Review & Interpretation

Review of Maleic–Itaconic Acid Copolymer Purported as Urease Inhibitor and Phosphorus Enhancer in Soils

S. H. Chien,* D. Edmeades, R. McBride, and K. L. Sahrawat

ABSTRACT

The fertilizer additive products Nutrisphere and Avail use a coating of maleic–itaconic acid copolymer and have been marketed worldwide. It is claimed that the copolymer (trade name: Nutrisphere) enhances the efficiency of urea-N use by inhibiting urea hydrolysis and reducing ammonia (NH_3) volatilization from urea. It is also claimed that the same copolymer (trade name: Avail) prevents or reduces the conversion of soluble P fertilizer to less soluble forms in the soil and thus enhances the efficiency of fertilizer P. Consequently, it is claimed that both additive products can increase crop yields by 10 to 15%. This review critically examines these claims by considering the basic polymer and soil chemistry, and agronomic effectiveness of these products in the field. It is found that the copolymer does not retard urea hydrolysis and the subsequent NH_3 volatilization. Theoretical calculations found that the amount of copolymer recommended for commercial use (0.25% of P fertilizers) is too small to have any significant effect on soil P chemistry. These results are consistent with evidence derived from field trials, which show that these products have very little practical effect on crop production. Accordingly, it is recommended that these products not be promoted to farmers as a means to either increase efficiency of fertilizer urea-N and fertilizer P or to enhance crop production.

Both N and P are essential macronutrients for plant growth and are essential inputs into agriculture to optimize and maintain crop production. Urea is the most widely used N fertilizer in the world because its high N content (46% N) reduces transportation costs compared with other commercial N fertilizers such as ammonium sulfate (21% N) and ammonium nitrate (30–34.5% N) (IFDC, 1998). However, urea has some disadvantages that reduce its agronomic efficiency [e.g., ammonia (NH_3) volatilization following urea hydrolysis in the soil] or, in some circumstances causes ammonia and nitrite toxicity to plant seedlings (Black, 1968). Considerable research has been directed toward overcoming these problems including (i) use of urease inhibitors to delay early urea hydrolysis, (ii) coating of urea to control release rate of urea-N to minimize early N loss via NH_3 volatilization, (iii) split applications of urea (basal and topdressing), and (iv) subsurface placement of urea (Chien et al., 2009).

The major P fertilizers traded internationally are the water-soluble products such as triple superphosphate (TSP, typically 0–48–0), mono-ammonium phosphate (MAP, prevalent median grade 11–52–0), and di-ammonium phosphate (DAP, typically 18–46–0) (IFDC, 1998). However, the agronomic efficiency of these water-soluble P fertilizers can be reduced due to the conversion of water-soluble P to less soluble forms such as Fe–Al–P in acid soils and Ca–P in alkaline soils (Syers et al., 2008). Chien et al. (2009) reported that recent research studies have been directed to improving P use efficiency by (i) coating of P fertilizer with polymers to slow down or reduce P release from the fertilizer granule; (ii) using additives to chelate soil Fe, Al, and Ca ions, which reduces formation of water-insoluble P in soils; and (iii) use of liquid MAP/DAP, instead of solid granular form, in calcareous soils because total and labile P from the liquid form diffused farther than did the granular form from the site of P application.

Recently, two new fertilizer additive products (Nutrisphere and Avail) have been released onto the international fertilizer market. Nutrisphere is manufactured by coating urea with a maleic-itaconic acid copolymer. Avail uses the same technology on water-soluble P fertilizers. It is claimed in respect to Nutrisphere that polymer coating reduces urea hydrolysis, thereby reducing NH_3 volatilization and increasing the agronomic efficiency of urea-based N fertilizers (Sanders et al., 2003, 2004). The polymer coating of Avail claims to reduce the conversion of soluble P to less soluble P forms in the soil, enhancing fertilizer P use efficiency. In the marketing of these products it is claimed that both products increase crop yields by 10 to 15% relative to the same products without the copolymer treatment (Sanders et al., 2003, 2004). However, there are no known basic data ever published in the peer-reviewed scientific journals from the producers of Nutrisphere

S.H. Chien, formerly with International Fertilizer Development Center (IFDC), Muscle Shoals, AL 35660; current address: 1905 Beechwood Circle, Florence, AL 35630; D. Edmeades and R. McBride, agKnowledge Ltd., P.O. Box 9147, Hamilton, New Zealand 3240; and K.L. Sahrawat, International Crops Research Institute for the Semi-Arid Tropics (ICRISAT), Patancheru, Andhra Pradesh, India. Received 27 Apr. 2013. *Corresponding author (nchien@comcast.net).

Published in Agron. J. 106:423–430 (2014)
doi:10.2134/agronj2013.0214

Abbreviations: CV, coefficient of variation; DAP, di-ammonium phosphate; JBU, jack bean urease; MAP, mono-ammonium phosphate; NBPT, *N*-(*n*-butyl)-phosphoric triamide; NBPT(o), *N*-(*n*-butyl)-phosphoric triamide in O-analog form; NBTPT(s), *N*-(*N*-butyl)-thiophosphoric triamide in S-analog form; TSP, triple superphosphate.

and Avail. For example, simple laboratory studies on the retarding effect of Nutrisphere on urea hydrolysis and enhancing effect of Avail on reducing soil P-fixation in soil incubation should be able to demonstrate that the two products act as urease inhibitor and P enhancer in soils, but they have not been scientifically reported by the producers of these products.

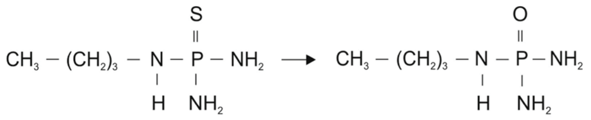
The purpose of this review article is to examine the veracity of these claims by posing two questions:

1. Considering the chemistry of the copolymer and the soil, can these claims be sustained?
2. Based on the agronomic results of these products in the field, can these products perform as claimed?

BASIC CHEMISTRY CONSIDERATIONS

Mechanism of Urease Inhibition

Several reports have been published regarding the reaction mechanisms of urease inhibitors of the phosphoramide derivatives with urease that results in the inhibition of urea hydrolysis (Manunza et al., 1999; Kot et al., 2001; Dominguez et al., 2008; Font et al., 2008). Manunza et al. (1999) discussed the binding mechanism of urea and *N*-(*n*-butyl)-phosphoric triamide (NBPT) in O-analog form, NBPT(o), at the urease active site. Its S-analog form, *N*-(*N*-butyl)-thiophosphoric triamide, NBTPT(s), (trade name: Agrotain) is currently the most widely used urease inhibitor (Chien et al., 2009). However, it is known that NBTPT(s) per se is a weak urease inhibitor but, it becomes very effective when NBTPT(s) (I) is converted to NBPT(o) (II) (McCarty et al., 1989) in the soil as shown in the following reaction:



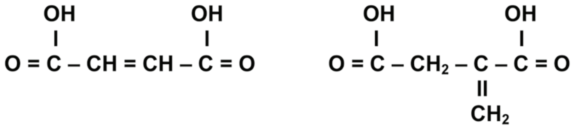
$$CH_3-(CH_2)_3-\underset{H}{N}-\underset{NH_2}{\overset{S}{\overset{\|}{P}}}-NH_2 \longrightarrow CH_3-(CH_2)_3-\underset{H}{N}-\underset{NH_2}{\overset{O}{\overset{\|}{P}}}-NH_2$$

NBTPT(s) (I) NBPT(o) (II)

Manunza et al. (1999) performed molecular dynamics calculations on the active site of urease from *Klebsiella aerogenes* (bacterium) and its adducts with urea and NBPT(o). They concluded that the NBPT(o) molecule coordinates with both the Ni atoms at the urease active site and a bidentate geometry. The oxygen atom and one amide group of the inhibitor molecule are engaged in the formation of a bridge between the two Ni atoms. Furthermore, another amide group of the NBPT(o) molecule forms a hydrogen bond with one oxygen atom of the carbamate bridge. This may explain why NBTPT(s) is a weak urease inhibitor due to lack of an oxygen atom. The stability of the bidentate complex is further strengthened by the formation of the hydrogen bond. As a result the inhibitor molecule binds the active site at three points (tridentate ligands). Consequently, the probability of urea reaching the Ni atoms is greatly reduced when the active site is locked by the NBPT(o) molecule. This may explain the known ability of the NBPT(o) molecule to act as a strong urease inhibitor (Manunza et al., 1999).

Based on the structural characteristics of urease activity site (Font et al., 2008) and the structural properties of the Ni ions of the urease (Ciurli et al., 1999), it has been concluded that phosphoramide derivatives are the most effective inhibitors with functional groups of P=O or P=S with P-connected to at least one free amide groups $(-NH_2)$. This was demonstrated by Dominguez et al. (2008), who designed, synthesized, and evaluated 40 phosphoramide derivatives. Recently, Balasubramanian and Ponnuraj (2010) investigated the molecular structure of the active site of crystallized jack bean urease (JBU) and concluded that the active site architecture of JBU is similar to that of bacterial urease containing a bi-nickel center. Jack bean urease has a bound phosphate and covalently tetrahedral density in JBU that exactly matches the position of the phosphate found in the phosphate-inhibited *B. pasterurii* urease structure. This may explain the essential role of P=O in the phosphoramide derivatives including NBPT(o) as effective urease inhibitors previously discussed.

Consider the following dicarboxylic molecular structures of maleic acid and itaconic acid:



$$O=\overset{OH}{\overset{|}{C}}-CH=CH-\overset{OH}{\overset{|}{C}}=O \qquad O=\overset{OH}{\overset{|}{C}}-CH_2-\underset{CH_2}{\underset{\|}{C}}-\overset{OH}{\overset{|}{C}}=O$$

Maleic Acid **Itaconic Acid**

It can be seen clearly that the maleic–itaconic acid copolymer does not have functional group with P=O or P=S bonds, and P-connected $-NH_2$ group as other effective urease inhibitors in the family group of phosphoramide derivatives.

The producers of Nutrisphere have claimed without data that the copolymer can chelate the two Ni metals of the active site of urease and thus deactivate the urease from hydrolyzing urea (Blaylock and Murphy, 2006). Sahrawat (1979) showed the lack of effectiveness of some chelating compounds including EDTA and carboxyl acids (citric acid and oxalic acid) to retard urea hydrolysis in soil. The strength of stability of chelating complexes for Ni follows the order of: EDTA (pK = 18.56) > > oxalic acid (pK = 5.16) > citric acid (pK = 4.8) > maleic acid (pK = 2.0) ≈ itaconic acid (pK = 1.8) (Sillen and Martell, 1974). Because all chelating compounds used by Sahrawat (1979), especially EDTA, are stronger than maleic acid and itaconic acid to chelate Ni showed ineffectiveness to retard urea hydrolysis, it can be concluded that maleic acid and itaconic acid are unlikely to chelate two Ni metals of urease and retard urea hydrolysis. Recently Goos (2013) tested 13 carboxylic acids including maleic–itaconic acid copolymer with a wide range of stability constants for Ni plus NBTPT(s). He added each of the compounds to the urea solution, followed by mixing with each of three soils. The results showed that all the compounds except NBTPT(s) failed to inhibit urea hydrolysis. This observation showed that the copolymer failed to chelate with the two Ni metals at the urease active site to inhibit urease activity, and this contradicts the claim by the producers of the copolymer. Indeed, laboratory incubation studies showed that the copolymer is not a urease inhibitor at all as shown in Fig. 1 (Franzen et al., 2011). The rate of urea hydrolysis was not reduced by the copolymer as compared with that of urea alone. It is also interesting to note that granulated urea treated with the copolymer somehow stimulated urease activity in Overly soil (fine-silty, mixed, superactive, frigid Pachic Hapludolls) that resulted in higher urea hydrolysis rate than that of urea alone as shown in Fig. 1(a) (Franzen et al., 2011). It is unknown as to why this stimulation of urease activity by the copolymer occurred in the soil.

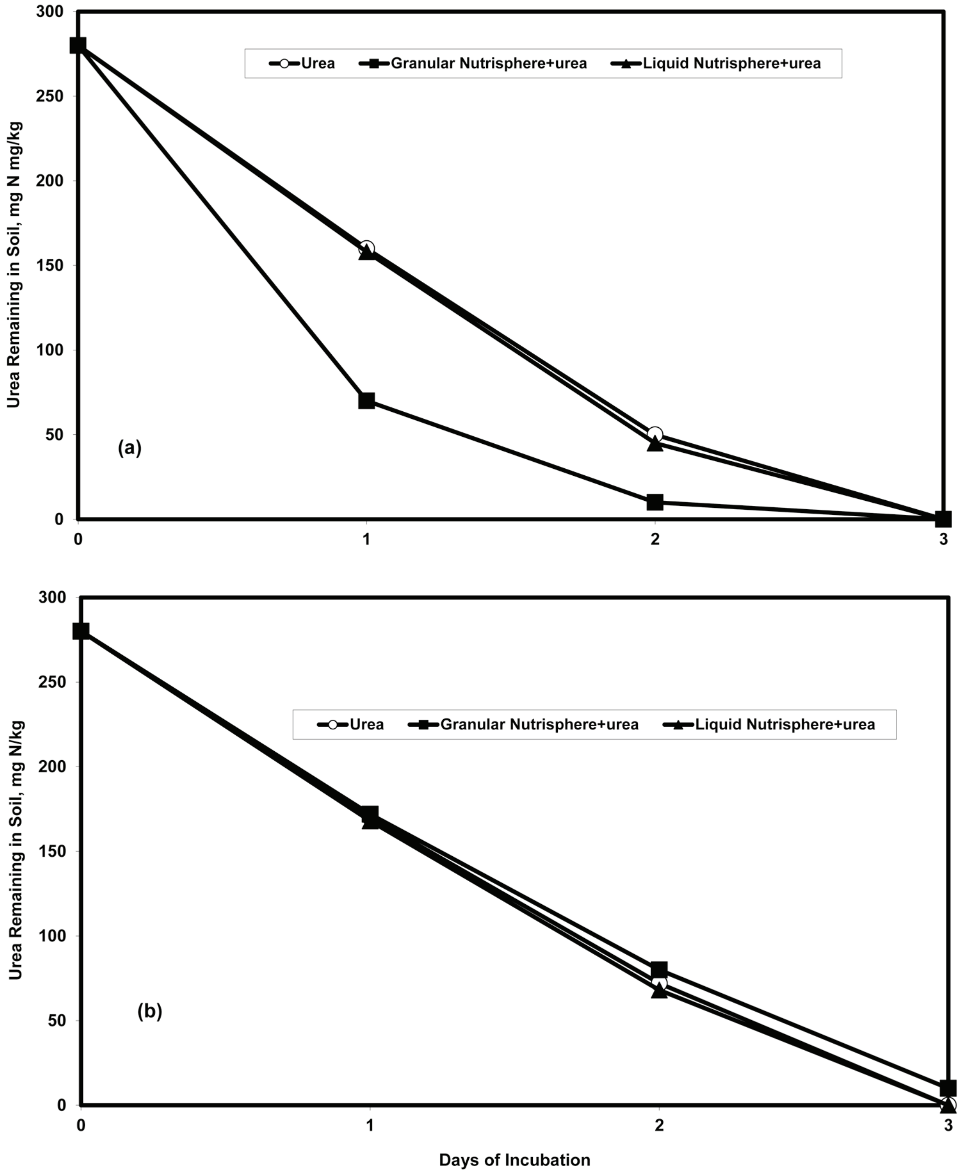


Fig. 1. Urea concentrations remaining in (a) Overly clay loam and (b) Renshaw sandy loam treated with urea alone or granular and liquid copolymer + urea fertilizers at 280 mg N kg^{-1} (adapted from Franzen et al., 2011).

Ammonia Volatilization

Ammonia volatilization can occur from surface-applied urea to acid, neutral, or alkaline soils due to the high alkalinity induced by the urea hydrolysis to NH_4HCO_3. If an inhibitor is effective, it is expected that NH_3 volatilization should be significantly reduced compared with urea alone. Data in Fig. 2 shows that NH_3 volatilization from urea treated with and without the copolymer did not differ, indicating that the copolymer did not reduce NH_3 volatilization from urea in Renshaw soil (fine-loamy over sandy or sandy-skeletal, mixed, superactive, frigid Calcic Hapludolls) (Franzen et al., 2011). The results in Fig. 3 and 4 show that the copolymer actually enhanced NH_3 volatilization of urea compared with urea alone, probably due to the stimulation of urease activity by the copolymer as shown in Fig. 1a. In contrast, NBTPT(s) reduced urea hydrolysis (Goos, 2013) and thereby reduced NH_3 volatilization compared with urea alone (Fig. 2–4). Thus, the lack of urease inhibition by the copolymer was confirmed by the measurements of urea hydrolysis (Fig. 1) and NH_3 volatilization (Fig. 2–4).

Soil Phosphorus Chemistry

Soluble P from applied fertilizers interacts with soil through processes including surface adsorption and/or solid precipitation (Syers et al., 2008) to become less soluble. The retained P, depending on the rate of P applied, types of soil and crop species, the effect of residual available P, can have relatively low, medium, or high availability for subsequent crops (Black, 1968).

The reactions of soluble P with Fe/Al ions and Ca ions are mainly responsible for P-retention in acid soils and alkaline soils, respectively. According to the producer's claim that "the maleic–itaconic acid copolymer can be used with soluble granular P fertilizers such as MAP and DAP as P enhancer because the very high cation-exchange capacity of the copolymer (1800 $cmol_c$ kg^{-1}) can exchange with soil Fe, Al, and Ca ion, and thereby prevent soluble P from being retained by the soil" (Specialty Fertilizer Products, LLC, Leawood, KS; www.sfp.com). We will begin to discuss the copolymer from the theoretical considerations to address whether there is a merit to use the copolymer as a P enhancer.

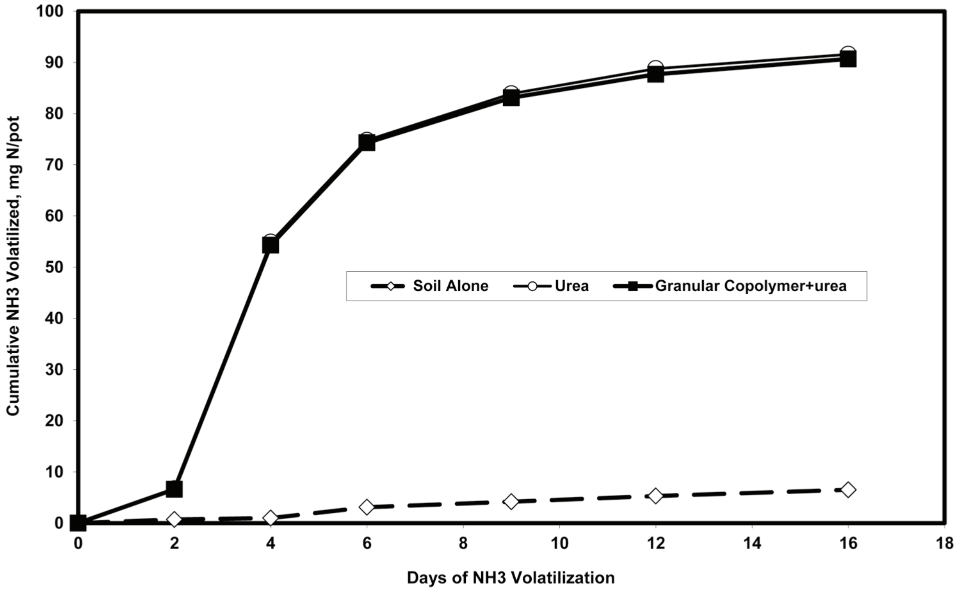


Fig. 2. Cumulative NH_3–N volatilized from Renshaw sandy loam treated with urea alone or copolymer + urea at 280 mg N kg^{-1} (adapted from Franzen et al., 2011).

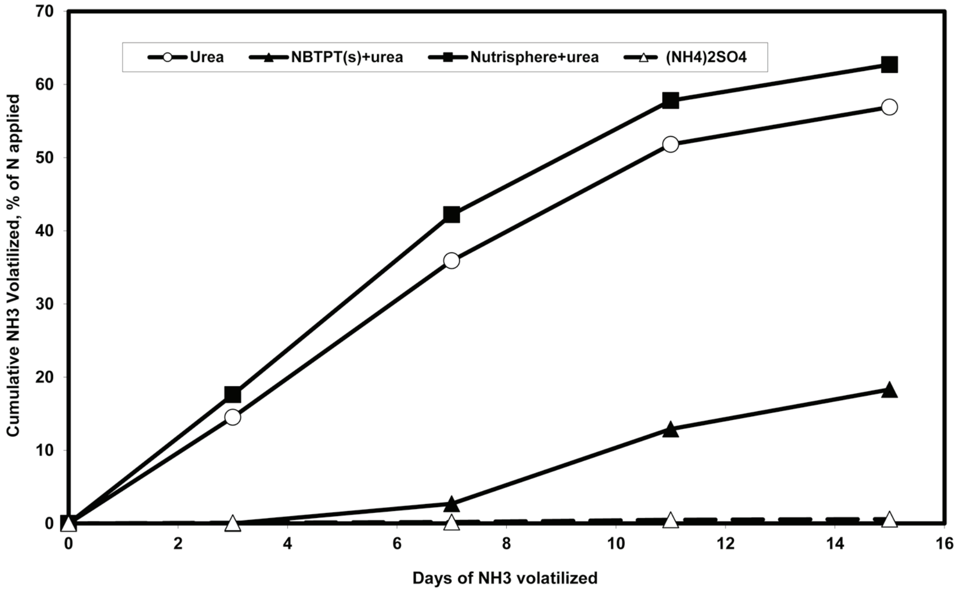


Fig. 3. Cumulative NH_3–N volatilized from Dewitt silt loam (fine, smectitic, thermic Typic Albaqualfs) treated with urea alone, copolymer+urea, or $(NH_4)_2SO_4$ at 202 kg N ha^{-1} (adapted from Franzen et al., 2011).

Soil P-retention greatly depends on the amounts at forms of amorphous Fe/Al oxide minerals, which are normally extracted by 0.2 M NH_4–oxalate pH 3 (Schwertmann, 1964).

Chien et al. (1987) reported that an acid (pH 4.7) Oxisol from Colombia with high Al saturation (90%) had low to medium P soil-retention capacity. The soil had 35 mg kg^{-1} soil of (Fe+Al) in amorphous Fe/Al oxides that was equivalent to 70.4×10^3 cmol$_c$ of (Fe+Al) ha^{-1} (factor = 1.65×10^6 to convert cmol$_c$ kg^{-1} to cmol$_c$ ha^{-1}assuming bulk density of soil = 1.1 g cm^{-3} in 15-cm depth). Based on the recommendation for commercial use of the copolymer (Sanders et al., 2003, 2004), the copolymer-coated DAP has 0.25% copolymer of DAP (or 2.0 L Mg^{-1} of DAP) or 2.5×10^{-3} kg of copolymer per kg of DAP or 2.5×10^{-3} kg of copolymer per 200 kg of P (DAP has 20% P). Since the copolymer solution used with DAP has only about 50% of the copolymer based on the recommended information, the CEC of copolymer-coated DAP thus has only 900 cmol$_c$ kg^{-1}. At 100 kg P ha^{-1} applied (considered a high P rate), it carries $(2.5 \times 10^{-3} \times 100/200) \times 900 = 0.12$ cmol$_c$ of CEC ha^{-1}. It requires three monovalent cation-exchange sites of the copolymer to exchange with one Al^{3+} or Fe^{3+} ions. So the maximum amount of Al^{3+} and Fe^{3+} ion that can be exchanged by the polymer = 0.12/3 is 0.04 cmol$_c$ ha^{-1}. In general, the soil volume that would be contacted with the commercial-grade DAP granules (–6+16 mesh or –3.35 + 1.00 mm size) is estimated up to 2% of soil volume in the plowed layer (15–20 cm depth) (Engelstad and Hellums, 1993). The amount of (Fe+Al) in the amorphous Fe/Al oxides thus is calculated as $70.4 \times 10^3 \times 0.02 = 1.4 \times 10^3$ cmol$_c$ ha^{-1}. Therefore, the maximum effect of binding Fe^{3+} and Al^{3+} ions of the amorphous Fe/Al oxides by the copolymer is [(0.04)/(1.4 ×

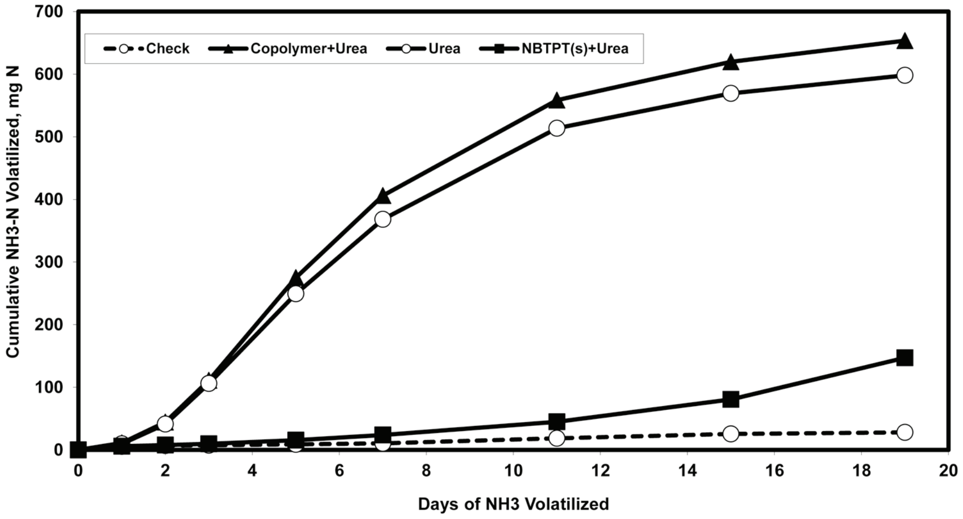


Fig. 4. Cumulative NH_3–N volatilized from a calcareous soil treated with urea alone, copolymer+urea, or NBTPT(s)+urea at 200 kg N ha^{-1} (S.H. Chien, personal communication, 2012).

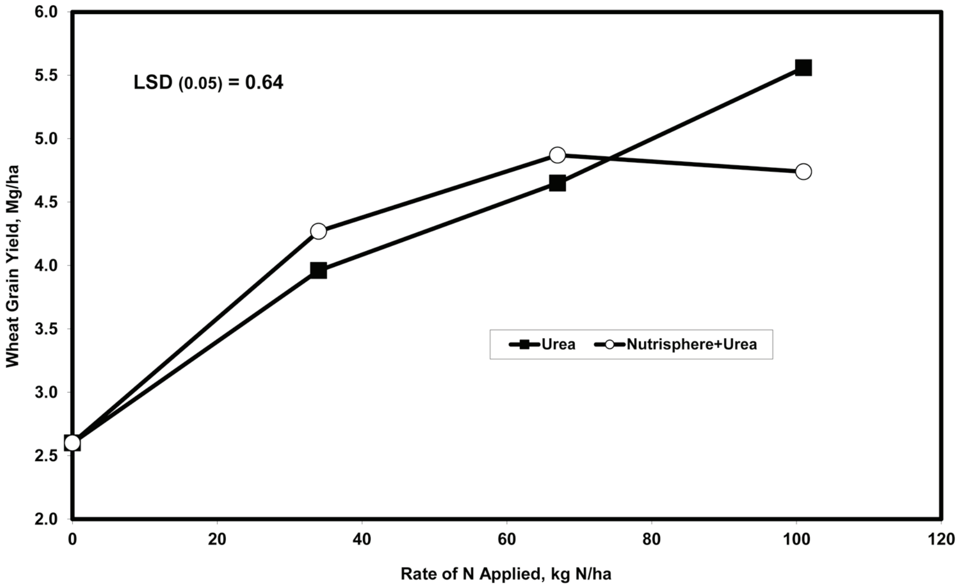


Fig. 5. Wheat grain yield obtained with surface application of urea and copolymer + urea to a calcareous soil (adapted from Franzen et al., 2011).

10^3)] × 100 = 0% of total Fe^{3+} and Al^{3+} of the amorphous Fe/Al oxides in the soil volume containing the copolymer with granular P fertilizers. In other words, the amount of the copolymer applied with DAP based on the commercial-use recommendation is too small to have any significant effect on reducing the level of soil P-retention capacity even in a soil with low P-retention capacity treated with high P rate.

We used similar assumptions that were used to calculate the unit of oxalate-extractable Fe and Al in $cmol_c\ kg^{-1}$ to the unit of $cmol_c\ ha^{-1}$ of exchangeable Ca of an alkaline (pH 7.7) Windthorst soil (fine, mixed, active, thermic Udic Paleustalfs) (exchangeable Ca = 10 $cmol_c\ kg^{-1}$) in Texas that contained no $CaCO_3$ (Chien et al., 2003).The amount of exchangeable Ca of the soil was calculated as 16.5 × 10^6 $cmol_c\ ha^{-1}$. It requires two cation-exchange sites of the copolymer to displace one exchangeable Ca ion of the soil. So the maximum amount of Ca^{2+} ion that can be exchanged by the polymer is 0.12/2 = 0.06 $cmol_c\ ha^{-1}$. Therefore, the maximum effect of binding exchangeable Ca^{2+} of the soil by the copolymer is [(0.06)/(16.5 × 10^6)] × 100 = 0% of total exchangeable Ca^{2+} in an alkaline soil containing no $CaCO_3$ treated with copolymer-coated DAP at high rate (100 kg P ha^{-1}). In other words, the amount of copolymer applied with DAP based on the commercial-use recommendation, is too small to have any significant affect on reducing the level of soil P-fixing capacity of the alkaline soils with or without $CaCO_3$.

Recently, a basic laboratory study on the effect of coating granular MAP with maleic and itaconic acids (at 1% by mass) was reported by Degryse et al. (2013). They reported that the two ligands had no significant effect on mobilizing P in soils (pH > 7). They also observed no significant effect of the ligands coatings on yield, P uptake, or shoot P concentration in wheat (*Triticum aestivum* L.) in a pot experiment with three P-responsive soils. Their theoretical calculations indicate that no effect is to be expected from the addition of the ligands to MAP at commercially realistic rates on P availability. Their conclusion agrees with ours that the amount of the maleic–itaconic acid copolymer added to

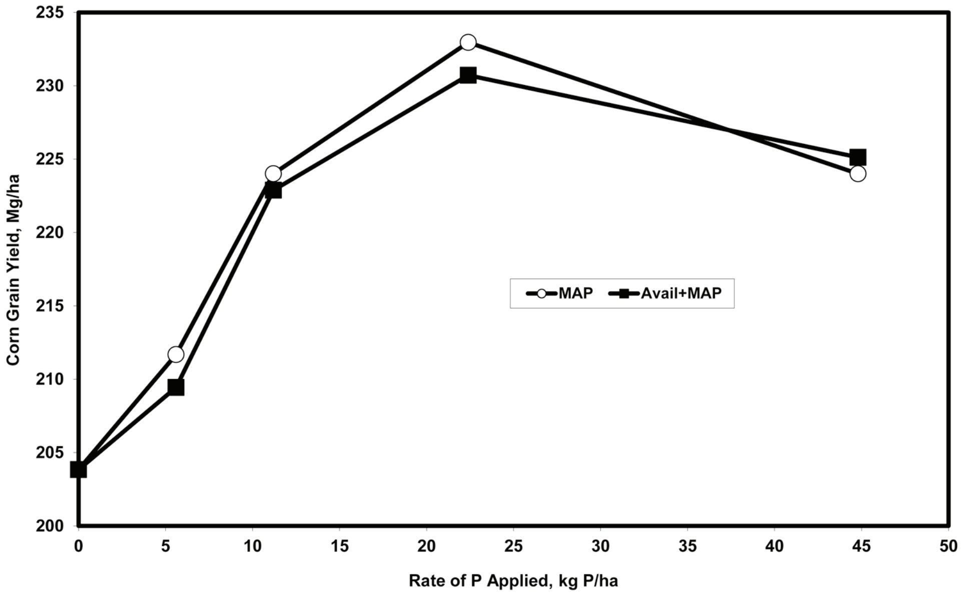


Fig. 6. Corn grain yield obtained with MAP and copolymer + MAP (adapted from Binford, 2008).

fertilizer P based on the recommendation is too small to have any significant effect on reducing P-retention capacity of any soils.

AGRONOMIC CONSIDERATIONS

There is some published scientific literature reporting the effects of Nutrisphere on crop production relative that of urea. Franzen et al. (2011) reported that within each of eight locations in North Dakota, there were no significant differences in wheat grain yield between similar rates of urea and copolymer + urea. For example, Fig. 5 shows that the wheat grain yields obtained with urea alone and copolymer + urea were about the same when surface applied to Langdon calcareous soil (mixed, mesic Lamellic Ustipsamments). Similarly, there were no significant differences in grain yield of flooded rice (*Oryza sativa* L.) between the two N sources at one location in Mississippi and two locations in Arkansas (Franzen et al., 2011). Connell et al. (2011) also reported that the treatment with maleic–itaconic acid copolymer was ineffectual relative to urea in improving Bermudagrass forage (*Cynodon dactylon* L.) production. Cahill et al. (2010) found that Nutrisphere was ineffective in increasing N efficiency for corn (*Zea mays* L.) and winter wheat. Norton (2011) reported that Nutrisphere did not enhance urea-N efficiency for sugarbeet (*Beta vulgaris* L.).

Karamanos and Puurveen (2011) reported neither a significant effect of treating MAP with the maleic–itaconic acid copolymer nor a significant interaction between the copolymer and rates of P were observed for wheat in Canada. Their explanation was the recommended rate of the copolymer impregnation (1%) was too low to have any effect on P retention by soil Ca. Grove (2011) reported that the copolymer did not improve DAP efficiency for soybean [*Glycine max* (L.) Merr.] grown on soils at soil test levels ranging from 4 to 8 mg P kg^{-1} (Mehlich III) in Kentucky. Binford (2008) also did not observe any significant effect of the copolymer on P efficiency for corn in Delaware (Fig. 6). Additional recent published reports that showed the lack of effect of Avail on fertilizer P efficiency at significant level ($p = 0.05$) can be found in Dunn and Stevens (2008), Cahill et al. (2013), Dudenhoeffer et al. (2012, 2013), and McGrath and Binford (2012).

The interpretation of results from field experiments is thwarted by difficulties especially when the potential effects of a given product on plant yield are similar to or less than the normal background variability, which occurs in all biological experimentation and is typically about 5 to 10% (expressed as the coefficient of variation, CV) in well designed, planned, and executed trials.

In these circumstances the measured effect of a given product on plant yield are frequently not statistically significant and hence the interpretation of such results are problematic—is the product having an effect but the experiment is not sufficiently accurate to detect it, or is the product having no effect and the observed treatment "responses" are due to the expression of the background biological variation?

The converse situation also arises when an individual result is statistically significant—is the effect due to the treatment of it due to the small but finite probability that product is having no effect and the observed "response" is due to the background variability? These possibilities give rise to the classic Type I and II errors associated with statistical testing (Snedecor and Cochran, 1967).

Reynolds (1987) has suggested a pragmatic solution to the above-mentioned problems. When a given product has been tested many times, as in this case of Nutrisphere and Avail, the frequency distribution of the measured treatment effects to be examined can be compared with a normal distribution with a mean of zero effect. For convenience, this can be achieved by plotting the % cumulative distribution function (y axis) against the observed % increase or decrease (x axis) in crop yield associated with the treatment with respect to that of the control (no treatment). Any displacement of the frequency distribution, either positive or negative, can be taken to indicate a real treatment effect.

Edmeades and McBride (personal communication, 2012) discovered that many field trials examining the agronomic efficacy of both Avail and Nutrisphere were unpublished. Therefore, they established a data-base of all the available research (published and unpublished) and conducted a meta-analysis of the results of 210 trials with Avail and 121 with Nutrisphere. These trials were then ranked as either: very reliable (trial design and full statistical

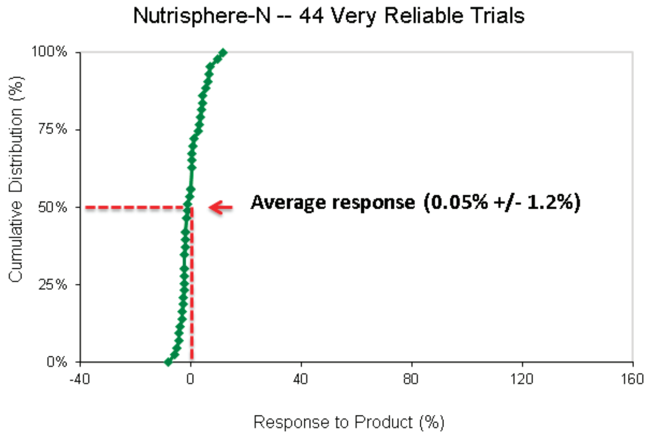


Fig. 7. The distribution frequency of plant yield response to copolymer + urea expressed as a decrease or increase (%) relative to control for a subset of trials that are defined as very reliable trials (Edmeades and McBride, personal communication, 2012).

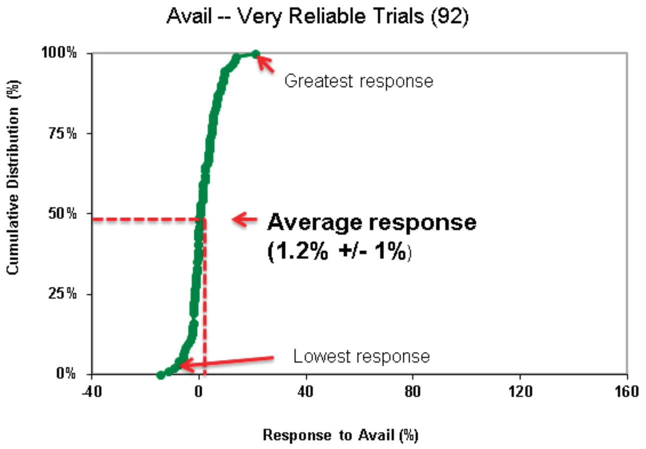


Fig. 8. The distribution frequency of plant yield responses to copolymer + P fertilizer expressed as a decrease or increase (%) relative to control for a subset of trials that are defined as very reliable trials (Edmeades and McBride, personal communication, 2012).

analysis were available), reliable (no information about the trial design but the statistical significance of the treatment effects was available), or not reliable (trials that were either non-replicated or with less than three replicates or the trial design was not known or no statistical information or analysis was available or if there was doubt as to whether the entire data set was presented).

From this data, the measured yield differences between the control and either Avail or Nutrisphere were calculated as a percentage of the control, either positive or negative. The rank and distribution, and hence the cumulative frequency distribution, of the observed product responses were then determined, together with the descriptive statistics of the distributions. A complete description of the methodology was reported (Edmeades, 2002; Edmeades and McBride, personal communication, 2012).

In formal meta-analyses, it is normal to give each trial a weighing dependent on the accuracy of the particular measurement of interest—in this case crop production. In the trials discussed in this article, the primary focus is on the effect of Avail and Nutrisphere on the relative crop production. The trials could then be weighed based on the LSD determined for each trial, or some other metric indicating the accuracy of the measurement to indicate whether any specific trial result was statistically different from zero. However, the quandary arising from Type I and II errors remains. By plotting the cumulative distribution of the responses, the focus is on the distribution of all of the observed responses relative to zero % effect. This provides that there is sufficient data (i.e., a sufficient number of trials) so that the weighing of any given trial is of secondary concern.

In any case, these sets of data were categorized into three classes based on the reported quality of the trial design. Only the most reliable set of data, and one assumes a subset of trials of similar weight, has been used for our conclusions.

Avail and Nutrisphere are promoted to and used by farmers who would normally expect, as a minimum, to get a return on his/her investment. Thus, small product responses of say <5%, although perhaps interesting to a research scientist developing a product, are likely to be of little consequence to a farmer.

The results with Nutrisphere (Fig. 7) show that yield responses were equally distributed (both positive and negative) around a mean of 0.05% (confidence interval 1.3%, $n = 44$). Similarly the results for Avail are shown in Fig. 8 and indicate that for this product the responses are equally distributed around a mean of 1.4% (confidence interval 1.1%, $n = 92$). Importantly, the occurrence of either positive or negative responses was not related to either soil P (Avail) or soil N (Nutrisphere) status. These results suggest that both products have little practical effect on crop production. The range in the observed response simply reflects the background variability, which is expressed in all field trials of this nature.

CONCLUSIONS

It is concluded from a meta-analysis of field research that neither Avail nor Nutrisphere performs as claimed. They have little practical effect on crop production, which is inconsistent with the claims made for these products. This conclusion is supported by a consideration of soil chemistry and the chemistry of the maleic–itaconic acid copolymer using a coating on P or N. Importantly, these two lines of enquiry are independent and mutually reinforcing. These products should not be recommended to farmers if their intention is to increase N or P use efficiency and/or increase crop production

REFERENCES

Balasubramanian, A., and K. Ponnuraj. 2010. Crystal structure of the first plant urease from jack bean: 83 years of journey from its crystal to molecular structure. J. Mol. Biol. 400:274–283. doi:10.1016/j.jmb.2010.05.009

Binford, G. 2008. Corn response to starter fertilizer and Avail on soils with high soil test phosphorus. University of Delaware Coop. Ext. Bull. 118.

Black, C.A. 1968. Soil-plant relationships. John Wiley & Sons, New York.

Blaylock, A., and L. Murphy. 2006. Optimizing N management without ammonium nitrate. Fluid J. 14(4):20–22.

Cahill, S., D. Osmond, R. Weisz, and R. Hieiniger. 2010. Evaluation of alternative nitrogen fertilizers for corn and winter wheat production. Agron. J. 102:1226–1236. doi:10.2134/agronj2010.0095

Cahill, S., D. Osmond, and D. Hardy. 2013. Evaluation of an organic copolymer fertilizer additive on phosphorus starter fertilizer response by corn. Crop Manage. doi:10.1094/CM-2013-0322-01-RS.

Chien, S.H., G. Carmona, J. Henao, and L.L. Prochnow. 2003. Evaluation of rape response to different sources of phosphate rock in an alkaline soil. Commun. Soil Sci. Plant Anal. 34:1825–1835. doi:10.1081/CSS-120023217

Chien, S.H., L.L. Hammond, and L.A. Leon. 1987. Long-term reactions of phosphate rocks with an Oxisol in Colombia. Soil Sci. 144:257–265. doi:10.1097/00010694-198710000-00004

Chien, S.H., L.I. Prochnow, and H. Cantarella. 2009. Recent developments of fertilizer production and use to improve nutrient efficiency and minimize environmental impacts. Adv. Agron. 102:267–322. doi:10.1016/S0065-2113(09)01008-6

Ciurli, S., S. Benini, W.R. Rypniewski, K.S. Wilson, S. Miletti, and S. Mangani. 1999. Structural properties of the nickel ions in urease: Novel insight into the catalytic and inhibition mechanisms. Coord. Chem. Rev. 190–192:331–355. doi:10.1016/S0010-8545(99)00093-4

Connell, J.A., D.W. Hancock, R.G. Durham, M.L. Cabrera, and G.H. Harris. 2011. Comparison of enhanced-efficiency nitrogen fertilizers for reducing ammonia loss and improving Bermuda grass forage production. Crop Sci. 51:2237–2246. doi:10.2135/cropsci2011.01.0052

Degryse, F., B. Ajiboye, R.D. Armstrong, and M.K. McLaughlin. 2013. Sequestration of phosphorus-binding cations by complexing compounds is not a viable mechanism to increase P efficiency. Soil Sci. Soc. Am. J. 77:2050–2059. doi:10.2136/sssaj2013.05.0165

Dominguez, M.J., C. Samartin, M. Font, J.A. Palop, S. San-Francisco, O. Urrutia, F. Houdusse, and J.M. Garcia-Mina. 2008. Design, synthesis, and biological evaluation of phosphoramide derivatives as urease inhibitors. J. Agric. Food Chem. 56:3721–3731. doi:10.1021/jf072901y

Dudenhoeffer, C.J., K.A. Nelson, P.P. Motavalli, B. Burdick, D. Dunn, and K.W. Goynef. 2013. Utility of phosphorus enhancers and strip-tillage for corn production. J. Agric. Sci. doi:10.5539/jas.v5n2p37.

Dudenhoeffer, C.J., K.A. Nelson, P.P. Motavalli, D. Dunn, W.E. Stevens, K.W. Goyne, M. Nathan, and P. Scharf. 2012. Corn production as affected by phosphorus enhancers, phosphorus source and lime. J. Agric. Sci. doi:10.5539/jas.v4n10p137.

Dunn, D.J., and G. Stevens. 2008. Response of rice yield to phosphorus fertilizer rates and polymer coating. Crop Manage. doi:10.1094/CM-2008-0610-01-RS.

Edmeades, D.C. 2002. The effects of liquid fertilizers derived from natural products on crop, pasture and animal production: A review. Aust. J. Agric. Res. 53:965–976. doi:10.1071/AR01176

Engelstad, O.P., and D.T. Hellums. 1993. Water solubility of phosphate fertilizers: Agronomic aspects– A literature review. Paper Series IFDC-P-17. IFDC, Muscle Shoals, AL.

Font, M., M.J. Dominguez, C. Sanmartin, J.A. Palop, S. San-Francisco, O. Urrutia, F. Houdusse, and J.M. Garcia-Mina. 2008. Structural characteristics of phosphoramide derivatives as urease inhibitors: Requirements of activity. J. Agric. Food Chem. 56:8451–8460. doi:10.1021/jf801786d

Franzen, D., R.J. Goos, R.J. Norman, T.W. Walker, T.L. Roberts, N.A. Slaton, G. Endres, R. Ashley, J. Staricka, and J. Lukach. 2011. Field and laboratory studies comparing Nutrisphere-N with urea in North Dakota, Arkansas and Mississippi. J. Plant Nutr. 34:1198–1222. doi:10.1080/01904167.2011.558162

Goos, R.J. 2013. A comparison of a maleic-itaconic polymer and n-(n-butyl) thiophosphoric triamide as urease inhibitors. Soil Sci. Soc. Am. J. 77:1418–1423. doi:10.2136/sssaj2012.0425

Grove, J.H. 2011. Impact of maleic-itaconic copolymer on phosphorus nutrition of soybean. ASA, CSSA, and SSSA Annual Meetings, San Antonio, TX. 16–19 Oct. Paper 382-2. http://scisoc.confex.com/scisoc/2011am/webprogram/Paper66136.html (accessed 27 Nov. 2013).

IFDC. 1998. Fertilizer manual. Kluwer Academic Publishers, Dordrecht, the Netherlands.

Karamanos, R.E., and D. Puurveen. 2011. Evaluation of a polymer treatment as enhancer of phosphorus fertilizer efficiency in wheat. Can. J. Soil Sci. 91:123–125. doi:10.4141/cjss10071

Kot, M., W. Zaborska, and K. Orlinska. 2001. Inhibition of jack bean urease by *N*-(*n*-butyl) thiophosphoric triamide and *N*-(*n*-butyl) phosphoric triamide: Determination of the inhibition mechanism. J. Enzyme Inhib. 16:507–516. doi:10.1080/14756360127569

Manunza, B., S. Deiana, M. Pintore, and C. Gessa. 1999. The binding mechanism of urea, hydroxamic acid and N-(N-butyl)-phosphoric triamide to urease active site. A comparative molecular dynamic study. Soil Biol. Biochem. 31:789–796. doi:10.1016/S0038-0717(98)00155-2

McCarty, G.W., J.M. Bremner, and H.S. Chai. 1989. Effect of *N*-(*n*-butyl) thiophosphoric triamide on hydrolysis of urea by plant, microbial and soil urease. Soil Biol. Fert. 8:515–519.

McGrath, J.M., and G.D. Bindford. 2012. Corn response to starter fertilizer with and without Avail. Crop Manage. doi:10.1094/CM-2012-0320-02-RS.

Norton, J.B. 2011. Nitrogen source, testing, and rate alternatives for furrow-irrigated sugarbeet. Crop Manage. doi:10.1094/CM-2011-0829-01-RS.

Reynolds, J. 1987. Submission to: Bell-booth Group Ltd v Her Majesty's Attorney General (in respect of the Ministry of Agriculture and Fisheries) and Broadcasting Corporation of New Zealand. High Court of New Zealand, Wellington.

Sahrawat, K.L. 1979. Evaluation of some chelating compounds for retardation of urea hydrolysis in soil. Fert. Technol. 16:244–245.

Sanders, J.L., J.M. Kimmerly, and G. Mazo. 2003. Anionic vinyl/dicarboxyl acids and uses thereof. U.S. Patent 6 515 090. U.S. Gov. Print. Office, Washington, DC.

Sanders, J.L., G. Mazo, and J. Mazo. 2004. Anionic polymers composed of dicarboxyl acids and uses thereof. U.S. Patent 6 703 469. U.S. Gov. Print. Office, Washington, DC.

Schwertmann, U. 1964. The differentiation of iron oxides in soils by a photochemical extraction with acid ammonium oxalate. Z. Pflanzenernaehr. Dueng. Bodenkd. 105:194–202. doi:10.1002/jpln.3591050303

Sillen, L.G., and A.E. Martell. 1974. Stability constants. Spec. Publ. 25. The Chemical Society, London.

Snedecor, G.W., and W.G. Cochran. 1967. Statistical methods. 6th ed. Iowa State Univ. Press, Ames, IA.

Syers, J.K., A.E. Johnston, and D. Curtin. 2008. Efficiency of soil and fertilizer phosphorus use. FAO Fertilizer and Plant Nutrition Bulletin 18. FAO, Rome.