Nitrogen Availability of Oxamide and Ammonium Nitrate Limestone

KARL DILZ
Dutch Nitrogen Fertilizer Industry, Wageningen, The Netherlands
and
JAN J. STEGGERDA
Central Laboratory, Staatsmijnen in Limburg, Geleen, The Netherlands

The low water solubility and slow hydrolysis of oxamide would indicate that it is a slow acting nitrogen fertilizer. Nitrogen availability from fine oxamide as compared with that from a mixture of ammonium nitrate and limestone (nitrolime) has been examined in pot trials in the open air on perennial ryegrass, flax, and spinach as test plants. Both rate of release and recovery of nitrogen were equal for the two fertilizers. However, especially in the case of spinach, a striking difference in physiological action could be observed. Nitrolime-fed spinach and perennial ryegrass were surprisingly stimulated both in dry-weight production and in nitrogen uptake by additional $CaSO_4$. An explanation for this phenomenon cannot be given. Oxamide is now far too expensive to compete with current nitrogen fertilizers; this substance might be, however, of interest for further research on nitrogen nutrition of plants.

Both in agriculture and horticulture there is a demand for nitrogen fertilizers from which nitrogen is gradually released in a form permitting it to be taken up by plants. Urea-formaldehyde condensates are being introduced as slow-acting fertilizers (*1*), but these materials cannot meet the nitrogen requirement of fast-growing crops, the nitrogen recovery being very low. Considering its low water solubility and slow hydrolysis to ammonium-oxalate, oxamide could be expected to be really slow-acting.

Results of pot experiments are presented in which the action of oxamide as a nitrogen fertilizer was compared with that of a mixture of ammonium nitrate and limestone (nitrolime), the latter being the most common nitrogen fertilizer in The Netherlands.

Oxamide, Preparation and Properties

Oxamide ($NH_2—C(=O)—C(=O)—NH_2$), the diamide of oxalic acid is a white, crystalline substance containing 31.8% nitrogen. Its solubility in water is very low, varying from 0.04 gram at 7° C. to 0.6 gram at 100° C. per 100 grams of water. As a consequence, oxamide is not hygroscopic. Both under acid and alkaline conditions, oxamide is hydrolyzed to ammonium oxalate. Its melting point is 420° C., but at temperatures above 230° C. oxamide decomposes into cyanogen ($N{\equiv}C-C{\equiv}N$) and water.

Oxamide can be prepared by the following reactions: by heating ammonium oxalate at 150° to 280° C.

$$H_4N—O—C(=O)—C(=O)—O—NH_4 \rightarrow H_2N—C(=O)—C(=O)—NH_2 + 2\ H_2O$$

by hydrolysis of cyanogen

$$N{\equiv}C—C{\equiv}N + 2\ H_2O \rightarrow H_2N—C(=O)—C(=O)—NH_2$$

Oxamide is not produced on a large scale. If it is to be used as a fertilizer, lowering of production costs seems to be essential. Perhaps the hydrolysis procedure may be of some value in this respect. Cyanogen can be prepared by oxidizing HCN; production costs of HCN-nitrogen are five times higher than those of NH_4-nitrogen. Consequently, as long as oxamide is produced on an HCN-basis, it will inevitably be more expensive than current nitrogen fertilizers. Cyanogen, however, can be prepared directly from N_2 and a carbon-containing compound. In the past, much attention has been paid to this procedure (*2*). If better yields could be obtained with this cyanogen synthesis, the position of oxamide in relation to conventional fertilizers could be greatly improved.

The oxamide, used in the authors' experiments, was made by reaction of pure dimethyloxalate with 25% NH_3 solution at 50° C.; the precipitate was filtered, washed with water and acetone, and dried with air at room temperature. The product was analyzed for C, H, and N. The results were: C: 27.4% (theoretical 27.3%); H: 4.64% (theoretical 4.55%); N: 31.4% (theoretical 31.8%).

In the pot experiments, this oxamide was compared with nitrolime (20.5% N). The oxamide and nitrolime were ground in a mortar and had an average grain size of 5 to 10 microns.

Description of Pot Experiments

In Experiment I, the release of nitrogen from oxamide as compared with that of nitrolime was estimated from nitrogen uptake by perennial ryegrass during a 3-month growth period.

In Experiment II, the effect of oxamide on three different plant species was compared with that of nitrolime.

Experimental

Experiment I. The trials were conducted in duplicate in Mitscherlich pots containing 6 kg. of sandy soil (pH 5.5). As a basic dressing, 3 grams of superphosphate (corresponding to 0.6 gram of P_2O_5) and 3 grams of "patentkali" (potassium magnesium sulfate, corresponding to 0.8 gram of K_2O and 0.3 gram of MgO) were mixed with the soil. Oxamide and nitrolime were supplied in amounts of 500, 1000, 1500, and 2000 mg. of N per pot. The pots were placed in the open air. The grass was sown on March 26 and cut on May 25 and June 22. When dry, the grass was weighed and analyzed for total nitrogen after oxidation with concentrated H_2SO_4 and 30% H_2O_2.

Experiment II. To examine whether the application of oxamide had any harmful effect on plant growth, trials were carried out in duplicate with three

Table I. Dry Weight (Grams/Pot) of Perennial Ryegrass and Nitrogen Yield (Mg. of N/Pot) in Herbage as Affected by Oxamide and Nitrolime

	1st Cut		2nd Cut		1st + 2nd Cut	
Nitrolime, Mg. of N	*Dry wt., grams*	*Total N, mg.*	*Dry wt., grams*	*Total N, mg.*	*Dry wt., grams*	*Total N, mg.*
500	9.21		10.47		19.68	
1000	18.97	558	14.17	151	33.14	709
1500	24.83		17.95		42.78	
2000	27.75	1091	22.00	296	49.75	1387
Oxamide, Mg. of N						
500	12.20		8.86		21.06	
1000	21.83	575	11.95	137	33.78	712
1500	27.95		14.92		41.87	
2000	29.64	1148	13.00	194	42.64	1342

Table II. Effect of Oxamide and Nitrolime on Dry Matter Yield of Flax, Grams per Pot

	Nitrolime		Oxamide	
Treatment, Mg. of N	*No $CaSO_4$, grams*	*$CaSO_4$, grams*	*No $CaSO_4$, grams*	*$CaSO_4$, grams*
1200	91	89	93	91
1800	103	104	98	97

Standard deviation, 1 to 2%.

Table III. Effect of Oxamide, Nitrolime, and $CaSO_4$ on Perennial Ryegrass

Nitrogen Treatment, Mg. of N	Nitrolime		Oxamide	
	No $CaSO_4$	*With $CaSO_4$*	*No $CaSO_4$*	*With $CaSO_4$*
		Dry Weight[a]		
1200	33.4	40.6	38.8	35.3
1800	47.4	46.9	47.9	41.0
		Nitrogen Yield[b]		
1200	810	900	851	839
1800	1313	1253	1219	1219

[a] Grams/pot.
[b] Mg. N/pot.

Standard deviation for dry weight and nitrogen yield, 3 to 8% and 2 to 4%, respectively.

Table IV. Effect of Oxamide, Nitrolime, and $CaSO_4$ on Spinach

Nitrogen Treatment, Mg. of N	Nitrolime		Oxamide	
	No $CaSO_4$	*With $CaSO_4$*	*No $CaSO_4$*	*With $CaSO_4$*
		Dry Weight[a]		
1200	14.2	18.6	19.8	18.3
1800	19.9	22.1	16.2	17.2
		Nitrogen Yield[b]		
1200	355	555	674	691
1800	601	876	887	914

[a] Grams/pot.
[b] Mg. of N/pot.

Standard deviation for dry weight and nitrogen yield, 4% and 3 to 8%, respectively.

different plant species, flax (*Linum usitatissimum*), perennial ryegrass (*Lolium perenne*), and spinach (*Spinacia oleracea*). All three crops were sown on March 26. The flax was harvested nearly ripe on July 13, the grass was cut on May 25 and June 22, and the spinach was harvested on May 21, just before it developed shoots. The same soil as in Experiment I was used, and identical quantities of superphosphate and patentkali were added. Oxamide and nitrolime were applied in amounts of 1200 and 1800 mg. of N per pot. It was to be expected that, after being added to the soil, oxamide would be hydrolyzed into ammonia and oxalic acid. This might lead to precipitation of calcium as calcium oxalate and to a reduction in the amount of calcium available to the plant. Therefore, in a parallel series of experiments, the supply of nitrogen was combined with a supplementary addition of $CaSO_4$. The rates of 1200 and 1800 mg. of N corresponded to 5830 and 8750 mg. of $CaSO_4$ per pot, respectively. These quantities are theoretically equivalent to the amounts of oxalic acid that might originate from the oxamide added. $CaSO_4$ rather than $CaCO_3$ has been used, owing to its neutral action on soil pH and its greater solubility.

The herbage was analyzed for nitrogen only in those cases where test plants showed a distinctly different reaction to the fertilizers.

Results

Experiment I. Dry weight and nitrogen yields in herbage are presented in Table I. Only samples from plants dressed with 1000 and 2000 mg. of N per pot were taken for analysis. Standard deviations for dry weight and nitrogen yield are 2 and 3%, respectively.

Oxamide treatment gave a distinctly higher, dry-weight production and nitrogen yield in the first cut of grass than nitrolime treatment. In the second cut, however, both dry weight and nitrogen yield were lower upon oxamide treatment. In this experiment, oxamide seemed to act slightly more rapidly than nitrolime.

Nitrogen recovery from the two fertilizers appeared to be almost equal.

Experiment II. FLAX. The flax was grown nearly to ripeness. The dry weights are presented in Table II.

At the lowest N-level, the oxamide-treated plants gave a slightly higher, dry-weight production than the plants dressed with nitrolime. At the highest N-level, however, it was just the reverse. The addition of $CaSO_4$ had hardly any effect.

At the highest N-level, the plant length was slightly reduced. Compared with nitrolime, oxamide had a somewhat decreasing effect on the straw length of the flax plants. Generally, however, the differences were of minor significance.

PERENNIAL RYEGRASS. Dry weight (grams per pot) and nitrogen yields (mg. of N per pot) are presented in Table III.

Both dry weight production and nitrogen yields of the oxamide-treated grass agreed with the data of Experiment I. Addition of $CaSO_4$ had a depressing effect on dry-weight production, but not on nitrogen recovery. Results of the nitrolime treatment differed slightly from the data obtained from Experiment I. The stimulating effect of $CaSO_4$ at the 1200-mg.-of-N level was quite unexpected. Both with respect to dry-matter production and nitrogen recovery, oxamide appeared to be equally valuable as a nitrogen fertilizer and as nitrolime. The addition of $CaSO_4$ had no beneficial effect.

SPINACH. Dry weight (grams per pot) and nitrogen yields (mg. of N per pot) are presented in Table IV.

The reaction of spinach as a test plant was rather complicated. Initially, the oxamide-treated plants developed much more slowly than the plants dressed with nitrolime. Furthermore, additional $CaSO_4$ proved to have a beneficial effect. The leaves were a dark bluish green and had a curled appearance. During the growth of the crop this picture changed completely. The initial delay in development was restored, and the favorable effect of $CaSO_4$ addition ceased to exist.

Analytical data showed that the dry weight of the oxamide-treated plants as well as their nitrogen uptake were only slightly affected by addition of $CaSO_4$.

Spinach dressed with nitrolime developed readily. Plants supplied with nitrolime only, turned yellow rather early in the season. After a combined nitrolime and $CaSO_4$ addition, however, the plants kept green for a considerably longer time. Dry-matter production and nitrogen uptake increased greatly.

In this experiment, there was hardly any relation between dry-matter production of the spinach and nitrogen uptake. At the 1800-mg.-of-N level, dry weight after addition of nitrolime was considerably higher than in the case of the oxamide supply; as to nitrogen yields, the reverse holds true. As a consequence, the spinach supplied with oxamide had a much higher nitrogen content than nitrolime-treated plants.

With respect to nitrogen recovery, oxamide appeared to be highly superior to nitrolime in this experiment.

Discussion

Experiment I shows that fine oxamide released slightly more nitrogen than did nitrolime. Especially at the 2000-mg.-of-N level, however, the oxamide-treated grass gave distinctly less total dry weight than nitrolime-treated grass. This points to a physiological difference as regards the source of nitrogen.

In Experiment II, the action of oxamide and nitrolime are compared with respect to their effect on three different plant species. In this experiment, a series with $CaSO_4$-supply has been introduced to make up a possible reduction in calcium availability caused by calcium oxalate precipitation. A favorable effect of oxamide combined with $CaSO_4$ could not be observed on the three plant species.

With flax, the differences between oxamide and nitrolime treated plants were of minor importance. At the 1800-mg.-of-N level, flax supplied with oxamide showed a slightly reduced straw length.

Both dry-weight production and nitrogen yields of the oxamide-treated grass were in agreement with the data of Experiment I. The results of nitrolime treatment, however, were somewhat different. At the 1800-mg.-of-N level, the unit quantity of nitrogen taken up from oxamide had a somewhat better effect on dry-matter production than the same quantity from nitrolime as a nitrogen source. This was not in agreement with the experience at the 2000-mg.-of-N level in Experiment I. The stimulating effect of $CaSO_4$ on the nitrolime-treated plants at the 1200-mg.-of-N level could not be explained, as deficiency in both calcium and sulfate was very unlikely under the experimental conditions.

The experiments with spinach showed a large difference in physiological action between oxamide and nitrolime as a nitrogen source. Per unit quantity of nitrogen taken up, nitrolime fed plants produced considerably more dry matter than those supplied with oxamide. On the other hand, nitrogen recovery from oxamide greatly exceeded that from nitrolime. The difference in physiological action seems to be due partly to nitrolime releasing both ammonium and nitrate nitrogen, oxamide nitrogen being mainly available as ammonium depending on nitrification rate. According to the authors' experience, growth of spinach is favored more by nitrate than by ammonium nitrogen.

In the case of the nitrolime supply, a striking increase both in dry weight and nitrogen uptake caused by additional $CaSO_4$ could be observed. $CaSO_4$ had an extending effect on the growth period of spinach. No explanation for this phenomenon can be given.

The experiment with spinach as a test plant was repeated during August and September. Series of nitrolime combined with $CaSO_4$ and minor elements have been included. In this experiment no effect of $CaSO_4$ or minor elements could be observed. Perhaps this $CaSO_4$ effect is related to special seasonal conditions.

The above experiments indicate that, as regards the rate of release and recovery of nitrogen, fine oxamide is generally similar to nitrolime. However, depending on the test plant, considerable differences in physiological action could be observed between the two fertilizers.

Recently, DeMent, Hunt, and Stanford (*3*) compared the nitrogen availability of oxamide, urea-formaldehyde, and ammonium nitrate over a wide range of granule sizes. They found that the rates of nitrogen uptake by corn from the fine oxamide and ammonium nitrate were equal, while the uptake from urea-formaldehyde was much less. Increasing granule size had no effect on nitrogen availability from ammonium nitrate and urea-formaldehyde, but greatly decreased the rate of nitrogen uptake from oxamide. They assumed that a mixture of large and small granules of oxamide might cover both immediate and long term needs. As to the rate of release of nitrogen from fine oxamide as compared with that from nitrolime, the authors' results agree with those of DeMent and co-workers. Their conclusion, however, "that the effectiveness of unit quantity of nitrogen taken up by the plants in increasing dry weight did not differ among fertilizers, etc." was not confirmed by the present experiments. In the case of spinach, particularly, pronounced differences in physiological action between the two fertilizers were observed. In this connection, it has to be emphasized that DeMent and co-workers obtained their results from greenhouse tests, whereas the present experiments were conducted in the open air.

Acknowledgment

The authors are greatly indebted to Maria A. Th. Steemers for technical and analytical assistance. The pot experiments have been carried out at the Laboratory of Microbiology, Agricultural University, Wageningen.

Literature Cited

(1) Winsor, G. W., Long, M. I. E., *J. Sci. Food Agr.* **9**, 185 (1958).
(2) Brotherton, T. K., Lynn, J. W., *Chem. Revs.* **59**, 841 (1959).
(3) DeMent, J. D., Hunt, C. M., Stanford, G., *J. Agr. Food Chem.* **9**, 453 (1961).

Received for review May 5, 1961. Accepted September 18, 1961.