## **SOIL ORGANIC MATTER**

# Effect of Wheat Straw, Nitrogenous Fertilizers, and Carbon-to-Nitrogen Ratio on Organic Decomposition in a Subhumid Soil

PURNA CHANDRA<sup>1</sup> and W. B. BOLLEN

Bacteriology Department, Oregon Agricultural Experiment Station, Corvallis, Ore.

Further information on effects of nitrogen fertilizers and straw on organic decomposition and nitrogen transformation is desirable for sound field practice. Water-soluble and -insoluble fractions of straw, rates of straw, and forms of nitrogen had significant effects on carbon dioxide evolution. Ammonium hydroxide produced more rapid decomposition than ammonium or calcium nitrate. Apparent utilization of nitrate as an oxidant by denitrifiers decreased the nitrates and lowered carbon dioxide evolution. Level of available carbon and form of nitrogen influence nitrogen balance as well as rate and extent of decomposition. The carbon-to-nitrogen ratio often fails to predict the rate of microbial decomposition and effects on soil nitrogen. Definition of carbon levels should indicate availability as well as total amount. Straw additions prevented significant decreases in total nitrogen.

**P**LANT RESIDUES ADDED to soil undergo more or less rapid and extensive decomposition by microorganisms, with liberation of carbon as carbon dioxide. The rate and extent of this mineralization is governed by the nature of the organic matter and by environmental factors, especially moisture, temperature, and available nitrogen. Determination of the rate and amount of carbon dioxide evolution from a soil provides a measure of the rate and extent of the organic matter decomposition under the particular conditions imposed.

Wheat straw residues are extensively used in trashy fallow or stubble-mulch farming on the subhumid soils of Oregon and other western states as an erosion control measure. Nitrogen fertilizers are generally used to avoid deficiency of this element. Decomposition studies on such residues are important for indicating probable duration and effects on carbonto-nitrogen relationships in the soil. As the nitrogen cycle and carbon cycle are biologically bound together and proceed simultaneously, organic matter decomposition is always accompanied by nitrogen transformations. The resulting changes in forms and availability of nitrogen lead to losses and gains, the balance being determined by carbon

<sup>1</sup> Present address, College of Agriculture, University of Baghdad, Abu-Gharib, Iraq.

sources, carbon-to-nitrogen ratio, and conditions of environment. Although much attention is given to carbon-tonitrogen ratio for its influence on decomposition and nitrogen availability, emphasis should be placed on the relative decomposability of the carbonaceous constituents of organic matter. Resistant material will have less pronounced and longer lasting effects. The significance of crop residues and nitrogen fertilizers in soil fertility may therefore be assessed more readily, if water-soluble as well as water-insoluble components are considered in relation to carbon and nitrogen changes resulting from additions of materials containing these elements.

## **Materials and Methods**

**Soil.** Walla Walla silt loam soil was selected for use in this study, because it is one of the most extensive and important wheat producing soils of Oregon (average annual rainfall is 15 to 18 inches). It is a Chestnut soil developed from fine-textured, wind-deposited material—loess. Accumulated humus from a native vegetation of bluebunch wheat grass (*Agropyron spicatus*) may be responsible for its dark color and exceptional fertility. Practically all of the soil is cultivated, and wheat is by far the most important crop. Summerfallow is commonly practiced.

Table I.	Analysis of Walla Silt Loam Soil	Walla
----------	-------------------------------------	-------

Analysis	Amount							
pH	6.7							
Nitrogen, p.p.m.								
Ammonium	10							
Nitrite	10							
Nitrate	4							
Total	1,030							
Total carbon, $\%$	1.51 14.66							
C:N ratio								
Cation exchange capac-								
ity, meq./100 g.	18.75							
Exchangeable cations,								
_ meq./100 g.	9.95							
Ca	3.12							
Mg	.52							
Na	1.49							
K Di lui luberbee	1.47							
Bicarbonate soluble phos-	12.5							
phorus, p.p.m.	12.5							
Water holding capacity,	48.7							
%	+0.7							
Mechanical analyses, $\%$	42							
Sand	38							
Silt	18							
Clay	10							
Microorganisms by plate								
count	88,500							
Molds, per gram	12							
Mucors, %	49							
Penicillium, %	11							
Aspergillus, % Demitaceae, %	24							
Trichoderma, %	4							
Bacteria, per gram	28,000,000							
Streptomyces, %	20,000,000							
Azotobacter, per gram	40,000							
Lotoration, per Brunn	,							

A bulk sample of the soil was collected in April 1956 from the Pendleton Branch Experiment Station. Random samples to a depth of 6 inches were composited from an alley along the end of a series of trashy fallow plots. The soil was brought to the laboratory, air-dried and passed through a 10-mesh sieve, and stored in covered 30-gallon galvanized iron cans for use as required. Moisture was determined each time soil was taken for an experiment, so that samples could be weighed out on the dry basis.

Chemical, physical, and microbial properties of the soil are shown in Table I. All data, except for pH, are given on the dry basis.

Exchange capacity and exchangeable cations were determined by the ammonium acetate method. Total phosphorus was determined by the bicarbonate method of Olson, Cole, Watanabe, and Dean (77).

For pH a soil-to-water ratio of 1 to 5 was used. Ten grams of soil, dry basis, and 50 ml. of distilled water were stirred in a 100-ml. beaker; after coarse particles had settled, readings were made with a Model N Beckman pH meter using a glass electrode.

Table II. Analysis of Straw

Tuble II. Analysis of 5	
Moisture, %	5.75
Water holding capacity, %	573.0
Total carbon, %	45.23
Water-soluble carbon, %	3.03
Total nitrogen, %	0.37
Water-soluble nitrogen, %	0.00
C:N ratio	122.2
pH, 1/20 aqueous suspension	5.1

#### Table III. Mechanical Analyses of Milled Wheat Straw

Tyler Standard Screen, Meshs/Inch	Wiley Mill, 10-Mesh Screen, %	Weber Hammer Mill, No. 800 Screen,ª %
+20	42.5	
+40	37.4	
+60	11.8	6.4
+80	4.1	18.4
+100	1.9	18.9
+150	1.0	16.7
+200	0.5	27.2
-200	0.8	12.1

<sup>a</sup> Approximately 60-mesh.

+ Indicates retained on screen.

- Indicates passing screen.

Table	IV.	Anal	ysis	of	Extract	and
	Extr	acted	Whe	at :	Straw	

Analysis	Wheat Straw Extract, %	Extracted Wheat Straw, %
Moisture Total solids Total carbon	1.01	2.9 40.9
Total nitrogen C:N ratio	0.00	0.36 113.3
pH <sup>a</sup> Of 1/20 water	8.1 r suspension	6.4ª

Ammonium nitrogen was determined by the method of Shirkhande (19), which employs distillation of the sample with phosphate buffer at pH 7.4. By avoiding the use of strong alkali, liberation of ammonia from amino acids and other intermediate decomposition products of proteins was prevented.

Nitrites were determined by the diazotization method with sulfanilic acid, 1-naphthylamine hydrochloride, and sodium acetate buffer.

Harper's (9) phenoldisulfonic acid method for nitrates was modified by use of ammonium carbonate to remove the excess calcium hydroxide remaining in a 1-to-5 soil-water extract after clarification.

Total nitrogen was determined by the official AOAC Gunning method. For soil, this was modified to include nitrate.

Total carbon was determined by combustion, using the AOAC procedure.

Moisture was determined as loss in weight by drying samples at 105° C. for 24 hours.

Water holding capacity was calculated from the amount of water retained by samples in Gooch crucibles wetted from below by immersion and then allowed to drain to constant weight in a moisturesaturated atmosphere.

Mechanical analysis was made by the pipet method (13).

Numbers of microorganisms were estimated by plating procedures. Peptone glucose acid agar was used for molds, and sodium albuminate agar was employed for bacteria and streptomyces. *Azotobacter* counts were made after growth on the medium recommended by Martin (14).

**Straw.** A 10-pound sample of wheat straw, Elmar variety, 1956 crop, from Pendleton was obtained and ground in a Wiley mill to pass a 10-mesh screen. This material was used in a greenhouse experiment to be reported later. A subsample was further reduced in a hammer mill through an approximately 60-mesh screen for use in the laboratory. The prepared samples were stored in screw-capped amber bottles.

Chemical analysis of the straw is shown in Table II.

Mechanical analyses of the prepared straw samples are indicated in Table III.

A sample of milled straw weighing 100 grams was fractionated in a stack of Tyler standard screens on a Porter sand shaker for 10 minutes; the percentage of each separate component was then determined by weight. As particle size affects reactivity and rate of decomposition it is considered important to present the mechanical analysis. The hammer-milled sample was used for all the experiments. While nearly all the sample passed 60-mesh, a major proportion was much finer. Use of material of a uniform size would be desirable, but it is likely that different mechanical fractions differ in chemical constituents and that no one fraction would represent the composition of the whole.

Extracted Straw and Straw Extract. To 25 grams of the hammer-milled straw in a liter bottle were added 500 ml. of distilled water which was shaken for 10 minutes on a Miller paint shaker, then allowed to stand overnight. Next day, it was filtered through a Whatman No. 2 paper on a Büchner funnel and another 500 ml. of water were added to the res-This was shaken for 10 minutes idue. and then passed through the same filter. The extraction process was repeated three times, after which the filtrate was colorless. Following a final washing, washings and filtrates were combined, concentrated on a steam bath, made up to a volume of 1000 ml., and stored in a bottle in the refrigerator for use as required.

The residue of extracted wheat straw on the Büchner funnel was carefully removed, air-dried, and stored in a bottle. Analysis of the extract and extracted wheat straw gave the results shown in Table IV.

Nitrogen Sources. The following sources and rates of nitrogen were used: ammonium hydroxide, ammonium nitrate, and calcium nitrate at 0, 100, 200, and 400 p.p.m. of nitrogen. The sources except ammonium hydroxide were of c.P. grade; the ammonium hydroxide was U.S.P., 28% nitrogen. Carbon-tonitrogen ratios of additions with straw were calculated to include the nitrogen content of the straw, but not of soil nitrogen.

## Experimental

Decomposition Studies. Portions of soil weighing 200 grams, dry basis, were placed in pint milk bottles and were treated in factorial combination with three rates of straw with three sources and four rates of nitrogen. A randomized block design was used with two replications. The straw was used at rates of 0, 5, and 10 tons per acreacre-furrow-slice, considered equivalent to 2,000,000 pounds dry soil-calculated on the dry basis. The 5-ton rate, corresponding to 0.5% of the soil by weight, is not much in excess of average field practice. Extracted straw and straw extract fractions were used in amounts equivalent to those supplied by whole wheat straw at 5 tons per acre. Additional treatments with extracted straw at a rate equivalent to total carbon in straw at 5 tons per acre were made also. The straw was mixed with the soil before transferring to bottles. Nitrogen sources and straw extract were added in solution, and the moisture in all treatments was made up to 50% of the water holding capacity of the soil. This was maintained by frequent addition of distilled water to restore loss of weight.

Temperature was maintained at  $28 \pm 1^{\circ}$  C. The experiment was set up in the incubator and connected to a modified Potter and Snyder (18) respiration apparatus designed by Bollen (1). The carbon dioxide evolved was absorbed in tubes containing 1N sodium hydroxide. The tubes were replaced at the end of 21, 42, 84 hours, and 7, 14, and 28 days.

The absorbed carbon dioxide was determined by differential titration with a Beckman automatic titrator. The end points used were those recommended by Cooper ( $\delta$ ): pH 8.5 for neutralization of excess sodium hydroxide and conversion of carbonate to bicarbonate; pH 5.0 to 4.6 for neutralization of bicarbonate, the particular end point varying according to the amount titrated. Sulfuric acid, 1N, in undetermined amount, was used to first bring the pH to about 8.5, after which 0.83N acid was used. Results are expressed as milligrams of carbon equivalent to carbon dioxide per 200 grams of soil on a cumulative basis.

Effect of Straw Fractions on Nitrogen Transformations. Eighty-gram portions of soil, dry basis, were used in pint milk bottles for each treatment. Treatments included straw at 0 and 5 tons per acre in factorial combination with the three sources of nitrogen at 0, 100, 200, and 400 p.p.m. nitrogen.

In each case the amount of soil was weighed and spread in a thin layer on a sheet of wrapping paper. The straw was added by sprinkling the weighed portion over the soil and then mixing well with a spatula, and rolling the mixture back and forth on the paper. It was transferred in four or five approximately equal portions to a pint milk bottle. Corresponding aliquots of distilled water, or solutions of the nitrogen sources when required, were added to each soil portion after it was placed in the bottle. Subsequent diffusion was relied upon to distribute the moisture and nitrogen treatments. This procedure was believed to give better distribution than mixing liquid additions with the soil before transfer to the bottle. It also avoided the risk of puddling. The bottles were capped, weighed, and marked before being placed in the incubator. Each cap was punctured with a 7-mm. hole to provide aeration. A table of random numbers was used in choosing nitrogen sources, in numbering treated bottles, and in selecting their position in the incubator.

Two replications were used. Because of the large number of treatments and analyses involved the replications were set up 7 days apart. The experimental design was a split-split plot with nitrogen sources as major treatments, dates as subtreatments, and nitrogen rates as subsubtreatments.

Soil from replicate bottles was analyzed at 0, 7, 14, and 28 days for pH, ammonium ion nitrogen, nitrite ion nitrogen, nitrate ion nitrogen, and total nitrogen.

## **Results and Discussion**

Effects of Rates of Wheat Straw and Nitrogen Fertilizers on Decomposition. The untreated soil showed the least production of carbon dioxide (Figure 1), which indicated that only 2.5% of the native organic matter was completely decomposed in 28 days. Addition of each nitrogen source, regardless of the rate of application to the soil, only did not significantly increase carbon dioxide evolution at the end of 28 days (Figure 2). There were, however, slight increases during the first day or so; with ammonium hydroxide and ammonium nitrate these became apparent earlier than with calcium nitrate.

To discuss and interpret these carbon dioxide data it is necessary to make certain assumptions, particularly that any excess carbon dioxide produced in a soil treated with plant residues is derived wholly from the organic addition. However, it has been shown that the addition to soil of plant material containing

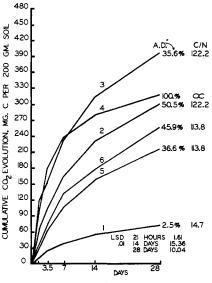


Figure 1. No nitrogen added

- . Soil only
- 2. Wheat straw 5 T/A 3. Wheat straw 10 T/A
- Wheat straw 10 T/A
   Extract from 5 T/A wheat straw 10 T/A
- Extract from 5 T/A wheat straw
   Extracted straw from 5 T/A wheat
- Extracted straw from 5 T/A wheat straw
   Extracted straw equivalent to total carbon
- in 5 T/A wheat straw \* A.D. = apparent decomposition

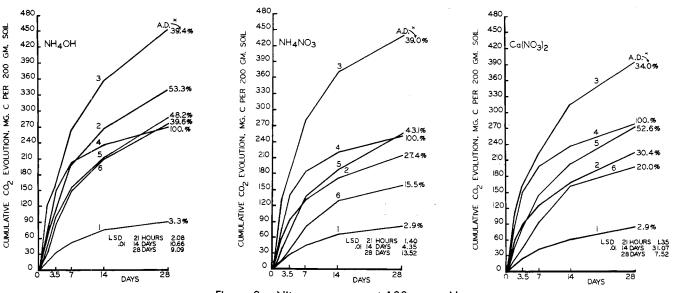


Figure 2. Nitrogen sources at 100 p.p.m. N

1. Soil + N, C: N = 13.4<sup>\*</sup> 2. Wheat straw 5 T/A + N, C: N = 19.1 3. Wheat straw 10 T/A + N, C: N = 33.0 4. Extract from 5 T/A wheat straw + N, C: N = 17.3 6. Extracted straw equivalent to total carbon in 5 T/A wheat straw + N, C: N = 17.3 6. Extracted straw equivalent to total carbon in 5 T/A wheat straw + N, C: N = 19.1

\*C:N ratios refer to straw-fertilizer additions

labeled carbon increases the decomposition rate of the soil organic matter (4, 8).

As these experiments were conducted without benefit of carbon-14 as a tracer, the increase in carbon dioxide production, when straw was added, was assumed to be due to decomposition of the straw itself. On this basis, added wheat straw was concluded to be extensively decomposed in 28 days. The extent of decomposition calculated from the carbon dioxide evolved and the total carbon added is referred to as apparent decomposition. Without added nitrogen, apparently one half of the total carbon in wheat straw at 5 T/A was converted to carbon dioxide, while about one third of the 10 T/A treatment was similarly decomposed. This is in accordance with the generally observed phenomenon that the greater the amount of mature plant material added to a soil, the longer time is required for a given percentage to decompose (4, 8).

Results obtained with the different nitrogen sources at 100 p.p.m. of nitrogen are shown in Figure 2. Data for the two higher rates are not presented, as they gave essentially the same pattern.

Ammonium hydroxide increased the rate of decomposition of 5 T/A straw additions, the higher rates of nitrogen having increased effects. In part, this could have been due to effect on pH, although preferential assimilation could be involved. Ammonium and calcium nitrate at all rates depressed the decomposition, the lowest rate in each case being most depressive. This suggests that much of the nitrate served as an oxidant for denitrification, rather than as a direct nutrient for microbes effecting the decomposition. The ammonium and calcium nitrate, however, had closely similar effects; all the nitrate of the former and a similar amount, or one half the total, of the latter could have been involved in oxidizing activities.

With wheat straw at 10 T/A all sources of nitrogen slightly increased the total carbon dioxide evolved at 28 days. Ammonium hydroxide at each rate produced small and similar increases. Higher rates of ammonium nitrate were less effective than at 100 p.p.m. of nitrogen in increasing carbon dioxide production. Increasing rates of calcium nitrate increased apparent decomposition; at 400 p.p.m. of nitrogen, it had the greatest effect of any of the sources. The amount of straw in proportion to added nitrogen sources is a factor influencing the rate of decomposition. Larger amounts of straw could be expected to increase nitrogen fixation, to increase aeration, and to decrease denitrification accordingly. This is consistent with results of total nitrogen determinations (Table V), which showed a greater decrease with no straw. However, carbon dioxide production and nitrates showed a negative correlation. Other investigators have reported conflicting results on the existence of parallels between nitrate formation and carbon dioxide (7, 17).

Decomposition of Water-Soluble and -Insoluble Fractions of Wheat Straw. The water-extract of wheat straw in an amount equivalent to that in whole wheat straw at 5 T/A was rapidly decomposed in all cases, even without added nitrogen (Figures 1 and 2). At 28 days, the carbon dioxide production was in excess of 100% apparent decomposition, indicating a simultaneously accelerated oxidation of the native soil organic matter. All sources and rates of added nitrogen significantly depressed the carbon dioxide evolution, which, however, was still more than enough to account for complete decomposition of the added water-soluble carbon. The larger the rate of nitrogen addition the less carbon dioxide was evolved. This suggests a sparing effect of nitrogen fertilizers on native organic nitrogen, microorganisms thus being relieved of the necessity for decomposing humus to satisfy nitrogen nutritional requirements.

Jansson, Hallam, and Bartholomew (17) and Jansson (10) reported the preferential utilization of ammonium nitrogen by bacteria in their studies on straw decomposition. This agrees with the results shown in Figure 2, which indicates that the ammonium nitrogen was generally more effective than the nitrate in promoting carbon dioxide production from added straw and straw fractions.

With the extracted wheat straw, containing no readily soluble carbon, addition of nitrogen increased the rate of decomposition as shown by carbon dioxide production. The increase in this case was least with ammonium hydroxide and greatest with calcium nitrate. Forms of nitrogen as well as resistance of organic matter thus seem to influence preferential utilization of these materials by soil microorganisms. Advantages of one form of nitrogen over another, as well as the function of each, are probably determined not only by the nature of the organic substance but also by the given set of environmental conditions.

Where extracted wheat straw was added at the higher rate, equivalent to total carbon supplied by whole straw at 5 T/A, the carbon dioxide evolution was less than from the whole straw at 5 T/A in all cases. With added nitrogen, less carbon dioxide was evolved from the higher application of the extracted straw, except with ammonium hydroxide at 400 p.p.m. nitrogen. Least carbon dioxide was produced with ammonium nitrate.

Effect of Straw Fractions on Nitrogen Transformations. Data showing changes in ammonium nitrogen, nitrification, denitrification, and total nitrogen are given in Table V. Essentially complete recoveries of added nitrogen were obtained at 0 days, within 1 hour after additions. The data for 7 and 14 days are omitted as the trends were in agreement with the results at 28 days. As changes in nitrate concentration can be due to more or less simultaneous denitrification and nitrification, and also to assimilation, the terms apparent nitrification and apparent denitrification are applied to the calculated percentage of these transformations as based on nitrate determination.

The data are in general consistent in showing that the added carbonaceous materials decreased nitrate accumulation. In the absence of straw, some nitrification occurred and ammonium hydroxide was appreciably nitrified, but nitrification of the ammonium ion of ammonium nitrate was overshadowed by nitrate disappearance in many cases. Nitrates disappeared rapidly and extensively from calcium nitrate. These results suggest that both denitrification and assimilation, even in absence of straw, are reasonable in view of the relatively wide carbon-to-nitrogen ratio of the soil. The amounts of ammonium ion nitrogen found in all cases were consistent with nitrate and total nitrogen changes.

Additions of wheat straw, straw extract, and extracted wheat straw gave differences significant at all times, at the 1% level between treatments. Replications showed no significant differences in either carbon dioxide evolution or nitrogen changes. Wheat straw extract had little effect on nitrate accumulation. As this extract provided only a relatively small amount of carbon, 310 p.p.m., it could induce only limited nitrogen assimilation; thus more nitrogen would be left for nitrification. Neither could this small amount of carbon be expected to retard nitrification. The generally accepted concept is that soluble carbonaceous material inhibits in pure cultures of nitrite- and nitrate-forming bacteria, but they can stand high concentrations of organic matter in soil, composts, and manure piles where the soluble carbonaceous material is higher. This tolerance is probably made possible by physical and chemical conditions of the soil and complex microbial associations.

Conflicting observations have been reported on the influence of water extract of straw on retardation of plant growth (5) and on nitrification in soil (12). Results reported in Table V agree with Jensen's (12) observations that the water soluble fraction of wheat straw did not interfere with nitrification.

With ammonium nitrate added to soil, with and without wheat straw and wheat straw fractions, there were decreases in nitrate during the first 7 days, followed by increases. This indicated a probable early assimilation of the nitrate fol-

### Table V. Effect of Wheat Straw and Its Water-Soluble and Water-Insoluble Fractions on Nitrogen Changes in Walla Walla Silt Loam Soil with Different Sources and Rates of Nitrogen

		NH₄OH							NH4NO3														
	Ap-			Days Ap-					Days				Ap-	Days									
Treatment         Days           Straw,         NH <sup>+</sup> <sub>4</sub> N, NO <sup>+</sup> <sub>3</sub> N,           tons/         N, P.P.M.           acre         p.m.         0         28         0         28		Р. М.	parent nitrifi- cation, <sup>a</sup> %	Total Nitrogen, P.P.M. 0 28		NH <sup>↓</sup> N, P.P.M. 0 28		NO <sup>-3</sup> N, P.P.M. 0 28		parent nitrifi- cation, <sup>b</sup> %	Total Nitrogen, P.P.M. 0 28		NH₄ N, P.P.M. 0 28		NO <sup>-</sup> 3 N, P.P.M. 0 28		parent denitrifi- cation,° %	Total Nitrogen, P.P.M. 0 28					
Whole																							
$0 \\ 0 \\ 0 \\ 0 \\ 5^{d} \\ 5 \\ 5$	0 100 200 400 0 100	6 105 198 394 7 104 199	61 118 2 6	5 5 5 5	42 104 125 174 3 76 109	62 41 33 34 31	1044 1138 1238 1450 1048 1154 1260	1055 1109 1220 1367 1118 1169 1294	201 8 51	3 7	5 48 98 197 5 45 106	42 99 117 184 2 33 88	14 -25 -29 -108 -54	1050 1146 1241 1446 1050 1154 1263	1058 1084 1178 1284 1130 1305 1360	9	9 8 4 13	5 104 204 402 4 98 204	45 51 102 258 2 35 84	94 72 47 110 81	1050 1153 1236 1436 1054 1169 1271	1060 1088 1168 1300 1121 1224 1337	
5	400			5	146	26	1458	1479			183	164	- 39	1452	1493		11		198	62	1463	1465	
Extrac 4.01 4.01 4.01 4.01	3 0 3 100 3 200 3 400	390	51 75 221		2 46 59 99	4 8 14	1048 1146 1249 1456	1110 1202 1300 1500	103	5 47 75 93	4 45 97 194	1 28 72 152	-128 30 55	1046 1149 1261 1449	1120 1208 1316 1490	34 23		4 98 195 391	3 46 75 212	99 85 58	1049 1141 1248 1447	1114 1221 1321 1494	
Extrac 5.3		C in 5		ie si 55	traw a 1	at 5 $T/A$	1043	1209	5	7	5	1		1047	1205	6	8	5	1		1049	1207	
5.3 5.3 5.3	5 100 5 200 5 400	104 203 400		5	42 46 76	0 2 9	1043 1146 1249 1442	1345 1141 1545	55 104	51 91	48 97 189	15 37 55	-26 40 33	1151 1250 1453	1263 1263 1329 1489	8 7	22 34		81 120 232	64 63 63	1049 1153 1254 1458	1291 1348 1489	
Extrac 0.9 0.9 0.9	4 0 4 100 4 200 4 400	106	25 42 135 246		56 97 113 157	55 36 28	1048 1144 1243 1440	1152 1220 1315 1416	104	25 44 75 144	5 49 99 199	56 101 144 224	118 102 91	1046 1143 1244 1442	1160 1213 1314 1424	17 19	46	5 105 204 402	55 29 66 99	116 90 87	1046 1146 1241 1443	1163 1200 1230 1420	
$-LSD_{0}$		w)	8 60	n	0.48			36.07		11.52		0.45			31.01		7.09		0.27			31.51	
$ (N \times \text{Straw}) \ 8.60 \ 0.48 \ 36.07 \ 11.52 \ 0.45 \ 31.01 \ 7.09 \ 0.27 \ 31.51 $ <sup>a</sup> Apparent nitrification, $\% = \frac{(\text{Increase in NO}_3^-\text{N in treated soil}) - (\text{NO}_3^-\text{N increase in soil only})}{\text{NH}_4^+\text{N}} \times 100 $ <sup>b</sup> Apparent nitrification. $\% = \frac{(\text{NO}_3^-\text{N at 28 days}) - (\text{NO}_3^-\text{N in soil only at 28 days}) - (\text{NO}_3^-\text{N added})}{\text{NH}_4^+\text{N} \text{ added}} \times 100 $																							
$^{b}$ A	oparen	t nitr	ificat	ion.	. % =	$=$ $(\mathbf{n}\mathbf{O}_{2})$	-18 at	20 UA	(5) -	(1103	NH <sup>1</sup>	-N ac	Ided	o uays,		10 <sub>3</sub> -	in au	<u>ueu</u> )	$\times$ 10	0			
<sup>o</sup> Apparent denitrification, $\% = \frac{(NO_3^-N \text{ added}) - (NO_3^-N \text{ at } 28 \text{ days}) - (NO_3^-N \text{ in soil at } 28 \text{ days})}{(NO_3^-N \text{ added})} \times 100$																							
<ul> <li><sup>4</sup> Equivalent to 2262 p.p.m. C.</li> <li><sup>e</sup> From wheat straw at 5 T/A; equivalent to 1952 p.p.m. C.</li> <li><sup>f</sup> Equivalent to C in whole straw at 5 T/A or 2262 p.p.m. C.</li> <li><sup>g</sup> From straw at 5 T/A; equivalent to 310 p.p.m. C.</li> </ul>																							

lowed by nitrification of the residual ammonium ion nitrogen.

Generally progressive decreases in nitrate ion nitrogen occurred in all treatments with calcium nitrate. The decreases were greater with all straw additions, but losses of total nitrogen were less, showing that assimilation exceeded denitrification. The assimilation followed fairly well the order of availability of carbon in the different straw and extract treatments.

Total Nitrogen Changes. Increases in total nitrogen over soil only were obtained in most cases where straw was added, even in the presence of nitrogen additions as high as 200 p.p.m. It should be emphasized, however, that changes in total nitrogen amounting to less than 40 p.p.m. as determined by the Kjeldahl method are of doubtful significance even though the least significant difference, values may be less than this amount (LSD) (Table V). Thus from results shown in this table it appears that appreciable nitrogen fixation occurred consistently only with the extracted straw applied at 5.35 tons per acre without added nitrogen and also with each nitrogen source at 100 and 200 p.p.m. of nitrogen. No fixation resulted where nitrogen was added at 400 p.p.m. Large amounts of available nitrogen are known to inhibit assimilation of free nitrogen.

Gains in total nitrogen following straw additions have been reported previously by Vandecaveye and Villanueva (20) for Palouse soils, by Newton (16) for Western Canada's gray wooded, black earth, and brown prairie soils, and by Jensen (12) for a large number of Australian soils. Amounts of straw added to the soil in these several investigations ranged from 0.2 to 5%. Jensen (12) also found that hot-water extract of wheat straw increased nitrogen fixation. Much of this fixation could be due to Clostridium rather than to Azotobacter (15). Indirect evidence for nitro-

gen fixation in soils of semiarid regions is presented in reports by Bradley (2) and Bracken and Greaves (3). Certain dry wheatland soils in eastern Oregon and Utah were found to show no decline in total nitrogen after years of cropping.

Increases in total nitrogen averaging 112 p.p.m. were obtained with the cold-water extract without added nitrogen sources. As the extract was used at a rate equivalent to the amount in a 5-ton per acre application of whole straw, the actual amount of carbon added was relatively small. Nevertheless nitrogen increases with the extract were comparable to fixation with the whole straw. This points to the importance of an initial influence of the watersoluble carbonaceous constituents.

Extracted wheat straw, especially at the higher rate, gave greatest increases in total nitrogen. This as well as the greater nitrate assimilation indicated in Table V is not in accordance with the presumably more resistant nature of the carbon. However, it should be pointed out that the actual amount of carbon, although water-insoluble, was much greater than that applied in the wheat straw extract. On the basis of unit amount of carbon, the amount of total nitrogen at the end of 28 days was generally greater for the soluble source of carbon, the only exceptions being at the higher rates of nitrogen added. Jensen (12) found that hot-water extracted straw did not favor any nitrogen fixation; it appears that cold-water extracted straw retains some available carbon sources for Clostridium if not for Azotobacter. Possibly hot and cold water have different effects on the physical structure and availability of the extracted straw.

The results of laboratory experiments, conducted under optimum conditions, are difficult to compare with results likely to occur in the field where distribution of straw, fertilizer, and moisture are irregular and variable. Nevertheless trends are indicated and inferences may be drawn. There is no doubt that straw additions influence nitrogen balance in the soil by promoting assimilation of

available nitrogen, by affecting nitrification, by favoring denitrification, and by stimulating nitrogen fixation. Summation of these transformations determines the net loss or gain of available and total nitrogen.

#### Literature Cited

- (1) Bollen, W. B., Iowa State Coll. J.
- Sci. 15, 353-74 (1941). (2) Bradley, C. E., J. Ind. Eng. Chem. 2, 138-9 (1910).
- (3) Bracken, A. F., Greaves, J. E., Soil Sci. 51, 1-15 (1941).
- (4) Broadbent, F. E., Bartholomew, W. V., Soil Sci. Soc. Am. Proc. 13, 271-4 (1948).
- (5) Collison, R. C., Conn, H. J., N. Y. Agr. Expt. Sta. Tech. Bull. 114 (1925).
- (6) Cooper, S. C., *Ind. Eng. Chem.*, *Anal. Ed.* **13**, 466–70 (1941).
- (7) Gainey, P. L., Soil Sci. 7, 293-311 (1919).
- (8) Hallam, M. J., Bartholomew, W. V., Soil Sci. Soc. Am. Proc. 17, 365-8 (1953).
- (9) Harper, H. J., Ind. Eng. Chem. 16, 180-3 (1924).

- (10) Jansson, S. L., Kgl. Lantbruks-Högskol. Ann. 24, 101-361 (1958).
  (11) Jansson, S. L., Hallam, M. J., Bartholomew, W. V., Plant and Soil, 6, 382-90 (1955).
- (12) Jensen, H. L., Proc. Linnean Soc.
- N. S. Wales 65, 1-222 (1940). (13) Kilmar, V. J., Alexander, L. T., Soil Sci. 68, 15-24 (1949).
- (14) Martin, W. P., Arizona Univ. Agr. Expt. Sta. Tech. Bull. 83 (1940)
- (15) Meiklejohn, J., Trans. 6th Intern. Congr. Soil Sci. 3, 243-8 (1956).
- (16) Newton, J. D., Ibid., 3, 213-33 (1956).
- (17) Olsen, S. R., Cole, C. V., Watanabe, F. S., Dean, L. A., U. S. Dept. Agr. Circ. 939 (1954).
- (18) Potter, R. S., Snyder, R. S., Soil Sci. 1, 76-99 (1916).
- (19) Shirkhande, J. G., Ind. Eng. Chem., 9) Shirkhande, J. C., Anal. Ed. 13, 187-8 (1941). S. C., Villanueva,
- (20) Vandecaveye, S. C., B. R., Soil. Sci. 38, 191-205 (1934).

Received for review May 4, 1959. Accepted September 11, 1959. Technical paper 1220, Oregon Agricultural Experiment Station, Oregon State College, Corvallis, Ore.

## SOIL MAGNESIUM ANALYSIS

# Elimination of Manganese Interference in the EDTA Titration of Exchangeable Soil Magnesium

H. H. CHENG and L. T. KURTZ Agronomy Department, University of Illinois, Urbana, Ill.

Manganese titrates quantitatively and interferes in the determination of magnesium by EDTA [disodium (ethylenedinitrilo)tetraacetate] titration. This interference can be conveniently eliminated by addition of ferrocyanide to precipitate the manganese. Exchangeable soil magnesium can be titrated by EDTA with Eriochrome Black T (EBT) as the indicator in the presence of 1 meq. of exchangeable manganese per 100 grams of soil. If larger amounts of manganese are present, the precipitate of manganese ferrocyanide obscures the end point and must be removed by filtration before magnesium is titrated.

The reagent EDTA [disodium(ethylenedinitrilo)tetraacetate] is widely used in the determination of calcium and magnesium. Cheng and Bray (1) adopted the procedures originated by Schwarzenbach, Biedermann, and Bangerter (3) to determine calcium directly and magnesium indirectly in plant materials and soils. To determine magnesium directly, calcium must first be removed. Tucker and Kurtz (4) obtained the most consistent results by tungstate precipitation of calcium.

Titrations with EDTA are subject to interference by foreign ions, such as aluminum, cobalt, copper, iron, manganese, and nickel, which are sometimes present in small but detectable amounts in soil and plant materials (1). Heavy metals such as cobalt, copper, nickel, and a small quantity of iron can be complexed with potassium cyanide (1). Pribil (2) screened aluminum from interference with triethanolamine, which also masked a small quantity of iron. When present in larger quantities, iron usually precipitates as the hydroxide at the pH specified for the titration.

Methods for eliminating manganese interference have not been convenient

or satisfactory. This paper proposes a convenient procedure for such elimination in the titration of magnesium with EDTA. In neutral and alkaline solutions, manganous ferrocyanide is insoluble, but the calcium and magnesium salts of ferrocyanide are highly soluble and ionized in solution. Ferrocyanide precipitation was very effective in removing manganese interference from the titration of calcium and magnesium with EDTA. This modification gave very reproducible results when used in the analysis of soil for exchangeable magnesium.