Litter effects on N dynamics and potential leaching in acid grassland soils

Muhammad Riaz, Ishaq A. Mian, Malcolm S. Cresser

Environment Department, The University of York, Heslington, York, UK. YO105DD. Emails mr548@york.ac.uk,

Abstract
A reconstituted microcosm study, from N-impacted acid grassland soils, was conducted to investigate the role of litter in N dynamics in winter. The study showed that, at UK winter temperatures, litter mineralization and retention of mineral-N from precipitation were the key sources of mineral-N in the mineral soil beneath the litter layer. NH_4^+-N produced in the litter layer was potentially mobile and resulted in significantly higher NH_4^+-N accumulation in the upper 5 cm of mineral soils from the surface litter treatment. Mixing of litter to 15 cm depth resulted in significant NH_4^+-N accumulation in sub-soils. NH_4^+-N retained in the soil profiles was strongly associated with dissolved organic carbon (DOC). The low nitrification corresponded to low temperature and acidic nature of the soils, however, mixing of litter with a high C:N ratio substantially retarded NO_3^--N production and favoured NO_3^--N immobilization. The latter was evident from markedly lower NO_3^--N concentrations in the drainage water.

Key Words
Nitrogen cycle; leaching; depth; retention; C: N ratio

Introduction
Litter decomposition rates and processes are generally considered key factors in cycling of N, P, S and other nutrients, and hence controls the sustainability of fertility and primary productivity of ecosystems (Henry *et al.* 2008). Dissolved organic carbon (DOC) is an immediate product of litter decomposition, entering the mineral layer (Kalbitz *et al.* 2000), and potentially retains and/or transports metals and organic compounds (Tipping *et al.* 2002). The N liberated from organic matter decomposition, if in excess of microbial and plant needs, would leach primarily as NO_3^--N, especially for ecosystems that have attained an N-saturation state (Aber *et al.* 1998). Soil organic matter is recognized as a potential sink for NH_4^+-N via retention on cation exchange sites so mobility of NH_4^+ is generally thought to be non-significant (Mian *et al.* 2009). Duckworth and Cresser (1991) described how the fate of ammonium and nitrate would be controlled by kinetics of their supply, availability of nitrogen and carbon, and the microbial populations associated with these transformations, together with inputs of competing cations. Riaz *et al.* (2008) showed that nitrification and immobilization of ammonium interacted to control the leaching of ammonium down the soil profile in freely draining acid grassland soils. Cresser *et al.* (2004) postulated that in heavily N-polluted upland areas of the UK, especially those with peaty and high organic matter content soils, nitrification and immobilization of ammonium are slow enough for NH_4^+-N to be in equilibrium with cation exchange sites. When this happens, NH_4^+-N concentrations in drainage water are similar to effective concentrations in precipitation, with only modification from mobile anion concentrations. In the same context, they also found low rates of nitrate transformations that facilitated leaching to adjacent streams. The present study, therefore, aimed to investigate in N-saturated acid grassland soils, the effects of litter on mineral-N production, mobility and retention in winter when biological uptake is low.

Methods
Site selection, soil sampling and microcosm construction
Soils were sampled from Hob Moor, an unfertilized permanent acid grassland near York, UK (53°57'30"N & 1°4'48"W). The site has been receiving ca. 25 kg N/ha/year from atmospheric deposition (Riaz *et al.* 2009). The grassland soils at Hob Moor range between slowly permeable clay loams and more freely draining (and more acidic) very fine sandy loams and loamy sands. In November, 2008, 10 soil profiles from the study area were selected at random and sampled to 25 cm depth in five 5-cm depth increments. Dried litter was cut into smaller pieces to pass through a 2.0 mm sieve. The microcosms were reconstituted using PVC pipes (length = 29.0 cm, inner diameter = 6.4 cm) with soils sampled from 5 depths. The experimental design used 3 treatments including: control (without addition of litter); surface litter application (20 g litter equivalent to 2 cm deep litter

layer); mixed litter (20 g litter was divided into 3 equal portions and a portion added to each of 0-5, 5-10 and 10-15 cm depths). Each microcosm was sealed at the bottom using a perforated plastic cap fitted with 140 μm nylon mesh under a layer of acid-washed quartz sand. The microcosms were then wetted and drained to bring them to field capacity. The experiment consisted of 3 replicates for each treatment and cores were set up under outdoor ambient winter conditions in York in early December under an open-sided roof structure. The cores were irrigated with 45 ml simulated rain (ca. 14 mm rain fall), twice a week and leachate was collected weekly. The formula for simulated precipitation was based upon mean composition of rainwater collected for previous 4 months over winter period.

Soil and litter initial analysis
Soil and litter pH was measured at a 1:5 m:v (soil:solution) ratio in 0.5M KCl with a pre-calibrated Thermo Orion 420 pH meter. Moisture contents were determined gravimetrically by oven drying soils overnight at 105°C. The same oven dried soil samples were ball milled to form a fine powder and used for measuring C, N and C/N ratio using an Elementar Vario Macro automated C and N Analyser.

Soil and litter analysis after 5 weeks
After 5 weeks, the soil cores were returned to the laboratory and were carefully removed from the PVC pipes. After removing the litter layer from the surface litter treatment, the soil cores then were cut into 5 equal depth sections corresponding to individual soil layers. pH and moisture content were measured using above described protocols.). Soils and litter samples were extracted for mineral-N (NH_4^+-N and NO_3^--N) determination using both 0.5M KCl and water, both at 1:5 m:v (soil:solution). The extracts were analysed for NH_4^+-N and NO_3^--N using a standard Bran & Luebbe Autoanalyser-3 protocol. The difference between KCl-extractable NH_4^+-N concentrations and water-soluble NH_4^+-N is viewed as NH_4^+-N retention index (ΔNH_4^+-N) in this study. The soil and litter water extractable-dissolved organic carbon (DOC) was determined by extracting 7-g field moist sub-samples with 35 ml deionised water. The filtered supernatants were analysed for DOC with an Elementar Liquitoc TOC analyser.

Leachate collection and analysis
Leachate (i.e. drainage water) pH and EC were measured on the day of sampling every week, and then leachates were analysed for mineral-N (NO_3^--N and NH_4^+-N) using a standard Bran & Luebbe Autoanalyser-3 manifold.

Results and discussion
Initial soil and litter physico-chemical characteristics
The soil pH (KCl) varied from 3.29 to 3.61 and soils remained substantially acidic even at 25 cm depth (Table 1). The surface soil layer (0-5 cm) had significantly higher moisture content, but moisture contents of soils from 5-25 cm depths showed no significant differences from each other. Organic carbon content consistently declined over depth, but differences were not always significant between adjacent sampling depths. The decrease in C/N ratio was significant and quite sharp over 0-20 cm depth. The KCl-extractable NH_4^+-N concentration in the litter horizon was more than 8-fold greater than that in the underlying soil, and this NH_4^+-N was highly soluble in water (data not shown).

Table 1. Initial characteristics of the soils used for the study.

Soil Layer/depth (cm)	pH (H_2O)	pH (KCl)	Moisture content (%)	C (%)	N (%)	C/N ratio
0-5	4.32[c]	3.29[e]	33.05[a]	7.97[a]	0.50[a]	16.08[a]
5-10	4.33[c]	3.36[d]	23.45[b]	3.82[b]	0.27[b]	14.17[b]
10-15	4.35[b]	3.48[c]	22.40[b]	3.07[bc]	0.23[bc]	13.46[c]
15-20	4.37[b]	3.57[b]	21.79[b]	2.47[c]	0.19[c]	12.79[d]
20-25	4.40[a]	3.61[a]	20.36[b]	2.61[c]	0.19[c]	13.44[cd]

All values are means of 4 analytical replicates. Values sharing different letters differ significantly from each other in each column excluding litter layer at p<0.05 (One-way ANOVA, Tukey's HSD post hoc test).

Litter controls on mineral-N production

The presence of added litter layer at the surface contributed significantly higher KCl-extractable mineral-N concentrations compared with the control and mixed litter treatments only at 0-5 cm depth (Figure 1). Mixing of litter, however, resulted in significantly higher mineral-N concentrations than the control at 5-10 cm depth, and higher than the surface litter application and control at 10-15 cm depth. Differences among treatments at 15-25 cm depths were non-significant. The mineral-N concentrations were dominated by NH_4^+-N in either of the litter treatments in 0-15 cm soil increments. NO_3^--N concentrations remained consistently lowered especially in the mixed litter treatment. However, soils from the control treatment showed enhanced NO_3^--N concentrations in the sub-soils. The significantly higher NH_4^+-N concentrations in the surface litter treatment could partially be the result of potentially mobile NH_4^+-N produced in the litter layer (Adamson *et al.* 1993). ΔNH_4^+-N showed strong association with DOC (Figure 2), indicating its potential in NH_4^+-N dynamics either as mobile anionic role or sorption to soil particles (Fernando *et al.* 2005). Burge and Broadbent (1961) also found a positive relationship between soil C and NH_4^+-N fixed in soils. Apart from the low pH and acidic nature of the soils, non-availability of such bound NH_4^+-N could explain limited nitrification in the mixed litter soils (Kudeyarov 1981). The consistent lower NO_3^--N production in the mixed litter treatment could also be the consequence of mixing high C:N ratio litter and associated N immobilization (Khalil *et al.* 2005).
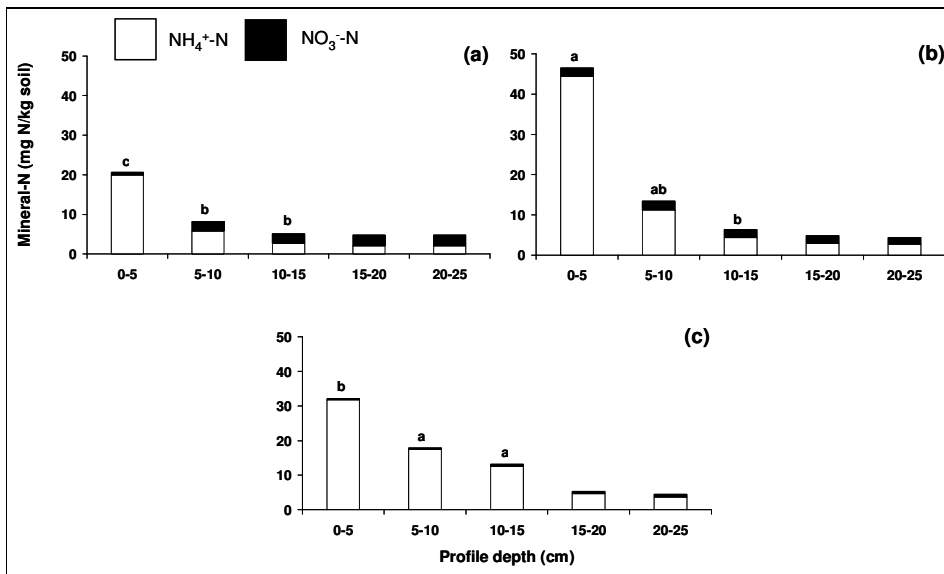

Figure 1. KCl-extractable mineral-N concentrations (mg N/kg soil) a) control, b) surface litter and c) mixed litter treatment. All values are means of 3 replicates. Bars sharing a different letter at specified depth for each treatment differ significantly from each other at p<0.05.
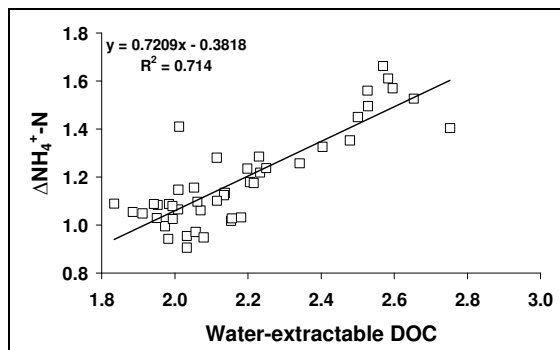

Figure 2. Linear relationship between water-extractable DOC and ΔNH_4^+-N. Regression analysis was performed on log transformed data (n=45). The R2 value was significant at p<0.001.
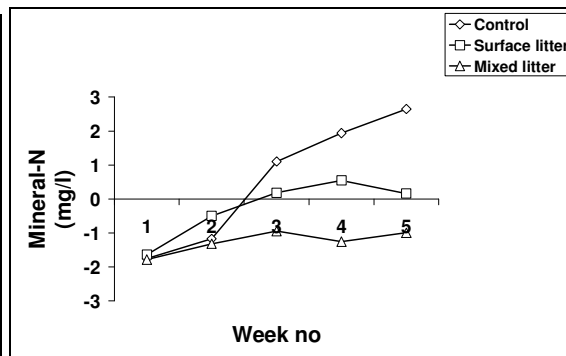

Figure 3. Changes in net mineral-N concentrations in the drainage water for each treatment over 5-week duration in winter. All values are means of 3 replicates.

Mineral-N concentrations in leachate

The net mineral-N (output-input) concentrations in leachate also clearly demonstrated remarkable N retention associated with litter additions (Figure 3). The control soils showed consistent increase in net mineral-N in leachate which indicates that mineral-N was relatively mobile in the absence of organic matter (litter) addition. However, the mixed litter treatment favoured N retention and reduced N concentrations in the leachate. This could be the result of incorporation of high C:N ratio residue which potentially immobilize N, thus reduced N leaching (Homyak *et al.* 2008).

Conclusions

A reconstructed microcosm study from acid grassland soils has shown that litter plays crucial role in mineral-N dynamics in winter. The presence of litter significantly enhanced mineral-N production in 0-15 cm soils. NH_4^+-N produced in litter layers was potentially mobile and its retention in the soil profiles was strongly associated with DOC. The mixing of litter effectively and consistently reduced mineral-N concentrations in leachate over winter, when N leaching could potentially occur to degrade water quality.

References

Aber J, McDowell W, Nadelhoffer K, Alison M, Berntson G, Kamakea M, McNulty S, Currie W, Rustad L, Fernandez I (1998) Nitrogen saturation in temperate forest ecosystems. *BioScience* **48,** 921-934.

Adamson JA, Hornung M, Kennedy VH, Norris DA, Paterson IS, Stevens PA (1993) Soil solution chemistry and throughfall under adjacent stands of Japanese larch and Stika spruce at three contrasting sites in Britain. *Forestry* **66,** 51-68.

Cresser MS, Smart RP, Clark M, Crowe A, Holden D, Chapman PJ, Edwards AC (2004) Controls on leaching of N species in upland moorland catchments. *Water, Air, & Soil Pollution: Focus* **4,** 85-95.

Duckworth CMS, Cresser MS (1991) Factors influencing nitrogen retention in forest soils. *Environmental Pollution* **72,** 1-21.

Fernando WARN, Xia K, Rice CW (2005) Sorption and desorption of ammonium from liquid swine waste in soils. *Soil Science Society of America Journal* **69,** 1057-1065.

Henry H, Brizgys K, Field C (2008) Litter decomposition in a california annual grassland: interactions between photodegradation and litter layer thickness. *Ecosystems* **11,** 545-554.

Homyak PM, Yanai RD, Burns DA, Briggs RD, Germain RH (2008) Nitrogen immobilization by wood-chip application: Protecting water quality in a northern hardwood forest. *Forest Ecology and Management* **225,** 2598- 2601.

Kalbitz K, Solinger S, Park J-H, Michalzik B, Matzner E (2000) Controls on the dynamics of dissolved organic matter in soils: a review. *Soil Science* **165,** 277–304.

Khalil MI, Hossain MB, Schmidhalter U (2005) Carbon and nitrogen mineralization in different upland soils of the subtropics treated with organic materials. *Soil Biology and Biochemistry* **37,** 1507-1518.

Kudeyarov VN (1981). In 'Terrestrial nitrogen cycles, Ecological Bulletin (Stockholm)'. (Eds. FE Clark, T Rosswall) Vol. 33, pp. 281-290.

Mian IA, Riaz M, Cresser MS (2009) The importance of ammonium mobility in nitrogen-impacted unfertilized grasslands: A critical reassessment. *Environmental Pollution* **157,** 1287-1293.

Riaz M, Mian IA, Cresser MS (2008) Extent and causes of 3D spatial variations in potential N mineralization and the risk of ammonium and nitrate leaching from an N-impacted permanent grassland near York, UK. *Environmental Pollution* **156,** 1075-1082.

Tipping E (2002) Cation Binding by Humic Substances. In 'Cambridge Environmental Chemistry Series' Vol. 12 (Cambridge University Press).