Recent Developments of Fertilizer Production and Use to Improve Nutrient Efficiency and Minimize Environmental Impacts

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Contents

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Abstract

This chapter provides information on some recent developments of fertilizer production and use that improve nutrient efficiency and minimize environmental impact. The nutrients discussed are mainly N, P, and S. Improving N nutrient efficiency includes use of (1) controlled-release coated urea products, (2) slow-release urea–aldehyde polymer products, (3) urea supergranules for deep placement, (4) nitrification inhibitors to reduce nitrate leaching and denitrification, (5) urease inhibitors to reduce ammonia volatilization from urea, and (6) ammonium sulfate to enhance N efficiency of urea. Improving efficiency of conventional P fertilizers includes use of (1) coated water-soluble P fertilizers, (2) urea supergranules containing P and K nutrients, and (3) fluid P fertilizers. Use of nonconventional P fertilizers includes (1) phosphate rock (PR) for direct application with a newly developed computer-based phosphate rock decision support system (PRDSS), (2) a mixture of PR and water-soluble P sources, (3) calcined nonapatite PR for direct application, and (4) nonconventional acidulated P fertilizers containing water-insoluble but citrate-soluble P compounds. The agronomic effectiveness of newly developed granular NP fertilizers containing elemental S to provide S nutrient is discussed. Two processes of producing (1) partially acidulated P fertilizers and (2) compound fertilizers of NP and K by bulk blending are recommended for reducing Cd uptake from P fertilizers by crops. The use of these nonconventional fertilizers may result in an increased relative economic benefit with respect to the use of conventional fertilizers in terms of saving fertilizer cost, enhancing nutrient efficiency, or increasing crop yield.

1. INTRODUCTION

For many years, the main goal of applying fertilizers was to provide nutrients to plants to increase or sustain optimal crop yield. Thus, improving fertilizer use efficiency in terms of nutrient uptake and crop yield is important to fertilizer producers and users. However, any fertilizer, whether in the natural, inorganic, or organic form, can harm the environment if misused. Recently, fertilizer use has been labeled by environmentalists as one source of polluting soil, water, and air environments. The main environmental impacts associated with fertilizer use have been linked to nitrate leaching into ground water, emission of greenhouse gases (nitrous oxides), soils

polluted with toxic heavy metals, and surface runoff of N and P nutrients causing aquatic eutrophication.

To ensure that proper use of fertilizer is beneficial to both crop production and the environment, researchers and fertilizer producers have tried to find ways to achieve the newly defined goal of fertilizer use, that is, improving fertilizer nutrient use efficiency and minimizing environmental impacts.

The purpose of this chapter is to examine literature reports of recent research and developments in technology for fertilizer production and use to improve nutrient efficiency and minimize environmental impacts. The elements to be discussed in this chapter are limited to only three important plant nutrients, N, P, and S. Possible toxic Cd associated with P fertilizer use will also be discussed.

2. Improving the Efficiency of Nitrogen Fertilizers

Nitrogen use efficiency is usually low. Dobermann (2005) used data from over 800 experiments to estimate that, on average, only 51% of the N applied was recovered by the aboveground parts of cereals. Similar results were compiled by Cantarella (2007) using ^{15}N data for maize in Brazil. However, N recovery may be even lower under certain management conditions. Fan et al. (2004) reported that the average N fertilizer recovery in cereals in China was 30–35%. Available data for perennial crops, such as citrus, show the same range of results; between 25% and 50% of the applied N was taken up by the plants (Quaggio et al., 2005).

Nitrogen derived from fertilizers and not taken up by plants may be immobilized in soil organic matter or may be lost to the environment. In this case, it has the potential to become a pollutant of ground or surface waters or to contribute to the greenhouse effect.

Loss of N to the environment usually takes place when high concentrations of soluble N forms are present in the soil solution in excess compared to the amount that plants can take up or when in periods or positions in the soil profile where there are no plants or roots to make use of the available N. These problems can be largely overcome with good management practices, which include selecting a rate of application compatible with plant needs, placing the fertilizer where plants can easily reach the nutrients, and choosing the right application time. In many cases for N, this implies splitting the application in two or more time intervals. Management practices will not be discussed in this text, except urea supergranules (USG) for deep placement in lowland rice soils.

Recently, the Association of American Plant Food Control Officials (AAPFCO) has adopted the term ''enhanced efficiency fertilizers'' (EEF) to

characterize products that can minimize the potential of nutrient loss to the environment, as compared to reference soluble sources (Hall, 2005). EEF includes ''slow-release'' or ''controlled-release'' fertilizers, which comprise coated, water-insoluble or slowly water-soluble products, and ''stabilized'' fertilizers which are those amended with additives that reduce the transformation rate of fertilizer compounds, resulting in an extended time of availability in the soil. The terms adopted by AAPFCO have shown wide international acceptance.

There are two important groups of fertilizers classified as slow- or controlled-release fertilizers (Trenkel, 1997). One group is formed by condensation products of urea and urea aldehydes, of which the most significant types on the market are urea formaldehyde (UF), isobutylidene diurea (IBDU), and crotonylidene diurea (CDU). The second group is comprised of coated or encapsulated fertilizers, such as S-coated urea (SCU) or polymer-coated urea (PCU). Examples of the stabilized nitrogen fertilizers are those treated with inhibitors, such as nitrification or urease inhibitors, that may avoid the rapid transformation of N into forms that are less stable in certain environments.

2.1. Controlled-release coated urea products

Although the terms slow-release and controlled-release are used interchangeably, it has become acceptable recently to apply the term controlled-release to coated or encapsulated fertilizers for which the factors determining the rate, pattern, and duration of release are known and regulated during fabrication, and slow-release be used for microbial decomposed N products such as UF (Shaviv, 2005; Trenkel, 1997).

SCU was developed by the Tennessee Valley Authority (TVA) and extensively studied compared to uncoated urea for different crops in the late 1960s to early 1980s as a controlled-release N fertilizer. Urea granules are coated with elemental S melted at about 156 °C, followed by a wax layer that acts as a sealant to cover fissures or cracks in the S coating, and finally by a conditioner layer. The pattern of N release of SCU depends on the thickness and quality of the coating. Cracks in the coatings, excess manipulation, and flaws in the manufacturing process may jeopardize the slow-release properties of the fertilizer (Gould *et al.*, 1986; Shaviv, 2005).

SCU with 7-day dissolution rates in water of 10%, 20%, and 30% were used in most of the agronomic tests. Despite the favorable results often reported in field trials (Allen, 1984; Gould *et al.*, 1986), the TVA SCU products required a 20–23% coating weight that resulted in a lower N content (35–37%) than uncoated urea (46% N) (Young, 1974), which would increase transportation costs on top of the additional cost for S coating. Consequently, SCU has not been accepted by farmers, especially

those growing food crops in developing countries. Lately some fertilizer companies (e.g., Regal, Simplot) have produced SCU products using a thin coating containing a higher N content (42–44%). Some commercialized products have a double coating of urea involving polymer-sealed S coating (e.g., ''TriKote'' by Pursell, ''Poly-S'' by Scotts, and ''Poly-Plus'' by Lesco) to reduce coating weight and maintain a higher N content.

Several companies have marketed thin PCU products as controlled-release N sources (e.g., ''POLYON''-coated urea by Pursell, ''ESN'' by Agrium, ''Osmocote'' by Scotts, Meister by Chisso-Asahi, and many others) (Trenkel, 1997). The coatings are usually resins or thermoplastic materials and their weight can be as low as <1% of the granule mass without significantly reducing the N content. Unlike SCU which releases urea through small pinholes that can result in a more difficult controlled–N release pattern, PCU releases N by diffusion of urea through the swelling polymer membrane. The release pattern is related to the coating composition and usually depends on soil moisture and temperature (Christianson, 1988), although some products are reported to be affected little by soil moisture content, pH, soil microbial activity, and even by temperature (Shaviv, 2005). It is possible, by changing or combining coatings, to formulate fertilizers which release 80% of their nutrients in pre-established time intervals such as 80, 120, 180, or even 400 days (Shaviv, 2005; Shoji et al., 2001; Trenkel, 1997; Wen et al., 2001).

There are many reports of favorable, as well as not so encouraging, results for the coated N fertilizers in the literature. In field trials, Singh et al. (1995) reported that grain yield of lowland rice from a single application of PCU was equivalent to or better than 3–4 well-timed split urea application. Fertilizer recovery with PCU was 70–75% compared with 50% with prilled urea (PU). The higher recovery of N from two PCU products was related to N release and subsequent N uptake by rice during the postanthesis stage (Fig. 1). A one-time application of PCU may have distinct advantages over prilled urea, not just in terms of labor saving, but also because PCU may provide a more stable and sustained N release in rainfed crop systems where well-timed split N applications may not be feasible due to variability in rainfall and soil moisture (Singh et al., 1995). Coated urea also performed better than regular fertilizers by promoting increased grain yield and N uptake in rice in Spain (Carreres et al., 2003), winter wheat in China (Fan et al., 2004), peanuts in Japan (Wen et al., 2001), potatoes in the USA (Munoz et al., 2005), and maize in Japan (Shoji et al., 2001). On the other hand, Carreres et al. (2003) found that some formulations of PCU were not efficient in increasing grain yield and N recovery by flooded rice in Spain, probably because of insufficient coating of the urea granule.
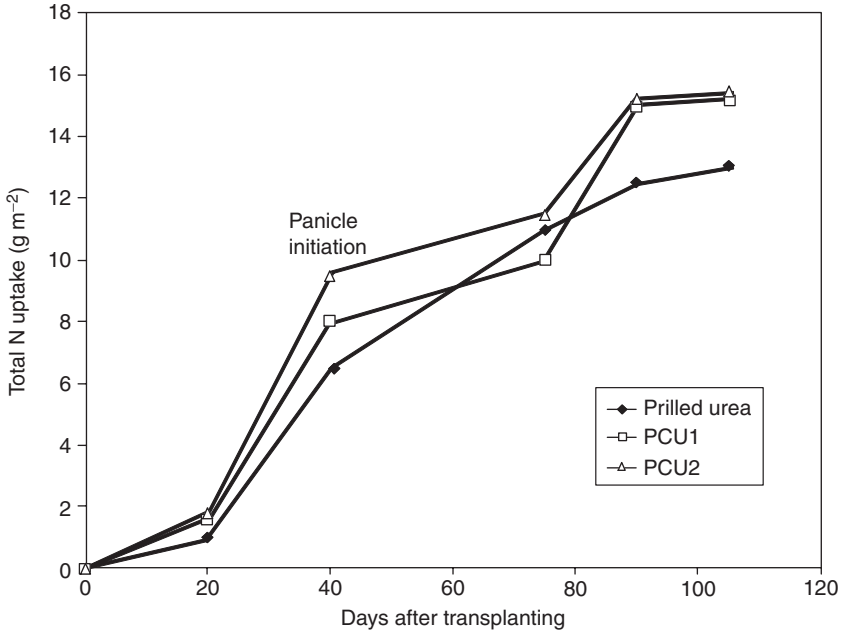
Figure 1 Lowland rice N uptake with crop age as affected by urea source. PCU1 and PCU2 are polymer-coated urea applied at planting; prilled urea was split in three applications. *Source*: data adapted from Singh *et al.* (1995).

2.2. Slow-release urea–aldehyde polymer products

Another approach for controlling N release to improve N efficiency and minimizing environmental impacts is to use urea formaldehyde-based polymer–N products. They can be either water-soluble (e.g., ''Nitamin'' by Georgia-Pacific) or water-insoluble (e.g., ''Nutralene'' by Agrium) or a mixture of both (''Sazolene'' by Sadepan Chimica). UF, IBDU, and CDU are marketed in several countries, but UF (38% N) is the most important fertilizer of this class. Urea–aldehyde condensation products may be combined with regular urea or with other fertilizers resulting in products with various N contents and release patterns. Urea–aldehyde polymers will become plant available only when mineralized to NH_4–N in the soil. However, there are complex factors such as solubility of polymer–N, soil temperature, moisture, microbial activity, texture, organic matter, etc., that can affect the mineralization rate and agronomic effectiveness of polymer–N (Christianson *et al.*, 1988). One distinct advantage of polymer–N products over urea is a reduction in NH_3 volatilization. The effectiveness in reducing NH_3 volatilization and also N release rate greatly depends on the ratio of urea and paraformaldehyde (PFA) used in the reaction (Carter *et al.*, 1986; Christianson *et al.*, 1988). For example, Christianson *et al.* (1988)

reported that NH_3 volatilization decreased as the percentage of PFA used increased from 0% to 6% (UF6) and 12% (UF12).

The agronomic performance of urea–aldehyde polymers has been studied by several authors (Allen, 1984; Gould et al., 1986). In general, this class of fertilizer is more efficient than soluble sources when the gradual supply of N is an advantage to crops such as grains, perennials, pastures, and turf grasses. However, Cahill et al. (2007) reported that the N of a fluid commercial UF polymer was released and hydrolyzed in only 1–2 weeks, and this UF formulation was equal to or outperformed with respect to urea ammonium nitrate (UAN) solution in eight field experiments with wheat and maize grown in the USA. More information on controlled-release polymer-sealed S-coated urea products, polymer-coated urea products, and polymer–N products can be found in recent review papers by Shaviv (2000, 2005).

Despite the potential to increase N use efficiency due to the gradual supply of N of the slow- or controlled-release fertilizers, the use of such products in commercial agriculture is limited by their cost compared to conventional fertilizers. SCU is probably the least expensive, but still costs twice as much as regular urea. The price of other slow- or controlled-release fertilizers varies from 2.4 to 10 times that of conventional soluble N sources, per unit of N (Shaviv, 2005; Trenkel, 1997). Therefore, currently the slow- or controlled-release fertilizers are marketed in niches such as nurseries, turf grass, and gardening. It has been estimated that slow-release fertilizers comprise only 8–10% of the fertilizers used in Europe (Lammel, 2005; Shaviv, 2005), 1% in the USA and only 0.25% in the world (Hall, 2005). However, this may change in the future. There is an effort by the fertilizer industry to search for less expensive EEF products, and world concerns about the environment may help to promote the use of less soluble N fertilizers.

2.3. Urea supergranules for deep placement

Work done by many researchers, especially by the International Fertilizer Development Center (IFDC), have conclusively demonstrated that compacted USG, that is, urea with 1–3 g granules, are an effective N source (Savant and Stangel, 1990). In general, one or more USG are deep placed (7–10 cm depth) by hand at the center of every four rice seedling hills in rice soils during or after rice transplanting. Savant and Stangel (1998) have shown that N loss is significantly reduced, which results in a significant increase in rice grain yield under flooded conditions compared with split-applied PU. For example, the average rice grain increase over control with USG was significantly greater than that with split-applied PU in 29 irrigated rice trials (Fig. 2). Deep placement of USG essentially cuts off NH_3 volatilization and also significantly reduces denitrification N loss compared to
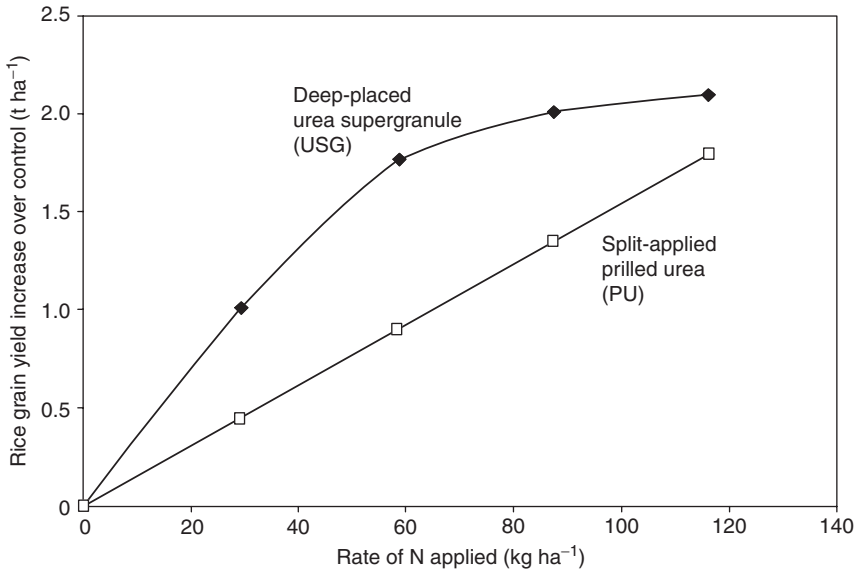
Figure 2   Yield increase of flooded rice grain over control (no N) obtained with USG and PCU. *Source*: data adapted from Savant and Stangel (1998).

surface application of PU. Furthermore, the N concentration of flooded water is greatly reduced when USG is deep placed, so that any water runoff from rice paddies does not contribute to N loss or to potential eutrophication problems (Savant and Stangel, 1990). The reason for producing USG is that it makes it easier for farmers to apply USG by hand. Use of USG has one great advantage in that it requires only one-time application after rice transplanting, whereas surface application of PU requires two to three split applications that can still result in significant N loss through NH_3 volatilization. One drawback of applying USG is that it is a labor-intensive practice that some rice farmers in developing countries are not willing to adopt, for example, China. Also, it is not an alternative to commercial rice farms in the USA, Europe, and Latin America due to high labor costs. However, the use of USG has been successfully promoted in several Asian countries, notably in Vietnam and Bangladesh. The Government of Bangladesh has announced that it will expand the use of USG to almost 1 million hectares of rice land, reaching about 1.6 million farm families (IFDC, 2007).

In contrast to flooded rice, little study has been done on the use of USG for upland crops, presumably due to difficulty in deep placement of USG in upland soils. Nevertheless, supergranules of NPK compound fertilizers containing urea have been commercially marketed by some fertilizer companies for tree crops, particularly fruits. Once the problem of deep placement in upland soils is solved, it is expected that deep placement of USG should also perform well as an N source for upland food crops.

2.4. Reducing nitrate leaching/denitrification by nitrification inhibitors

As early as the 1960s and 1970s, various chemical compounds were extensively tested for their nitrification retarding properties to inhibit oxidation of NH_4–N to NO_3–N, and thus reduce NO_3–N leaching/denitrification N losses. Decreasing denitrification of NO_3–N to N_2O and NO can also benefit the environment, as N_2O and NO are now considered a part of the greenhouse gases that are responsible for global warming (Snyder et al., 2007).

There are many compounds known as nitrification inhibitors (Trenkel, 1997), but three products have come out on a commercial basis. These are (1) 2-chloro-6-(trichloromethyl) pyridine (Nitrapyrin) with the trade name "N Serve," (2) dicyandiamide (DCD, $H_4C_2N_4$), which is available with several commercial names, and (3) 3,4-dimethylpyrazole phosphate (DMPP) with the trade name "ENTEC." A different type of potent nitrification inhibitor, acetylene gas, was reported by Hynes and Knowles (1982) and Walter et al. (1979). The addition of wax-coated calcium carbide (CaC_2), which reacted with water to produce acetylene gas to urea fertilized soil, reduced nitrification and increased yield, or recovery of N, in irrigated wheat, maize, and cotton, and flooded rice as summarized by Freney (1997). Numerous reviews on nitrification inhibitors have been reported in the literature (e.g., Amberger, 1986; Edmeades, 2004; Freney et al., 1995a; Hoeft, 1984; Prasad et al., 1971; Scharf and Alley, 1988; Trenkel, 1997), and therefore there will be no further discussion on nitrification inhibitors in this chapter.

2.5. Reducing ammonia volatilization by urease inhibitors

Urea-based N products (e.g., urea, UAN) are N fertilizers used worldwide for crop production today, especially urea due to its high N content (46% N). However, NH_3 volatilization can be a significant N loss mechanism for urea when applied to the surface, especially for neutral, alkaline, and flooded soils, at the early stage of plant growth. Hydrolysis of urea [$(NH_2)_2CO$] to NH_4HCO_3 produces high pH that induces NH_3 volatilization under conditions of high wind, moistened soil surface, low plant canopy, high temperature, etc. The use of urease inhibitors to reduce NH_3 volatilization from urea hydrolysis has thus been considered one effective strategy to increase N efficiency of urea-based N products, and more than 14,000 compounds or mixtures of compounds with a wide range of characteristics have been tested (Kiss and Simihaian, 2002) and many patented as urease inhibitors.

Many metals are able to inhibit urease activity, among them Ag, Hg, Cd, Cu, Mn, Ni, and Zn (Bayrakly, 1990; Reddy and Sharma, 2000; Shaw, 1954; Tabatabai, 1977; Tyler, 1974). Boric acid was also reported to have an inhibitory effect on urease (Benini et al., 2004). It appears that metals react with sulfhydryl groups of the urease enzyme rendering it inactive

(Shaw, 1954; Tyler, 1974), whereas boric acid appears to show competitive inhibition with urea (Benini *et al.*, 2004). However, the effectiveness of these inorganic products is somewhat low (Bayrakly, 1990; Bremner and Douglas, 1971; Reddy and Sharma, 2000; Tabatabai, 1977) and some of them are heavy metals which have restrictions for soil application. Further–more, in some studies the rates of application were too high to justify their use in commercial fertilizers (Bayrakly, 1990; Purakayastha and Katyal, 1998; Tabatabai, 1977). On the other hand, micronutrients added to urea at rates compatible with nutrient recommendations may have some appeal if they could show urease inhibition in addition to that of more effective organic inhibitors. Ammonium thiosulfate, which is an S and N fertilizer, also presents a capacity to inhibit nitrification and urea hydrolyses (Goos, 1985), but its effectiveness is low and the compound is required at high rates (Goos and Fairlie, 1988).

Many organic compounds are capable of inhibiting urease activity. Up to the early 1970s, hydroquinone and some benzoquinones were shown to be urease inhibitors (Bremner and Douglas, 1971), but later studies showed that the compounds of the group of structural analogues of urea were more effective (Martens and Bremner, 1984a,b; Radel *et al.*, 1988; Watson, 2000).

One potent urease inhibitor that received extensive investigation in the early days, after it had been patented by East German researchers in 1976, was phenyl phosphorodiamidate (PPDA). Experiments were conducted with this product under laboratory conditions (e.g., Martens and Bremner, 1984a,b) and also in different field and greenhouse studies (e.g., Broadbent *et al.*, 1985; Byrnes *et al.*, 1983; Fillery *et al.*, 1986; Snitwongse *et al.*, 1988; Vlek *et al.*, 1980). In a review article on urease inhibitors, Byrnes and Freney (1995) reported that application of PPDA significantly increased rice grain yields in only two out of eight flooded–field rice trials. One of the reasons they attributed was a rapid degradation of PPDA due to high pH or temperature of flooded water. Broadbent *et al.* (1985) found that adding PPDA to a urea solution applied to corn did not affect the rate of urea hydrolysis, N uptake of corn or corn yield. However, Joo and Christians (1986) found that 2% PPDA added to liquid urea increased the fresh weight of Kentucky bluegrass turf by 20–31%.

Lately attention has been focused on the most widely tested urease inhibitor, N–(*n*-butyl) thiophosphoric triamide (NBTPT), trade named ''Agrotain.'' In a greenhouse study, Byrnes (1988) reported that NBTPT was more effective than PPDA at retarding urea hydrolysis (Fig. 3A) and reducing the ammonium–N concentration in flooded water (Fig. 3B).

Similar results that showed NBTPT was more effective than PPDA in retarding urea hydrolysis were also reported by Beyrouty *et al.* (1988), Bremner and Chai (1986), Bremner *et al.* (1991), Bronson *et al.* (1989), Buresh *et al.* (1988), and Lu *et al.* (1989). Addition of NBTPT increased flooded rice grain yield by an average of 40% over unamended urea
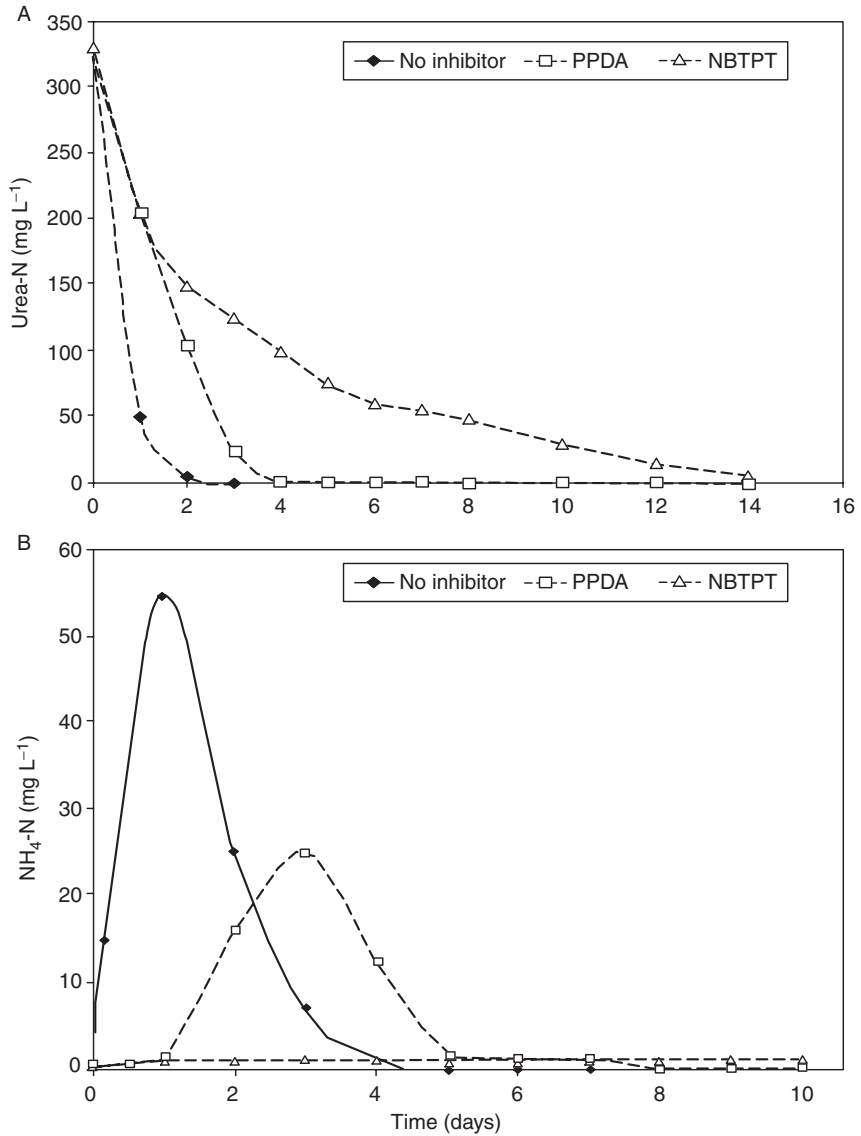
Figure 3 Concentrations of (A) urea–N and (B) NH_4–N in floodwater treated with urea as affected by urease inhibitors. *Source*: Byrnes (1988).

(Byrnes, 1988). However, the yield provided by NBTPT use was not significantly greater than that of PPDA. In field experiments, application of NBTPT seldom resulted in significant increases in flooded rice grain yields as summarized by Byrnes and Freney (1995). They attributed this to the requirement for the conversion of NBTPT in sulfur-analog form

[NBTPT(s)] (I), which is not an effective urease inhibitor *per se*, to NBPT [*N*-(*n*-butyl) phosphoric triamide] in oxygen-analog form [NBPT(o)] (II), which becomes active to retard urea hydrolysis in soil (McCarty *et al.*, 1989) as shown in the following reaction:

$$
\underset{\substack{\text{NBTPT(s)}\\\text{(I)}}}{CH_3 - (CH_2)_3 - \underset{\underset{H}{|}}{N} - \underset{\underset{NH_2}{|}}{\overset{\overset{S}{\|}}{P}} - NH_2} \longrightarrow \underset{\substack{\text{NBPT(o)}\\\text{(II)}}}{CH_3 - (CH_2)_3 - \underset{\underset{H}{|}}{N} - \underset{\underset{NH_2}{|}}{\overset{\overset{O}{\|}}{P}} - NH_2}
$$
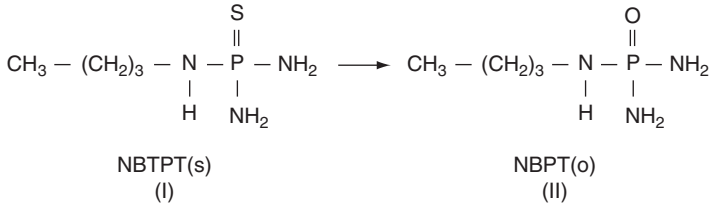
However, NBPT(o) (II) is too unstable to be used to treat urea directly (Quin *et al.*, 2005), so the NBTPT(s) (I) form is employed in the commercial formulation.

The rate of conversion of NBTPT(s) (I) to NBPT(o) (II) in soil depends on several factors, including soil properties, moisture, temperature, microbial activity, and concentration of inhibitors (Byrnes and Freney, 1995; Carmona *et al.*, 1990; McCarty *et al.*, 1989). Under flooded conditions, the conversion of NBTPT(s) (I) into NBPT(o) (II) may be impaired (Byrnes and Freney, 1995). In many situations, it appears that much of the urea has been hydrolyzed before sufficient conversion of NBTPT(s) (I) to NBPT(o) (II) has occurred (Freney, 1997). This may explain the inconsistent results of the agronomic beneficial effect of NBTPT(s) on increasing crop yield from application of urea-based products reported in the literature.

One potential way to enhance the effectiveness of urease inhibitors in paddy rice is by combining PPDA and NBTPT (Luo *et al.*, 1994). It appears that during the time when PPDA actively retarded urea hydrolysis, part of NBTPT(s) was being converted to NBPT(o), which inhibited urease activity as the concentration of PPDA declined later due to degradation. Phongpan *et al.* (1995) showed that daily NH_3–N volatilized in a flooded-field rice soil was higher with NBTPT than PPDA for the first 7 days, whereas the reverse was observed after 8 days (Fig. 4). A combination of NBTPT and PPDA reduced NH_3–N volatilization more than either NBTPT or PPDA alone. The rather low NH_3–N volatilized from urea (15%) in the study was, in part, due to the addition of algicide to all treatments that controlled algal growth and maintained floodwater below pH 8.3. Without algicide, the pH of floodwater reached 8.7–9.3 in the daytime, which could have induced higher NH_3–N volatilization from urea hydrolysis.

Lu *et al.* (1989) reported that the effectiveness of urease inhibition of NBTPT was enhanced by aerobic, in contrast to anaerobic, conditions. In fact Byrnes and Freney (1995) found that the conversion of NBTPT(s) to NBPT(o) could be detected within a few minutes in four aerobic soils in
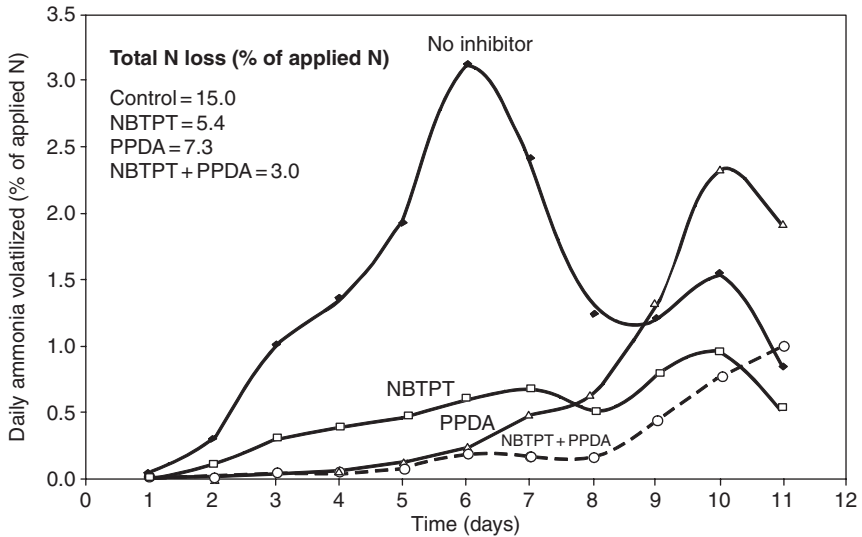
Figure 4 Ammonia volatilization as affected by urease inhibitor treatments in flooded rice soil. *Source*: data adapted from Phongpan *et al.* (1995).

the USA. Byrnes and Freney (1995) summarized that in 21 field experiments with maize from 1989, mostly in the Midwestern United States, NBTPT increased average grain yields by 750 kg ha^{-1} (9%) at an average fertilization rate of 100 kg ha^{-1} N. The yields with NBTPT were equivalent to those resulting from 80 kg ha^{-1} N of additional urea–N without NBTPT. In southern Illinois, maize yields were increased by an average of 525 kg ha^{-1} (9%) for 13 field experiments with broadcast urea and 750 kg ha^{-1} (14%) for nine experiments in which urea was placed in bands on the soil surface. Trenkel (1997) summarized the results of over 400 field trials with NBTPT and showed that on average, treating urea or UAN with NBTPT brought about maize grain yield increases of 0.89 and 0.56 t ha^{-1} compared to yields obtained with untreated fertilizers (Table 1).

In the same way as many inhibitors of the urea analogue family, NBTPT is efficient at low concentrations (Keerthisinghe and Blakeley, 1995; Watson *et al.*, 1994). Also, NBTPT presents solubility and diffusivity properties similar to those of urea (Radel *et al.*, 1988; Watson, 2000), which are important characteristics for a fertilizer additive. NBTPT has been tested in several countries, usually with satisfactory results (Antisari *et al.*, 1996; Grant and Bailey, 1999; Rawluk *et al.*, 2001; Watson, 2000; Watson *et al.*, 1994). Recent studies in New Zealand also showed that the coating of urea with NBTPT or adding NBTPT to urea suspensions significantly increased pasture yields (Quin *et al.*, 2005; Zaman *et al.*, 2005). In Brazil, Cantarella *et al.* (2005) reported that the reduction of

Table 1 Response of maize to urea or UAN treated with the urease inhibitor NBTPT in the USA

N source	Number of field trials	Grain yield (t ha^{-1})		
		With NBTPT	Without NBTPT	Yield increase due to NBTPT
Urea	316	8.02	7.13	0.89
UAN	119	8.21	7.62	0.56

Source: data adapted from Trenkel (1997).
Data are an average of 11 years of field research.

Table 2 Ammonia volatilization losses evaluated in field trials carried out in Brazil

Crop/site	NH$_3$ volatilization (% of applied N)	
	Urea	Urea–NBTPT[a]
Maize (site 1)	45	24 (47)
Maize (site 2)	37	5 (85)
Maize (site 3)	64	22 (65)
Maize (site 4)	48	34 (29)
Pasture (site 1)	18	6 (69)
Pasture (site 2)	51	22 (56)
Pasture (site 3)	18	3 (83)
Pasture (site 4)	18	2 (89)
Average	37	15 (60)

[a] Values in parentheses are % reduction compared with urea.
Source: Cantarella *et al*. (2005). Fertilizers were surface applied to no-till maize or to *Brachiaria* pastures.

NH$_3$ volatilization from surface-applied urea due to NBTPT ranged from 29% to 89%, with an average of 60%, compared to no inhibitor, in eight field trials (Table 2). Most of the volatilization with untreated urea took place within 2–3 days after fertilizer application. The addition of NBTPT postponed volatilization by 2–8 days, depending on the soil moisture and temperature conditions, and slowed down the rate of ammonia loss. In another set of seven trials with N fertilizers applied on top of sugarcane trash blankets by Cantarella *et al*. (2008), an average reduction in NH$_3$ volatilization of 26% was observed when NBTPT-treated urea was compared to regular prilled urea. Under prevailing dry weather conditions, the effect of NBTPT tended to be smaller than that observed in the rainy season, because after the inhibitory effect on urease subsided, urea fertilizer remained unincorporated into the soil and was still subject to volatilization losses (Fig. 5). The effect of NBTPT on increasing crop yields obtained with
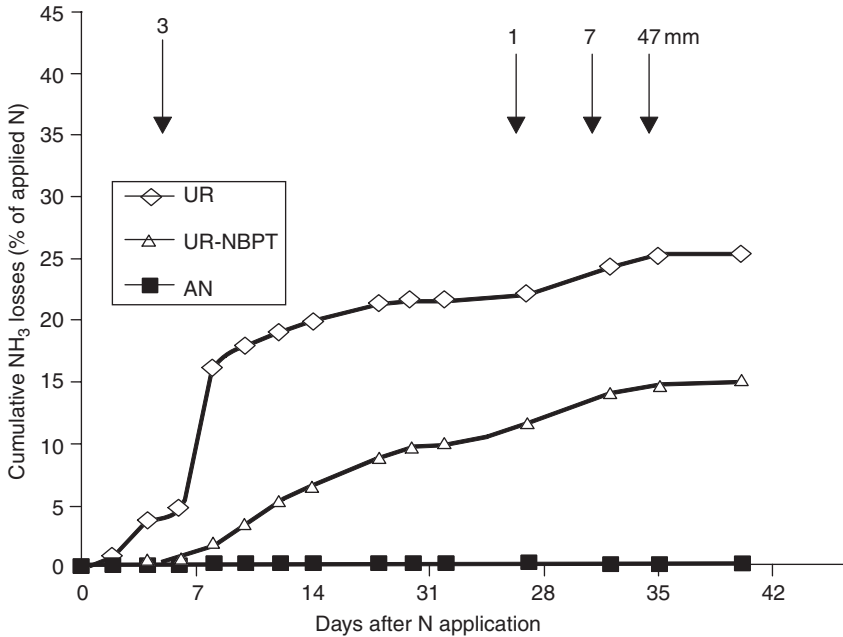
Figure 5 Cumulative ammonia loss from urea (UR), ammonium nitrate (AN), and NBTPT-treated urea (UR–NBTPT) surface applied to a trash-covered sugarcane soil. Arrows indicate the amount (mm) and the date of rain events after N application. *Source*: Cantarella *et al.* (2008).

Table 3 Grain yield response to N as urea, NBTPT-treated urea, or ammonium nitrate surface applied to maize grown under no-till conditions in southeastern Brazil

N source	Grain yield[a] (kg ha^{-1})	Grain yield increase (kg ha^{-1})
Urea	7054a	–
Urea + NBTPT	7405b	351
Ammonium nitrate	7526b	472

[a] Means followed by the same letter are not significantly different at $p \leq 0.05$ by the Tukey test.
Source: H. Cantarella (unpublished data). Data are average of three N rates (40, 80, and 120 kg ha^{-1}) in seven N-responsive sites.

urea in no-till field trials conducted in Brazil is shown in Table 3 (H. Cantarella, unpublished data).

In laboratory studies, Chien *et al.* (1988a) and Christianson *et al.* (1990) found that cyclohexylphosphoric triamide (CHPT) in oxygen-analog form was a very effective inhibitor of urease activity, and this finding was confirmed in a field experiment with flooded rice that showed CHPT was even more effective than NBTPT in reducing daily NH_3–N volatilization (Fig. 6) and total N uptake, but not in rice grain yield (Freney *et al.*, 1995b).
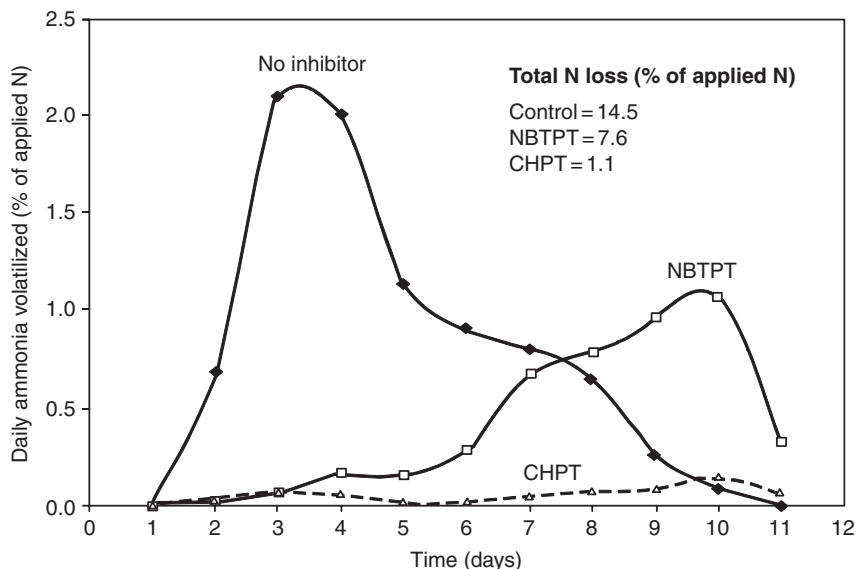
Figure 6 Ammonia volatilization from urea as affected by urease inhibitors in flooded rice soil. *Source*: data adapted from Freney *et al.* (1995a,b).

Both NBTPT and CHPT retarded NH_3–N volatilization for the first 3 days, but CHPT was more effective than NBTPT between 4 and 10 days. For the whole course of 11 days, CHPT was able to sustain lower NH_3–N volatilization losses than NBTPT.

To compare the effectiveness of sulfur and oxygen analogs of two urease inhibitors, Christianson *et al.* (1990) synthesized four compounds: two sulfur analogs, NBTPT(s) and CHTPT(s), and two oxygen analogs, NBPT(o) and CHPT(o). At 0.1% concentration (w/w in urea), NH_3–N volatilized in 12 days from urea applied to the surface of a soil with pH 6.2 were as follows: control $\gg$ CHTPT(s) > NBTPT(s) = NBPT(o) = CHPT(o). At a concentration lower than 0.01%, the order was as follows: control > CHTPT(s) > NBTPT(s) > NBPT(o) = CHPT(o). The results showed that, similar to NBTPT(s), CHTPT(s) was a weak urease inhibitor and became more effective when it was converted to CHPT(o) in soil as shown in the following reaction:

$$C_6H_{11}-N-\overset{\overset{\textstyle S}{\|}}{P}-NH_2 \longrightarrow C_6H_{11}-N-\overset{\overset{\textstyle O}{\|}}{P}-NH_2$$

CHTPT(s)   CHPT(o)

(III)   (IV)
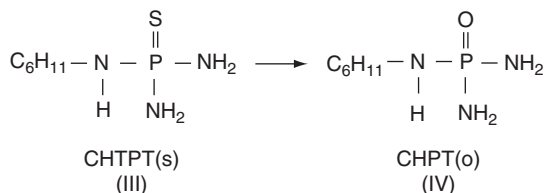
Both NBPT(o) (II) and CHPT(o) (IV) were equally effective in reducing NH_3–N volatilization. Unlike NBPT(o) (II), which is an unstable

compound, CHPT(o) (IV) is rather stable. However, there are no commercial products with either CHTPT(s) (III) or CHPT(o) (IV) available yet.

New urease inhibitors of the phosphoroamide family are being developed. Domingues et al. (2008) reported that eight phosphoroamide-derived compounds presented higher *in vitro* urease inhibitory activities than NBTPT, the commercial product used as a reference; two of the compounds tested (4-methyl-2-nitrophenyl phosphoric triamide and 2-nitrophenyl phosphoric triamide) showed marked differences from NBTPT in acidic soils, whereas the commercial inhibitor is reported to be less effective.

The interest in urease inhibitors is well justified because urea is the most important conventional N fertilizer worldwide and the risks of NH_3 volatilization loss significantly contribute to low fertilizer use efficiency. However, the data available show that urease inhibitors cannot completely control NH_3 loss when urea is surface applied to soils because the inhibitory effect depends on soil physical and chemical characteristics and also on environmental conditions. The urease inhibitors available so far can prevent urea hydrolysis for at most 1 or 2 weeks, during which time the fertilizer should ideally be incorporated into the soil by water (rain or irrigation) or mechanical methods; however, that does not always happen. The short-lived effect of the inhibitor is also a limitation when urea is surface applied to flooded rice. Nevertheless, despite only a partial capacity for reducing NH_3 losses, urease inhibitors represent an alternative that cannot be disregarded due to the growing presence of urea in the fertilizer market.

2.6. Reducing ammonia volatilization and nitrate leaching/denitrification by combining urease and nitrification inhibitors

Because ammonia volatilization and nitrate leaching/denitrification are mainly responsible for potential N losses from application of urea–based products, it seems logical to expect that combining urease inhibitors and nitrification inhibitors may yield the least amount of N loss. In an interesting field experiment in New Zealand, Zaman et al. (2005) compared the treatment of combined NBTPT (urease inhibitor) and DCD (nitrification inhibitor) against NBTPT or no inhibitor in terms of N loss in a soil (pH 5.7) fertilized with urea for pastures comprised mainly of perennial ryegrass and white clover. The results (Table 4) showed that NBTPT reduced more NH_3 volatilization than no inhibitor did, whereas DCD resulted in less NO_3–N leaching and denitrification loss from the soil fertilized with urea. The authors explained that the overall low losses of NO_3–N leaching for the treatments were due to inadequate drainage (30 mm) to remove the bulk of the nitrate from the 30-cm soil depth during the period of the trial. Combining NBTPT and DCD, however, somehow enhanced NH_3 volatilization comparing to NBTPT alone. Similar results

Table 4 Effect of different inhibitors on N status, losses, and dry-matter yield in a soil fertilized with urea for pasture

Measurement	No N	No inhibitor	NBTPT	NBTPT + DCD
Soil ammonium–N ($mg\,kg^{-1}$ N) (on 14th day)	5	52	23	95
Soil nitrate–N ($mg\,kg^{-1}$ N) (on 14th day)	2.0	24.5	15.5	3.8
Ammonia volatilized ($kg\,ha^{-1}$ N) (over 14 days)	1.2	7.7	4.2	10.0
Nitrate leaching ($g\,ha^{-1}$ N) (over 82 days)	5	375	200	50
N_2O flux ($kg\,ha^{-1}$ N) (over 82 days)	0.8	2.4	2.3	1.5
Total dry-matter yield ($t\,ha^{-1}$) (three cuts)	7.5	9.5	11.0	10.8

Source: data adapted from Zaman *et al.* (2005).

were reported by Gioacchini *et al.* (2002) and Nastri *et al.* (2000). It is not clear whether DCD affects the inhibiting properties of NBTPT or if by decreasing denitrification DCD enhanced NH_3 volatilization loss due to an increase in NH_4–N concentration on the soil surface. However, Clay *et al.* (1990) found that DCD did not affect NH_3 volatilization when mixed with urea or urea plus NBTPT; however, in their work the ratio of DCD to urea was somewhat low (2:160). In the study of Zaman *et al.* (2005), the dry-matter yield of pasture follows the order: no N < no inhibitor < NBTPT = NBTPT + DCD. In this study, no additional benefit was shown for combining a urease inhibitor and a nitrification inhibitor compared to urease inhibitor alone in terms of pasture production with urea application.

Radel *et al.* (1992) found that thiophosphoryl triamide [$(NH_2)_3PS$ or TPTA] had a dual effect on inhibition of urea hydrolysis and nitrification. They compared TPTA with DCD (nitrification inhibitor) and NBTPT (urease inhibitor) in terms of retardation of urea hydrolysis or nitrification in a soil treated with urea or $(NH_4)_2SO_4$ during a 5-week incubation. Urea was completely hydrolyzed in 1 week in the treatment without inhibitor, in 2 weeks with DCD, and in 5 weeks with TPTA, whereas NBTPT effectively retarded urea hydrolysis for the incubation period (Fig. 7). TPTA was 95% and 81% as effective as NBTPT for weeks 1 and 2, respectively, on retarding urea hydrolysis. Since NH_3 volatilization from urea hydrolysis generally occurs during the first 2 weeks after urea surface application, TPTA seems to be an effective urease inhibitor for reducing NH_3 volatilization. As expected, NH_4–N from added $(NH_4)_2SO_4$ significantly decreased
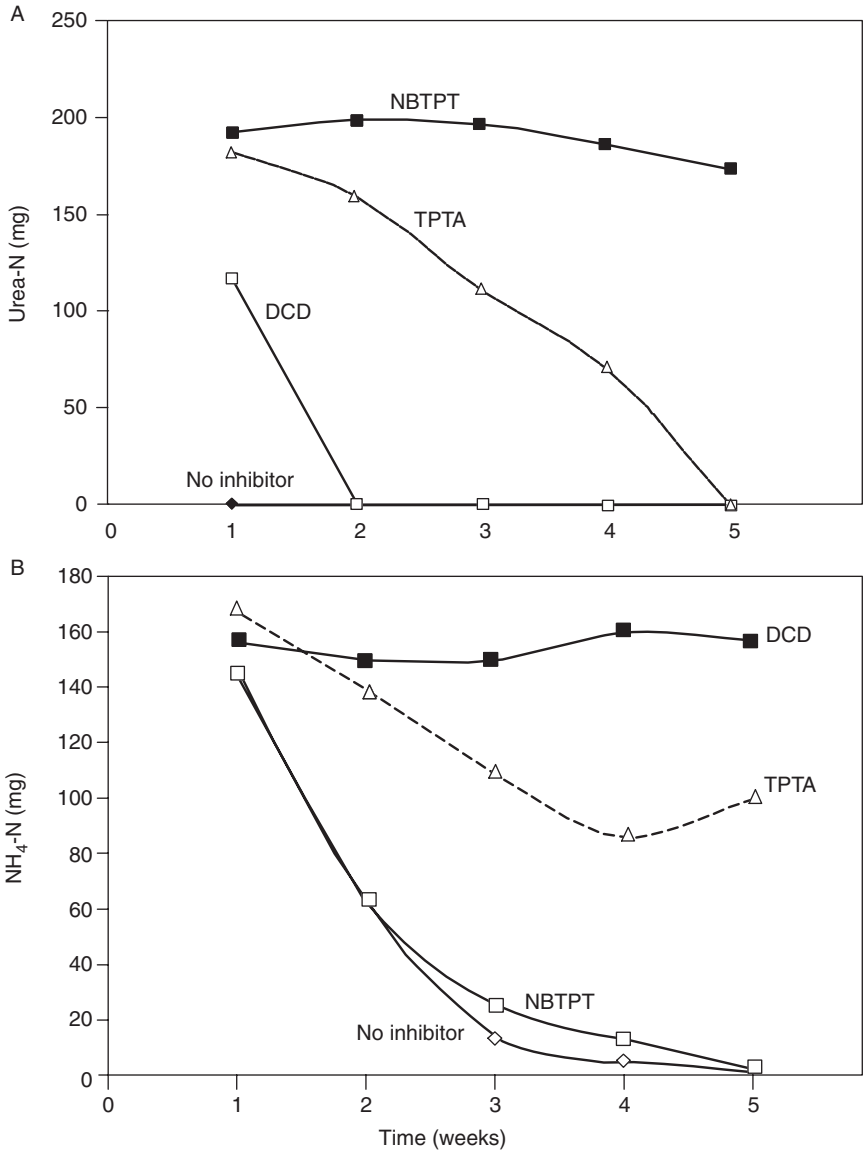
Figure 7 Effect of inhibitors on urea hydrolysis and nitrification in a soil treated with (A) urea and (B) ammonium sulfate during incubation. *Source*: data adapted from Radel *et al*. (1992).

after 2 weeks in the soil treated without inhibitors or with NBTPT (Fig. 7). DCD effectively retarded nitrification during the course of incubation, whereas TPTA was 55% as effective as NBTPT after 5 weeks. When the same soil was treated with urea, Radel *et al*. (1992) found that the percentage

of nitrification inhibition for NBTPT was 85%, for DCD was 90%, and for TPTA was 97% after the 5-week incubation. Thus TPTA could be an effective dual inhibitor for urea hydrolysis and nitrification, although slightly less effective than NBTPT and DCD with regard to their sole inhibition properties. However, no agronomic studies of TPTA versus DCD and NBTPT in soil treated with urea have been reported in the literature.

2.7. Use of ammonium sulfate to enhance N efficiency of urea

Ammonium sulfate $[(NH_4)_2SO_4$ or AS] is a weakly acidic salt that is not prone to NH_3 volatilization in acidic and neutral soils. It is also a common source of N fertilizer, and therefore several studies have been conducted to investigate whether use of AS could enhance the agronomic N efficiency of urea by reducing NH_3 volatilization. Fleisher and Hagin (1981) hypothesized that pretreatment of soil with an NH_4^+ salt could increase the population of nitrifiers that could reduce NH_3 volatilization from subsequently applied urea. They found that pretreatment with AS reduced NH_3 loss from a subsequent urea application by half in a neutral soil (pH 6.2). In a field study in India, Kumar and Aggarwal (1988) also found that pretreatment of soil (pH 8.2) with AS 2–4 weeks prior to urea application reduced NH_3 loss by half, and led to a yield increase of pearl millet. Recently, Goos and Cruz (1999) observed a similar effect of AS pretreatment 2 weeks before urea on reducing NH_3 volatilization from the subsequent urea application to soils varying widely in soil properties. The concept of this approach could be utilized in crop systems that receive more than one urea topdressing if AS is used before the first application (Goos and Cruz, 1999), although it is not always possible to coincide the fertilizer applications in the same spots under field conditions.

Another approach to enhance the N efficiency of urea is to partially substitute AS for urea in the mixture. Several studies have shown that mixing AS with urea reduced NH_3 volatilization losses (Lara-Cabezas *et al.*, 1992, 1997; Oenema and Velthof, 1993; Vitti *et al.*, 2002). Lower NH_3 losses are expected when AS is added to urea because AS is unlikely to contribute to NH_3 losses under neutral or acidic soil conditions; moreover, the dilution effect of AS–N should be taken into account since NH_3 volatilization is greater with increased urea concentration and/or rate of application (Cantarella *et al.*, 2003; Nelson, 1982). However, in some studies the decrease in NH_3 volatilization loss due to the addition of AS is greater than the proportion of $NH_4^+ - N$ in the AS–urea mixture (Lara-Cabezas *et al.*, 1992; Vitti *et al.*, 2002). For instance, in a recent study, Vitti *et al.* (2002) mixed different amounts of AS (0, 75, 150, 225, and 300 mg N) with a constant amount of urea–N (330 mg N). After 23 days of soil incubation, the total amounts of NH_3–N volatilized from urea decreased with increasing amounts of AS added, along with a decreasing soil pH from 6.2 to 5.2. Apparently the acidic nature of AS caused a reduction in NH_3

volatilization from urea in the mixtures (Lara-Cabezas et al., 1992; Oenema and Velthof, 1993; Vitti et al., 2002).

Studies with plants have also shown that the mixture of urea and AS may increase fertilizer N efficiency. Watson (1988), in a pot experiment, measured N uptake by ryegrass from mixtures of AS and urea using ^{15}N-labeled fertilizers, and observed that N derived from urea increased by 38% when AS was present in the same granule, as compared with urea alone; however, the uptake of AS-derived N decreased 14% in the presence of urea. The net effect of the fertilizer mixture on N uptake was still positive. In another study with maize in a sandy soil in Brazil, Villas Boas (1990) concluded that the mixture of AS and urea in the same granule tended to promote higher recovery of N fertilizer and increased grain yield compared to plants treated only with urea; the N fertilizers were surface applied to soils with no incorporation.

The extent of the response to the addition of AS to urea is not always significant and there are reports showing no effect of the fertilizer mixture compared with urea alone. Lara–Cabezas et al. (1992) in a field experiment observed a reduction of NH_3 volatilization due to the addition of AS to urea in a sandy Oxisol with 14.9% and 25.3% moisture content, but not with 18.3% moisture content. In another study with maize under field conditions, Lara–Cabezas et al. (1997) found lower NH_3 losses with AS + urea compared with urea alone when the fertilizers were applied before, but not after, sprinkle irrigation (28 mm). The reasons for these results are not clear, but could be associated with experimental error in field trials. In an experiment with sugarcane, Costa et al. (2003) reported no difference in NH_3 volatilization loss in plots treated with urea or with a mixture of urea and AS (loss of about 35% of the surface-applied N). In the same way, Villas Boas et al. (2005) did not find differences in uptake by maize plants of ^{15}N–labeled AS + urea and urea alone, although in their experiment conditions were not conducive to NH_3 volatilization losses.

In some cases, it appears that the proportion of AS in the fertilizer mixture may affect N fertilizer efficiency when N is surface applied. For instance, Watson (1987, 1988) observed an increase in urea–N uptake by ryegrass when the amounts of urea and AS (w/w) were 1 + 1 (Watson, 1988), but not when they were 3 + 1 (Watson, 1987). Great reductions of NH_3 volatilization reported by Lara–Cabezas et al. (1992) were obtained when AS accounted for 42% N of the urea + AS mass (25% of total N as $NH_4^+ - N$), but the differences were less pronounced compared to those of urea when the mixture contained only 21% AS (11% of total N as $NH_4^+ - N$). Similarly, the greater the amount of AS added, the lower the volatilization loss of urea–N observed in the study of Vitti et al. (2002). Although high amounts of AS in urea + AS formulations do not always guarantee decreased NH_3 loss or increased N uptake by plants, in most studies with positive results reported in the literature, the proportion of N

from AS in the urea + AS mixture was relatively high: 50% (Watson, 1988), 42% (Lara-Cabezas *et al.*, 1992), 65% (Lara-Cabezas *et al.*, 1997), and 41–48% (Vitti *et al.*, 2002). It should be pointed out that the reason for urea being widely used as an N fertilizer worldwide is its lower price per unit N due to its high N content (46% N), compared to those of ammonium nitrate (35% N) and AS (21% N), which reduces the transportation cost of urea–N fertilizer. Thus, any attempts to use AS with urea to enhance the N efficiency of urea should also consider the economic aspects, including (1) increase in the transportation cost for AS compared to urea, (2) saving the cost of urea–N by reducing NH_3 volatilization loss, and (3) a possible increase in crop yield by mixing AS and urea compared to urea alone. An additional reason to mix AS and urea is to supply S along with N. AS has an N:S ratio much higher than that of most plants (N:S ratios 8:1–10:1), but urea lacks S. However, it takes only about 21% AS in the AS + urea mixture to produce a formulation with an N:S ratio of 8:1, or approximately 5% S. Mixtures containing 42% AS and 58% urea (about 10% S and an N:S ratio of 3.7:1) could be justified for situations with high S demand.

3. Improving the Efficiency of Conventional Phosphorus Fertilizers

It is known that water-soluble P (WSP) can be converted to water-insoluble P after reaction with soil minerals, which can result in a decrease of P availability. Several terminologies, such as P sorption, adsorption, retention, fixation, precipitation, and immobilization, have been used to describe this process. The forms of reaction products depend on P sources and soil minerals. In general, Fe–Al–P minerals form in acidic soils containing Fe–Al–oxide minerals, whereas Ca–P minerals form in alkaline or calcareous soils. The P reaction process involves surface adsorption and/or precipitation. Often the Fe–Al–P precipitates, if they indeed occur, are in the amorphous instead of crystalline form, which makes identification of mineral species rather difficult (Hsu, 1982a,b). In alkaline and calcareous soils, often more crystalline Ca–P and/or NH_4–Ca–P compounds from TSP, SSP, DAP, and MAP can be physically identified (Lindsay *et al.*, 1989). There has been some interest in research and development on modifying the physical characteristics of conventional WSP fertilizers to reduce P fixation by soil, and thereby increase the P efficiency for plant uptake. Some of the recent findings are discussed below.

3.1. Coated water-soluble phosphorus fertilizers

Recently, some fertilizer companies have developed thin coating of WSP fertilizers (DAP, MAP, TSP) with water-insoluble polymers, with or without S (e.g., trade name "DAP-Star" by Hi Fert), as a slow-release

P fertilizer. Another type is coated with water-soluble polymers (e.g., trade name ''Avail'' by SFP) to reduce the rate of WSP conversion to water-insoluble P by soil fixation. Gordon and Tindall (2006) claimed that Avail is a polymer with a very high surface charge density (about 1800 cmol kg^{-1} of cation exchange capacity) that can inhibit P precipitation by acting as a platform for sequestration of P-fixing cations, such as Ca and Mg in high pH soils and Fe and Al in low pH soils. One study conducted by the University of Georgia (G. J. Gascho, unpublished data) showed that MAP coated with this polymer performed significantly better than uncoated MAP when MAP was broadcast, but it did not when banded (Table 5). Since soil fixation of WSP is higher when broadcast than when banded, as evidenced by the lower grain yield of uncoated MAP when broadcast than when banded, the result showed the benefit of MAP by polymer coating. However, there is little information on the soil chemistry of this polymer-coated P fertilizer published in the peer-reviewed scientific journals and questions remain unanswered regarding the mechanisms of reducing P fixation by the polymer. For instance, it is known that WSP is adsorbed or precipitated on the solid surfaces of Fe and Al oxide minerals in acid soils and $CaCO_3$ in alkaline soils (Lindsay et al., 1989). What mechanism causes these Fe, Al, and Ca cations to dissolve from their minerals and diffuse to the dissolved polymer-coated WSP granule sites, be adsorbed by the polymer via ionic exchange, and thereby protect the WSP from precipitation? Furthermore, shouldn't the soluble cations associated with the WSP fertilizers (Ca ions from SSP and TSP, and NH_4 ions from MAP and DAP) be first adsorbed by the polymer and thereby reduce the polymer's capacity to sequester soil Fe, Al, and Ca ions? Research is needed to address these questions in order to understand the merit of using WSP fertilizers coated with water-soluble or water–insoluble polymers. If indeed P release meets the crops' needs, and at the same time minimizes P fixation, the coated WSP fertilizers may be effective for crop production provided the cost/benefit is feasible compared to the uncoated WSP fertilizers.

Table 5 Grain yield of maize obtained by polymer-coated and -uncoated MAP as influenced by the placement method

P rate (kg ha^{-1} P)	Method of placement	P source	Grain yield (t ha^{-1})
0	NA	Control	3.7
11.6	Band	MAP	8.5
11.6	Band	Polymer–coated MAP	9.2
11.6	Broadcast	MAP	7.0
11.6	Broadcast	Polymer–coated MAP	10.1
LSD (0.10)	NA	NA	1.2

Source: G. J. Gascho (unpublished data).

3.2. Urea supergranules containing phosphorus and potassium nutrients

Savant and Chien (1990) first showed that available P from DAP in USG by deep placement was as effective as broadcast and incorporation of DAP or TSP for flooded rice. Although initial P accumulation in young rice leaves from deep-placed USG-containing DAP was lower than that of incorporated TSP, P uptake from both P sources was the same 40 days after rice transplanting (Savant *et al.*, 1997). In the same study, practically no ^{32}P activity was detected in the floodwater when USG-containing ^{32}P-tagged DAP was deep placed. This observation clearly suggests that runoff losses of P in solution and/or P adsorbed on clays suspended in the flowing floodwater would be reduced substantially, thus practically eliminating the problem of water pollution or eutrophication due to P runoff from paddy fields.

Results of several farmer-managed field trials conducted in India demonstrate that USG–DAP management can make the fertilizer agronomically more efficient, economically more attractive with less risk, and reduce the loss of nutrients compared to the conventional use of PU and WSP fertilizers (Savant and Stangel, 1998). For example, the grain yield of rainfed rice obtained with USG–DAP by deep placement in an Ultisol was higher than that obtained with basal incorporated SSP plus split-applied PU (Fig. 8).
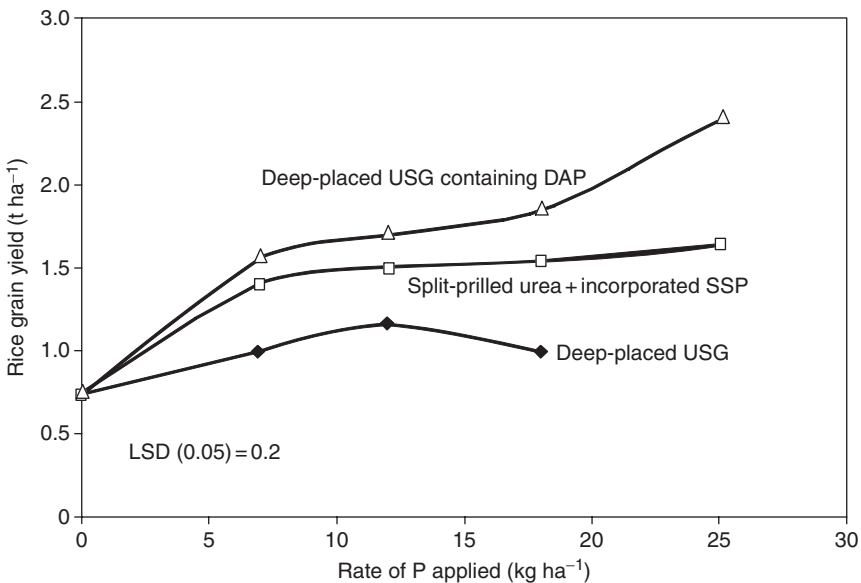

Figure 8   Grain yield of flooded rice obtained with different NP treatments (each N rate = four times each P rate). *Source*: Savant and Stangel (1998).

A recent study (Kapoor *et al.*, 2008) showed that deep placement of USG-containing DAP and KCl performed better than broadcast application of urea (three splits), DAP, and KCl for rainfed rice in a Vertisol. Significantly higher grain yields and straw yields, total N, P, and K uptake, and N and P use efficiencies were observed with deep placement of N–P–K compared to broadcast of N–P–K. Furthermore, the amounts of N, P, and K in the floodwater in the deep–placement treatments were negligible—similar to floodwater N, P, and K contents without fertilizer application. Thus, urea-based N–P–K compound fertilizers may be agronomically and economically feasible in supergranule form by deep placement for flooded rice production.

3.3. Fluid versus granular water-soluble phosphorus fertilizers

Numerous studies have been reported in literature on the comparison of agronomic effectiveness of fluid versus granular or nongranular WSP fertilizers. As Engelstad and Terman (1980) pointed out, for a valid comparison of fluid and solid fertilizer P, the P should be supplied in the same chemical compounds in both cases and be similarly placed. However, many reported greenhouse and field trials do not comply with these requirements and often the results are conflicting. For example, many studies claimed that fluid ammonium polyphosphates (APP) are agronomically superior to ammonium phosphates when based on different P compounds in the two P sources (polyphosphates vs orthophosphates). Most results in the USA and other countries show equal P availability from these two P sources to crops grown on most soils (Terman, 1975). A recent study by Ottman *et al.* (2006) also showed that there were no significant differences in alfalfa yield obtained with fluid APP and granular MAP on a calcareous soil over 3 years. According to Engelstad and Terman (1980), some favorable results with APP on neutral to alkaline soils may have been caused by appreciable amounts of micronutrients such as Fe or Zn in the APP. On the other hand, P of APP would become plant available only when polyphosphates are hydrolyzed to orthophosphate in soils that depends on soil biological activity. For example, Engelstad and Allen (1971) reported that APP was less effective than MAP at a colder temperature (16 °C), but there was no difference at a warmer temperature (24 °C). Earlier, after summarizing many field trials in the USA, Lathwell *et al.* (1960) also concluded that P in solution form is as satisfactory as in comparable solid sources.

Recently, renewal interest in research work on fluid versus granular forms of the same P fertilizers has been reported, especially in Australia. Holloway *et al.* (2001) showed that commercial fluid P fertilizers, for example, MAP, DAP, and APP, were more effective than the same commercial granular P fertilizers in increasing crop yield in calcareous and alkaline soils. Hettiarachchi *et al.* (2006) and Lombi *et al.* (2004) used highly

sophisticated instruments to study P mobility of surface-applied granular versus fluid MAP in a calcareous soil at 60% of field capacity. They found that total and labile P from the liquid MAP diffused farther (1.35 cm) than did the granular MAP (0.75 cm) from the site of P application. This may explain the better agronomic performance of fluid MAP over granular MAP in field trials as reported by Holloway *et al.* (2001). They claimed that P diffusion and isotopic lability from granular MAP were reduced compared with equivalent liquid MAP because precipitation reactions osmotically induced the flow of soil moisture into the MAP granule. Also, a significant amount of the initial P still remains in the granule even after some time of dissolution, partly due to the presence of water–insoluble Fe–Al–P minerals in the granule, and also due to the precipitation *in situ* of similar minerals resulting from the diffusion of Ca and Al into the granule. In contrast, there is significantly less fixation of P from the fluid P fertilizers, and hence a greater concentration of labile P (Lombi *et al.*, 2004). Black (1968), however, showed that P could diffuse up to 1.50 cm from the site of solid KH_2PO_4 applied to the surface of a calcareous soil at 100% field capacity. Apparently, P diffusion greatly depends on soil moisture content (% of field capacity) and water content of the liquid P fertilizers. Furthermore, in the studies conducted in Australia, the researchers only reported total P content, but did not report the proportion of WSP and water–insoluble P content, when comparing the same fluid with granular P fertilizers. For example, Lombi *et al.* (2004) compared commercial granular MAP with commercial fluid technical grade MAP, but they did not report whether the two sources had the same P compounds or water solubility, a caution that was emphasized by Engelstad and Terman (1980).

In short, a comparison of fluid with granular WSP fertilizers in agronomic effectiveness depends on many factors. Some of them are (1) chemical compounds of P sources, (2) proportion of WSP and water–insoluble P in P sources, (3) soil pH, (4) soil P-fixing capacity, (5) soil biological activity, (6) soil moisture or rainfall, (7) crop species (e.g., rooting system), (8) rate of P applied, (9) P placement method (e.g., incorporation vs band, no–till vs till), (10) initial versus residual P effect, and (11) cropping systems. One benefit of applying fluid ortho- or polyphosphate sources as compared with solid P sources may be that fluid P sources can increase soil concentration of available P with depth. Kovar (2006) suggested that fluid P sources, especially polyphosphates, which are known to sequester from soil adsorption, applied to the soil surface after crop harvest would move into the soil profile where it may be less subject to loss in runoff or by erosion, which may minimize the environmental impact of P during the winter months, and yet be available to plants the following growing season. In light of the recent renewal of interest in research comparing the agronomic effectiveness of fluid to granular WSP fertilizers in Australia (Evans, 2008; Holloway *et al.*, 2006), it may be worthwhile to take up similar research for different soils in other countries.

4. Use of Nonconventional Phosphorus Fertilizers

4.1. Phosphate rock for direct application

Direct application of phosphate rock (PR) can be an effective agronomic and economic alternative to the use of more expensive WSP fertilizers for crop production under certain conditions, especially in acidic soils of tropical and subtropical developing countries. The agronomic use of PR has been extensively studied and reported over the past 50 years. Some PR sources have been commercialized for export from Tunisia, Jordan, Algeria, Egypt, Morocco, Israel, China, and Christmas Island (Australia) to Malaysia, Indonesia, New Zealand, and Brazil, mainly for pastures and tree crops. Some indigenous PR sources are marketed for local use, for example, Burkina Faso, Colombia, Chile, Nigeria, Mali, and Tanzania (Kuyvenhoven *et al.*, 2004). Recent work done by researchers, particularly the work done by the IFDC, has provided more insight on the agronomic effectiveness of PR compared with the use of WSP fertilizers. Several in-depth reviews of this subject have been reported by Chien (2003), Chien and Menon (1995b), Hammond *et al.* (1986), Khasawneh and Doll (1978), Rajan *et al.* (1996, 2004), and Truong (2004). Therefore, there will be no further discussion on the agronomic use of PR in this chapter, except the most recent developments on PR use as described below.

The major factors affecting the agronomic effectiveness of PR are (1) chemical and physical properties of PR that affect the solubility of PR, (2) soil properties, (3) management practices, (4) climate, and (5) crop species. Despite hundreds of agronomic trials that have been conducted worldwide in the past, there is a need to integrate all of these factors in a comprehensive system to understand how these major factors affect the agronomic effectiveness of PR. Use of a phosphate rock decision support system (PRDSS) is a means to solve this problem. Because it is designed to be practical, PRDSS can be used in developing countries, especially those countries with endowed indigenous PR deposits, to assist in making decision to use WSP fertilizers or PR to supply P needed by crops.

Researchers in New Zealand (e.g., Metherell and Perrott, 2003) and Australia (e.g., Gillard *et al.*, 1997) have developed different versions of PRDSS. However, their models are mainly aimed at the use of reactive PR sources for pasture production. Recently, IFDC has developed and published its own PRDSS model for PR sources varying in reactivity for different crop species (Smalberger *et al.*, 2006). Based on this model, the FAO/IAEA has posted the PRDSS on the IAEA Web site (http://www-iswam.iaea.org/dapr/srv/en/resources). The current PRDSS version, however, only applies to the initial relative agronomic effectiveness

(RAE) of PR with respect to the conventional WSP fertilizers. To optimize agronomic and economic use of PR, IFDC, and FAO/IAEA have advanced the current PRDSS version by incorporating the residual RAE of PR, since the residual PR effect is very important when comparing the use of PR versus WSP. By including the residual PR effect and further validating or modifying the current PRDSS version, it will make the future FAO/IAEA Web-based PRDSS a more powerful and useful tool to researchers, extension workers, fertilizer companies, and government decision makers on the feasibility of the agronomic use of PR, whether locally produced or imported, compared to the use of WSP fertilizers. Figure 9 shows that the latest validation of an updated PRDSS in initial and residual RAE agrees well between the predicted and observed RAE values within 10% of a 1:1 line across different PR sources, types of soil, and crop species (U. Singh and S. H. Chien, unpublished data). The updated PRDSS version will be posted on the same IAEA Web site later. It should be noted that the current residual RAE of PR of the updated PRDSS version represents only the average of residual RAE values of a PR over several years or crops. In the future, more work will be needed to model a residual RAE of PR for a given residual crop in a given time.

Recently, eutrophication of aquatic environments (creeks, ponds, rivers, lakes, etc.) caused by excessive P from soil surface runoff has drawn many researchers to find strategies to mitigate the P pollution problem. Preliminary studies done in New Zealand and the USA have suggested that the use of reactive PR can not only sustain crop productivity but also may minimize the eutrophication problem compared to the use of WSP sources, because of lower P availability from PR for algal growth (Hart *et al.*, 2004; Shigaki *et al.*, 2006, 2007). Table 6 shows that both cumulative total and dissolved reactive P losses from surface runoff from three soils were significantly lower with reactive North Carolina PR than TSP, indicating less eutrophication would be encountered with reactive PR (Shigaki *et al.*, 2007). However, more work, including field studies, is needed to validate this supposition.

Another new field of PR research is the increasing use of PR for organic farming worldwide, since chemical P fertilizers are not allowed to be used on organic farms (Nelson and Mikkelsen, 2008). Mixing elemental S, which is also allowed as an input for organic farming, with PR may be a potential source of P and S for organic crop production. Oxidation of elemental S to H_2SO_4 may enhance PR dissolution, which has been studied for many years with inconclusive results due to many variables (Rajan *et al.*, 1996). It should be pointed out that use of PR with or without elemental S for organic farming, similar to conventional farming, greatly depends on the reactivity of PR sources used. Thus organic farmers should be aware that not all PR sources are the same in reactivity. The general rule is that the higher the reactivity of PR, the better it is as a P source for organic farming. For example, an indigenous igneous PR from Ontario, Canada, with very low reactivity has
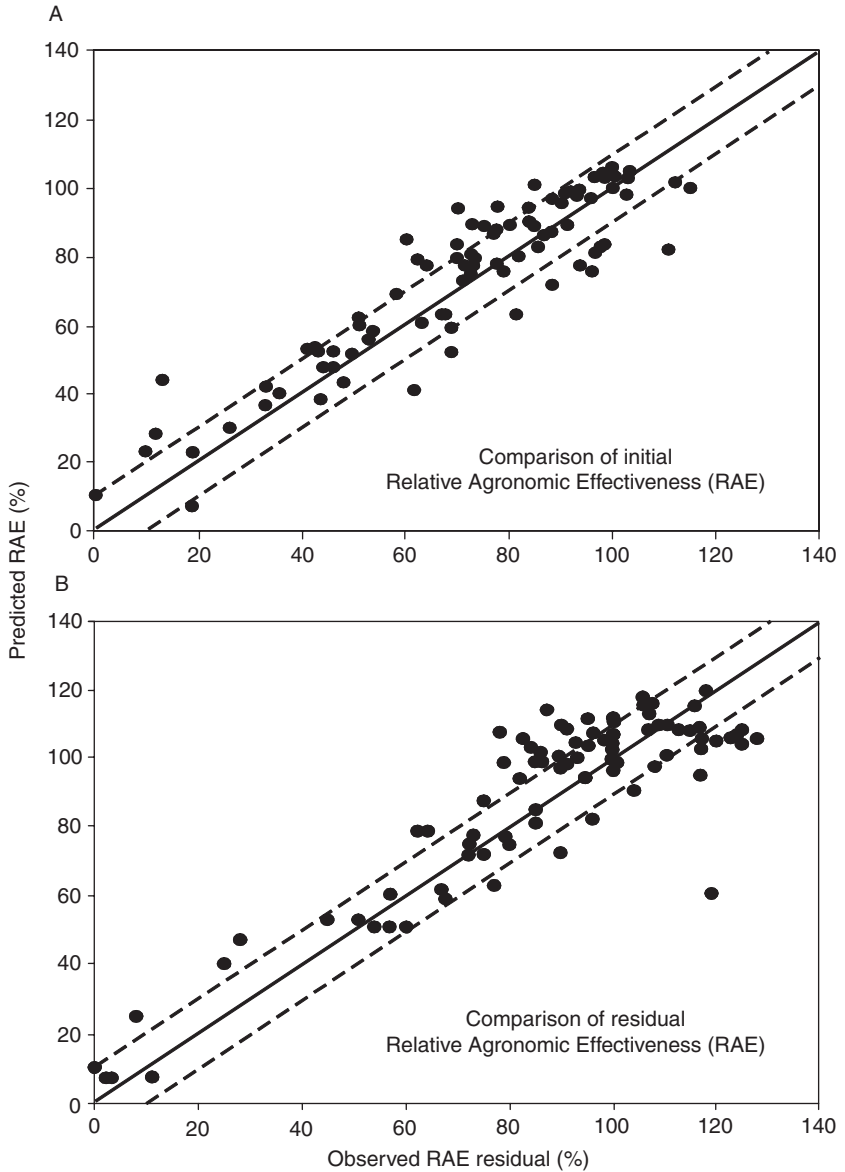
Figure 9 Comparison of observed and predicted relative agronomic effectiveness (RAE) for (A) initial and (B) residual applications of PR and WSP. The spread ($\pm$10%) along the one-to-one line (dashed line) is shown by dotted lines. *Source*: U. Singh and S. H. Chien (unpublished data).

Table 6 Cumulative loss of dissolved reactive and total P from surface runoff from three soils treated with phosphate rock (PR) or triple superphosphate (TSP)

Soils	P sources		
	Control	North Carolina PR	TSP
Cumulative dissolved reactive P (DRP) loss (kg ha^{-1})			
Alvira	0.28	0.52	32.2
Berks	0.18	0.39	14.5
Watson	0.23	0.43	16.2
Average[a]	0.23c	0.45b	20.9a
Cumulative total P loss (kg ha^{-1})			
Alvira	0.35	0.83	33.2
Berks	0.30	0.68	15.5
Watson	0.31	0.72	19.6
Average[a]	0.32c	0.74b	22.7a

[a] Average DRP and total P loss followed by the same letter are not significantly different at $p < 0.05$.
Source: Shigaki *et al.* (2007).

been marketed for organic farming due to its high P content. However, the total P content is irrelevant to PR reactivity for direct application (Chien, 1995). In fact, most igneous PR sources are high in P content but very low in reactivity due to little carbonate substitution for phosphate in apatite structure (Chien, 2003), and therefore they are not suitable for direct application. Another example is an organic strawberry farm in Canada once imported a highly reactive PR from North Africa, but the crop was grown on alkaline soils, and therefore the PR was not effective as a P source for the organic crop. Factors affecting the agronomic effectiveness of PR for organic farming should be considered more or less the same way as for conventional farming. One major exception is that in the case where PR is used with composting for organic farming, it is likely that the chelation of organic matter with Ca ions derived from apatite is the main mechanism responsible for PR dissolution (Chien, 1979), rather than soil acidity in the case of conventional farming. Thus the PR reactivity and the effectiveness of composts to chelate with Ca ions are important factors to the success of organic farming using PR as a P source. However, little information on the use of PR for organic farming has been published in the peer-reviewed scientific journals.

4.2. Mixture of phosphate rock and water-soluble P

Under certain conditions, such as low PR reactivity, high soil pH, or short-term crop growth, agronomic use of PR may not be as feasible as WSP (Chien and Menon, 1995a). Mixing PR with WSP can sometimes be an agronomically and economically effective P source under these conditions.

Partial acidation of low-reactive PR (PAPR), which consists of unacidulated PR and acidulated WSP, is one way to achieve this goal (Chien and Hammond, 1988). Another way is to mix PR with WSP by dry granulation (compaction) (Menon and Chien, 1996). For example, the agronomic effectiveness of a low-reactive Patos PR (Brazil) compacted with SSP at a 50:50 P ratio was as good as SSP in dry-matter yield of wheat and ryegrass (Prochnow et al., 2004). The explanation is that WSP can provide initially available P to plants (starter effect) that results in better plant root development that in turn may utilize PR more effectively later than if PR is applied alone (Chien and Hammond, 1988). The direct evidence of the starter effect of WSP on increasing PR effectiveness was reported by Chien et al. (1996) using an isotopic dilution technique with radioactive ^{32}P-tagged P sources. In the study by Prochnow et al. (2004), P uptake from Patos PR in the presence of WSP was higher than that from Patos PR alone, indicating the starter effect of water-soluble P on improving the effectiveness of Patos PR (Fig. 10).

The results of many studies, particularly those of the IFDC, have provided valuable information on the factors affecting the agronomic effectiveness of mixtures of PR and WSP. These include (1) PR reactivity, (2) the degree of acidation (IFDC's recommendation is 50% with H_2SO_4 or 20% with H_3PO_4, based on agronomic and economic considerations), (3) the degree of Fe and Al impurities of PR [if they are high, e.g., Capinota PR (Bolivia), the compaction process is preferable because the effectiveness of PAPR is lower than that of compacted PR with water-soluble P, whereas the two types of mixtures would have the same effectiveness if PR has low Fe and Al impurities, e.g., Huila PR (Colombia), shown in Fig. 11 as reported by Menon and Chien (1990).], (4) the effect of soil properties such as pH and P-fixing capacity (more favorable for soils with high P-fixing capacity) (Chien and Hammond, 1989), (5) the starter effect of water-soluble P on PR effectiveness (Chien et al., 1996), (6) the effect of crop species (Chien and Menon, 1995b), and (7) the initial and residual P effect. Figure 12 shows that RAE of PAPR increases with soil P-fixing capacity and it can be even more effective than TSP in soils with very high P-fixing capacities (Chien and Hammond, 1989). More information on the use of mixtures of PR and water-soluble P in terms of production, soil chemistry, and agronomic effectiveness can be found in several reviews (Chien, 2003; Chien and Hammond, 1989; Chien and Menon, 1995a; Hammond et al., 1986; Menon and Chien, 1996).

4.3. Calcined nonapatite phosphate rock for direct application

Most PR sources used for the chemical acidation process or direct application contain Ca–P minerals in the form of apatite. There are limited PR deposits in the world that contain Ca–Fe–Al–P minerals in the form of crandallite. Due to its high Fe and Al content, the nonapatite PR is not

A

B
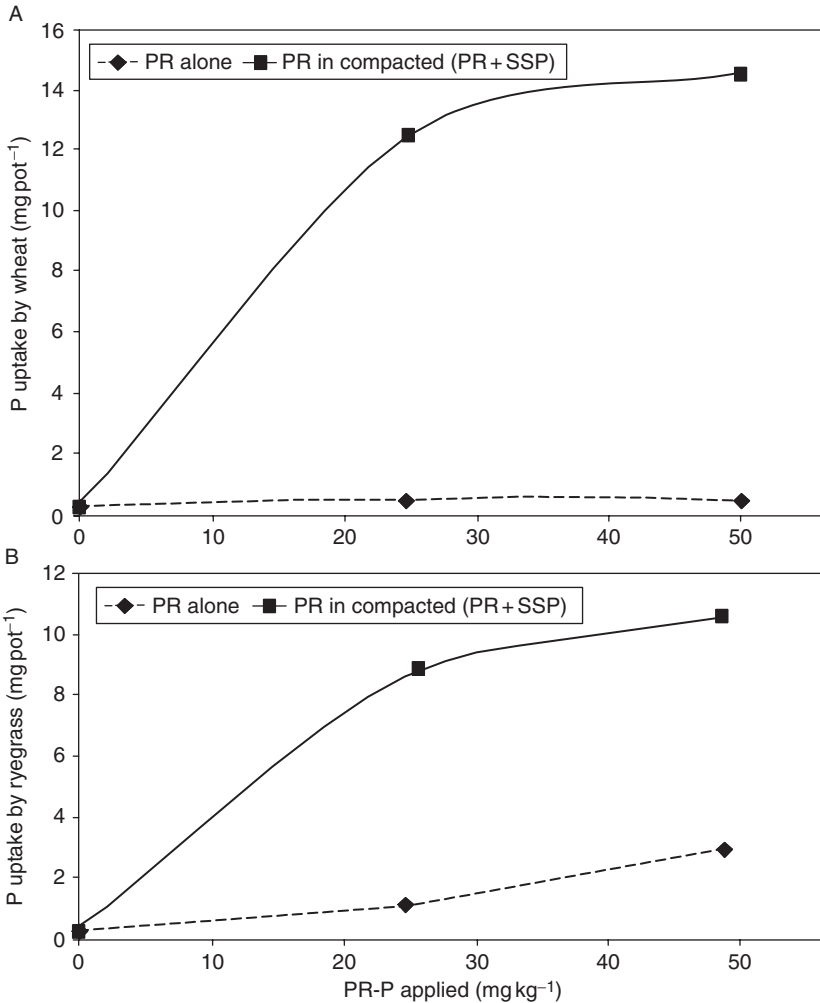
Figure 10 Phosphorus uptake by (A) wheat and (B) ryegrass from PR alone or PR in compacted (PR + SSP) applied at the same PR–P rate. *Source*: Prochnow *et al.* (2004).

suitable for the conventional chemical acidulation process. The natural crandallite PR sources are very low in reactivity and therefore, not suitable for direct application. The reactivity, however, can be significantly increased upon calcination at temperatures ranging from 450 to 700 °C, after the hydrated water molecule of the crandallite structure is driven off and the structure becomes amorphous (Hoare, 1980). In the past, commercial calcined crandallite PR products were marketed from Christmas Island (trade named ''Calciphos'' and ''Citrophos'') and Senegal (trade named ''Phospal''), but without success due to high energy costs and poor agronomic response for upland crops (Bolland and Gilkes, 1987).
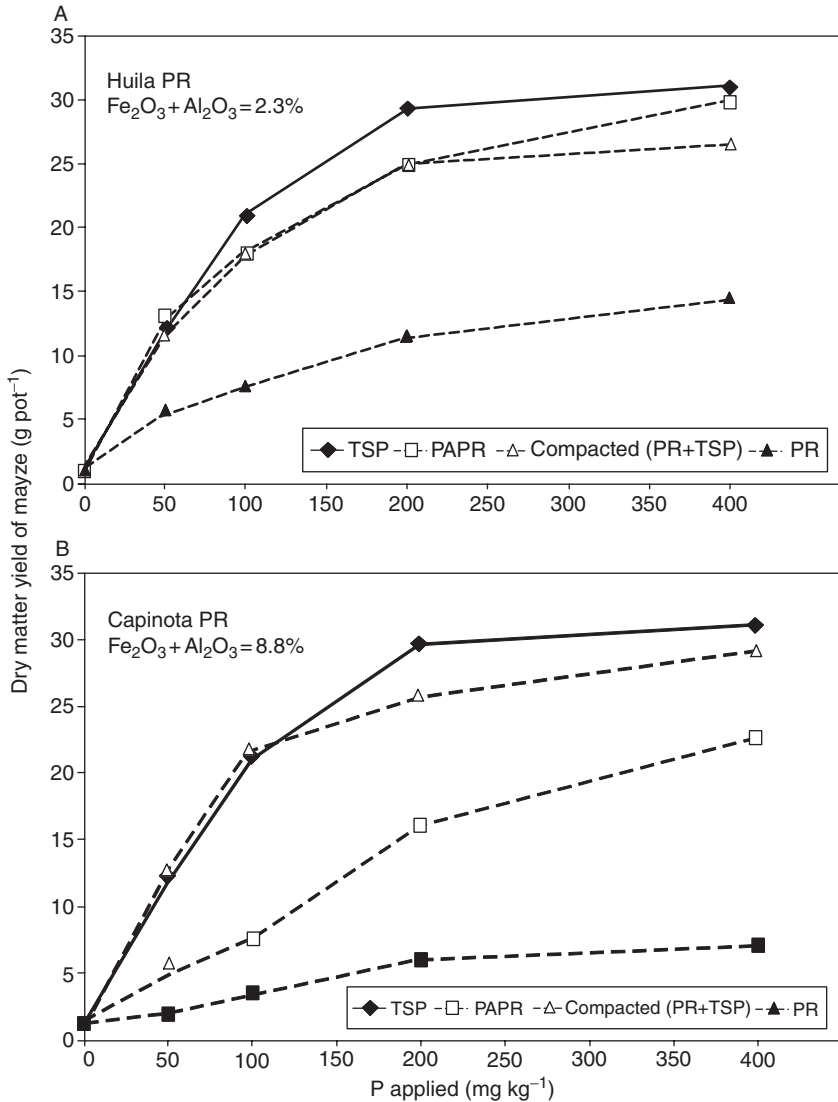
Figure 11 Dry-matter yield of maize obtained with TSP and modified PR products made from (A) Huila PR and (B) Capinota PR. *Source*: Menon and Chien (1990).

Chien (1998) reported that the calcined Christmas Island PR performed well compared to TSP for flooded rice. The explanation was that flooding could (1) create reduced soil conditions that convert Fe^{3+} to Fe^{2+}, which could in turn increase Fe–P solubility, and (2) increase soil pH, which could increase the solubility of Fe–Al–P. Later, S. H. Chien (unpublished data) found that a calcined crandallite PR was able to provide both P and Fe

Figure 12   Relative agronomic effectiveness (RAE) in dry-matter yield and P uptake of maize obtained with PAPR-50% H_2SO_4 as related to soil P-fixing capacity. *Source*: Chien and Hammond (1989).

nutrients to upland rice, whereas TSP failed due to Fe deficiency in an alkaline soil deficient in both P and Fe nutrients. Recently, two studies were reported by Francisco *et al.* (2008a,b) on the characterizati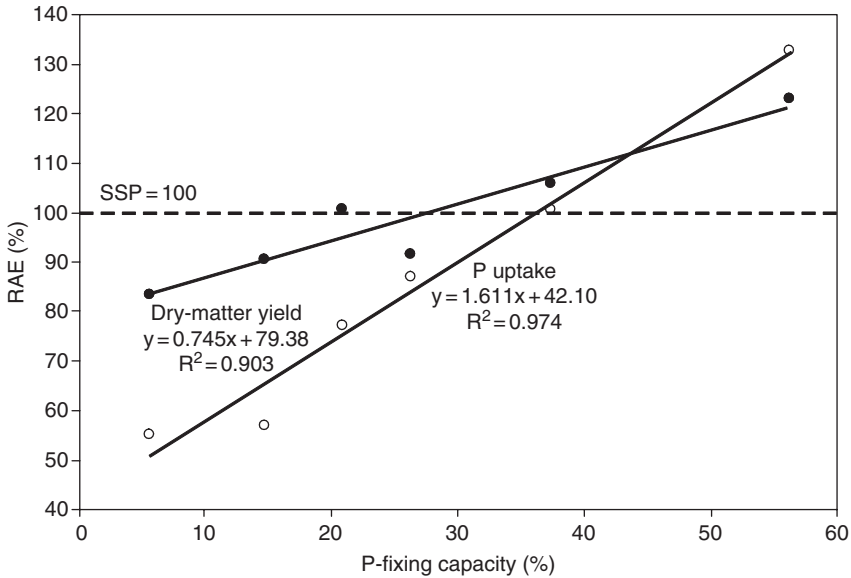on and agronomic evaluation of several calcined crandallite PR sources from Brazil. In the study by Francisco *et al.* (2008b), the solubility of two calcined PR sources (Juquia and Sapucaia) in neutral ammonium citrate (NAC) increased and reached a maximum at 500 °C upon calcination (Fig. 13). Their RAE values in terms of rice grain yield compared to WSP (RAE = 100%) were 66–72% for flooded rice, whereas the RAE of highly reactive Gafsa PR (Tunisia) was 0%. For upland rice grown in an acidic soil (pH 5.3), the RAE values of these two calcined PR sources were 83–89%, whereas the RAE was 95% for Gafsa PR. The results showed that the calcined PR sources can indeed be used for upland and flooded rice. However, economic analysis is needed to assess the feasibility of using these nonconventional P sources compared to conventional WSP fertilizers or other highly reactive PR sources containing apatite.

4.4. Agronomic effectiveness of nonconventional acidulated phosphate fertilizers

The amounts of premium quality PR available to produce conventional acidulated P fertilizers (SSP, TSP, MAP, and DAP) are rapidly decreasing worldwide. As the P industry becomes more dependent on lower quality
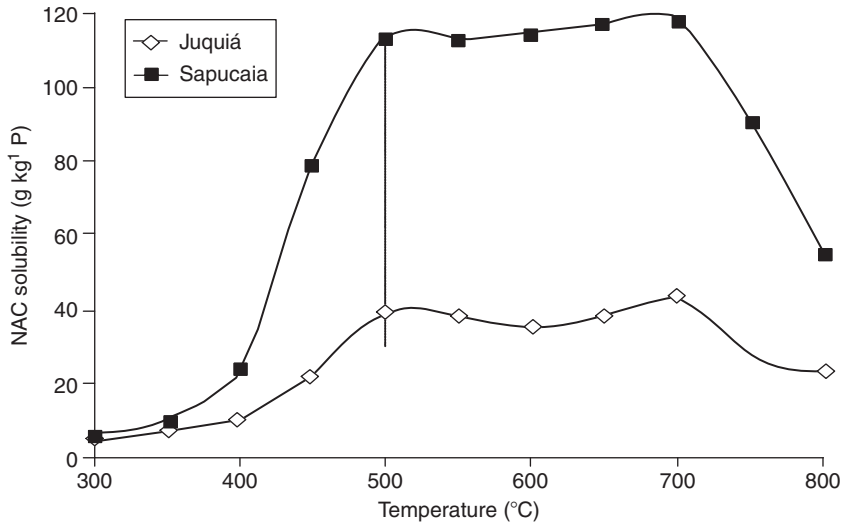
Figure 13 Effect of thermal treatment on neutral ammonium citrate (NAC) solubility of crandallite minerals from Juquia PR and Sapucaia PR deposits, Brazil. *Source*: Francisco *et al.* (2008b).

PR ore, higher levels of P impurity compounds can be expected in the final acidulated P fertilizers (Lehr, 1980; Mullins and Sikora, 1995). These impurities are generally water-insoluble forms of Ca–P or Fe–Al–P, and their composition is determined by the mineralogical constitution of the ore and also by the process of fertilizer production (Gilkes and Lim–Nunez, 1980; Lehr, 1980).

There has been some concern regarding the effect these impurity compounds may have on P fertilizer effectiveness. Gilkes and Lim–Nunez (1980), for example, stated that raw materials and manufacturing procedures used to produce superphosphates should be studied to limit the development of impurities, mainly the compounds $Ca(Fe,Al)H(HPO_4)_2F_2 \cdot 2H_2O$ and $(Fe,Al)(K,Na)H_8(PO_4)_6 \cdot 6H_2O$. In fact, preliminary agronomic studies showed that some Fe–Al–P compounds in acidulated P fertilizers, when applied *per se*, were less effective when compared to the WSP compounds normally found in superphosphates and ammonium phosphates (Bartos *et al.*, 1991; Gilkes and Lim–Nunez, 1980; Gilkes and Mangano, 1983; Mullins *et al.*, 1990; Prochnow *et al.*, 1998; Sikora *et al.*, 1989). Legislation in some parts of the world has established the minimum legal content of WSP in acidulated P fertilizers. As an example, Brazil set the minimum content levels of WSP in acidulated P fertilizers to approximately 90% available P [NAC plus WSP as adopted by AOAC (1999)], which amounts to 7.0%, 16.2%, 16.6%, and 19.2% WSP in SSP, TSP, DAP, and MAP, respectively (Brasil, 1982). Also, for many years Europe adopted a minimum of 93% WSP in the available P fraction for TSP (European Community, 1975).

Although the impurity compounds do not provide P to plants as WSP compounds when they are mixed with reagent-grade MAP or MCP, under experimental conditions that simulated acidulated P fertilizers, the results suggested that these fertilizers may contain higher proportions of impurity compounds than those expected and normally used in commercial fertilizers (Bartos *et al.*, 1992; Mullins and Sikora, 1995; Mullins *et al.*, 1995; Prochnow *et al.*, 2003a,b, 2008). Bartos *et al.* (1992) isolated water-insoluble impurity compounds from five MAP fertilizers, representing the primary U.S. sources of PR (Florida, North Carolina, and Idaho). These impurities were used to simulate MAP fertilizers containing 0%, 20%, 40%, 60%, 80%, and 100% of the total P as reagent-grade MAP (i.e., 0–100% WSP). When a Mountview silt loam soil with a pH of 6.7 was evaluated under greenhouse conditions, the MAP fertilizers, at 80 mg kg^{-1} P, did not require more than 75% WSP to obtain 90% of the maximum sorghum–sudangrass forage yield.

Mullins and Sikora (1995) conducted a similar study utilizing water-insoluble impurities isolated from two commercial TSP fertilizers (manufactured from Floridian and Moroccan PR) to determine if soil pH would affect the requirement for WSP to reach maximum yield. TSP fertilizers were simulated by mixing the fertilizer impurities with MCP to supply approximately 0%, 20%, 40%, 60%, 80%, and 100% of the AOAC-available P as MCP (AOAC, 1999). In a greenhouse study using wheat, the simulated TSP fertilizers required as little as 37% WSP to reach maximum yields when applied at a soil pH of 5.4, whereas at soil pH 6.4 the fertilizers required at least 63% WSP for maximum yields. To achieve 90% of maximum yield, the values were only 23% and 38% for pH 5.4 and 6.4, respectively. The authors stated that the pH dependence suggests that some of the P in the water-insoluble P fractions of TSP fertilizers may be some type of Ca–P compound(s), although no chemical characterization was provided on these compounds.

Prochnow *et al.* (2008) conducted another study with four nonconventional acidulated P sources produced from Brazilian PR. The requirement for WSP was once again P source and pH dependent. At a soil pH of 5.2, the fertilizers required 73–95% WSP to reach the maximum dry-matter yield, while they required 60–86% WSP at pH 6.4. To reach 90% of the maximum yield, all superphosphate fertilizers required <50% WSP (Fig. 14; Table 7). It should be noted that the results show that higher levels of water-insoluble P as compounds of the Fe–Al–P type can be tolerated in acidulated P fertilizers when applied to slightly acid soils than when applied to strongly acid soils, while, as shown by Mullins and Sikora (1995), the opposite was true when the water-insoluble P fraction is composed of forms of Ca–P. It may be noted that the results of several studies consistently show that it is not always necessary to have high water solubility as required by legislation in many countries.

Research has provided already valuable information regarding the possible agronomic use of some nonconventional acidulated P fertilizers.
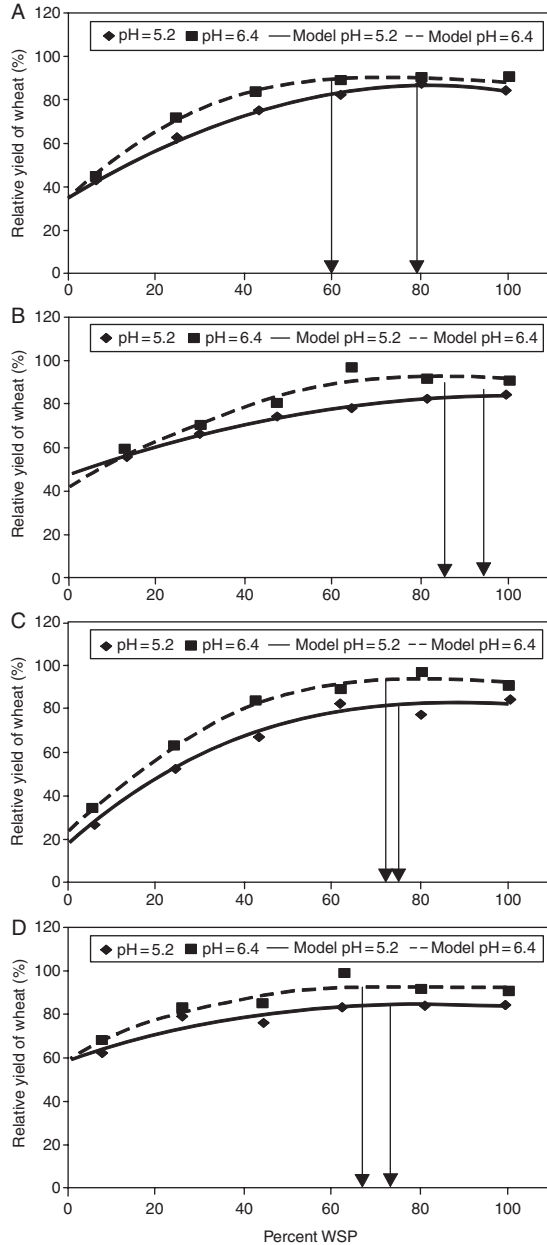
Figure 14 Relative dry-matter yield of 101-day-old wheat plants at initial soil pH values of 5.2 and 6.4, as affected by the percentage of water-soluble phosphorus (WSP) for the P sources (A) triple superphosphate (TSP) produced from Tapira phosphate rock (PR), (B) TSP produced from Jacupiranga PR, (C) low-quality single superphosphate (SSP) produced from Araxa PR, and (D) low-quality SSP produced from Patos de Minas PR, applied at a rate of 40 mg available P kg^{-1} soil. Arrows show the WSP percentage needed to reach the plateau. *Source*: Prochnow *et al.* (2008).

Table 7 Segmented regression models for P sources in each soil pH condition describing the relationship between dry-matter yield of wheat (DMY; Y = g pot^{-1}) or relative yield of wheat (RY; Y = %) and the rate of P applied (X = mg kg^{-1}) for the MCP and relative yield of wheat (RY; Y = %) and the percentage of water-soluble P (X = %) for the P sources TSP1, TSP2, SSP1, and SSP2

| P source[a] | pH | Segmented regression model | | | P rate (mg kg^{-1}) required to reach[b] | | WSP (%) required to reach[c] | |
		Quadratic equation (R^2)	SE[d]	Plateau	Plateau	90% of plateau	Plateau	90% of plateau
MCP–DMY	5.2	$Y = 0.94 + 0.957X - 8.8 \times 10^{-3}X^2$ (0.98)	1.25	26.9	54.3	36.8		
MCP–RY	5.2	$Y = 3.27 + 3.337X - 30.0 \times 10^{-3}X^2$ (0.97)	4.37	93.9	54.3	36.8		
MCP–DMY	6.4	$Y = 0.70 + 1.447X - 19.3 \times 10^{-3}X^2$ (0.97)	1.45	27.8	37.4	25.4		
MCP–RY	6.4	$Y = 2.44 + 5.047X - 67.4 \times 10^{-3}X^2$ (0.95)	5.05	96.9	37.4	25.4		
TSP1–RY	5.2	$Y = 35.44 + 1.249X - 7.9 \times 10^{-3}X^2$ (0.97)	1.57	84.9			79	46
TSP1–RY	6.4	$Y = 34.13 + 1.830X - 15.3 \times 10^{-3}X^2$ (0.96)	2.66	88.8			60	36
TSP2–RY	5.2	$Y = 47.98 + 0.745X - 3.9 \times 10^{-3}X^2$ (0.97)	2.14	83.5			95	49
TSP2–RY	6.4	$Y = 42.97 + 1.161X - 6.8 \times 10^{-3}X^2$ (0.96)	5.04	92.9			86	48
SSP1–RY	5.2	$Y = 17.93 + 1.705X - 11.4 \times 10^{-3}X^2$ (0.97)	3.62	81.6			75	48

SSP1–RY	6.4	$Y = 24.42 + 1.897X - 13.1 \times 10^{-3}X^2$ (0.97)	2.21	93.2	72	46
SSP2–RY	5.2	$Y = 58.76 + 0.683X - 4.7 \times 10^{-3}X^2$ (0.96)	4.02	83.7	73	31
SSP2–RY	6.4	$Y = 60.97 + 0.926X - 6.9 \times 10^{-3}X^2$ (0.95)	5.24	92.1	67	31

[a] P Source: MCP, reagent-grade monocalcium phosphate; TSP1, triple superphosphate produced from Tapira PR; TSP2, triple superphosphate produced from Jacupiranga PR; SSP1, low-quality single superphosphate produced from Araxa PR; SSP2, low-quality single superphosphate produced from Patos de Minas PR.

[b] Rate of P (mg kg^{-1}) needed to obtain the plateau or 90% of the plateau of the segmented model.

[c] Percentage of water-soluble P (WSP) needed to obtain the plateau or 90% of the plateau of the segmented model.

[d] Standard error for comparing predicted values.

Source: Prochnow *et al.* (2008).

As a result, legislation was modified to make the presence of water–insoluble phosphate compounds more flexible. In Europe, the legislation was changed to decrease the requirement for water solubility in TSP. Instead of 93%, the limit was lowered to 85%. Also in Brazil, the SSP water solubility requirement was lowered from 16% to 15%, and new categories of P fertilizers, such as multimagnesium phosphates (MMP) fertilizers, were added to the legislation to legally permit the commercialization of fertilizers containing lower WSP amounts compared to conventional SSP, TSP, MAP, and DAP. MMP fertilizers are P sources containing as low as 50% water solubility in the total amount of P soluble in water and NAC.

It is necessary to recognize that a great variety of new, nonconventional acidulated P products may be offered in the future due to differences in PR chemical composition and process of production. An example of differences in chemical composition of SSP sources, and how to evaluate on a percent basis the different compounds in this type of fertilizer, can be found in the publication of Prochnow *et al.* (2003c). Accessing this type of information for the various fertilizers will be essential. Due to distinct chemical compositions, the fertilizers will have to be tested and approved individually. A better understanding of how the water-insoluble P compounds will form, the final chemical composition of the P fertilizers, and also how these different nonconventional acidulated P fertilizers will react in the soil is essential for P fertilizer producers, legislators and final users to obtain and manage these heterogeneous fertilizers in a cost-effective manner. Only agronomic research will provide the necessary guidance. Better utilization of PR is anticipated as a result of this type of research.

5. New Granular Nitrogen and Phosphorus Fertilizers Containing Sulfur Nutrient

Soil S deficiency has become a major problem for crop production in many countries due to the extensive and popular use of high-analysis NP fertilizers, for example, urea, MAP, DAP, and TSP that contain little or no S nutrient. Because elemental S (ES) is almost 100% S, incorporation of ES will not significantly decrease N and P contents of these NP fertilizers compared to the incorporation of SO_4–S, such as $(NH_4)_2SO_4$ or $CaSO_4$. Thus, some fertilizer companies have been marketing products by incorporating ES to NP fertilizers. For example, ES–enriched urea fertilizer was introduced to the market over 25 years ago. The product is manufactured by injecting molten ES into liquid urea and prilling the melt; it contains 36% N and 20% S. Boswell and Friesen (1993) provided a comprehensive review on the use of ES fertilizers, including effects of incorporation of ES into NP fertilizers on crops and pastures. The present chapter, therefore,

will discuss only the most recent developments in new NP fertilizers containing ES.

It is known that ES is not plant available unless it is oxidized to SO_4–S by soil microbes, and the rate of S oxidation greatly depends on the particle size of ES (Boswell and Friesen, 1993). For this reason, some fertilizer companies have been developing processes to micronize the particle size of ES being incorporated into granular NP fertilizers. The new idea assumes that once the fertilizer granules dissolve and ES disperses back to the original fine particle size, it may rapidly enhance rate of S oxidation in soils. However, it should be pointed out that there is still the so-called ''locality'' effect; that is, all the very fine ES particles will still be localized at the applied site when the granule disintegrates. The rate of S oxidation will still be slowed due to limited contact between ''clustered'' ES particles and soil microbes, unless the ES particles are thoroughly mixed with the soil. Figure 15 shows little S oxidation of granulated ES with bentonite clay (90% ES) during incubation compared to powdered ES in a sandy soil, despite the fact that the granular ES disintegrated and ES particles dispersed into the soil (S. H. Chien, unpublished data). Chien et al. (1987) reported that the grain yield of flooded rice decreased from 96% with powdered ES to 58% with a granular urea–ES melt when surface applied with respect to that of gypsum. When all S sources were incorporated, the effectiveness was 87% with powdered ES and 61% with granular urea–ES melt. Therefore, S-enriched NP granular fertilizers may not provide adequate initial S nutrient for the first crop. However, once the soil is mixed (e.g., plowing)
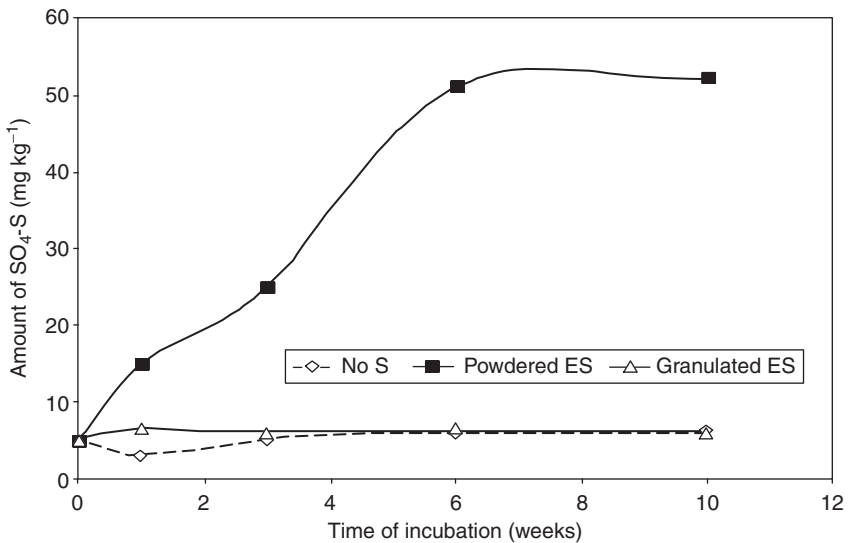

Figure 15 Amounts of SO_4–S obtained with check (no S), powdered ES, and granulated ES with bentonite. *Source*: S. H. Chien (unpublished data).

between the first and second crops, ES applied to the first may become available to the second crop due to S oxidation by mixing ES with the soil, as reported by Chien *et al.* (1988b). In this study, incorporation of powdered ES was as effective as gypsum for flooded rice, whereas deep-placed powdered ES was ineffective due to a lack of S oxidation under reduced soil conditions. The soil was subsequently mixed after the first rice crop and the results showed that both previously deep placed and incorporated powdered ES were equally effective as gypsum for the second flooded rice crop.

The negative "locality" effect of granular S-carrier products on S oxidation when incorporated can be seen in Fig. 16 as reported by Friesen (1996). In this study, ES was cogranulated with TSP, DAP, urea, or bentonite. All granules had the same size (1.68–3.36 mm diameter) and contained fine ES (<0.15 mm) homogeneously mixed throughout each product. The results showed that all granular ES–carrier products were much less effective than gypsum in dry-matter yield of maize, despite all the granules of disintegrated ES particles being dispersed in the soil. Furthermore, P carriers (TSP, DAP) were significantly better than a non-P carrier (urea), which was better than an inert carrier (bentonite), presumably attributable to the effect of P and N nutrients on S-oxidizing microorganisms.

Surface application of granular S-enriched NP fertilizers may perform better than incorporation because rainfalls may break up the granules and disperse S particles, which may enhance S oxidation. However, this still may
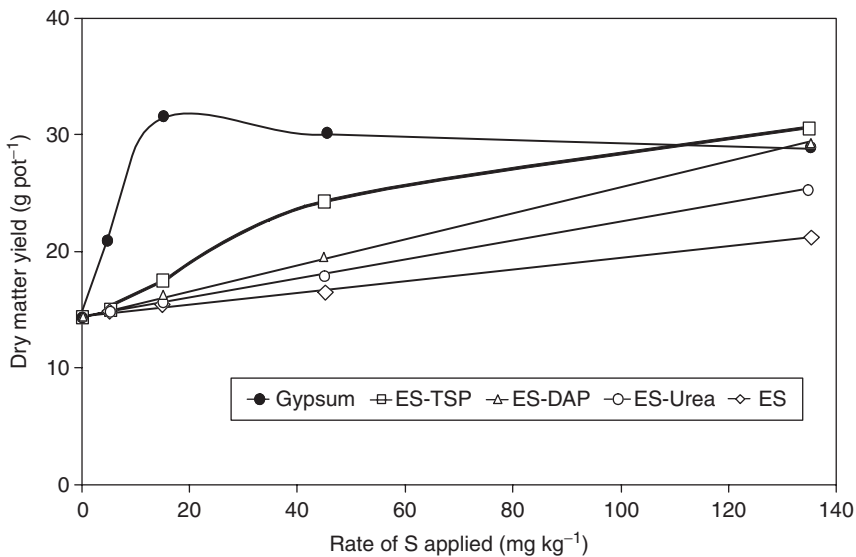

Figure 16   Dry-matter yield of maize obtained with different granular S fertilizers. All the S fertilizers had the same granule size (1.68–3.36 mm diameter). *Source*: data adapted from Friesen (1996).

Table 8 Dry-matter yield of maize obtained with different granular S fertilizers during consecutive maize cropping

	Dry-matter yield of maize (g pot^{-1})[a]				
Granular S source	First	Second	Third	Fourth	Fifth
No S	10.6b	1.6c	31.0a	4.1c	5.7b
ES–bentonite	10.6b	2.1c	31.5a	5.3c	8.4ab
(ES + AS)–MAP[b]	13.4a	14.2b	33.1a	17.1a	10.1a
AS	13.8a	17.8a	27.2a	12.8b	5.2b

[a] Means followed by the same letter are not significantly different at $p < 0.05$.
[b] ES, elemental S; AS, ammonium sulfate. S ratio of ES:AS = 50:50.
Source: Prochnow *et al*. (2007).

not be effective for the initial S effect for deep-rooted cereal crops, for example, maize, sorghum, etc., usually the consequence of inadequate downward movement of SO_4–S to plant roots caused by restricted rainfall (Boswell and Friesen, 1993). The exception may be grazed pastures with shallow-rooted crops. Grazing may also affect the rate of S oxidation, probably attributable to the roaming of grazing animals, which may help break up and disperse the S-enriched NP granules to facilitate S oxidation. To overcome the relatively low agronomic effectiveness of granular ES-enriched NP fertilizers due to slow S oxidation, these fertilizers may be required to include some SO_4–S for early plant establishment. In other words, SO_4–S can provide for early S requirement, while ES can provide available S later after S oxidation to SO_4–S in the soil. The concept is similar to that of mixing WSP and PR to enhance the agronomic effectiveness of PR, as discussed previously. In a recent greenhouse study, Prochnow *et al*. (2007) compared granular AS, granular MAP containing 7.5% S as AS and 7.5% as ES, and ES granulated with bentonite (90% S) as the S source for five consecutive maize crops. Table 8 shows that granular S-enriched MAP was as effective as or better than AS, whereas granular ES was not effective due to slow S oxidation of ES in increasing the dry-matter yield of maize. Field trials of these new granular NP fertilizers containing ES or a mixture of ES and SO_4–S are needed to assess factors affecting their agronomic potential to provide plant-available S nutrient.

6. Cadmium Uptake by Crops from Phosphorus Fertilizers

Cd is one of the heavy metals that may be potentially toxic to human health. There is an increasing concern over the use of Cd-containing P fertilizers for crop production because Cd uptake by plants can be one

possible avenue of Cd entry into the human food chain through consumption of plants directly or indirectly by man.

Depending on the sources of PR, Cd content associated with apatite minerals can vary widely. If a PR source contains a significant amount of Cd, a significant amount of Cd can be found in SSP or H_3PO_4 upon acidulation of the PR with H_2SO_4. If the H_3PO_4 is used to acidulate the same PR, the resultant TSP would have a high Cd content. Ammoniation of the Cd-containing H_3PO_4 would also result in Cd-containing DAP and MAP.

6.1. Effect of acidulation levels of phosphate rock on cadmium uptake by crops

A study by the IFDC showed that Cd uptake by upland rice was increased by raising the degree of acidulation of Togo PR that contained a significant Cd content (Iretskaya *et al.*, 1998). The results showed that Cd concentration in upland rice grain was 0.051 μg g^{-1} Cd with 50% acidulation with H_2SO_4, compared to 0.114 μg g^{-1} Cd with 100% acidulation, whereas the two P sources produced the same rice grain yield (Table 9). Cd was associated with Ca and P in the apatite structure based on the data of P and Cd uptake (Iretskaya *et al.*, 1998). The study also showed that a high Cd-containing reactive North Carolina PR was agronomically as effective as fully acidulated SSP produced from the same PR in increasing rice grain yield, but Cd uptake was lower from the directly applied PR (Table 9). The results suggest that if PR and PAPR are as agronomically effective as fully acidulated P sources, the former may also contribute less to Cd uptake by crops than the use of WSP sources.

Table 9 Upland rice grain yield and Cd uptake by grain from various P sources applied at 200 mg kg^{-1} P to Wavely soil (pH 5.6)

P source[a]	Cd rate added (μg g^{-1})	Grain yield[b] (g pot^{-1})	Uptake of Cd by grain[b] (μg pot^{-1})	Concentration of Cd in grain[b] (μg pot^{-1})
NC–PR	70.5	25.3a	1.68b	0.066b
NC–SSP	79.0	24.5a	3.25a	0.135a
Togo–PAPR	57.8	27.6a	1.44b	0.051b
Togo–SSP	69.3	25.6a	2.88a	0.114a

[a] NC = North Carolina; PAPR = PR acidulated at 50% with H_2SO_4; SSP = 100% acidulation of PR with H_2SO_4.
[b] Means followed by the same letter in each column are not significantly different at $p < 0.05$.
Source: Iretskaya *et al.* (1998).

6.2. Cadmium uptake by crops from granulated versus bulk-blended phosphorus and potassium fertilizers

Recently, field experiments conducted in Australia have shown that increased chloride (Cl) content in irrigated waters would have a high risk of producing crops with high Cd concentrations. These researchers have proposed that Cl ions form relatively strong complexes with Cd^{2+} in the form of $CdCl^{1+}$ and $CdCl_2^0$ in solution, and results in enhanced Cd uptake (McLaughlin et al., 1997; Smolders et al., 1998). Based on these observations, it would be expected that if a WSP fertilizer contains a high Cd content, granulation of this WSP fertilizer with KCl may result in a higher Cd uptake by crops compared to the same, but bulked-blended, PK fertilizer. The explanation is that, in the granulated PK fertilizers, KCl- and Cd-containing P fertilizers are in the same granule and thus are in close contact, thereby increasing the possibility of forming $CdCl_2^0$ and $CdCl^{1+}$ complexes. Likewise, it would be less likely that the complexes would form when KCl and Cd–containing P granules are physically separated in bulk-blended PK fertilizers.

The above hypothesis was tested and confirmed by Chien et al. (2003) in a preliminary greenhouse study. In this study, all P and K sources produced by either granulation or bulk blending had the same granule size (1.68–3.36 mm diameter). Upland rice and soybean were grown to maturity and *Brachiaria* grass was cut four times in an acidic soil (pH 5.2). The results showed that the agronomic effectiveness in increasing crop yield was the same with Cd-containing SSP and the reagent–grade MCP (0% Cd), whether granulated or bulk blended with KCl (Tables 10–12). Concentrations of Cd in plant tissue samples of all crops were much lower for MCP than for SSP. In all the plant tissue samples, except grain samples of upland rice, Cd concentrations obtained with granulated (SSP + KCl) fertilizers were significantly higher than that with bulk-blended (SSP) + (KCl) fertilizers. Bulk blending of Cd-containing P fertilizers with KCl can thus reduce Cd uptake by crops compared to the same, but granulated, PK

Table 10   Grain yield of upland rice and Cd concentrations in rice, grain, and straw

		Cd concentration[b] (mg kg^{-1})	
PK source	Grain yield[a,b] (g pot^{-1})	Grain	Straw
Granulated (SSP + KCl)	22.6a	0.13a	1.53a
Bulk–blended (SSP) + (KCl)	23.1a	0.12a	1.18b
Bulk–blended (MCP) + (KCl)	25.1a	0.01b	0.20c

[a] Grain yield of check (no P and K = 1.2 g pot^{-1}).
[b] Means followed by the same letter within the columns are not significantly different at $p < 0.05$.
Source: Chien et al. (2003).

Table 11 Grain yield of soybean and Cd concentrations in soybean, grain, straw, and root

| PK source | Grain yield[a,b] (g pot^{-1}) | Cd concentration[b] (mg kg^{-1}) | | |
		Grain	Straw[c]	Root
Granulated (SSP + KCl)	27.1a	0.54a	1.66a	1.34a
Bulk-blended (SSP) + (KCl)	29.5a	0.35b	0.88b	0.99b
Bulk-blended (MCP) + (KCl)	23.8a	0.06c	0.26c	0.27c

[a] Grain yield of check (no P and K) = 1.4 g pot^{-1}.
[b] Means followed by the same letter within the columns are not significantly different at $p < 0.05$.
[c] Combined leaf, stem, and pod samples.
Source: Chien *et al.* (2003).

Table 12 Dry-matter yield and Cd concentration of *Brachiaria* grass

PK source	Dry-matter yield[a,b] (g pot^{-1})	Cd concentration[b] (mg kg^{-1})
Granulated (SSP + KCl)	43.9a	0.24a
Bulk-blended (SSP) + (KCl)	42.8a	0.21b
Bulk-blended (MCP) + (KCl)	41.5a	0.08c

[a] Dry-matter yield of check (no P and K) = 4.1 g pot^{-1}.
[b] Means followed by the same letter within the columns are not significantly different at $p < 0.05$.
Source: Chien *et al.* (2003).

fertilizers. Although PK sources, instead of NPK sources, were used in the study, it is expected that inclusion of N will not affect the results. If this is proven to be true, the process of bulk blending, compared to that of granulation in decreasing Cd uptake, would also apply to NPK compound fertilizers. Due to the simplicity of the bulk-blending process and its relatively low investment and operating cost, bulk blending has become popular worldwide. This is an area that some researchers and fertilizer companies may want to pursue for future production and use of NPK compound fertilizers, and at the same time, minimize Cd uptake by crops.

7. General Conclusions

Fertilizers, whether from inorganic or organic sources, will be continuously used to increase and sustain crop production in order to meet the demand of the growing population worldwide in the future. At the same

time, however, the potential impacts of fertilizer use on environmental quality due to inappropriate application of fertilizers should also be addressed. Research and development shall continue to pursue new alternative innovative technology in terms of fertilizer production and use to achieve these goals, that is, sustaining crop production and minimizing environmental impacts.

Another issue that should be pointed out is that the prices of conventional fertilizers have steadily increased. For example, urea increased from US $277/t in early 2007 to US $672/t in early 2008, and DAP increased from US $252/t to US $1230/t (IFDC, 2008). The use of the nonconventional fertilizers discussed in this chapter may result in an increased relative economic benefit with respect to the use of conventional fertilizers in terms of saving fertilizer cost, enhancing nutrient efficiency, or increasing crop yield. More detailed economic analysis is needed to address this issue.

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