilisers. Closer inspection of the experiments included in these meta-analyses reveals that the vast majority were designed to evaluate N_2O emissions, and thus used only one N fertiliser rate, typically the recommended N fertiliser rate for the local crop production system. We suggest that EENFs are unlikely to increase yields beyond conventional N fertilisers when the control fertiliser treatment is applied at the recommended rate for achieving maximum N-limited yield. To demonstrate our perspective, we re-evaluated data from only those studies comparing yield responses to conventional N fertiliser with those of the nitrification inhibitors dicyandiamide (DCD) and 3,4-dimethylepyrazole phosphate (DMPP) and the urease inhibitor N-(*n*-butyl) thiophosphoric triamide (NBPT) that included a sub-optimal N rate as well as a control 'recommended' N rate. While only 11 published studies met these criteria, the available data suggested that EENF products achieve significantly higher yields over conventional N fertilisers at suboptimal N rates, with the greatest yield difference (11%, $P < 0.05$) generated at 50% of the recommended N rate. Due to the additional costs of EENF products per unit N applied, the question asked should not be 'can EENFs increase yields?' but rather 'to what extent can N application rate be reduced by applying EENFs without loss of yield, and is this economically viable?' To obtain such information, further studies across a range of crops and environments are needed to more accurately derive agronomic response curves for EENFs and simple calculator tools that factor in the cost of a given EENF at a given time can be used to determine economic viability. Finally, holistic assessment should also consider additional benefits of lower N application rates, such as a reduction in the rate of nitrate leaching-induced soil acidification which has associated longer term management costs.

1. Introduction

Nitrogen (N) is a key plant nutrient and is typically one of the most limiting nutrients for crop production. In addition to an estimated 33–46 million t of N fixed from the atmosphere by legumes per year worldwide (Herridge et al., 2008), almost 115 million t of fertiliser-N is expected to be applied to crops across the globe in 2016/17 to sustain current production levels (Heffer and Prud'homme 2012). Unfortunately, the recovery of fertiliser-N by crops is typically low, with the three major global cereal crops rice, wheat and maize typically recovering only 30–50% of applied N in the season of application (Herrera et al., 2016), with < 10% of the residual N recovered in subsequent years (Ladha et al., 2005). The losses of fertiliser-N from the system as nitrate (NO_3^-) or in gaseous forms including ammonia (NH_3), nitrous oxide (N_2O) and molecular nitrogen (N_2) represent a significant loss of resource investment to farmers. Environmental consequences include eutrophication of waterways (leaching of NO_3^- and deposition of NH_3), greenhouse gas emissions (N_2O) (Forster et al., 2007) and ozone depletion (N_2O) (Ravishankara et al., 2009).

In light of the limited recovery of applied N fertiliser by crops, there has been increased interest in using enhanced efficiency N fertilisers (EENFs) which aim to slow the supply of NO_3^-. These include slow release fertilisers such as polymer coated urea (PCU) and N fertilisers that contain chemicals which inhibit biological processes including hydrolysis of urea (urease inhibitors) or oxidation of NH_4^+ (nitrification inhibitors) (Chalk et al., 2015). Several recent reviews have concluded that on the whole, the use of nitrification and urease inhibitors in N fertiliser products can significantly lower soil N_2O emissions in

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http://dx.doi.org/10.1016/j.agee.2017.10.008
Received 27 July 2017; Received in revised form 3 October 2017; Accepted 12 October 2017
Available online 05 November 2017

upland (i.e. non-flooded) crops compared to conventional N fertiliser sources (Halvorson et al., 2014; Ruser and Schulz, 2015). Using a meta-analysis approach Akiyama et al. (2010) concluded that nitrification inhibitors lowered N_2O emissions by 38% on average compared to N fertilisers without nitrification inhibitors, while Gilsanz et al. (2016) concluded that the nitrification inhibitors dicyandiamide (DCD) and 3,4-dimethylepyrazole phosphate (DMPP) lowered N_2O emissions on average by 42 and 40%, respectively.

While meta-analyses broadly suggest that nitrification and urease inhibitors can lower N_2O emissions, the effect of these inhibitors on agronomic efficiency (i.e. yield and crop N-uptake) is less clear. Using meta-analysis with data sets from 27 studies, Abalos et al. (2014) reported an average crop yield increase of 7.5% when DCD, DMPP or the urease inhibitor N-(*n*-butyl) thiophosphoric triamide (NBPT) were used in comparison to conventional N fertilisers without inhibitors. In a more recent meta-analysis, Yang et al. (2016) reported that DCD increased yields by an average 6.5% (based on 102 data sets) while DMPP only increased yield by an average of 1.2% (based on 66 data sets). Other recent meta-analyses have concluded that nitrification inhibitors including DCD, DMPP and nitrapyrin increased grain yields by 7% (Thapa et al., 2016) or 9% (Qiao et al., 2015), or increased crop yields (grain or biomass) by 4.4% (Feng et al., 2016). Essentially, the large reductions in N_2O emissions observed in these meta-analyses do not translate into large increases in agronomic efficiencies. While N_2O emissions are of importance to the net greenhouse gas balance from the system, they are of less importance to agricultural crop production. Depending on the agroecosystem, the emission factor for N additions from mineral fertilisers, organic amendments and crop residues, and N mineralised from mineral soil as a result of loss of soil carbon, is on average 1% (De Klein et al., 2006). Ultimately, enhanced crop N uptake at a given N fertiliser application rate is only likely if the inhibitors are able to mitigate N losses from the major loss pathways, these being NH_3 volatilisation, NO_3^- leaching and N_2 losses. While the meta-analyses clearly identify that EENFs reduce N losses from volatilisation and in some cases leaching, these savings only translate into modest yield increases of 1–9% (Abalos et al., 2014; Feng et al., 2016; Qiao et al., 2015; Yang et al., 2016). One possible explanation for the relatively low yield increases is that the reference experiments employ control treatments with sufficient N to achieve maximum N-limited yields. Any potential N-fertiliser savings arising from EENF application would not therefore contribute to additional yield. This issue is the focus of this opinion piece, and our perspective is that future meta-analyses need to explicitly discuss the issue with reference to the potential biases that may result from including data sets where comparisons of standard N fertiliser and EENFs were made at the optimal/recommended N fertiliser rate.

2. Interpreting the results of recent meta-analyses

As reported by Wolt (2004) in an extensive review, and references therein, much of the early work conducted with the nitrification inhibitor nitrapyrin aimed to determine whether using N fertiliser products that contained nitrapyrin were likely to increase crop N uptake and yields compared to conventional N fertilisers, and generally investigated crop yields at multiple N fertiliser rates. However, closer inspection of data sets used in the recent meta-analyses focussing on DCD, DMPP and NBPT (Abalos et al., 2014; Feng et al., 2016; Qiao et al., 2015; Thapa et al., 2016; Yang et al., 2016) indicates that most of the studies cited and used in the meta-analyses were primarily designed to investigate the role of the inhibitors in lowering soil N_2O emissions, and as such, often only used a single N fertiliser rate in the experiments. These studies often lacked a nil N control or indeed a suboptimal N dose. For example, in the meta-analysis of Abalos et al. (2014), only three of the studies used in the meta-analysis compared N fertiliser products with and without DCD, DMPP or NBPT at a suboptimal N rate in addition to a control (or recommended) N fertiliser rate. The remaining 24 studies either used a single rate which was the locally recommended N rate or used a single N rate without any explanation or justification for the selection of this N rate. In most agricultural systems in developed countries, the recommended rates of N fertiliser are generally those that give maximum grain yields. If experiments are conducted at the locally recommended N rate for maximising biomass or grain yields, the question arises as to whether it is reasonable to expect a yield increase with the use of EENF products.

To develop N fertiliser recommendations for farmers, yield responses to N fertiliser application are fitted over multiple seasons, and models developed to incorporate the prices of N fertiliser and expected value of the commodity (e.g. Rochester and Bange, 2016). Because of seasonal variation, the recommended N fertiliser rate may be a slight overestimate of crop requirements in some seasons and conversely, a slight underestimate in other seasons. As such, even when locally recommended N fertiliser rates are used, there is a chance that crops may respond to increased soil N supply in any given season but the magnitude of the response is likely limited. Thus, the inclusion of studies comparing products with inhibitors and conventional N fertilisers at only the recommended N rate in meta-analysis studies diminishes the chance of any overall yield response to N fertilisers, and heavily biases the outcome of the meta-analysis.

We suggest that meta-analyses on the agronomic efficiency of EENFs would be greatly improved if only data sets where conventional N fertilisers and EENFs were applied using at least one sub-optimal N rate were included in the analysis. Where meta-analyses are conducted using data sets that only included one N rate in the treatments, the studies could be improved by providing explicit discussion on the limitations associated with the use of these data sets. In the study of Abalos et al. (2014), where only three of the 27 studies used in the meta-analysis included defined suboptimal N rates in their treatment structure, N application rates were grouped into three categories − low ($\leq$150 kg N ha^{-1}), medium (150–300 kg N ha^{-1}) and high ($\geq$300 kg N ha^{-1}) − in attempt to tease out the impact of N rates (see also Yang et al., 2016). Abalos et al. (2014) state in the discussion: "It could be argued that at higher N rates the yield response to inhibitors would be less pronounced because N rates may be above optimal and as such yields may not respond positively to an inhibitor's application". However, data presented in Fig. 3a in Abalos et al. (2014) indicate that greater productive gains were observed in experiments with higher N rates (> 300 kg N ha^{-1}). We believe that this highlights a critical issue, namely that the rate of N used in a given site/season/crop is not indicative of the probability of a response to N fertiliser at the site. That productivity responses with EENFs were observed in experiments that used > 300 kg N ha^{-1} (Fig. 3a − Abalos et al., 2014) suggests that yields in the conventional N fertiliser treatments at 300 kg N ha^{-1} were still N-limited. Conversely, it is entirely possible that the use of low ($\leq$150 kg N ha^{-1}) or medium (150–300 kg N ha^{-1}) N rates at a given site may be sufficient to achieve the maximum N-limited yield. For example, maximum dryland crop yields are often achieved at N fertiliser rates < 100 kg N ha^{-1} (Halvorson and Reule 1994; van Herwaarden et al., 1998). Thus, N fertiliser rate alone may not be sufficient to determine whether any N rate applied at a given site/season was sub-optimal. As an example, Abalos et al. (2012) investigated the effect of the urease inhibitor NBPT on N_2O emissions and grain yields in a barley crop compared to urea by applying N at a rate of 120 kg N ha^{-1} for both treatments, and included a nil N fertiliser control treatment. Ultimately, the use of both N fertiliser products increased grain yields above the nil N treatment, but there was no significant increase in grain or biomass yields of barley due to NBPT, despite significant abatement in N_2O emissions in the NBPT treatment (Abalos et al., 2012). However, in the absence of additional N rates to derive an N response curve, there is no way of knowing whether 120 kg ha^{-1} of N applied as urea was already sufficient for maximum grain yields given other soil constraints to production, in which case it would be unreasonable to expect a yield increase if the NBPT treatment provided more available N to the crop.

Where EENFs have been compared to conventional N fertilisers at the locally recommended N rate in conjunction with at least one sub-optimal N rate, several positive yield outcomes have been reported at suboptimal N rates in the EENF treatment. For example, Zhang et al. (2010) reported that while maize yields declined when urea was added at 70% of the recommended rate (126 kg N ha^{-1} vs 180 kg N ha^{-1}), there was no loss of yield when DMPP was used in conjunction with the 70% application rate compared to the treatments that received the recommended N rate. Similar results have been obtained in pasture systems where urea was compared with urea + DMPP (Entec ™): while a yield loss was observed when urea rates were cut by 30% compared to urea at the recommended N rate, no yield loss was observed in the corresponding DMPP treatment (Koci and Nelson, 2016; Rowlings et al., 2016).

3. Results from a re-evaluation of the literature

We examined the studies used in recent meta-analyses (Abalos et al., 2014; Feng et al., 2016; Qiao et al., 2015; Thapa et al., 2016; Yang et al., 2016) and other recent studies to investigate yield responses to nitrification or urease inhibitors when suboptimal N rates were applied. Given the uniqueness of flooded crop systems such as rice cultivation, we only examined upland, or aerobic crop and pasture systems, and we focussed on commercial N fertiliser products that contain DCD, DMPP and NBPT because of their widespread availability. In total, we were only able to identify 11 published studies that applied both conventional N fertiliser and the EENF products at a control (recommended N rate) and one or more sub-optimal N rate (Table 1). Notably, two studies included in the data base − Zhang et al. (2010) and Kawakami et al. (2012) − included a comparison of standard N and EENF products at a suboptimal rate but did not include an EENF treatment at the highest (control) N rate. These studies were included because the treatments still established circumstances that would enable any potential yield response from EENFs at a suboptimal rate to be observed.

Data from the selected studies were extracted and yield data were converted to percentage of maximum yield and N fertiliser rates were converted to percentage of recommended rate for maximum yield. Quadratic, quadratic-plateau and exponential fertiliser response curves (Cerrato and Blackmer, 1990) were fitted to these data using the nls function in R (R Core and Team, 2016). Confidence intervals were estimated by propagating errors for model parameters using a Monte Carlo simulation with 10000 iterations via the predictNLS function in the R package *propagate* (Spiess, 2014). Quadratic-plateau models did not improve upon fits provided by the simple quadratic models and are excluded from further discussion. Both quadratic and exponential models suggest a significant ($P < 0.05$) divergence in yields between conventional N products vs EENF products when N fertiliser rates are 25–90% of the recommended N fertiliser rate (Fig. 1A,B). A maximum yield difference between EENFs and conventional fertiliser was estimated to occur at 48% of the recommended N rate under an exponential model, which was similar to the yield difference estimated by the quadratic model at this N rate ($P < 0.05$). Although the magnitude of the yield benefit (~11%) is similar to that estimated by other meta-analyses on this subject (Abalos et al. (2014), Qiao et al. (2015), Feng et al. (2016), and Yang et al., (2016)) three of these analyses found the yield benefit of using an EENF to be greater under higher N rates (Abalos et al., 2014; Feng et al., 2016, Yang et al., 2016). The key issue here is that different crop/environment/soil/management combinations will have different N requirements for maximum yield, meaning that the role of 'N rate' in explaining yield variation in these meta-analyses is somewhat confounded by other factors. In our analysis, scaling of the actual N rate against the optimum N rate accounts for some of the variation driven by crop type/soil type/environment, thereby limiting the contribution of these confounding factors to yield variation. However, a significant drawback to our analysis is the limited number of studies fitting the criteria of including suboptimal N rates. This prevents a thorough investigation of the role of other factors, including crop type, soil characteristics and environmental variables, in moderating the effect of EENFs on yields. Nevertheless, we believe our results are sufficient to warrant a renewed effort in assessing the agronomic effectiveness of EENF products using trials designed specifically for the purpose of quantifying yield responses, as opposed to targeting N_2O emissions.

Table 1
Published studies that compared crop yields using standard N fertiliser products and N fertiliser products containing DMPP, DCCD or NBPT at a suboptimal N fertiliser rate in addition to the recommended N fertiliser rate for inhibitor and control products.

Reference	Crop	Inhibitor
Zhang et al. (2010)	maize	NBPT, DMPP, NBPT + DMPP
Zaman et al. (2013)	ryegrass/clover pasture	NBPT, NBPT + DCD
Kawakami et al. (2012)	cotton	NBPT, NBPT + DCD
Khan et al. (2013)	wheat	NBPT, NBPT + DCD
Khan et al.(2014)	maize	NBPT
Thapa et al. (2016)	wheat	Nitrapyrin, NBPT + DCD
Rowlings et al.(2016)	ryegrass/kikuyu	DMPP
Koci and Nelson (2016)	ryegrass/setaria/kikuyu	DMPP
Lester et al. (2016)	sorghum	DMPP
Alonso-Ayuso et al. (2016)	maize	DMPP
Wang et al.(2016)	Sugarcane	DMPP

4. Are N fertiliser products with inhibitors economically viable?

Enhanced efficiency N fertiliser products typically cost more than conventional N fertilisers such as urea, and given the extra cost, it is likely that the use of these products will be limited to countries where farmers can afford and have ready access to N fertilisers, or where fertiliser costs are subsidised. In these production systems, N fertiliser is usually applied at rates that are sufficiently high that N is not the limiting factor for crop or pasture yields. Thus, the question asked should not be 'can EENFs increase yields?' but rather 'to what extent can EENF application rates be reduced without yield loss and is the EENF economically viable at that rate?' While studies with one sub-optimal rate are sufficient to demonstrate that a given EENF product can be effective in a particular scenario, they do not provide sufficient information to resolve what rate of the EENF is needed to achieve maximum non-N-limiting yields, which further precludes a valid economic analysis. To derive the appropriate data, N rate response curves need to be generated for a given crop/environment over multiple sites/seasons. From these data sets, simple calculator tools that factor in the cost of a given EENF can be used to estimate the economic viability of using an EENF at a particular rate. To the best of our knowledge, the only published study that has examined urea vs DMPP, DCD or NBPT products at multiple N rates over multiple seasons is the study of Lester et al. (2016), which found no evidence that lower rates of DMPP + urea (Entec ™) could be used to achieve maximum sorghum grain yields across five sites/seasons. We suggest that further studies across a wider range of crops and environments are needed, and that any economic analyses arising from these studies should account for other additional benefits of lower N application rates. While NO_3^- leaching leads to environmental damage off-farm that is not a direct cost to the landholder, it is also the greatest contributor to the accelerated rate of soil acidification in agricultural systems (Tian and Niu, 2015). Acidification from NH_4^+-based fertilisers can result in decreases in cation exchange capacity (CEC), base saturation, and exchangeable Ca^{2+} and Mg^{2+} (Barak et al., 1997), impacting soil productivity. Costs associated with soil acidification include yield losses and the cost of remediation (i.e. liming). It should be noted also that even regular liming does not

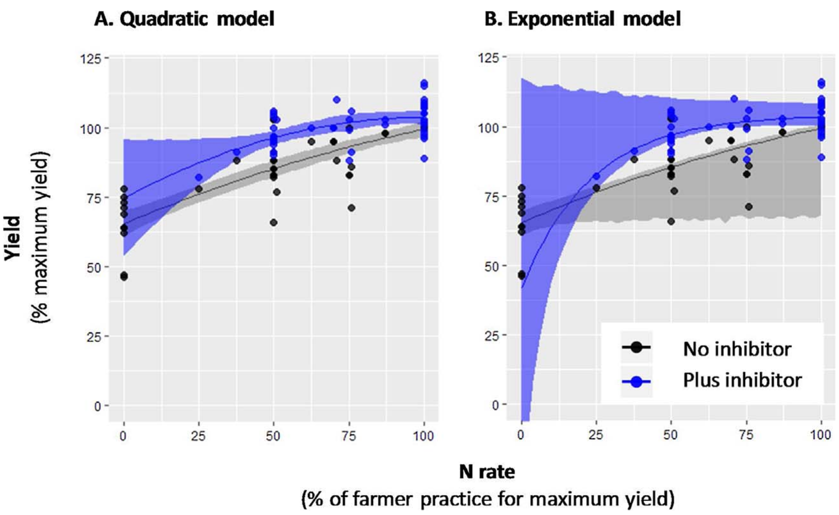

Fig. 1. Quadratic (A) and exponential (B) yield response curves to EENFs and conventional N fertiliser. Note that compiled data have been normalised with respect to optimum N fertiliser requirements as stated in references provided in Table 1.

always correct soil acidification, particularly sub surface acidity (Moody and Aitken, 1997), further highlighting the advantages of minimising its production in the first place, best achieved by lowering inorganic N application. These are direct costs to the landholder which should be accounted for in any economic analysis of the viability of using EENFs.

5. Conclusions and outlook

We conclude that the results from recently published meta-analyses on the agronomic efficacy of the NIs DCD and DMPP and the urease inhibitor NBPT need to be interpreted with caution, since the inclusion of data sets that only used one N rate − frequently the recommended N rate − may fail to achieve agronomic responses because N is not the limiting constraint to production. While we only identified 10 published studies with DCD, DMPP or NBPT vs standard N fertiliser that investigated yields at suboptimal N rates, data from these studies suggest that EENF products may be able to achieve higher yields *cf* conventional N fertiliser at suboptimal N fertiliser rates. Ultimately, further studies across a range of crops and environments are needed to more accurately derive agronomic response curves for EENFs. Once this is achieved, economic models can be implemented allowing farmers to make informed decisions on the price differential between products.

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