

Availability of Urea, Ammonium, and Nitrate Applied to Pine Bark

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Abstract. Initial availability of NO₃, NH₄, and urea applied to limed or unlimed pine bark as well as the form of N available over a period of 21 days was determined. Nitrate was not present in significant amounts when N was supplied as either urea or NH₄, and the extractable amounts of both urea and NH₄ declined significantly over the course of the experiment. Urea was the least effective of the N forms in supplying N in an extractable form. With NO₃ as the N source, addition of lime to pine bark resulted in significant reductions in extractable NO₃. Applications of NH₄ gave relatively equal amounts of extractable N as NH₄ from limed and unlimed pine bark after 21 days. It was concluded that N interaction and N transformations with these N forms in pine bark would influence total available N as well as the form of N available for plant growth.

Commercial N fertilizers used in the production of crops in soilless media are composed of one or more of three N forms (NO₃, NH₄, and urea), with urea and/or NH₄ generally being the primary N form. Although N frequently is applied in large quantities to crops produced in soilless media, the interactions of the different N forms with bark-based media have not been clearly delineated.

The interaction of urea with pine bark, as well as the rate of urea conversion to NH₄, are unknown. Urea is only weakly adsorbed in soils, and its adsorption is directly correlated to soil organic matter content (3). Reactions of urea with pine bark may be quite complex, as many organic compounds, including waxes, straight- and branched-chain aliphatic compounds, many N compounds, and resins are known to form complexes with urea (3). Studies evaluating plant response to NH₄ in a pine bark medium revealed a significant interaction between NH₄ and pine bark, with reduced N availability resulting from use of ammoniacal fertilizers (1, 9, 12). Niemiera and Wright (10, 11) reported that nitrification rates were important in the nutrition of container-grown plants with (NH₄)₂SO₄ as the N source. Nitrate retention and availability are also unknown, although rapid loss by leaching and denitrification is thought to occur (9).

Because the pH of pine bark is naturally acidic (pH 3.2 to 4), use of lime (calcitic or dolomitic) in bark-amended media to supply Ca and raise the medium pH to the 5.0 to 6.5 range has become an industry standard. The objective of this study was to evaluate

the influence of N form and lime additions on N retention and transformation in a pine bark medium.

Laboratory evaluations were performed with 65 cm³ of aged, air-dried pine bark placed in 125-ml Erlenmeyer flasks. The bark in one-half of the flasks was amended with dolomitic lime (100-mesh) at the rate of 212 mg Ca(OH)₂/flask. Flasks were divided into three groups labeled 24 hr and 10 and 21

days, respectively, with each group containing 15 limed and 15 unlimed bark samples. Nitrogen treatments consisted of C(NH₂)₂O, (NH₄)₂SO₄, and Ca(NO₃)₂. Each N form was added to five flasks each in limed and unlimed bark samples, in a 75-ml modified Hoagland's solution at a rate of 600 ppm N/flask. Control flasks (five limed and five unlimed) received 75 ml of deionized water/flask.

All flasks were agitated and placed in a vacuum desiccator for 24 hr to remove air from interior pore spaces and allow movement of N solution into internal pore space. After vacuum infiltration, the excess solution was extracted by gravity flow and analyzed for remaining N forms (Table 1).

The 24-hr group of 30 flasks was placed in a freeze-dryer, temperature was lowered to -40°C, and samples were dried under vacuum to 10.1 kPa. Immediately after freeze-drying, 75 ml of deionized water containing 5 mg-liter⁻¹ of phenyl-mercuric acetate and 50 mg-liter⁻¹ of N-Serve 24E was added to each flask to inhibit urease activity, nitrification, and denitrification during extraction and analysis. Flasks were placed under vacuum for 24 hr to promote equilibrium between the external solution and solution in the bark pore spaces, and the excess solution was extracted by gravity flow.

The remaining two groups of flasks (10 and 21 days) were sealed with Parafilm and

Table 1. Initial interaction of N form with limed and unlimed bark samples and the form of N recovered (Nitrogen additions labeled "stock").

Form of nitrogen added and lime treatment	Nitrogen form recovered (ppm)			pH
	Nitrate-N	Ammonium-N	Urea-N	
Nitrate				
Stock	600	0	0	3.6
Limed	683	0	0	5.5
Unlimed	628	0	0	3.1
Ammonium				
Stock	0	600	0	4.1
Limed	2	391	0	5.5
Unlimed	0.4	480	0	3.4
Urea				
Stock	0	0	519	6.3
Limed	5	11	408	5.9
Unlimed	1	6	426	3.5
Water (control)				
Limed	6	0	0	6.3
Unlimed	1	0	0	3.7
Orthogonal comparison				Significance
Nitrate concentrations				
NO ₃ -stock vs. NO ₃ -treated bark				**
NO ₃ -stock vs. Limed NO ₃ -treated bark				**
NO ₃ -stock vs. Unlimed NO ₃ -treated bark				*
NO ₃ /limed bark vs. NO ₃ /unlimed bark				**
Ammonium concentrations				
NH ₄ stock vs. NH ₄ bark				**
NH ₄ stock vs. limed NH ₄ bark				**
NH ₄ stock vs. Unlimed NH ₄ bark				**
Limed NH ₄ bark vs. unlimed NH ₄ bark				**
Urea bark vs. NH ₄ bark				**
Urea concentrations				
Urea stock vs. urea bark				**
Urea stock vs. limed urea bark				**
Urea stock vs. unlimed urea bark				**
Limed urea bark vs. unlimed urea bark				**

** Significant at the 1% and 5% levels, respectively.

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Table 2. Interaction of N source with lime and incubation time on nitrate in solution extract.

Lime treatment	Urea	Nitrate-N recovered (ppm)	
		Nitrogen source	
		Ammonium	Nitrate
		<i>24 hr</i>	
Limed	6	0	290
Unlimed	6	0	309
		<i>10 days</i>	
Limed	4	0	40
Unlimed	0	0	299
		<i>21 days</i>	
Limed	1	0	36
Unlimed	0	0	231
Orthogonal comparisons			Significance
NO ₃ source: NO ₃ recovered			
Limed vs. unlimed at 24 hr			NS
10 days			**
21 days			**
NH ₄ source: NO ₃ recovered			
Limed vs. unlimed at 24 hr			NS
10 days			NS
21 days			NS
Urea source: NO ₃			
Limed vs. unlimed at 24 hr			NS
10 days			NS
21 days			NS
24 hrs vs. 10 days			NS
10 days vs. 21 days			NS
N-sources: NO ₃ recovered			
NO ₃ vs. NH ₄ and urea at 24 hr			**
10 days			**
21 days			**

NS, **Nonsignificant and significant at the 1% level, respectively.

Table 3. Interaction of N source with lime and incubation time on ammonium in solution extract.

Lime treatment	Ammonium-N recovered (ppm)	
	Nitrogen source	
	Urea	Ammonium
	<i>24 hr</i>	
Limed	91	189
Unlimed	142	293
	<i>10 days</i>	
Limed	51	162
Unlimed	56	239
	<i>21 days</i>	
Limed	38	142
Unlimed	38	165
Orthogonal comparisons		Significance
Urea source:		
Limed vs. unlimed at 24 hr		*
10 days		NS
21 days		NS
24 hr vs. 10 days		NS
10 days vs. 21 days		NS
NH ₄ source:		
Limed vs. unlimed at 24 hr		**
10 days		**
21 days		NS

*, **, NS Significant at the 5% or 1% levels or not significant, respectively.

placed in an incubator at 30°C. After 10 or 21 days, flasks were placed in a freeze-dryer (as described previously), after which 75 ml of the N-Serve/phenylmercuric acetate solution was added, the flasks were then placed under vacuum for 24 hr, and 10- and 21-day solutions were extracted by gravity flow.

low that required for optimum plant growth (35 ppm) within 10 days of the addition of NO₃-N.

Ammonium conversions. Extracts from both limed and unlimed NH₄-treated bark were significantly lower in NH₄ levels than originally applied (Table 1.) The rapid loss of NH₄ from the initial stock solutions applied to the bark samples without an increase in NO₃ in the extract strongly suggests some binding on NH₄ to pine bark. Microbial tie-up of NH₄ in this short time (24 hr) seems unlikely. Although some NH₄ may have been volatilized in the lime treatments due to localized pH effects, similar results were obtained with the unlimed bark treatments, where the low pH precludes volatilization as an explanation of the drop in NH₄ concentration. Either cation exchange or other chemical reactions with bark may be responsible for the reduced NH₄ levels, as the extract solutions pH decreased in the unlimed bark samples in comparison to the water-treated unlimed bark solution extracts (Table 1), possibly indicating displacement of H⁺ from the bark.

Ammonium concentration in the solution extracts exhibited a pattern of declining concentration in both limed and unlimed bark sample, although the concentration of leachable NH₄ was consistently lower in limed bark (Table 3). This difference cannot be readily attributed to nitrification, since no NO₃ was detected in any of the NH₄-treatment leachates. Either denitrification was proceeding at a rate equal to the rate of nitrification, or relatively little nitrification occurred.

Urea conversions. Urea concentration in the solution extracts from unlimed bark samples were significantly lower than that supplied by the stock nutrient solution (Table 1). The addition of lime further reduced the amount of urea in the solution extracts. Since insignificant amounts of NH₄ and/or NO₃ were detected in the initial solution extracts, the rapid disappearance of urea was attributed to a binding reaction with the pine bark. Significant amounts of NH₄ were present in the solution extracts after 24 hr (Table 3), indicating urease activity. Differences between limed and unlimed treatments were apparent after 24 hr with recovery of urea lower and extractable NH₄ higher in unlimed than in limed solution extracts. After 10 days, no free urea was detectable in any solution extracts, and NH₄-N had decreased significantly without any corresponding increase in NO₃-N (Tables 2-4).

Rapid decreases in urea concentration in initial solution extracts and a decline of urea concentration to undetectable levels in all solution extracts within 1 week indicates rapid binding of urea in pine bark. Liming apparently increased urease activity, as indicated by the NH₄ concentration in 24-hr solution extracts, but later measurements show no net difference between limed and unlimed treatments. Stoichiometric conversion of urea to NH₄ was unlikely, since, under these circumstances, the NH₄ content in the urea solution extracts would be much higher and

Table 4. Interactions of urea with lime and incubation time on urea in solution extract.

Lime treatment	Urea-N recovered (ppm)		
	24 hr	10 days	21 days
Limed	91	0	0
Unlimed	75	0	0
Orthogonal comparisons			
Limed vs. unlimed at 24 hr			**
10 days			NS
21 days			NS
24 hr vs. 10 days			**
10 days vs. 21 days			NS

** . NS Significant at the 1% level or not significant, respectively.

closer to that of the NH_4 treatments. On the contrary, total soluble N in urea-treatment leachates after 10 to 21 days was only one-fourth to one-third of the amount present in the NH_4 -treatment leachates. Some microbial immobilization of urea, perhaps by organisms that use urea directly without its prior conversion to NH_4 , may have occurred, as large microbial populations have been reported in media containing bark (5). However, this effect is not due to differences in pH, as the same differences occur in the presence or absence of lime.

Results from this study suggest that each N-form tested would react differently in pine bark and that these interactions and N transformations would influence nitrogen and N-form availability to plants growing in a pine bark-based medium. Significant concentrations of NO_3 in the initial and 10- and 21-day solution extracts were obtained only when NO_3 was the N source provided to the medium. However, liming the bark caused a reduction in NO_3 -N about six to seven times lower, which, in previous studies, has been attributed to either microbial tie-up or denitrification (9). Initial leaching losses of applied NO_3 fertilizers would be significant if the applied fertilizer NO_3 is repelled by negative sites on pine bark, as indicated in this study. Physical entrapment in pore spaces has been suggested as a possible mechanism of retention of NO_3 ions in bark (12), but these data indicate selective exclusion of NO_3 from bark. Leaching losses plus the significant loss of NO_3 through denitrification in a bark medium, as previously reported (12), would create a stress for many plants grow-

ing in pine bark without frequent NO_3 applications.

Urea and NH_4 reactions in bark differ greatly. Though urea is converted rapidly to NH_4 in most soils, stoichiometric conversions of urea to NH_4 did not occur in pine bark, and a significant amount of the applied urea could not be accounted for. Urea may react directly with the bark, and/or urea may selectively stimulate microbial activity in a manner different from that occurring with NH_4 . Strong initial adsorption of NH_4 in large quantities may account for some of the later differences in NH_4 -N in the solution extracts, but it is unlikely that the differences were due entirely to NH_4 adsorption. Physical reaction of NH_4 may be due to ion exchange and/or more integral combinations of N and organic compounds in the bark, perhaps covalent bonding.

Since NH_4 and urea concentrations in the solution extracts were reduced significantly below that originally supplied to the pine bark medium, the availability of these two N forms would depend on the capacity of plants to extract NH_4 or urea that is physically or chemically tied up in the bark. Reduced plant growth due to limited N availability has been reported in 100% pine bark with NH_4 provided as the sole N source. Nitrification of NH_4 and hydrolysis and nitrification of urea did not occur at rates sufficient to provide significant amounts of NO_3 in the leachates, even after 3 weeks of incubation. These results differ from those of Niemiera and Wright (10, 11), in which they found that NO_3 -N was present in container grown crops in which bark was the medium. The difference may

be due to the presence of a plant in their study and/or saturation of the sites binding the ammonium ion over time. However, the results presented in this study may explain why plants do not respond or grow well initially in pine bark. At the N level used in this study, N would be limiting to crop growth with all N forms evaluated during the time investigated.

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