

# SUPPLY AND TURNOVER OF N, P, AND K IN RECLAIMED COAL MINE WASTE IN SCOTLAND

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**Abstract.** Field trials were established in 1980 on coal mine spoil at Baads Colliery, West Lothian, to assess the effect of various organic treatments on nitrogen, phosphorus, and potassium levels. Chicken manure, sewage sludge, a seaweed-based soil conditioner, and peat were applied to limed and unlimed plots. Chicken manure and sewage sludge supplied large amounts of nitrogen and phosphorus initially, but this effect did not last beyond the sixth year after establishment. Carbon and nitrogen turnover showed little variation between treatments. The ratio of C:N mineralized was high in all cases, suggesting a deficiency of nitrogen. Spoil and herbage analyses suggested a deficiency of phosphate, but no response to added P was obtained. A survey of sites in Central Scotland was made to assess which parts of the nitrogen cycle function in coal mine spoil. Spoils of widely varying properties were sampled and showed high rates of carbon turnover, but little nitrogen mineralization. Nitrification occurred only on sites of pH > 5.5, but was not measured on all sites with these pH values, presumably due to the absence of nitrifying bacteria. Ammonium fixation by clay minerals was high on some sites. Extractable inorganic nitrogen values were generally low.

## INTRODUCTION

A major long-term factor to be considered when reclaiming coal mine waste is the supply of sufficient amounts of nutrients for plant requirements. Fertilizers are routinely added at seeding and provide immediate benefit. If a site is subsequently managed for agricultural or recreational use, the nutritional level may be maintained by further applications of fertilizers. Very often, however, reclamation does not have a specific aim, other

than cosmetic purposes, and so management ceases after the establishment period. In this case it is important to initiate nutrient cycling so that a system develops which can sustain a reasonable plant cover. The difficulty is that coal mine waste tends to be a system of low nutrient turnover, which lacks a humified organic matter component. This latter is particularly important for N and P supply.

It has generally been found that reclaimed coal mine waste is deficient in nitrogen and phosphorus, but reasonably sufficient in potassium (Fitter and Bradshaw 1974, Pulford and Duncan 1978, Bloomfield et al. 1982). Of these three macronutrients, nitrogen has undoubtedly received the greatest attention. It has

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been suggested that nitrogen in the waste coal and shales may be made available to plants on weathering (Cornwell and Stone 1968), and attempts have been made to characterise the various N fractions in spoil (Palmer et al. 1985). More commonly, the supply of N to plants by various treatments has been measured (Palmer and Chadwick 1985, Palmer et al. 1986), as have N transformations such as mineralization and nitrification (Williams and Cooper 1976, Reeder and Berg 1977). Bradshaw (1983) has estimated that a nitrogen capital of about 1,600 kg N/ha is required to sustain a vegetation cover. This is based on a requirement of 100 kg N/ha/annum and an organic matter decomposition rate typical of temperate soils. Broadly, two main strategies are used to supply N in sufficient amounts over the longer term, a single supply of manures at a high rate, which may also supply some P, and the use of legumes to fix atmospheric nitrogen. In this study, organic amendments were applied to a limed acid spoil to assess the long-term supply of nitrogen, phosphorus, and potassium to plants.

#### MATERIALS AND METHODS

Experimental plots were set up at Baads Colliery, West Lothian, in 1980 with the following treatments, chicken manure, sewage sludge, a seaweed-based soil conditioner, peat, and no organic amendment, applied to limed (25 and 50 t/ha) and unlimed plots. All plots received 300 kg/ha of a 15:10:10 NPK compound fertilizer. Samples were taken from the plots which had received the organic amendments and 25 t/ha lime, and from the no amendment plots which had received 0 and 25 t/ha lime.

Spoil pH was measured in a 1:2.5 spoil: water suspension, using a combination pH electrode. Extractable P and K were measured in a 2.5% acetic acid extract (1:10 spoil:extractant); N, P and K contents of herbage were determined in the dried grass by Kjeldahl digestion. N and P were measured by automated colorimetric analysis, and K by flame photometry.

For C and N turnover measurements, 50g fresh spoil was incubated in a 1.5-l Kilner jar, with a beaker containing 20 cm<sup>3</sup> 1 M NaOH. Carbon dioxide evolved was determined by the method of Jenkinson and Powlson (1976). Inorganic N was extracted with 0.5 M K<sub>2</sub>SO<sub>4</sub> solution at a 1:20 spoil: solution ratio, and measured by automated colorimetric methods. For ammonium fixation and nitrification measurements, the spoils were treated with 100 mg NH<sub>4</sub>-N/kg prior to incubation.

#### RESULTS AND DISCUSSION

Table 1 shows the yields of herbage for the treated plots, expressed as a percentage of the control yield in each year (100%), so that annual variations can be removed. This shows that the addition of the manure-type amendments (chicken manure

and sewage sludge) resulted in much higher yields initially, but these declined so that by the seventh year there was no difference between any treatment and the controls. The peat and soil conditioner treatments gave poorer herbage yields in the first year, but thereafter these treatments behaved similarly to the controls. The N, P, and K content of the herbage did not differ greatly between treatments, but the large differences in herbage yield resulted in corresponding differences in N, P, and K in the standing crop.

Acetic acid extractable levels of P and K were measured in the spoil in 1983 and 1984 (table 2). Except for the chicken manure-treated spoil, extractable P levels were very low. This agrees with the general findings of previous studies that extractable P is low in colliery spoil. Palmer (1978) used a number of standard P extractants on spoil from the Yorkshire coalfield, and found that the levels of P removed were too close to zero to be of value. Fitter et al. (1974) reported a mean of 5.5 mg P/kg for bicarbonate-extractable P in Lancashire spoil. Using spoil from the Scottish coalfield, Pulford (1976) could find no acetic acid-extractable P in acid spoil. Lister (1987), using the Bray method (0.1 M HCl + 0.05 M NH<sub>4</sub>F) also on Scottish spoil, found that extractable P ranged from zero to 19.3 mg P/kg, with a mean of 6.2 mg P/kg. The value of such extractable P figures in coal spoil is questionable however, due to the ability of many spoils to adsorb large amounts of phosphate, particularly under acid conditions (Pulford and Duncan 1975). A mean value for maximum P adsorption of 1.5 mg P/g was measured for spoil from this site. Assuming 2,000 tonnes of spoil per hectare, this is equivalent to a P adsorption capacity of 3 t P/ha. The chicken manure used in this study contained a high level of organic P which was apparently made available for plant uptake, and which was held in the spoil in an extractable form (table 2). The extractable P levels were much higher in the chicken manure- and sewage sludge-treated spoil in 1984. This may be due to mineralization of P from the manures. It may also suggest that phosphorus which had been taken up into the vegetation was returned to the spoil in the autumn, and remained in the spoil in an extractable form (Pulford et al. 1984).

The amounts of K extracted from the spoils were more variable from year to year. Although fairly low when compared to acetic acid-extractable K in a soil, these levels probably represent an adequate supply for the plants. Potassium is usually found in reasonably high amounts in coal spoil as it is a constituent of the shale and is released during weathering. Pulford (1976) found a mean for acetic acid-extractable K of 152 mg K/kg, and Lister (1987) measured a mean of 136 mg K/kg exchangeable K (both of these studies being on spoil from Scotland). The low levels of K in the unlimed sample are attributed to acid leaching

Table 1. Vegetation yield and N, P, K recovered in the grass for treated plots, expressed as a percentage of the control plots (no organic amendment) plots for each year.

	1980	1982	1983	1984	1986
<u>Vegetation yield</u>					
Chicken manure	722	499	310	226	85
Sewage sludge	226	288	250	227	116
Soil conditioner	34	88	106	157	150
Peat	62	105	83	112	99
<u>Nitrogen recovered</u>					
Chicken manure	-	308	278	161	101
Sewage sludge	-	223	209	173	103
Soil conditioner	-	93	96	133	113
Peat	-	90	84	102	109
<u>Phosphorus recovered</u>					
Chicken manure	-	524	411	272	130
Sewage sludge	-	299	289	245	144
Soil conditioner	-	110	78	136	130
Peat	-	110	100	109	115
<u>Potassium recovered</u>					
Chicken manure	-	-	357	165	102
Sewage sludge	-	-	284	185	98
Soil conditioner	-	-	106	133	108
Peat	-	-	100	108	95

Table 2. Acetic-extractable P and K' in Baads spoil, with and without treatments.

	mg P/kg		mg K/kg	
	1983	1984	1983	1984
Chicken manure	17.0	37.9	54.8	107
Sewage sludge	1.5	4.2	41.5	71.4
Soil conditioner	1.0	1.1	54.0	83.1
Peat	1.1	1.0	56.0	73.6
No organic amendment	3.3	1.0	42.4	59.1
No lime, no organic amendment	0.3	0.4	1.0	3.6

Table 3. Carbon and nitrogen mineralised over 10 weeks

Treatment		Amount of element mineralized (mg/kg) mean and (standard deviation)			
		1982	1983	1984	
Chicken manure	C	782 (161)	1907 (312)	1940 (647)	
	N	-	33.3 (13.8)	34.1 (15.7)	
	C:N	-	57	57	
Sewage sludge	C	696 (140)	1501 (205)	1784 (342)	
	N	-	19.4 (5.9)	24.1 (7.0)	
	C:N	-	77	74	
Soil conditioner	C	700 (189)	1586' (137)	1431 (310)	
	N	-	17.0 (7.5)	29.5 (13.6)	
	C:N	-	93	49	
Peat	C	730 (209)	1650 (51)	1873 (927)	
	N	-	18.0 (6.4)	23.0 (11.9)	
	C:N	-	92	82	
No. org. amendment	C	451 (238)	1128 (498)	1508 (226)	
	N	-	22.8 (8.3)	31.6 (14.5)	
	C:N	-	49	48	
No lime, no org. amendment	C	119 (40)	143 (27)	160 (51)	
	N	-	4.0 (3.4)	1.5 (2.8)	
	C:N	-	36	133	

(Pulford and Duncan 1978).

Whereas the status of P and K in the spoil can be assessed using extraction data, that of nitrogen is more difficult to interpret. Total N levels mean very little as there is a significant amount of nitrogen in the organic component of the shale. Although this "fossil nitrogen" may be released on weathering, the rate at which this occurs is so slow, except under extremely acid conditions, that the amount of N made available for plant uptake is insignificant. The levels of extractable inorganic  $\text{NH}_4^+$  and  $\text{NO}_3^-$  reflect the nitrogen status of a very small fraction of total N at a particular stage of the nitrogen cycle. For these reasons it was felt to be preferable to measure the amount and rate of N mineralized from spoil during incubation over a fixed time period. As this is a microbiologically mediated process, the amount of carbon turned over during the same period was also measured.

Table 3 shows the amounts of C and N mineralized over a 10-week period of incubation. In all cases, large amounts of carbon were turned over in comparison to nitrogen, which is reflected by the high values of the C:N ratios. There was considerable variation in the levels of C and N mineralized between samples. Within any one year, there was no significant difference between treatments for the limed plots, but significantly less C and N were mineralized in the unlimed control plots. Comparison of these results with those of previous studies is difficult due to the variety of methods used. For example, Reeder and Berg (1977), Palmer and Chadwick (1985) and Fyles and McGill (1987) all used air-dried spoil, whereas in this study fresh spoil was used. Similarly there are a number of incubation systems which have been used. Despite these variations, however, it has usually been the case that far more carbon than nitrogen is released in this type of incubation. Even though the levels of N measured are low, they may represent the most important pool of N available to plants. Palmer and Chadwick (1985) found that mineralizable nitrogen was the fraction most highly correlated with herbage nitrogen.

Cumulative plots of carbon and nitrogen mineralized showed that after an initial flush, due to disturbance on sampling and handling the spoil, the release of carbon dioxide was linear from weeks 4-10, allowing an estimate of the rate of release at equilibrium to be made. There was initially immobilization of nitrogen, but the rate of release was linear for weeks 1-10, allowing an estimation of the rate of N release. These zero order rate constants for C and N release are shown in table 4. As in the study of Fyles and McGill (1987), nitrogen mineralization did not follow first order kinetics, and so values of potentially mineralizable nitrogen ( $\text{N}_0$ ) could not be measured

(Stanford and Smith 1972), Reeder and Berg (1977). C:N ratios calculated on the basis of rates of mineralization were lower than for those calculated from total carbon and nitrogen mineralized, due to the initial immobilization of nitrogen.

The evidence from the levels of extractable P and K, and the rates of turnover of C and N suggest that nitrogen and phosphorus are very deficient in these spoils. A fertilizer response trial showed vegetation yield increased significantly ( $p < 0.05$ ) only when 100 kg N/ha was applied (table 5). No effect on vegetation yield was measured by additions of P or K alone, or by 50 kg N/ha. Similarly, when a combination of N, P, and K were added, there was a significant response only at the high rate of N. A yield response to added N has commonly been recorded (Bradshaw 1983); the effect of P is less clear. Fitter and Bradshaw (1974) and Doubleday and Jones (1977) both showed an increase in vegetation yield with added P. Pulford and Duncan (1978) measured only a slight decrease in yield in two spoils, and no effect in a third spoil, when no phosphate was added in a pot trial. Addition of 60 kg P/ha, alone or with N and K, increased the phosphorus content of the vegetation; therefore some of this added P was available and taken up. Moreover, where a high level of N with no added P led to a yield increase, the phosphorus content of the grass did not decline, implying that additional P was taken up and so was not limiting to growth.

A detailed study was carried out on various transformations in the nitrogen cycle on 90 samples of coal mine waste from sites throughout central Scotland, representing a wide range of properties (table 6). Carbon dioxide evolution and nitrogen mineralization rates showed that a high level of carbon, but little nitrogen, was turned over. Nitrification was measurable only on about half of the sites studied, and was, as expected, highly pH dependent, being inhibited below approximately pH 5.5. However, even on sites above this pH, nitrification was not invariably measured, suggesting that the introduction of nitrifying bacteria into the spoil was also an important factor. Some N was lost due to ammonium fixation by the clay minerals of the shale. In the spoils which showed the highest degree of ammonium fixation, up to 23% of the 100 mg/kg  $\text{NH}_4\text{-N}$  added was lost in this way. Low levels of extractable inorganic N were found.

Table 4. Zero order rate constants for C and N turnover during incubation at 22°C.

Treatment	Zero order rate constants		
	mg CO <sub>2</sub> -C released per kg spoil/week	mg N released per kg spoil/week	C:N
Chicken manure	146.4	3.80	39
Sewage sludge	127.5	2.72	47
Soil conditioner	101.4	3.29	31
Peat	143.6	2.48	58
No organic amendment	102.0	3.46	29
No lime, no org. amendment	16.5	0.68	24

Table 5. Fertilizer response plots - herbage yield and NPK content

N (kg/ha)	P (kg/ha)	K (kg/ha)	Herbage yield* (t/ha)	Herbage content		
				N	P	K
0	0	0	1.7 <sup>a</sup>	1.16	0.16	1.46
50	0	0	1.6 <sup>a</sup>	1.17	0.18	1.04
100	0	0	3.3 <sup>b</sup>	1.37	0.19	1.16
0	30	0	1.2 <sup>a</sup>	1.53	0.22	0.85
0	60	0	1.2 <sup>a</sup>	1.44	0.32	1.09
0	0	30	1.8 <sup>a</sup>	1.11	0.20	0.73
0	0	60	1.3 <sup>a</sup>	1.34	0.20	0.76
50	30	30	1.3 <sup>a</sup>	1.29	0.24	0.85
100	60	60	2.6 <sup>b</sup>	1.50	0.30	1.17

\*Values with the same letter following are not significantly different at the 5% level using a Fisher LSD test.

Table 6. Survey of nitrogen status of 90 experimental sites on coal spoils.

	Minimum	Maximum	Mean
pH (in water)	3.0	8.8	5.9
CO <sub>2</sub> Evolution (mg C/kg/wk)	19.5	181.4	62.6
N Mineralization (mg N/kg/wk)	0.0	3.2	0.8
Nitrification (mg N/kg/day)	0.0	10.2	3.6
NH <sub>4</sub> <sup>+</sup> Fixation (mg/kg)	0.0	22.9	6.0
Inorganic N (mg/kg)	0.1	31.4	3.4

\* Only 46 of the 90 sites investigated showed detectable nitrification. The mean is calculated on the basis of those 46 sites only.

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