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Abstract

Urea has become the leading form of N fertilizer worldwide. Historically there has been concern about biuret formed during the manufacturing of urea fertilizer and the potential adverse effect of biuret on plant growth. In this paper, the fate of biuret in soils and its phytotoxicity is reviewed. Biuret is mineralized by many soil microorganisms, but the process is much slower than for urea. Excessively high biuret concentrations can damage seedlings and, like urea, should not be placed in close proximity to germinating seeds. Crop tolerance to biuret varies according to the plant species, soil conditions, fertilizer placement, and method of application. Biuret applied to soil or to plant foliage interferes with N metabolism and protein synthesis. The current standards in the fertilizer industry supply adequate protection against biuret-induced damage to crops.

Introduction

There are many reasons for the rapid rise in the relative importance of urea as the leading form of N fertilizer (Fig. 1). Its high N content (46% N) makes it economical to produce, transport, and distribute throughout the world [Harre and Bridges, 1988]. However, the wide acceptance of urea fertilizer is a relatively new phenomenon. Early users of urea had to learn to manage two problems associated with its use. First, when

urea is surface-applied to soils, considerable amounts of the applied N may be lost through NH_3 volatilization, with an accompanying loss in fertilizer value [Gasser, 1964]. Second, early methods of manufacturing urea fertilizer often resulted in relatively high concentrations of biuret which are potentially harmful to plant growth [Starostka and Clark, 1955].

When applied to soil, urea undergoes a series of chemical, physical, and biological transformations following hydrolysis by the enzyme urease [Bock and Kissel, 1988]. After this occurs, the urea-derived N is readily available for plant uptake. In addition to soil application, urea solutions are widely used as a foliar N fertilizer. The use of urea as a foliar spray is attractive due to its non-ionic composition and high N content [Wittwer et al., 1963]. Solutions of urea form a relatively low osmotic nutrient source which reduces the risk of foliar scorch due to salt damage, compared with many other N sources.

When urea is heated near or above its melting point (132°C), NH_3 is slowly evolved and several different substances, including biuret, are formed (Fig. 2). Conditions under which biuret and other urea derivatives are formed during the fertilizer manufacturing process were discussed by Shen [1959] and Kaasenbrood et al. [1963].

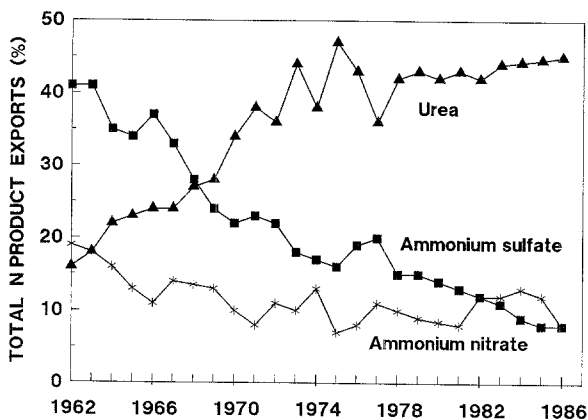


Fig. 1. World exports of selected N fertilizers (adapted from Harre and Bridges, 1988).

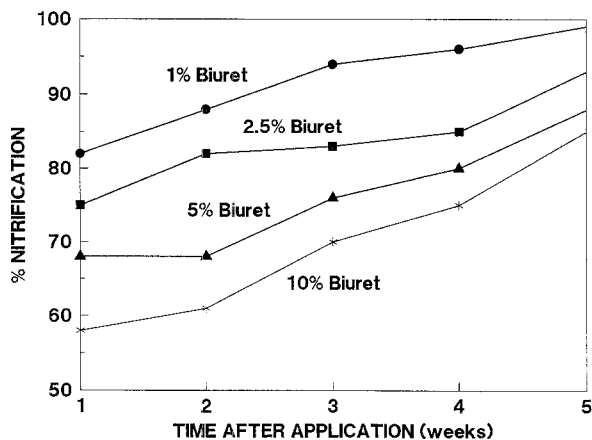


Fig. 3. Relative nitrification of urea containing various concentrations of biuret compared with urea alone (adapted from Sahrawat, 1977).

and development [Brage et al., 1960]. This was first demonstrated by Smika and Smith [1957] who found that soaking seeds in a urea + 2.5% biuret solution greatly reduced wheat germination compared with seeds that had been soaked in a urea-containing solution alone. They also found that the presence of biuret increased the time required for emergence. However, Hunter and Rosenau [1966] soaked maize seeds in biuret-containing urea solution and found that germination was not affected, except at very high biuret concentrations (>5% biuret). They observed that seeds soaked in a biuret solution appeared to germinate normally, but the subsequent growth processes were impaired. As the solution biuret concentrations increased to 10%, toxicity symptoms became more severe, ranging from rolled, twisted leaf tips to darkening of the radicle and coleoptile, and death of the seedling before emergence from the sand. It appears that biuret enters the germination seed or the seedling roots and obstructs metabolic processes in some way as to prevent normal development.

The seedling damage caused by urea + biuret fertilizer placed with the seed in soil may partially be due to free NH_3 liberated following urea hydrolysis. Hunter and Rosenau [1966] reported that NH_3 evolved from urea fertilizer was toxic to nearby seeds, but that no NH_3 was evolved from biuret when applied alone. This demonstrates that urea may have harmful effects on

seedling development independent from biuret damage.

The placement of the urea + biuret fertilizer with respect to the seed is important in determining biuret toxicity to seedlings. For example, Haque et al. [1970] placed urea (containing 1.5% biuret) either with maize seeds, 2.5 cm from the seed row, or mixed into the surface 5 cm of soil. Yield reductions were only found when the biuret-contaminated urea was placed in direct contact with the seed, and this damage may have been caused by the urea alone. Field research conducted on the effects of biuret on the germination of barley and maize showed that plant populations were reduced 30% when 22 kg urea-N/ha containing 2.5% biuret was applied with the seed [Brage et al., 1960]. However, 180 kg urea-N/ha containing 10% biuret caused no damage to these same crops when applied to the soil surface.

Researchers have questioned whether the concentration of biuret in the urea fertilizer or the total quantity of biuret applied is the critical factor influencing biuret toxicity to seedlings. Smika and Smith [1957] concluded that the critical factor in determining the harmful effects on seedling emergence was the biuret concentration of the urea fertilizer. They found that applying 4 kg urea-N/ha with 15% biuret caused a complete loss of germination. However, applying the same total quantity of biuret with urea fertilizer containing a lower biuret concentration always allowed some germination to occur.

It is evident that biuret can cause damage to seedlings when placed in direct contact with seeds. The severity of biuret damage to seedlings depends on the sensitivity of the crop, the total amount and concentration of biuret applied, and the fertilizer placement. Thus, urea which contains biuret should be used like biuret-free urea and not placed directly with the seed. If the fertilizer is separated from the seed by a small volume of soil, toxicity concerns are greatly diminished.

Soil application of biuret

Considerable effort has been spent to determine the maximum biuret concentration tolerable in urea fertilizer before crop production suffers.

The Tennessee Valley Authority (TVA) Technical Library lists over 150 papers on the subject of biuret in urea fertilizer published between 1954 and 1981 [TVA, 1981]. Unfortunately, many of these studies are difficult to compare due to the widely varying conditions under which the tests were performed. Since crop sensitivity to biuret depends on many factors such as plant species, soil properties, method and timing of fertilizer application, and both the concentration and total amount of biuret applied, it is difficult to clearly define any exact permissible limits. However, some general guidelines become clear when this research is viewed as a whole.

Many crops can tolerate large amounts of biuret applied with urea if it is not in direct contact with the seed (Table 1). A general guideline for safe use of urea applied to soil would permit a maximum 2% biuret [Mithyantha et al., 1977]. Many crops are not adversely affected until biuret concentrations far exceed this level. The effort by the fertilizer industry to keep biuret concentrations in urea less than 0.8% may be overly restrictive for N fertilizer intended for soil application. Excessive concern regarding the biuret content of urea fertilizers can lead to increased production costs and possible oversight of other important product quality factors. The

Table 1. Examples of allowable biuret concentrations for crops fertilized with soil-applied urea

Crop		Damaging biuret concentration	Reference
Bermuda grass	<i>Cynodon dactylon</i> Pers.	>20%	Jackson & Burton [1959]
Barley	<i>Hordeum vulgare</i> L.	>2%	Kondrat'ev & Podkolzina [1967]
Celery	<i>Apium graveolens</i> Mill.	>5%	Drinkwater & Pickering [1958]
Citrus		<2.5%	Jones et al. [1955]
Cotton	<i>Gossypium hirsutum</i> L.	>10%	Starostka & Clark [1955]
Cotton		>2%	Kondrat'ev & Podkolzina [1967]
Flax	<i>Linum usitatissimum</i> L.	>2%	Luzzati [1970]
Maize	<i>Zea mays</i> L.	>4%	Abdel-Hadi et al. [1983]
Maize		>10%	Starostka & Clark [1955]
Maize		>15 kg/ha	Gadet et al. [1959]
Maize		>5%	Drinkwater & Pickering [1958]
Maize		>2%	Kondrat'ev & Podkolzina [1967]
Oat	<i>Avena sativa</i> L.	>10%	Starostka & Clark [1955]
Oat		>2%	Luzzati [1970]
Pasture grass		>4.6%	Devine & Holmes [1963]
Pepper	<i>Capsicum</i> spp.	>5%	Drinkwater & Pickering [1958]
Potato	<i>Solanum tuberosum</i> L.	4 kg/ha	Gadet et al. [1959]
Potato		>1%	Sharma et al. [1975]
Potato		>1.3%	Singh et al. [1979]
Potato		<3.7%	Murphy & Goven [1966]
Potato		>2%	Kondrat'ev & Podkolzina [1967]
Rice	<i>Oryza sativa</i> L.	>4%	Abdel-Hadi et al. [1983]
Rice		>1.5%	Jain et al. [1972]
Rice		<2%	Bhargava [1978]
Rye	<i>Secale cereale</i> L.	<2%	Kondrat'ev & Podkolzina [1967]
Snapbean	<i>Phaseolus vulgaris</i> L.	>5%	Drinkwater & Pickering [1958]
Sugar cane	<i>Saccharum officinarum</i> L.	>2.5%	Innes [1960]
Sugar Beet	<i>Beta vulgaris</i> L.	>2%	Kondrat'ev & Podkolzina [1967]
Sunflower	<i>Helianthus annuus</i> L.	<3%	Mayr & Barbier [1963]
Tobacco	<i>Nicotiana tobacum</i> L.	<3%	Mayr & Barbier [1963]
Tomato	<i>Lycopersicon esculentum</i> Mill.	>5%	Drinkwater & Pickering [1958]
Tomato		>10%	Starostka & Clark [1955]
Tomato		>5%	Tanew et al. [1973]
Tomato		>2%	Kondrat'ev & Podkolzina [1967]
Wheat	<i>Triticum vulgare</i> L.	<4%	Abdel-Hadi et al. [1983]
Wheat		>6 kg/ha	Gadet et al. [1959]
Wheat		>2%	Kondrat'ev & Podkolzina [1967]

majority of crops [with a few possible exceptions such as citrus (*Citrus* spp.) and pineapple (*Ananas comosus* (L.) Merrill)] are likely capable of utilizing urea fertilizer with a biuret content higher than is generally found in most commercial urea fertilizers (0.8 to 0.9% biuret).

The soil properties on which the biuret-fertilized crop is grown are important in determining potential toxicity. Biuret is not retained in soil [Ogata, 1962] and is easily leached [Gadet et al., 1959]. Plants are generally less sensitive to biuret when it is applied to soils containing appreciable amounts of clay or organic matter or of low pH [Jurkowska, 1967].

There have been questions regarding the specific toxic agent associated with biuret in the root zone. It has been considered that cyanuric acid or NO_2^- may accumulate following addition of biuret to soil. Terman et al. [1964] mixed cyanuric acid with soil and found that although it was temporarily harmful to the growth of bermuda grass, it later became a good nutrient source. Hunter and Rosenau [1966], however, observed no damage to maize seedlings from cyanuric acid when it was placed 4–5 cm from the germinating seed. Nitrite that has accumulated in soil following biuret decomposition may also be harmful to plants [Goyal and Huffaker, 1984]. Although these compounds may be injurious to plant growth, Hunter and Rosenau [1966] demonstrated in sand culture experiments that biuret by itself is detrimental to plant growth.

Whether the concentration of biuret in the fertilizer urea or the total quantity of biuret added determines the threshold toxicity to plants has not been completely resolved.

Foliar application of biuret

Researchers first identified the harmful effects of biuret in urea solutions for foliar application to plants when injury symptoms were noted on avocado (*Persea americana* Mill.) [Hass and Brusca, 1954], citrus [Jones, 1954] and pineapple [Sanford et al., 1954]. Since that time, considerable effort has been devoted to discovering the safe threshold concentrations of biuret in urea sprays. As with soil applications of biuret, some plant species are more tolerant of biuret than others, but the allowable concentration of biuret

in urea intended for foliar sprays is much lower than for soil application.

Foliar application of urea can be extremely beneficial in some circumstances for plants. For example, the quality of citrus fruit may be improved with foliar N applications beyond that possible with soil fertilization alone. Jones and Embleton [1957] recommended that the biuret concentration of urea spray for citrus not exceed 0.25%, or 'yellow leaf' symptoms would appear 2 to 8 weeks after application. This concentration of biuret in urea (0.25%) has become a 'safety' guideline for foliar sprays for many crops.

Gadet et al. [1959] illustrated the wide range of tolerance that different plant species have to biuret. They reported that foliar sprays should contain <150 mg biuret/L to avoid damage to grapes (*Vitis* spp.) and pears (*Pyrus communis* L.). Peach (*Prunus persica* (L.) Batsch.) trees could tolerate 400 mg biuret/L and wheat up to 5000 mg biuret/L in foliar sprays without visible damage.

Following foliar application of urea containing 0.5% biuret to potatoes, Sharma et al. [1975] observed visual symptoms of yellow leaves, upward rolling and necrotic leaf margins. Similar biuret-damage symptoms are typical in perennial crops. Impey and Jones [1960] reported that when citrus developed the yellow leaf symptom following application of a biuret-containing spray, the yellow leaves never regained their normal color, although the new flush of growth appeared normal.

Jain et al. [1972] conducted an experiment to examine the interaction between biuret applied to soil and biuret which was foliar-applied to rice. They found no adverse effects resulting from soil application of 50 kg urea-N/ha containing 1.5% biuret. However, when an additional 30 kg urea-N/ha was foliar-applied, even the presence of 0.3% biuret caused plant damage. Foliar application of biuret delayed ear emergence, the number of tillers, ear length, number of grains per ear, and the yield of both straw and grain. However, there was no interaction between soil and foliar applications of biuret. Tolerance of foliar-applied biuret generally is much lower than soil applications of biuret, because the modifying effects of soil are not present and

the applied biuret is absorbed by the plant over a short period of time.

Because biuret is not easily metabolized by plants, repeated spray applications of urea and biuret may have a cumulative effect, especially with perennial crops. Jain and Verma [1974] applied 20 kg urea-N/ha (containing from 0 to 9% biuret) to rice foliage in four weekly sprays. Although both growth and yield were adversely affected by biuret (Fig. 4), no visual symptoms of biuret toxicity were observed even at biuret concentrations up to 9%. Other researchers have, at times, failed to observe toxicity symptoms following application of concentrated biuret solutions [Ehrendorfer, 1962]. This may be due to the relatively low total quantity of biuret applied at one time, rather than the biuret concentration of the urea fertilizer. For example, at the highest biuret concentration (9% biuret), Jain and Verma [1974] only applied 3.9 kg biuret/ha and observed no visible toxicity symptoms, although yields were greatly reduced.

Bhargava and Ghosh [1976] applied 60 or 120 kg urea-N/ha containing from 0 to 4% biuret to wheat. Two-thirds of the N was applied to the soil and the remaining one-third portion was applied to foliage in four increments. The magnitude of the adverse effect of biuret on the crop was nearly the same for both rates of N application, even though at a given biuret concentration, the 120 kg N/ha treatment received twice the total amount of biuret than the 60 kg N/ha treatment. These results support the hypothesis that the concentration of biuret may be more im-

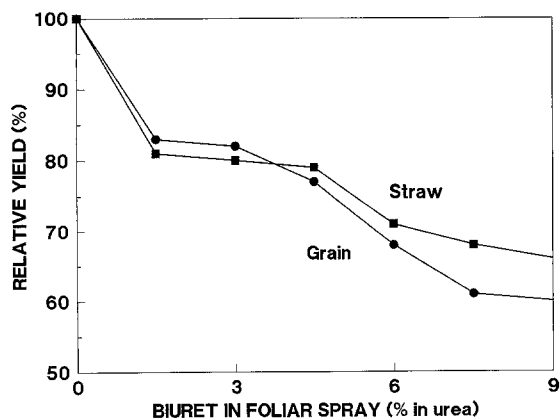


Fig. 4. The effect of foliar applications of biuret in urea on the growth and yield of rice (adapted from Jain and Verma, 1974).

portant in predicting potential damage than the total quantity of biuret applied.

Effects of biuret on plant metabolism

Plants seem unable to metabolize biuret [Clark and Wallace, 1961]. Following foliar application of a biuret-containing solution, biuret was still present in the leaves of orange trees after 8 months [Impey and Jones, 1960]. Soil-applied biuret similarly accumulates in plants for long periods of time. While the precise mechanism of biuret damage to plants is still unclear, considerable evidence of its effects on plants has been gathered.

Webster et al. [1957] studied the effect of biuret on protein synthesis in *Xanthium pennsylvanicum* leaves. They found that biuret does not promote leaf protein decomposition, but inhibits protein formation. Ogata [1962] confirmed that the presence of biuret in plants inhibits protein synthesis. It is interesting that a compound so closely related to urea is harmful to so many plant species.

Biuret in plants interferes with N metabolism. Impey and Jones [1960] found for oranges, the apical portion of the leaf was the most sensitive to biuret damage. In damaged leaves, they found lower total N, lower concentrations of protein-N, lipid-N, and chlorophyll than in healthy leaves. They measured higher concentrations of water-soluble N and total amino-N in these same damaged leaves. Similar depressing effects of N uptake resulting from biuret application have been reported by other researchers [Tanev, 1979; Singh et al., 1979].

When biuret was the sole N source for tomatoes growing in hydroponic culture, significant changes in enzyme activity occurred [Krisper et al., 1972]. The activity of peroxidases, esterases, and acid phosphatases in the roots were increased by biuret nutrition. In the shoots, the activity of some enzymes was diminished, but the activity of leucine aminopeptidase was enhanced. These results suggest that biuret may influence proteolysis and protein synthesis. They also noted a marked increase in urease activity in both roots and shoots in the biuret-treated plants. Shaw and Kistiakowsky [1950] observed that biuret was hydrolyzed by urease. Perhaps

the ability of a particular plant species to internally produce urease is related to its tolerance to biuret.

Although biuret in urea can be damaging to plants when present at high concentrations, modern manufacturing processes have greatly reduced the extent of this problem. Early urea fertilizer manufacturing facilities often produced urea containing >5% biuret. Modern urea fertilizer plants typically produce urea containing <0.5% biuret. This relatively low biuret concentration should be safe for the majority of agricultural uses. However urea containing especially low concentrations of biuret may be required for foliar fertilization of some sensitive crops.

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