



# Applying Nanotechnology to Fertilizer

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Rationales, research, risks and regulatory challenges<sup>1</sup>



Institute for  
Agriculture &  
Trade Policy

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October 2017

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Published October 2017

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# OVERVIEW

Dependence on more efficient use of synthetic fertilizers to increase crop yields poses technical, economic and environmental challenges. This article summarizes three proposed applications of nanotechnology enabled fertilizers (NEFs). Each one of them is intended to increase fertilizer nutrient efficiency uptake in plants and reduce the percentage of nitrogen that leaches into ground and surface water as nitrates and volatilizes as nitrous oxide. (Nitrous oxide makes up only about five percent of all greenhouse gases, but is about 300 times as potent as carbon dioxide.<sup>2</sup>) One application would use a nano-composite polymer to bind fertilizer nutrients into pellets that would improve nutrient use efficiency more than current Controlled Release Fertilizers (CRFs). The second is a proof of concept application that would rely on a nano-biosensor embedded in a biopolymer fertilizer coating to release nutrients (just in time) in response to chemical signals from soil microbes in a plant's root system (rhizosphere). A third, laboratory tested approach, is to amend soil samples with nano-clays, which create soil micro-structures to reduce and delay nitrate loaded runoff and release of ammonia and nitrous oxide.<sup>3</sup> This mini-survey presents some of the technical problems and environmental risks of each approach. It also offers insights regarding broader economic challenges related to use of nanotechnology enabled CRFs for row crops.

To the extent that industrial scale crop production depends on synthetic fertilizers—and forgoes intensified crop rotation and systemic use of cover crops to reduce negative environmental consequences—nanotechnology is likely to be among the technologies of precision agriculture that are hoped to make the intensification of crop production environmentally sustainable. This brief survey by a non-scientist is intended to help inform an interested lay public of the status of nano-fertilizer development and environmental risk assessment.

Some agri-nanotechnology researchers have sounded a loud note of caution about the research and development challenges to manufacturing and safe use of NEFs. A recent article by researchers at the International Fertilizer Development Center states, “large scale industrial production of nano-fertilizers is yet to be realized,” adding that among their concerns are “toxicity associated with nanoscale materials; scant nanofertilizer research with key crop nutrients; inadequacy of soil or field-based studies with nanofertilizers; [which] types of nanomaterials to produce as nanofertilizers; how to efficiently and effectively apply nanofertilizers at the field scale; and the economics of nanofertilizers.”<sup>4</sup> Our review of the studies summarized here affirms these concerns and adds to them.

However, the urgent need to increase nutrient uptake efficiency and greatly decrease environmental harms from synthetic fertilizer use, particularly from nitrogen-based fertilizer, will continue to drive research and investment into NEFs. It remains to be seen whether nano-fertilizer researchers will be patient enough to learn from plant physiology and soil science the risk and hazards that some nano-materials may pose to soil, plant and human health.

One research team described an underlying cause of poor performance by fertilizers:

the gap between the intended fertiliser functionality and their actual impact arises from the fact that fertilisers are made by chemists, chemical engineers and industrial processing technologists, following laws of physical and chemical processes, with little input from the knowledge of plant physiology and need for agro-ecological specificity of crop nutrition. A renewed impetus is, therefore, needed, to arrive at novel ways of packaging and delivering nutrients to plants, based on a better integration of the plant physiological and ecological processes related to the different modes of nutrient uptake, transport and metabolism.<sup>5</sup>

Understanding specific applications of nanomaterials in fertilizer is critical to preventing inadequately researched, field tested and regulated products from exacerbating current environmental and public health problems associated with industrial scale use of synthetic chemicals. Scientists are under enormous pressure to deliver technologies to increase yields that are not only technically reliable but cost-effective for the fertilizer industry and for farmers.<sup>6</sup> The public has an important role to play to ensure that any new nano-fertilizer products are not rushed to market before their environmental and public health impacts can be determined, reliably validated, and diminished, if not eliminated, through regulation and product re-design.

## THE ROLE OF FERTILIZER IN EXPANDING EXPORTS AND INCREASING YIELDS

The reports of the Global Harvest Initiative (GHI), “a private sector policy voice for increasing productivity and sustainability throughout the agricultural value chains for food, feed, fiber and fuel”<sup>7</sup> illustrate a global agribusiness approach intended to increase crop yields and exports of those crops. GHI members include Monsanto, Mosaic (a fertilizer company that was formerly part of Cargill), Dow Elanco Animal Health, John Deere, Novozymes, DuPont, and Farmland Partners, a

large and fast-growing agricultural Real Estate Investment Trust.<sup>8</sup> Consulting partners to the members include universities, nongovernmental organizations, corporations, and publicly funded development banks, such as the Inter-American Development Bank (IADB).

The GHI project originates in Washington DC and aims to be applied globally. The Latin American regional version of the GHI reports and analytic framework have been facilitated, adapted and translated by IADB. Brazil is an important case study for the application of nanotechnology to increase yield in export crops, particularly soybeans. Among GHI members, the Brazilian Agricultural Research Corporation (EMBRAPA) investment in nanotechnology includes the development of a nanotechnology enabled controlled release fertilizer. The application of nano-clay composites to urea, the richest source of nitrogen fertilizer, is designed to reduce nitrate leaching into surface and ground water, and its volatilization as the powerful greenhouse gas, nitrous oxide. According to a press release, “Intelligent fertilizer,” following successful laboratory and field trial experiments, “is ready to be transferred to the private sector for adjustments to stages of scale production and of trade.”<sup>9</sup>

Before analyzing the technical reporting of NEFs and their possible environmental and farm worker health impacts, it is helpful to understand the institutional and agricultural economic context in which commercial release of a nano-fertilizer or nanotechnology enabled soil amendment would take place.

The Brazilian report, “O próximo celeiro global: Como a America Latina pode alimentar o mundo” [“The next global granary: how Latin America can feed the world”] repeats the GHI solution to a GHI forecast shortfall in agricultural productivity for low income countries:<sup>10</sup> “The path to follow: invest in Latin American/Caribbean Agriculture”, the report declares. The areas of investment include agricultural technologies to realize an environmentally sustainable intensification of crop and animal production and exports of that production to low-income countries.<sup>11</sup> The GHI tacitly assumes that low income countries will have the hard currency, usually dollars, with which to pay for imported agricultural products as advocated by GHI members and associates. It also tacitly assumes that imports are economically, culturally and environmentally preferable to further development of domestic agricultural production.

The Brazilian government advocates for and invests in precision agriculture for major export crops with the goal of increasing yields by up to 67 percent, although there is no target date by which this increase is to be realized.<sup>12</sup> The assumption of ever greater yields on ever more planted hectares<sup>13</sup> would entail ever greater use of fertilizer. The

International Plant Nutrition Institute reports the application of the macro-nutrients, nitrogen, potassium and phosphorus in Brazil went from about 7.4 million metric tons in 2000 to about 15.2 million metric tons in 2014.<sup>14</sup> Part of this increase is due to the two to three crops per season that can be harvested in much of Brazil.<sup>15</sup>

However, scientists have raised serious concerns about the future availability of phosphorus and potassium, two of the three major macro-nutrients for crops.<sup>16</sup> The 37 certified fertilizer companies in the International Fertilizer Industry Association’s (IFA) “Protect and Sustain Hall of Fame”<sup>17</sup> have agreed on production standards for fertilizer manufacture in 45 countries to improve efficient use of those raw materials. The IFA also has nutrient stewardship programs to teach farmers how to reduce fertilizer overuse.<sup>18</sup> To the extent that industrial scale agriculture for export depends on chemically fertilized monocrops, even with improved fertilizer manufacturing and farmer application techniques, the synthetic fertilizer foundation of industrial agriculture could be exhausted within two generations.

Intensive use of cover crops and crop rotation have proven to increase soil health and reduce the need for chemical fertilizers (and their attendant high costs of production and environmental harms).<sup>19</sup> Despite this success, industry continues to research technological fixes that will be extend the profitability of agribusiness by perpetuating mono-cropping and agricultural trade of a few grains and oilseeds. The application of nanotechnology and nano-scale materials to fertilizer is one such proposed technological fix.

## RATIONALES FOR APPLYING NANOTECHNOLOGY TO FERTILIZER

A U.S. researcher neatly summarized the agri-nanotechnology proponents’ imperative for applying the technology to enable more sustainable intensification of agricultural production along the lines of the GHI agricultural productivity forecasts: “The population is increasing, the climate is changing, making agriculture hard to do. The role of nanoparticles is to help us address this major problem. We just can’t produce enough food.”<sup>20</sup> The econometric projections underlying this claimed imperative, which assumes global food production must double by 2050—have long been controversial and recently rebutted.<sup>21</sup> Whether this neo-Malthusian assessment is accurate or not, nanotechnology is among the tools of precision agriculture that its proponents hope will

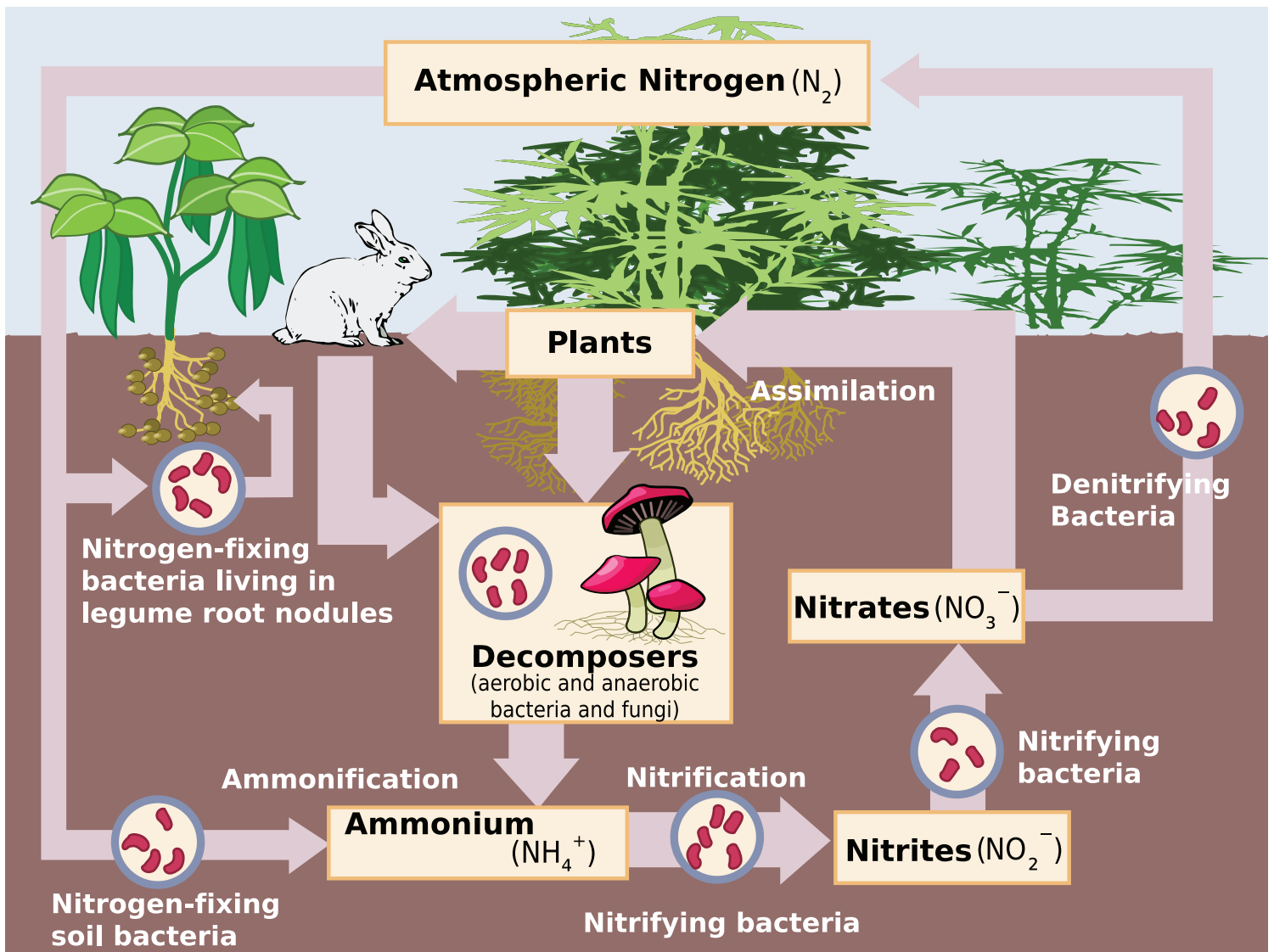


Illustration 1: Atmospheric Nitrogen ( $N_2$ )

Source: Dréo, Johann, "The Nitrogen Cycle," *Environmental Protection Agency*, September 27, 2009. Accessed October 08, 2017, [https://en.wikipedia.org/wiki/Denitrification#/media/File:Nitrogen\\_Cycle.svg](https://en.wikipedia.org/wiki/Denitrification#/media/File:Nitrogen_Cycle.svg).

increase agricultural production while reducing negative environmental consequences of fertilizer use. An increase in production resulting in part from an increase in fertilizer use with current product technologies would exacerbate current negative environmental effects of that use.

According to Professor Stephen Carter, globally "We've changed nitrogen and phosphorus cycles vastly more than any other element . . . [The increase in the nitrogen and phosphorus cycles] is on the order of 200 to 300 percent. In contrast, carbon has only been increased 10 to 20 percent and look at all the uproar that has caused in the climate."<sup>26</sup> The cycle describes the processes by which nitrogen and phosphorus are changed into various chemical forms, part of which nourishes plant life and the excess of which is "lost" to the

environment. The U.S. Department of Agriculture's Natural Resource Conservation Service (NRCS) estimated in 2006 that an average of about 40 percent of nitrogen in fertilizer was lost annually on U.S. crop acreage, with about 18 percent of the total loss coming in the form of greenhouse gases.<sup>27</sup>

These estimates are based on computer simulations of modeled assumption scenarios that extrapolate from field observation data. A USDA researcher notes, "In general, the accuracy of model predictions cannot exceed the accuracy of the input data used in the analysis."<sup>28</sup> The NRCS estimates vary widely by crop planted and by region with nitrogen losses as high as 115 pounds per acre for corn planted in the Southeastern United States and as low as 12 pounds per acre for grass hay planted in the Northern Great Plains states. A

## An alternative to doubling global agriculture production for export to low income countries: improving post-harvest storage

As far back as 1975, the United Nations General Assembly resolved that UN member governments would reduce by 50 percent agricultural crop losses by 1989. In 2006, the African Union resolved to reduce crop losses to 10 percent of production by 2015.<sup>22</sup> Regrettably, these goals have been far from realized. One 2016 study reports that the estimated post-harvest loss of South Saharan African agricultural production is equal in value to that of SSA agricultural imports.<sup>23</sup> Former UN Secretary General Kofi Annan has long advocated improving post-harvest storage to reduce agriculture production losses and increase food security, particularly in Africa. Secretary General Annan outlined nine steps as crucial to achieve food security, particularly in Africa. Increasing agricultural productivity is just one.<sup>24</sup> Proponents of increasing agricultural production through greater investment in agricultural technology maintain, based rate of return policy scenarios and econometric estimates, that investment in post-harvest technology is a complementary but subordinate strategy to improving food security, compared to increasing agricultural production.<sup>25</sup>

recent article in *Science* forecasts a 19 percent increase in global nitrogen in the form of nitrates and greenhouses gases by the end of this century, under a Business As Usual scenario.<sup>29</sup> Whether viewed globally, in terms of nitrous oxide released as a greenhouse gas, or more locally, in terms of nitrates that runoff from agricultural fields into streams, rivers, lakes and subterranean aquifers, the negative environmental impacts of current chemical fertilizer use and practices are undeniable.

In the United States, at least five decades of voluntary programs to reduce fertilizer runoff from polluting lakes and rivers, including the Mississippi River, have failed.<sup>30</sup> Minnesota's Department of Agriculture (IATP is headquartered in Minnesota) has proposed the first in the nation nitrogen fertilizer rule, scheduled for adoption by the fall of 2018. The rule would ban fall and frozen ground application of nitrogen fertilizer on land where the soil type and geomorphology easily transport nitrate runoff.<sup>31</sup> Minnesota is also part of a new state-federal partnership program for voluntary certification of agricultural water quality. Farmers and landowners that meet the requirements of the Minnesota Agricultural Water Quality Certification Program "are deemed to be in compliance with new water quality rules for 10 years."<sup>32</sup>

Other state efforts to reduce nitrogen loss are meeting powerful resistance. For example, a lawsuit against ten rural water districts by the Des Moines, Iowa (U.S.) municipal water works, which spent approximately \$1.5 million in 2015 to filter agricultural nitrates out of drinking water, was dismissed by a U.S. federal judge in March 2017. The judge ruled that water quality and safety was a problem for the Iowa state legislature to solve.<sup>33</sup> The legislature's initial response, which was to consider the dissolution of the Des Moines municipal water works,<sup>34</sup> suggests that a legislative solution to nitrate pollution is not forthcoming.<sup>35</sup>

If neither voluntary fertilizer application and agricultural runoff programs nor lawsuits result in measures to reduce nitrate pollution of surface and subterranean waters, will NEFs succeed? Nano-fertilizer research offers the prospect of a technological solution to nitrate contamination of drinking water and the production of a very potent greenhouse gas. Adoption of NEFs could be profitable for the fertilizer companies and enable the growth of current production and agricultural exports sought by the GHI and related agribusiness companies. The prospect of a profitable agro-environmental technology that enables current cropping and trade practices, however, may be realized only if successful research, development and commercial deployment of NEFs overcome large and persistent problems.

The high percentage of fertilizer nutrient loss,—notwithstanding the fertilizer production methods certification<sup>36</sup> and nutrient stewardship seminars of the International Fertilizer Industry Association<sup>37</sup>—drives investment in high tech solutions to reduce that loss and the resulting pollution of urban and rural water by nitrates. Engineered Nanoscale Materials (ENMs) in fertilizer have not yet been detected and characterized in commercially available fertilizers and/or soil amendment products. However, the EMBRAPA press release mentioned above points to the imminence of commercial application of its "Intelligent fertilizer." Internet advertising for "NanoAg" and similar soil treatments<sup>38</sup> further indicates that nanotechnology enabled fertilizer may soon be commercialized, if it is not already.



Image used under Creative Commons license via Flickr user NOAA glerl.

In 2017, Lake Erie experienced harmful levels of algae mega bloom, largely resulting from fertilizer nutrient runoff

## CONTROLLED RELEASE FERTILIZERS (CRFS): THE ECONOMICS THAT LIMIT CRF USE IN ROW CROPS TO REDUCE NITRATE RUNOFF AND NITROUS OXIDE VOLATILIZATION

If nanotechnology enabled fertilizer is soon to be put in the marketplace, its marketers will face economic challenges at least as challenging as those faced by marketers of existing controlled release fertilizers (CRFs). Indeed, one proof of concept study for a micro-nutrient NEF (reviewed below) if successfully realized, would offer a much more precise form of CRF. But before jumping to the conclusion that

nanotechnology will succeed as a technological fix for industrial agriculture and the fertilizer industry, it is necessary to review the current economics of fertilizer use.

CRFs, which have been commercialized and applied to ornamental gardens and lawns for at least twenty years, are designed to increase the efficiency of fertilizer nutrient use and reduce nitrate runoff in water. The CRFs are polymer coated. The thickness of the coating or coatings and the mix of nutrients that are coated determine the release rate of the fertilizer nutrients. For example, different formulations of Osmocote®, a Scott Sierra product, can release nutrients over a three or four month to a 14 or 16 month period, according to the company.<sup>39</sup> However, CRF is about a third more expensive than the uncontrolled release fertilizer applied to row crops (calculation outlined below). The controlled release fertilizer global market, valued at about \$2.2 billion in 2014, was projected to grow to about \$3.2 billion by 2020.<sup>40</sup> Yet even

with that forecasted growth, the CRF market is dwarfed by the \$175 billion uncontrolled release global fertilizer market of 2013.<sup>41</sup> Why?

For U.S. farmers, who are regularly compelled to sell their crops to agribusiness processors and traders at prices below the cost of production, adding to that cost by using more expensive CRFs would drive them further in debt.<sup>42</sup> Whether farmers are in Brazil, the United States or elsewhere, fertilizers are a major production cost. For example, in 2014, fertilizer costs were about 40 percent of all U.S. farm operating costs for planting maize (about \$149 of about \$357 per acre planted).<sup>43</sup>

To appreciate the economic challenges of applying a new fertilizer technology, consider the situation of U.S. farmers, whose production is heavily subsidized. The U.S. Department of Agriculture reports U.S. farmers lost an average of \$86.62 per acre maize planted in 2014 and \$58.46 in 2016.<sup>44</sup> To some degree, U.S. taxpayers compensate farmers for the agribusiness market's failure to pay prices above the cost of production. For example, the Congressional Budget Office estimated that maize farmers would receive \$4.1 billion in revenue insurance payments in Fiscal Year 2014-2015.<sup>45</sup> Such payments keep the maize and other row crop systems economically sustainable for governments that can afford to pay them. The calculation of the revenue insurance payment crucially depends on crop yield, which to some extent depends on fertilizer use.

CRF technology applied to urea for growing maize is becoming more affordable for U.S. farmers, in large part due to Environmental Quality Incentives Program (EQIP) payments of \$5-15 per acre.<sup>46</sup> (EQIP is a government contract based voluntary participation program to improve the natural resource base of agriculture, e.g. water quality.<sup>47</sup>) These payments could partly offset the considerable price difference between CRF urea and the conventional uncoated urea commonly applied to maize. From 2009 to 2015, the per pound price of uncoated urea averaged \$0.54.<sup>48</sup> According to an agronomist at Agrium, CRF urea costs \$0.18 to \$0.20 per pound more than the conventional urea.<sup>49</sup> Farmers must estimate whether the extra 33-36 percent of CRF urea cost will be covered by a combination of EQIP payments, increased cash receipts from increased yields, and revenue from yield related government insurance programs.

Fertilizer company agronomists tell farmers that an increase in yield will more than offset the extra cost of CRF use for maize. According to the agronomy manager of Agrium (the manufacturer of a polymer coated urea marketed as Environmentally Smart Nitrogen [ESN]), "Farmer surveys show yield and convenience [of application] will drive sales of ESN. . . Farmers are concerned about the environment, but it doesn't drive their [fertilizer purchase and use] decisions."<sup>50</sup> Indeed,

because the U.S. Farm Bill's commodity program payments are tied to a formula of a farm's "base acres" and a Farm Bill defined average revenue or a legislatively determined reference price for covered crops,<sup>51</sup> the calculus for fertilizer use is to increase yield and thus "farm income," which the U.S. Department of Agriculture defines as cash receipts plus government payments.<sup>52</sup>

EQIP payments are not designed, however, to offset the public and environmental health costs of the well-documented contribution of fertilizer use to greenhouse gas production and nitrate contamination of water.<sup>53</sup> For example, this taxpayer funded compensation will not cover the 2010 estimated costs of \$88 million for the San Joaquin (California) Valley, a major agriculture production area, to improve its filtration infrastructure to make drinking water potable.<sup>54</sup>

Public health and environmental costs are huge outside the U.S. "The estimated cost of environmental damage from reactive nitrogen emissions is between €70 billion and €320 billion in the European Union alone."<sup>55</sup>

Current U.S. agribusiness prices and government payments for crops do not provide a consistent and clear economic incentive to expand the use of the more expensive CRF to commercial grain and oilseed agriculture. However, non-nanotechnology research to reduce nitrogen release is reporting promising laboratory results, e.g., a 75 percent reduction in nitrous oxide emissions by coating urea with nitrification inhibitors.<sup>56</sup> Whether such results can be replicated in field conditions and whether nitrification inhibitors can be manufactured at a cost and for a price that is affordable for farmers will influence whether non-nanotechnology or nanotechnology enabled fertilizers to reduce nitrogen loss will be adopted by farmers.

In the below cost of production price environment for row crops, at least in the United States, adoption of CRFs entails government subsidies beyond EQIP and additional programs to improve and conserve the natural resource base of agriculture. The likelihood of raw material cost increases for commercial fertilizer production is driving research into applications of nanotechnology to reduce the volume of raw material use, improve the nutrient uptake efficiency and reduce the negative environmental and public health costs of fertilizer use and overuse. Whether farmers adopt nanotechnology enabled fertilizers or non-nanotechnology means to reduce their fertilizer costs and negative environmental impacts of nitrogen fertilizers may be determined by crop prices and subsidies, at least as much by the technical efficacy of new fertilizers and fertilizing methods.



# NANOTECHNOLOGY ENABLED FERTILIZER: ALL GOOD NEWS?

The trade press reporting on nanotechnology enabled fertilizer indicates that technology developers have gone beyond laboratory and greenhouse scale experiments to field trials. Researchers report impressive reductions in nitrogen related environmental harms and an increase in nitrogen use efficiency, resulting in crops yield increases.<sup>57</sup> For example, a Sri Lankan research group reports, “Initial trials on rice farms have revealed that a savings of up to 50 percent in urea consumption can be obtained by using urea-HA NP [Hydroxyapatite NanoParticle] hybrids. The farm field trials were extended to three seasons, and a similar trend in crop yield improvement was observed (Figure 7). . . In the farm field trial data, 50 percent reduction in urea use allows the yield to be maintained at ~7.9 tons/hectare, which is notably higher than the yields for the urea only rice crop yields (7.3 tons/hectare) using the recommended levels of urea.”<sup>58</sup> The reported results of these farmer field trials followed laboratory experiments in pots, and then in research plot trials.

Here is how the experimental design is described. HA is a bio-ceramic compound that is used in medical and dental applications to provide calcium, phosphate and other minerals to bone and other hard mammal tissues. Urea coated HA NPs slow the release of nitrogen because of the chemical bonding properties between nitrogen and HA, increasing the plant’s uptake of urea. In the experiments, the NPs formed nano-rods, 100-200 nanometers in length and 15-20 nanometers in diameter.<sup>59</sup> The researchers state, “There was no evidence of HA NPs entering into the plant.”<sup>60</sup> Although they conducted a leaf nutrient analysis for nitrogen, phosphorus and potassium, there is no indication of how they concluded that there was no evidence that the rice plants did not uptake some HA nano-rods.

Intuitively, the plant uptake of calcium, phosphate and other minerals in the commercially available nano HA<sup>61</sup> seems unproblematic. However, what is unproblematic in the macro scale may be problematic in the nano scale. A European

Commission Scientific Opinion on consumer safety states that an article it reviewed on laboratory rat consumption of nano HA “indicated that needle-shaped crystals of hydroxyapatite can be a concern in relation to acute toxicity.”<sup>62</sup> Whether the crystalline structure of the urea coated HA nano-rods in the Sri Lankan experiments are needle shaped is unclear from the NP visualization infrastructure used to photograph them. The Scientific Opinion authors found no data to review on sub-chronic toxicity (90 days of oral exposure) or chronic toxicity (one year exposure) related to nano HA.<sup>63</sup> Furthermore, the authors stated, “No study has been identified that would allow the identification of a point of departure for risk assessment.”<sup>64</sup> So according to European Commission and Organization for Economic Cooperation and Development nanomaterial safety working group standards, there were no studies that would enable risk assessment of HA NP even in the research and development phase of products.

Given the number of nanomaterials that have been shown to be taken up into plant roots and translocated throughout plants<sup>65</sup>, it is surprising that HA NPs would not be taken up to some extent in the field trial rice plant samples of the Sri Lankan research team. Further research to understand any possible negative effects in the use of HA NPs in fertilizer prior to commercialization is a critical task for product developers, exposure scientists and those involved with fertilizer policy, investment and use. The very important role of rice production in food security and the urgent need to reduce nitrate contamination of water and urea volatilization as nitrous oxide makes it imperative that further research be

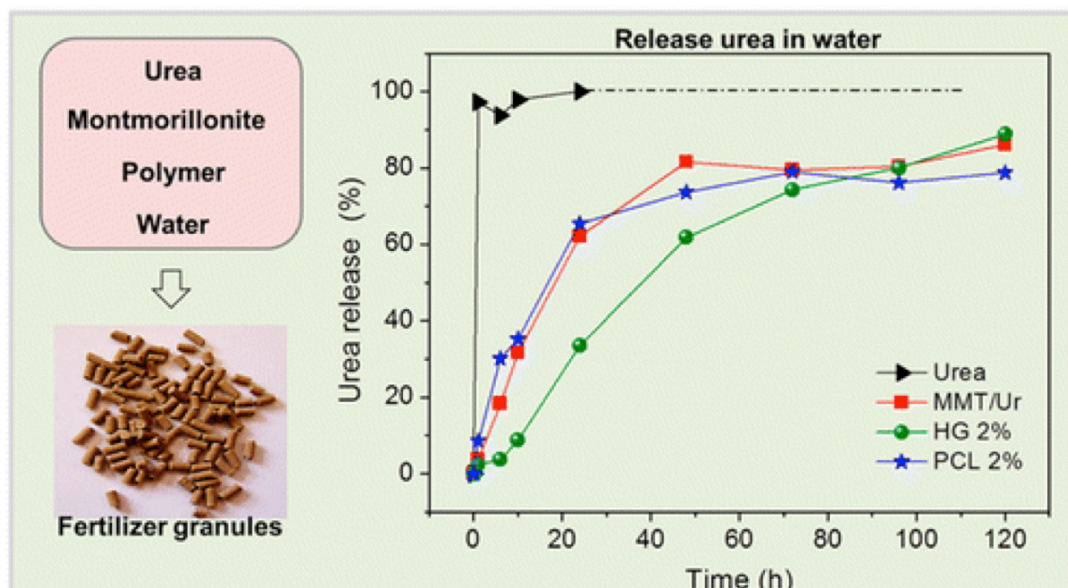


Illustration 2: Novel Slow-Release Nanocomposite Nitrogen Fertilizers: The Impact of Polymers on Nanocomposite Properties and Function

Source: Elaine L. Pereira et al, “Novel Slow-Release Nanocomposite Nitrogen Fertilizers: The Impact of Polymers on Nanocomposite Properties and Function,” *Ind. Eng. Chem. Res.*, 2015, 54 (14), pp 3717–3725. <http://pubs.acs.org/doi/abs/10.1021/acs.iecr.5b00176>.

undertaken to verify (or not) all or part of the Sri Lanka team's HA NP nitrogen fertilizer experiments from laboratory to field trial.

A reviewer of the Sri Lanka paper wrote, "The important goal and challenge for this technology going forward is to fine-tune the urea-HA nanohybrid to maximize its potential in a variety of soil types, while making this simple approach to the global nitrogen issue commercially viable."<sup>66</sup> The reviewer's enthusiasm for this nanotechnology enabled fertilizer application is understandable. But more work to determine the impacts of the HA nano-rods on soil health and plant uptake should take place before any fine tuning begins. Furthermore, the method of applying this nanotechnology enabled fertilizer will mediate the risks to farmworker health and inform the design of protective equipment to mitigate those risks. For example, it seems unlikely that nanotechnology enabled fertilizer could be broadcast or even side-dressed without farmworker inhalation of nanoparticles not bound in the fertilizer. Airborne fertilizer NPs could put the farmer at risk of damage to lungs and other organs.

## NANOTECHNOLOGY ENABLED FERTILIZER AND POSSIBLE TOXICITY TO SOIL HEALTH

As a snapshot of possible risk to soil health of a nanotechnology enabled fertilizer, consider Brazil's EMBRAPA research, first as reported by the USDA. EMBRAPA claimed that by adding a nanocomposite polymer to urea, "[I]n a field experiment nitrous oxide emissions were reduced by more than 50 percent compared to emissions when the same amount of urea was applied as fertilizer to a winter wheat crop."<sup>67</sup> (EMBRAPA agri-nanotechnology research, such as that reported by USDA, is published in peer reviewed journals.<sup>68</sup> Summaries of research projects are available in its website news articles.<sup>69</sup>)

One of the polymers used in the EMBRAPA nanotechnology enabled urea fertilizer, polycaprolactone (PCL), has the technical virtue of being degraded slowly by micro-organisms (e.g., bacteria and fungi) and the economic virtue of being easy and cheap to manufacture.<sup>70</sup> The PCL binds a nano-scale exfoliated clay mineral, montmorillonite, and urea in CRF pellets. Because PCL has become a polymer of choice for use in drug delivery for implanted medical devices, EMBRAPA researchers were able to explore how results from experiments on slow release drug delivery might inform the use

of PCL to help deliver slow release of fertilizer nutrients. However, technical and economic virtues of PCL do not address environmental sustainability in field conditions.

One of the materials incorporated into the pelletized fertilizer is polyacrylamide hydrogel, a chemical used to reduce water usage in landscape gardening. Because non-amended montmorillonite swells to retain water<sup>71</sup> and other liquids, such as nitrates, the hydrogel improves the montmorillonite's water retention performance. However, as the polymer breaks down, the resulting acrylamide, "is a lethal neurotoxin and has been found to cause cancer in laboratory animals."<sup>72</sup> The breakdown is accelerated in combination with fertilizer salts, which raises the question of whether the hydrogel that binds urea nutrients to nano-clay in fertilizer pellets may harm micro-arthropods and other engineers of soil health. Could chronic exposure to minute amounts of acrylamide released from the hydrogel also harm the smallest soil engineers, the bacteria, protozoa and fungi?

An article on well-controlled laboratory experiments to measure hydrogel polymer bio-degradation reported, "Synthesized hydrogel was completely degraded within 70 days using composting method, while it was 86.03 percent degraded within 77 days using soil burial method."<sup>73</sup> The authors explained, "The candidate polymer has been evaluated as a device for controlled release of urea and enhancement of moisture content of soils."<sup>74</sup> The authors reported success of the polymer for both purposes, claiming, "Because of its [the hydrogel polymer's] stability for long duration and no harsh impact on soil fertility such devices are very useful in agriculture sector."<sup>75</sup> But the authors limit the metrics for measuring "no harsh impact on soil fertility" to measuring "pH of soil, organic carbon, phosphorus and potassium content" in control (non-amended) soil loam and clay samples compared to soil and clay samples in which the hydrogel polymer has biodegraded.<sup>76</sup> Their conclusion that hydrogel polymers are useful for the agriculture sector, therefore, is inadequately supported by other necessary metrics, e.g., measurements of microbial biomass that could indicate adverse effects of the hydrogel polymer bio-degradation on soil fertility.

Life cycle exposure assessments (LCEA) of this nanotechnology application in field conditions should be a pre-requisite to regulatory review for commercialization.<sup>77</sup> LCEA applies a Life Cycle Assessment methodology (historically used to estimate global environmental impacts) to the exposure science that attempts to measure exposure to minute chemical quantities. LCA is defined in the Safe Nano project: "Life cycle assessment (LCA) is a quantitative assessment of emissions, resources consumed and the potential impacts on health and the environment that can be attributed to a product over its entire life cycle, from raw material extraction, raw material

# NANO-BIOSENSOR CONTROLLED RELEASE FERTILIZER

conversion, manufacture of product, distribution, through to its use and end-of-life processes.”<sup>78</sup> An LCA approach to exposure assessment of engineered nanomaterials in consumer products has not made great progress, according to a presentation at a 2015 National Nanotechnology Initiative meeting. Professor Paul Westerhoff gave LCEA low marks for achievement when compared to the objectives of a 2008 NNI strategy on understanding environmental, health and impacts of nanomaterial exposure.<sup>79</sup>

In the example above, an LCEA of the hydrogel polymer would attempt to quantify the exposure of biological engineers of soil health—from earthworms to bacteria—to the polyacrylamide hydrogel during various stages of its bio-degradation. A research group experiment with hydrogel polymer as a non-nanotechnology enabled soil amendment used in field conditions to enhance water retention in soil concludes

Acrylamide, a monomer used for hydrogel preparation is neurotoxic, but polyacrylamide itself is non-toxic. The polyacrylamide can never reform its monomer. Hence there is no residual amount of acrylamide present in the soil after degradation of hydrogel, especially when cellulose is used as backbone. Acrylamide residue is also not detected in crop products which are grown with hydrogel application.<sup>80</sup>

This conclusion, contradicting my concern about the impact of bio-degradation on the polyacrylamide, could be good news for soil health. There remain important questions, however, regarding the origin of acrylamide in food crops grown in soil which is purported to be residue free. Potatoes, for example, can form acrylamide through heat induced food processing.<sup>81</sup>

Risks of worker exposure to acrylamide used in the preparation of the hydrogel remain. Because acrylamide can be absorbed through the skin or inhaled, exposure scientists must determine whether repeated inhalation and/or dermal exposure of fertilizer manufacturing workers and farmers to the fertilizer nutrients bound in pellets with polyacrylamide hydrogel might result in cancers or other harm to human health. At the very least, exposure and hazard assessment of this fertilizer, based on the released polyacrylamide hydrogel, both for soil health, and laboratory animal testing for human health, is a pre-requisite for regulatory approval to commercialize this novel fertilizer.

A CRF that reduces nitrous oxide emissions by 50 percent—if technologically realized and cost effective for farmers, however desirable—is still far from the ideal of 100 percent fertilizer nutrient use efficiency, with no nitrate run-off or greenhouse gas volatilization. In the CRF product referenced above, the polymer coating of nitrogen nutrient pellets is triggered to release nutrients with the addition of water. However, this trigger and the nutrient release are not specifically synchronized to the nutrient needs of the plant’s root system in real time.

A nanotechnology application to greatly increase the control of the plant over the nutrient release rate was proposed in 2012 by a Canadian research team as “Intelligent NanoFertilizer.”<sup>82</sup> The application builds on a long history of soil science, including the discovery of a root exudation of chemical signals corresponding to a decrease in nitrogen.<sup>83</sup> This highly interdisciplinary project has evolved from a focus on incorporating a nano-biosensor in a polymer that coats the fertilizer to release urea, to a focus on increasing macro-nutrient uptake efficiency by putting nano-biosensors in a polymer that coats micro-nutrients, such as iron and zinc. However, the project’s authors note, “Many of the effects of NMs (Nanomaterials) and NPs (Nanoparticles) on crop yield and quality, human health, plant-beneficial soil microorganisms, and environmental risks remain largely unknown.”<sup>84</sup>

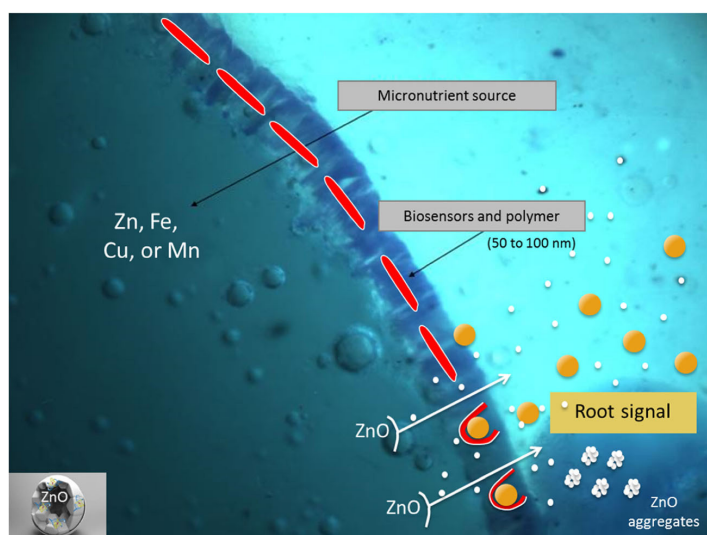
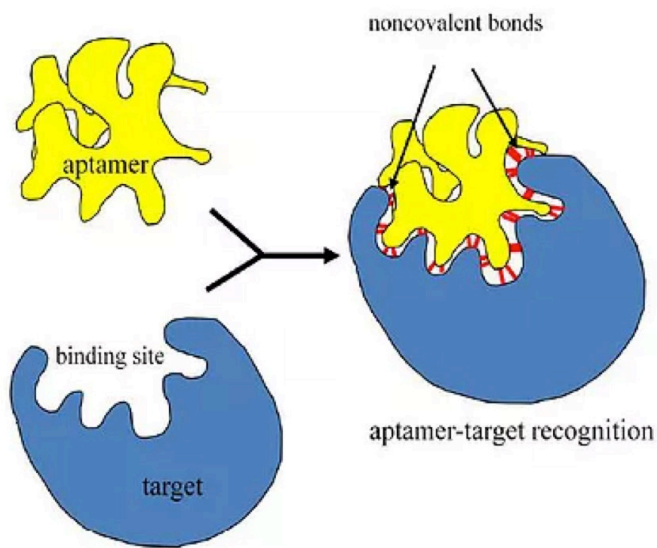


Illustration 3: “Conceptual release of ZNO2 NPS”

Source: Carlos Monreal, et al, “Nanotechnologies for increasing the crop use efficiency of fertilizer-micronutrients,” *Biology and Fertility of Soils*, October 2015, DOI: 10.1007/s00374-015-1073-5.



Simplified schematic diagram illustrating aptamer-target interactions.

*Illustration 4: DNA Aptamer*

Source: Caleb Acquah et al, « A review on immobilised aptamers for high throughput biomolecular detection and screening » *Analitica Chimica Acta* 888, July 2015. <https://www.researchgate.net/publication/280068079>.

This precautionary preface to incorporating a nano-biosensor into a polymer coated fertilizer is dictated by the complex and not well understood interactions among soil micro-organisms and plants. The Intelligent Nano-Fertilizer project has selected DNA aptamers as the optimal nano-biosensors from many possible nano-devices. The aptamers “are synthetic nucleic acids that fold into unique three-dimensional structures capable of binding tightly to a target of interest,”<sup>85</sup> in this case chemical signals from the soil micro-organisms in the rhizosphere of a plant. The aptamer targets for binding the chemical interactions between the root system and the soil-micro-organisms. Several research projects show that a polymer becomes more permeable in response to the binding of the aptamer with the target. The polymer responds by becoming sufficiently permeable to deliver a “payload” of a medication or a nutrient. Based on an encyclopedic literature review and their own experiments, the Intelligent Nano-Fertilizer project authors conclude, “intelligent nanodevices or biosensors may help deliver macronutrient and NMs, according to the temporal and spatial crop requirements during the growing season.”<sup>86</sup>

One of the many challenges for this project team is for the aptamer to identify accurately specific chemical signals between the soil microbes and plant rhizosphere. Misidentification could result in no nutrient release or a sub-optimal amount of release. The Intelligent Nano-Fertilizer scientists have accomplished this identification for 12 root chemical signals, some for canola and some for wheat, in greenhouse experiments.<sup>87</sup> Apart from the questions entailed in scaling

up greenhouse experiments to field experiments, the researchers are also asking “Can an aptamer still bind its target while immobilized in a nanoscale film?”<sup>88</sup> If not, the aptamer might misread the chemical signal, leading to too much or too little nutrient delivery or even no delivery at all.

Furthermore, they ask, “Can aptamer target binding influence the properties of these films?”<sup>89</sup> If a polymer designed to be permeable in response to the rhizosphere chemical signal becomes less permeable or even impermeable because of the effect of the target binding on the properties of the polymer, the polymer simply would degrade, releasing the nutrients in an unintelligent fashion. Could impurities in the nutrient payload result in the aptamer misreading the chemical signal and binding incompletely with the target, leading to an inaccurate or partial delivery of the nutrient? And no doubt many more questions need to be asked and answered.

Can the Intelligent Nano-Fertilizer project succeed in developing a commercial product that can be effectively applied to deliver nutrients to plants without harming the engineers of soil health? If so, it will be because the researchers will have convinced their funders and those who convert that research into commercial fertilizer products that researching the environmental health and safety impacts of nano-fertilizer must be done by the product developers as the product is developed. Health and safety impact assessment by government or academic scientists, showing adverse impacts only after the product has been commercialized, will make withdrawal of a soil health harmful product from the market far more difficult.

As the Intelligent NanoFertilizer researchers summarize the scope of the work to be done: “nano-biotechnology approaches to enhance MUE [Micronutrient Use Efficiency] in soil-crop systems need to be accompanied by research dealing with the interactions of not only NPs, polymer films, and nanodevices with heterogeneous soil phases, such as electrically charged humic substances and clay colloidal surfaces, but also with active soil microorganisms and fauna.”<sup>90</sup> This summary indicates that the research and development pathways for Intelligent NanoFertilizer remain long and that commercialization is not imminent, at least if that commercialization follows a risk analysis informed regulatory process.

In any case, farmers are unlikely to adopt this technology, if the economic benefits do not significantly outweigh the costs, even if those costs are subsidized. The National Nanotechnology Initiative held a workshop in September 2014 that addressed the technical challenges of developing nano-biosensors, as well as the economic challenges of attracting investors to support that development from proto-type to a commercially viable product.<sup>91</sup>

Perhaps the most relevant presentation for agri-nanotechnology was by a John Deere engineer who discussed the company's process for evaluating which nano-biosensors might be incorporated into Deere's farm machinery for gathering and reporting data on soil moisture, pesticide residues, fertilizer residues and even to determine when hydraulic fluids in farm machinery needed to be changed. However, given the dust, vibration, and uneven topography of agricultural fields, whatever might work in an engineering laboratory should be tested with farmers in industrial scale field trials. Convincing farmers to pay for nano-biosensing technology in a below cost of production crop price environment, (when Deere was laying off employees because of low commodity prices and reduced farm machinery purchases), has turned out to be a difficult value proposition challenge.<sup>92,93</sup> Fertilizer companies will likewise face a similar value proposition challenge in persuading farmers to pay more for nano-technology enabled fertilizers, even if the cost of purchasing those fertilizers is subsidized by taxpayers.

## RESTRUCTURING SOIL TO RETARD RELEASE OF NITROGEN IN WATER AND AIR

Prominent on the list of possible applications of engineered nanotechnology materials (ENMs) to amend soil is the application of nano-composite clay to re-structure soil in a way that retards nitrate and nitrous oxide flows.<sup>94</sup> Nano-clays have thermal and mechanical properties that have many industrial uses, e.g., building micro-structures to strengthen and resist the aging of cement.<sup>95</sup> Not surprisingly, then, nano-material composites have also been shown to strengthen and stabilize the geological properties of soil.<sup>96</sup>

Understanding how nano-clay composites affect the inorganic-organic material soil interface presents analytic and practical challenges. According to one survey article, "By their nature and surface properties, [natural] nanoparticles in soil participate in essential ecological services, ranging from regulating water storage and element cycling, through sorbing and transporting chemical and biological contaminants, to serving as a source or sink of organic carbon and plant nutrients."<sup>97</sup> It is crucial to gain a understanding of how ecological services and bacterial and micro-fauna engineers of those services will be affected by engineered nano-clay composites. What will the effect be of applying the composites at a scale and frequency sufficient to reduce significantly

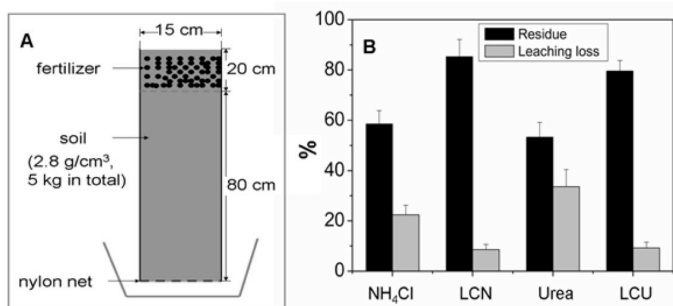
the nitrate contamination and greenhouse gas production resulting from multiple applications of chemical fertilizers each growing season?

A perhaps less environmentally beneficial, but nearer to commercialization, approach to addressing negative environmental impacts of fertilizer use is to use ENMs to build nano-scale networks in soil that reduce the amount and rate of release of nitrogen. A group of Chinese researchers claimed, "Since 2006, LCF [Loss Control Fertilizer] has been widely applied (more than 3.4 million hectares) in China, presenting outstanding agricultural (yield increases more than 10 percent) and environmental effects (N loss decreases more than 20 percent) compared with traditional fertilizer with equal nutrition."<sup>98</sup> It appears that this claim is made for traditional LCFs in general and not for nanotechnology enabled LCFs. However, the authors report having successfully field-tested nanotechnology enabled and laboratory tested LCF, as described below, to grow wheat, cotton, corn and rice on 200 acres of test plots distributed among five Chinese counties, representing four soil types (Supplementary figures 11-12).

(The article reporting their research has been cited just nine times in peer-reviewed journals since its publication in January 2014, which may point to a difficulty in reproduction of their methodology and results by other researchers or which may reflect a scientific preference for other applications of nanotechnology to control nitrogen loss in soil.)

The objective of their experiments is to measure nitrogen loss from Loss Control Urea (LCU) and Loss Control Nitrogen (LCN) ammonium as compared to nitrogen loss from a control of traditional ammonium and urea fertilizers. The researchers write, "LCU is a ternary system comprised of attapulgite [a clay], [the aforementioned] polyacrylamide (P) and urea (U),"<sup>99</sup> which has the highest nitrogen content of commonly used fertilizers.<sup>100</sup> The addition of polyacrylamide, together with other (oxidation and hydrothermal) processing of attapulgite, "increases the pore space in soils with clay" and stops "erosion and water runoff," among other functions. Water soluble polyacrylamide has been used as a soil conditioner to control erosion on agricultural land since the mid-1980s.<sup>101</sup> Without the addition of polyacrylamide and the other treatments, attapulgite rods, measuring 20-50 nanometers in diameter and about a micron (one thousand nanometers) in length would agglomerate, preventing the creation of micro-structures to retard nitrogen loss.

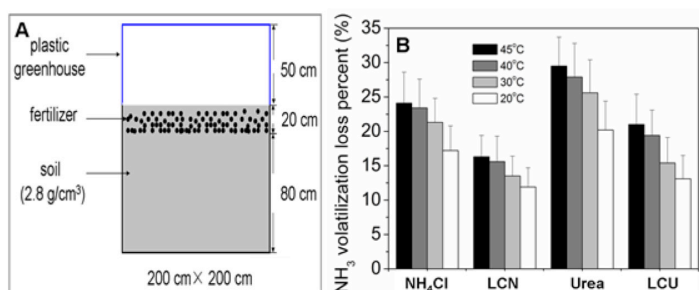
The experimental design measures nitrogen loss to the air in the form of ammonia and N losses in the form of liquid nitrates in sub-surface leaching and surface agricultural runoff. The volatilized N loss is captured in a mini-greenhouse, whereas the leached nitrogen loss and nitrogen runoff are captured in



**Supplementary figure 8. Comparison of the leaching performance of LCF (LCN and LCU) with traditional fertilizer (NH<sub>4</sub>Cl and urea) in soil column. A.**

*Illustration 5: Experimental design to compare nitrogen leaching performance of nano-clay modified Loss Control Fertilizer with nitrogen leaching of traditional fertilizer*

Source: D. Cai et al, "Controlling nitrogen migration through micro-nano networks," *Scientific Reports*, January 14, 2014, 2. <http://www.nature.com/articles/srep03665#s1>.



**Supplementary figure 10. Comparison of the NH<sub>3</sub> volatilization performance of LCF (LCN and LCU) with traditional fertilizer (NH<sub>4</sub>Cl and urea) from soil pool.**

*Illustration 6: Experimental design of a micro-greenhouse to compare ammonia volatilization of nano-clay amended Loss Control Fertilizers with traditional Urea and Ammonium Chloride fertilizers*

Source: D. Cai et al, *Op cit*.

beakers. The polyacrylamide modified attapulgite is mixed separately with urea and ammonium chloride (NH<sub>4</sub>Cl), another source of nitrogen in fertilizer.<sup>102</sup> The LCU and LCN are mixed in soil columns in a 20cm. wide band near the surface of the soil column. (Supplementary documents 8 & 10 refer to a "soil column", whereas Supplementary documents 3 & 6 refers to a "sand column"). Distilled water is poured on to the LCU mixed soil and LCN mixed soil columns which acts as filters. The water activates the self-assembly of the soil microstructures that reduce nitrogen loss. The authors report, "Under simulated conditions, about 50 percent leaching (Fig. 6A), 36 percent volatilization losses (accumulating for 20 days) (Fig. 6B) and 45 percent surface runoff (Fig. 6C) of N can be reduced by this loss control technology."<sup>103</sup>

The article does not provide a description of the methodology for how the soil/sand samples were selected or whether and how the samples were treated to ensure a uniform soil filtering environment for both the LCU and LCN and their traditional fertilizer counterparts. Figure 6 refers to filtering LCN and NH<sub>4</sub>Cl through perlite, a mineral used in horticulture to prevent soil compaction and aid filtration.<sup>104</sup> The use of perlite would appear to add a degree of nitrogen loss reduction above and beyond that of the LCU and LCN. Unless the experimental design and/or reporting of the experiment has been misstated or misunderstood by me, it is reasonable to question whether the use of perlite could have compromised the accuracy of the reported reductions in N loss resulting from the nanotechnology enabled fertilizers.

Supplementary figure 8 shows the experimental design and results comparing liquid N loss of the nano-clay modified with the control. Supplementary figure 10 shows the experimental design and results comparing volatilized N loss of the LCU and LCN with that of the traditional urea and ammonium fertilizers.

Perhaps the most important experimental finding common to the volatilization, runoff and leaching experiments is that the densest nitrogen retaining nano and microstructures are self-assembled when the aqueous solution filtered through the LCU and LCN modified soil is in the five to seven pH (potential Hydrogen) range. The optimal soil pH for growing most crops is five to seven pH, which indicates that the LCU and LCN soil amendments could be applied to a broad range of soil types that grow a broad range of crops. The techniques that visualize these nano and microstructures and the extent to which the experimental design simulates the effect of rain-water and irrigation on soil are visually compelling. However, success in the controlled laboratory environment does not necessarily translate to field trial success. The scientists did not indicate a near term field trial for their nanotechnology enabled soil amendment. Among the challenges of field trial methodology will be how to ensure the consistency of soil amendment application, and how to adjust the amendment per soil type and topography.

This summary of experimental objectives, design and results is by no means complete and hence may be less than completely accurate. But the summary can serve as a basis for discussing some methods for determining environmental risks of nanotechnology enabled fertilizers and for regulating the application of such fertilizers.

# LIFE CYCLE ASSESSMENT OF EXPOSURES TO NANOTECHNOLOGY ENABLED FERTILIZERS

Life Cycle Assessment estimates the release of ENMs during each phase of a nanotechnology enabled product's life from nanomaterial fabrication, to incorporation into a product, to ENM release during a product's use to ENM release during its recycling phase, e.g., in a landfill.<sup>105</sup> Computer modeling LCA for exposures from nitrogen in fertilizer is particularly difficult. According to a recent pioneering study, "One of the major challenges in environmental life cycle assessment (LCA) of crop production is the nonlinearity between nitrogen (N) fertilizer inputs and on-site N emissions resulting from complex biogeochemical processes."<sup>106</sup>

Nitrogen in fertilizer is transformed by bacteria, fungi, protozoa and other agents in the biogeochemical process of denitrification. ENMs are transformed by the matrix in which they are inserted, whether that matrix is a biopolymer, fluids or tissues in the human body or elements of the natural environment. Estimating nitrogen emissions resulting from N fertilizer inputs is difficult. Estimating nitrogen emissions from nitrogen fertilizer modified by ENMs will add a further degree of difficulty, since the laboratory measurements of nitrogen emissions cannot be extrapolated to test plots or field trials with a high degree of confidence.

The current state of the art in evaluating environmental exposures of ENMs in products used as fertilizer is research on nano-silver and nano metal oxides in waste water treatment residues (called "biosolids" by the U.S. Environmental Protection Agency) that are applied as fertilizer. Controlled experiments in greenhouse mesocosms enable field like simulation of exposure impacts of NPs on plants and soil.<sup>107</sup> Because tons of biosolids are applied as fertilizers, this research is of great importance for understanding the fate and transport of NPs. These exposures include inhalation by farmworkers applying dried biosolids and their uptake into food crops as well as possible health consequences of bio-accumulation of nano-silver and nano-metal oxides in the human body.

IATP reported on some of this research in 2013.<sup>108</sup> One surprising consequence of the interaction between silver nanoparticles (AgNPs) mixed with biosolid slurry and the soil microbial community is a dramatic increase in nitrous oxide (N<sub>2</sub>O): "The N<sub>2</sub>O flux was 350 percent higher in the Slurry plus AgNPs treatment than in the Slurry only treatment on Day 8 [of the 50 Day experiment], a dramatic increase given

that N<sub>2</sub>O is both an important greenhouse gas with 296 times the warming potential of CO<sub>2</sub> and N<sub>2</sub>O is the dominant ozone depleting substance."<sup>109</sup>

The LCA methodology and instrumentation to quantify and characterize ENM exposures in biosolids' release, transport and fate can be applied with modification to the LCA analysis of nanotechnology enabled fertilizers. A research group at the Center for Environmental Implications of Nanotechnologies has proposed and illustrated a functional essay framework to forecasting nanomaterial risk in "prescribed systems," such as soil and water subjected to system limitations in greenhouse environments.<sup>110</sup> That framework could be applied to nanotechnology enabled fertilizer applications in distinct soil types and agronomic conditions.

However, such studies of ENMs in biosolids used as fertilizer are distinct from doing LCAs of exposures to nanotechnology enabled fertilizers of conventional macro and micro-nutrients. LCA of exposures of such fertilizers would have two primary purposes: 1.) to determine whether chronic exposure to the ENM composites (e.g., in the pelletized fertilizer) harm the capacity of bacteria and fungi to process biogeochemical nutrients to feed the soil and 2.) to determine whether the nanotechnology Loss Control Fertilizer nutrients are retained longer for plant growth and with less and retarded runoff, leaching and volatilization as greenhouse gases.

Some LCA fertilizer studies focus on the metrics of nutrient use efficiency for production, rather than on metrics designed for understanding environmental or public health impacts.<sup>111</sup> For example, studies that consider N loss from organic agriculture with manure based fertilizers as compared to conventional agriculture with chemical fertilizers do so to determine the N loss per unit of production. They conclude that lower yields in organic agriculture require more acreage to achieve the same units of production, leading to more N loss. Some of these studies are commodity specific.<sup>112</sup>

One possible approach to doing LCA of nanotechnology enabled fertilizers to estimate environmental impacts is to start with LCA of current fertilizer products. One review of LCA of fertilizer studies states, "When LCA is used in agriculture, the functional unit most often chosen is the weight of the raw material or product (e.g. 1 kg, 1 t) or surface area (e.g. 1 ha)."<sup>113</sup> However, because the mass of NPs is super minute and the mass to surface ratio of NPs is so huge, traditional metrics for LCA fertilizer studies are largely irrelevant for understanding the ENM exposures, and hence the environmental impacts of nanotechnology enabled fertilizers or ENM amendments to soil.

Nevertheless, LCA studies of fertilizer composition, product types, manufacture and uses can inform at least the objectives, phases and methods of LCA exposure studies on nanotechnology enabled fertilizers and soil amendments. A recent study focused on fertilizer composition, manufacture and use techniques aimed to show how to reduce five kinds of environmental impacts: climate change; acidification; eutrophication; fossil fuel depletion and nutrient resource depletion. For example, regarding climate change, the study's authors write that "new catalytic reduction techniques for the manufacturing of nitrogen (N) containing fertilizers are available that can lead to drastic reductions of N<sub>2</sub>O emissions."<sup>114</sup> If scenario analysis of fertilizer manufacture using catalytic reduction techniques does produce "drastic" reductions of N<sub>2</sub>O emission in the manufacturing phase of fertilizer products, would such estimated emission reductions increase further if the products were nanotechnology enabled?

The authors state that the catalytic reduction techniques are not applicable to urea based fertilizers, the commonest form of nitrogen. Even with this major limitation in applicability of fertilizer manufacture techniques, the authors claim that their LCA study shows, "With an optimized fertilization strategy the environmental burden can be reduced up to 15 percent."<sup>115</sup> Is such an estimated reduction enough to make agriculture (and, indeed, the fertilizer industry) environmentally sustainable, at least regarding fertilizer use? If not, is the application of nanotechnology to fertilizers and soil amendments necessary to make the use of synthetic fertilizers sustainable in agriculture?

## RISK ASSESSMENT AND REGULATION

LCA ENM exposure data bases, if gathered and validated by agreed metrics and methods, can help inform the risk assessments of ENMs in their conditions of use. This was a key message of exposure scientists to National Nanotechnology Initiative (NNI) and White House officials during the Obama administration.<sup>116</sup> Will this message be heeded by a Trump administration whose policy agenda<sup>117</sup> and proposed budget demonstrates a profound hostility to regulation, and particularly environmental regulation?<sup>118</sup>

The first and thus far only regulatory action taken by the Trump administration on nanotechnology was to delay compliance with a rule to require the reporting and record keeping of ENMs used or intended for use in manufactured products.<sup>119</sup> In August 2017, the EPA issued guidance to industry on how to report ENMs,<sup>120</sup> indicating that the rule will be implemented. Still, similar delays have been used to

give the EPA time to determine whether a rule comports with the Trump administration agenda to make regulation and regulatory science less costly to business in the short term.

Unfortunately, the ENM LCA information required for risk assessment across all product categories remains inadequate not just in the United States, but also in other member countries of the Organization for Economic Cooperation and Development (OECD). A recent NGO commissioned analysis of 11,000 pages of studies and documents submitted by OECD member data for 13 of the "most representative" (i.e. those in greatest industrial use) ENMs, concluded "most of the information made available by the sponsorship programme is of little to no value in identifying hazards of the nanomaterials or in assessing their risks."<sup>121</sup> The OECD environment health and safety manager defended the OECD's nanomaterial safety program, begun in 2007, by saying that its ENM "testing programme was not designed to evaluate risks, to perform round-robin tests or to deliver exposure data."<sup>122</sup> Instead, the OECD program had worked for a decade to agree on "the appropriate methods for assessing nanomaterials."

This OECD defense of decade-long objectives of and member government contributions to its nanomaterial safety program is discouraging. How can OECD member countries agree on standards for regulating ENMs and nanotechnology enabled products if the literature and data reviewed in the OECD's nanomaterial safety intergovernmental working group is not usable for estimating exposures to and assessing risks from nanotechnologies? Will OECD government regulators allow nanotechnology enabled fertilizers to be commercialized by a largely self-regulated industry without risk assessments informed by considering life cycle exposures of ENMs in fertilizers in greenhouse limited experiments?

In an Obama administration NNI meeting on how to accelerate commercialization of nanotechnology products, there was no mention of risk assessment or regulation as core components of commercialization.<sup>123</sup> The NNI funded research programs on environmental, health and safety impacts of ENMs are subordinated to the NNI strategic objective of the "responsible development of nanotechnology." However, as IATP noted in its comment on the NNI draft strategic plan for 2017-2020, a consistent and effective approach to enable such responsible development requires government risk assessment, regulation and guidance industry.<sup>124</sup>

Is there any prospect for the regulation of nanotechnology enabled fertilizer and its application to agricultural fields? In the long list of Environmental Protection Agency<sup>125</sup> regulations that apply to farm operations, fertilizer is not listed. Rather, the EPA seeks to protect water quality under the Clean Water Act by setting fertilizer nutrient limits in that water,



## CONCLUSION

e.g., to prevent toxic algae blooms and nitrate contamination that results in ‘blue baby’ syndrome from consumption of the nitrate contaminated water. The fertilizer industry sued EPA to prevent application of CWA authorized regulations in state water bodies that would result in less fertilizer use.<sup>126</sup> The Trump administration has begun to impede the implementation of the Clean Water Act in the Obama administration’s Waters of the U.S. regulation.<sup>127</sup> The U.S. Department of Agriculture maintains a data base of fertilizer consumption and prices,<sup>128</sup> but does not regulate on-farm fertilizer use practices, except regarding the use of synthetic fertilizer in the USDA National Organic Program. Self-regulation is the extent to which the fertilizer industry is currently regulated.

As summarized earlier, in the current U.S. judiciary, it appears that nitrate contamination from fertilizer overuse will continue to be protected by ignoring or non-enforcement of the Clean Water Act. A major lawsuit brought by the Des Moines Water Works against ten rural drainage districts argued that the water from tiled fields of the drainage districts must be regulated under the Clean Water Act as a point control source of pollution. On March 17, 2017, a U.S. district judge dismissed the facts of a case and indeed, the whole case, contending that the early 20th century Iowa law that established the drainage districts did not require them to regulate nitrates. Regarding evidence presented and the redress sought by the Water Works the judge recommended “these contentions are best addressed to the Iowa legislature” and declared the drainage districts immune from any lawsuit, provided they fulfill their legal purpose of draining fields to increase production.<sup>129</sup> On April 11, the Board of the Water Works decided not to appeal the case, noting that the judge failed to address its argument under the Clean Water Act and that the legislature was considering a bill to dismantle the Water Works for having filed the lawsuit.<sup>130</sup>

Because nitrates will continue to pollute rural, as well as urban municipal, water it is likely that another lawsuit to prevent that pollution and/or to recover damages for the environmental clean-up and public health costs will be filed, though probably not in Iowa. If neither the courts nor regulation nor voluntary fertilizer stewardship programs succeed in reducing nitrate pollution and nitrous oxide emissions, will nanotechnology enabled fertilizers reduce water contamination enough to comply with the Clean Water Act, so that legal action to reduce nitrate pollution becomes a moot point of law? At present, the economics of below cost of production prices for crops suggest that only massive government subsidies will enable U.S. farmers to use these fertilizers, even if they are technically effective and do not damage further what is priceless to agriculture—microbial soil health.

Agri-nanotechnology applications are initiated and implemented in an institutional framework and economic context that this article has illustrated. Comments and questions about a few proposed applications of nanotechnology to nitrogen fertilizer likewise suggest that there is more research needed to understand the environmental and farm worker and public health impacts of these proposed applications to reduce nitrous oxide emissions and nitrate contamination of water and to increase nutrient efficiency uptake in agricultural crops. Most of the best questions are asked by the researchers themselves, particularly in the case of the Intelligent NanoFertilizer research group.

However, non-nanotechnological means to reduce nitrogen emissions and increase nutrient uptake efficiency should be evaluated for field application by researchers, farmers and the broader public, even if nanotechnology enabled fertilizers prove to be technically and economically feasible. Such an evaluation is mentioned only in passing here. However, a comprehensive and comparative agricultural technology policy assessment would not assume that there is an economic or neo-Malthusian imperative for governments to invest and technically support the development of nanotechnology enabled fertilizers, to the exclusion of investments in non-nanotechnology means to reduce negative nitrogen impacts. Such a technology policy assessment should—yet is unlikely—to be undertaken by the U.S. government in the near term. Nevertheless, research to evaluate nanotechnology enabled fertilizers, relative to achieving agronomic and natural resource conservation objectives, is an ongoing and urgent task.

## ENDNOTES

1. This article originated as a presentation in Spanish via Skype to an international seminar of the Brazilian Research Network on Nanotechnology, Society and Environment (Renanosoma) on October 26, 2016 at the University of Chapeco School of Law. I wish to thank Renanosoma’s coordinator Dr. Paulo Martins, and Professor Reginaldo Perreira, Dean of the Law School, for the opportunity to make this presentation. An early and partial draft of this article was published in English in the seminar proceedings, *A governança dos riscos socioambientais da nanotecnologia e o marco legal de ciência, tecnologia e inovação do Brasil*. <https://editorakarywa.wordpress.com/2017/03/29/a-governanca-dos-riscos-socioambientais/#more-236>
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