

REVIEW ARTICLE

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Soluble organic nitrogen in agricultural soils

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Abstract The existence of soluble organic forms of N in rain and drainage waters has been known for many years, but these have not been generally regarded as significant pools of N in agricultural soils. We review the size and function of both soluble organic N extracted from soils (SON) and dissolved organic N present in soil solution and drainage waters (DON) in arable agricultural soils. SON is of the same order of magnitude as mineral N and of equal size in many cases; 20–30 kg SON-N ha⁻¹ is present in a wide range of arable agricultural soils from England. Its dynamics are affected by mineralisation, immobilisation, leaching and plant uptake in the same way as those of mineral N, but its pool size is more constant than that of mineral N. DON can be sampled from soil solution using suction cups and collected in drainage waters. Significant amounts of DON are leached, but this comprises only about one-tenth of the SON extracted from the same soil. Leached DON may take with it nutrients, chelated or complexed metals and pesticides. SON/DON is clearly an important pool in N transformations and plant uptake, but there are still many gaps in our understanding.

Key words Dissolved organic nitrogen · Soluble organic nitrogen · Nitrogen transformations · Nitrogen loss · Leaching

Dedicated to Prof. K. Vlassak on the occasion of his 65th birthday

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Introduction

The forms of N present in the soil and lost in drainage have been the subject of research for many years. Lawes and Gilbert (1881) made gravimetric analyses of the organic and inorganic contents of lysimeter drainage waters after laboriously distilling >100-l samples. They reported that the amount of dissolved organic N (DON; N dissolved in soil solution and drainage water collected from agricultural land) leached was no more than 2 kg N ha⁻¹ and mostly <1 kg N ha⁻¹ out of a total leached of 50 kg N ha⁻¹, and that it was highly nitrogenous, with a mean C:N ratio of 2.6:1. They said that: “Respecting the nature of these nitrogenous organic bodies, and the part they possibly play in plant nutrition, very little is at present known.” Russell and Richards (1919) reported analyses of N in rainwater. They calculated that rainwater deposited ca. 1.5 kg organic-N ha⁻¹, one-quarter of the total N deposited at the beginning of this century. Thus it was known almost 100 years ago that rain and drainage waters contained DON. What progress have we made? Fortunately labour-intensive distillation and gravimetric analysis is a thing of the past and we are beginning to understand the composition and dynamics of DON. This paper reviews that progress.

The plough layer of arable soils may contain >3000 kg N ha⁻¹ (Stevenson 1982; Streeter and Barta 1988), but most of this is composed of a continuum of complex organic forms, which can be divided conceptually into a number of pools (Paul and Juma 1981). These pools may include organic N which is virtually inert (Hsieh 1992) as well as N present in the living bodies of the soil microbial biomass (SMB) (Jenkinson and Powlson 1976). Mineral N comprises only a small part of the total N in the soil (Harmsen and Kolenbrander 1965; Bremner 1965), usually about 1% in arable soils (Jarvis et al. 1996), except after fertiliser application. But mineral N cycles rapidly. It is supplied by the mineralisation of soil organic matter, as well as from

fertiliser, manure and atmospheric deposition, and depleted by plant uptake and immobilisation by microorganisms, by denitrification and by leaching. Although microbial N comprises only 3–5% of total N in soil, mineralisation, immobilisation and denitrification are all microbially mediated processes.

The importance of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ in crop nutrition, and the environmental and possible health impacts of NO_3^- in groundwater has focused attention on the study of mineral N (Archer et al. 1992). However, a pool of soluble forms of organic N of equal size to mineral N (about 0.3–1% of total organic N in arable soils; Mengel 1985) also exists in soil. Only recently has interest in soluble organic N (SON; N extracted from soil by water, KCl, etc.) and DON increased. We make the distinction between SON and DON because, as we shall show later, the two pools are neither the same size nor of the same composition. Soluble pools of organic N are composed, at least partially, of easily mineralisable N, and so have a major impact on the usually very small but rapidly cycling N pools such as $\text{NH}_4^+\text{-N}$ (Mengel et al. 1999). SON is therefore likely to be an important pool in N transformation pathways and plant uptake (Németh et al. 1988). The flux of N through the microbial biomass is large compared to its size and the size of the mineral N and SON pools at any given time. Determination of the relative importance of mineral N and SON in specific N transformation pathways and crop nutrition is essential for a proper understanding and prediction of the production, transformation and fate of N in agricultural systems.

In forest systems increased levels of atmospheric deposition have increased the N content of soil and brought many forest soils close to N saturation (Aber et al. 1989; Aber 1992; Currie et al. 1996; Koopmans et al. 1997; Goulding et al. 1998). Quite large pools of DON have been measured in leachates from forest floors (Yavitt and Fahey 1986; Stevens and Wannop 1987; Qualls et al. 1991; Currie et al. 1996). Qualls et al. (1991) found that 94% of the dissolved N leaching through a deciduous forest soil was present in organic form. Yu et al. (1994) also found that SON was the dominant form of N in a coniferous forest soil. SON has been identified as a key pool in soil-plant N cycling in forest systems (Qualls and Haines 1991), arctic tundra (Atkin 1996) and subtropical wet heathland (Schmidt and Stewart 1997) and DON represents a major input of N to surface water in forested watersheds (Wissmar 1991; Hedin et al. 1995), suggesting that the leaching of organic N could be a major pathway for N loss from at least some soils.

Compared to semi-natural systems, little is known about the form and function of SON/DON and the role that it plays in soil N cycling in agricultural soils. Here we review the progress that has been made since Lawes and Gilbert (1881) first analysed rain and drainage waters. We review methods of extraction, pool sizes and the role of SON and DON in N transformations and losses.

Measuring SON and DON

Extraction of SON from soil

Soluble forms of N can be extracted from soils by shaking with water. However, such extractions cause the dispersion of clays and it can be difficult to obtain clean solutions for analysis (Young and Aldag 1982). A range of salt solutions have been used for extracting N from soils, most commonly solutions of CaCl_2 , KCl and K_2SO_4 . Salt extracts may disturb adsorption equilibria on soil surfaces and release organic N, which was not originally dissolved (Fig. 1). The SON pool in soils cannot be measured directly by extraction, but instead is determined by subtracting the mineral N concentration from the total soluble N (TSN) concentration. Kjeldahl digestion was first used in this way to determine TSN in seawater; it has also been used for soil solutions (Beauchamp et al. 1986). This method is based on the reduction of N to $\text{NH}_4^+\text{-N}$ in an acid solution, and has been described in detail by Bremner and Mulvaney (1982). However, the method is slow and cumbersome, and large N contents in control samples can decrease the accuracy and sensitivity of the procedure (Smart et al. 1981).

The development of simple, rapid and automated methods by which TSN can be routinely analysed has encouraged more measurements of SON to be made in recent years. Persulphate ($\text{K}_2\text{S}_2\text{O}_8$) oxidation was originally used for the analysis of seawater (D'Elia 1977; Koroleff 1983) but has been modified to determine TSN in fresh water (Solórzano and Sharp 1980) and soil extracts (Ross 1992; Cabrera and Beare 1993; Sparling et al. 1996). $\text{K}_2\text{S}_2\text{O}_8$ oxidation is based on the principle that, in the presence of a strong oxidising agent, both $\text{NH}_4^+\text{-N}$ and SON are converted to $\text{NO}_3^-\text{-N}$. Complete oxidation is achieved by autoclaving the soil extract or by ultra-violet digestion (Cabrera and Beare 1993; Williams et al. 1995; Sparling et al. 1996). Both approaches are suitable for the processing of large batches of samples (100 per day) and require only simple laboratory equipment. This technique has become popular in recent years for determining SMB-N from the difference in TSN between chloroform-fumigated and non-fumigated soils (Ross 1992; Sparling and Zhu 1993; Murphy

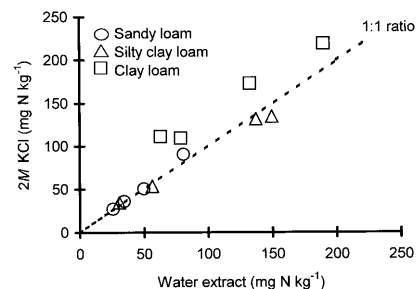


Fig. 1 Effect of extractant on the size of the soluble organic N pool in soils of differing texture

et al. 1998a). By also measuring the mineral N content in non-fumigated soil, SON can be estimated by difference (Jensen et al. 1997; McNeill et al. 1998). Alternatively, KCl extracts are routinely used to measure mineral N in soil to support fertiliser recommendations (Shepherd et al. 1996; Wilson et al. 1996). It is possible to use samples of the same soil extract for determination of TSN, mineral N and thus SON (Bhogal et al. 1999).

Smart et al. (1981) reported that $K_2S_2O_8$ oxidation was more precise than Kjeldahl digestion for measuring TSN in samples collected from a range of aquatic habitats. Studies employing water and 0.5 M K_2SO_4 soil extracts, comparing Kjeldahl digestion and $K_2S_2O_8$ oxidation, have found no significant difference in the amount of TSN determined (Cabrera and Beare 1993; Yu et al. 1994; Sparling et al. 1996). However, in 1 M KCl soil extracts, TSN was overestimated at low concentrations and underestimated at higher concentrations by $K_2S_2O_8$ oxidation compared to Kjeldahl digestion (Cabrera and Beare 1993). More recently, Merriam et al. (1996) proposed a high-temperature catalytic oxidation technique to measure TSN and found that results compared well to those of $K_2S_2O_8$ oxidation.

Our measurements of arable and cultivated ley crops growing on a sandy loam soil suggest that the extractant has only a slight influence on the size of both the mineral N and SON pools in this soil type. Extractions made with routine procedures for mineral N (2 M KCl) or SMB-N (0.5 M K_2SO_4) all show the same quantitative differences in the effects of management on N pool size and distribution; all are suitable for determining SON. However, other measurements of TSN on three contrasting soil types, sandy loam, silty clay loam and clay loam (Fig. 1) suggest that water and KCl extract comparable amounts of SON from non-clay soils, but that clay soils contain TSN only extractable with KCl. This is likely to be NH_4^+ -N or organic N adsorbed on cation exchange surfaces on the clay.

Measuring SON by electroultrafiltration

Electroultrafiltration (EUF) applies an electric field to soil suspensions to separate fractions of soluble N by forced diffusion through membrane filters (Németh 1979, 1985). The method removes both mineral (EUF- NO_3) and organic (EUF- N_{org}) N, and is therefore considered by its advocates to remove all forms of N that are available for plant uptake, loss or microbial transformations over the short term. The advantage of EUF is that the rate of nutrient release can be determined, whereas soil extraction determines only pool sizes (Németh 1985). However, EUF is labour intensive, costly, and produces variable results compared to soil extraction (Houba et al. 1986). Houba et al. (1986) found that amounts of N extracted by EUF and 0.01 M $CaCl_2$ were highly correlated, and concluded that the two techniques were interchangeable. Feng et al. (1990) found

that the EUF- N_{org} fraction was larger than the pool of N extracted with $CaCl_2$ 1 week after the incorporation of ground and dried rape tops into soil. Recent results from Mengel et al. (1999) indicated that EUF removed a larger N_{org} fraction than $CaCl_2$ in 13 of 20 soils. Thus EUF appears to measure SON plus a part of some other soil N pool.

DON in soil solution

Dissolved mineral and organic N in soil solution is found in mobile water flowing through pores, cracks and channels, and in immobile water within pores in soil peds. Sampling techniques must be selected to extract the pool of interest. Centrifugation of soil at natural soil moisture contents has been shown to be a suitable method for obtaining solutions containing dissolved organic C similar in composition to the soil solution in macro-, meso- and micro-pores (Raber et al. 1998). However, most measurements are made to estimate leaching losses, and these can be made in a number of ways, summarised below (Addiscott et al. 1991; Goulding and Webster 1992; Titus and Mahendrapa 1996). All of the methods have limitations, especially in structured soils with heterogeneous preferential flow through soil macropores.

Suction cups (also called porous cups, porous probes and, by some, lysimeters) are made of a hydrophilic material containing small pores, typically kaolin clay. When they are buried in the soil and connected to the surface by one or more narrow tubes, soil solution can be collected by creating a vacuum in the cup (Grossmann and Udluft 1991). They have been very widely used to measure NO_3^- -N leaching, but only work well in homogeneous (e.g. sandy) soils where water flow is not dominated by cracking and preferential flow. In such soils, solute movement as measured by suction cups and monolith lysimeters is in close agreement (Webster et al. 1993). They do not work well on poorly drained, heavy clay soils because they have been found to preferentially sample immobile water from soil peds (Goulding and Webster 1992; Hatch et al. 1997), whereas macropores are the dominant drainage route, especially after heavy rain (Grossmann and Udluft 1991) or irrigation. However, suction cups may still be useful for determining the composition of the pool of water that plant roots utilise.

It is difficult to determine the volume of soil from which suction cups remove solution; the reproducibility of both the volume of water removed and the concentration of solutes in it is often unsatisfactory (Addiscott et al. 1991). Suction cups with ceramic heads are normally used to obtain soil solution for the analysis of NO_3^- -N (Webster et al. 1993; Poss et al. 1995; Hatch et al. 1997) but their use is questionable for measuring a strongly adsorbed ion such as PO_4^{3-} (Hansen and Harris 1975). Because DON contains molecules that adsorb and absorb strongly, ceramic suction cups are unlikely

to be suitable for measuring DON. Quartz/Teflon samplers are inert (Zimmermann et al. 1978) and are now widely used, especially in P leaching studies (Bottcher et al. 1984). However, they are approximately 10 times more expensive than ceramic cups.

DON in drainage water

Nutrient and pollutant losses have been extensively studied by collecting drainage water from field drains (Lawes et al. 1882; Tyson et al. 1997), and lysimeters (Smolander et al. 1995; Titus and Mahendrappa 1996). However, field drains may only partially intercept soil drainage, the rest percolating to the aquifer when subsoils are permeable. Drains also require constant (preferably automatic) sampling. Very detailed results are available from experimental systems of fully automated, hydrologically isolated plots such as the Brimstone experiment (Cannell et al. 1984; Vinten and Redman 1990). Such experiments enable all drainage to be collected and analysed, giving a quantitative water and solute budget from plots on which agricultural operations can be carried out as normal, but at great cost (Cannell et al. 1984). Lysimeters are in the middle price range at approximately one-tenth of the cost of a field drainage system but 10 times the cost of porous cups. Although subject to soil shrinkage problems, they are the most reliable and economic tools with which to measure total water and solute loss from a block of soil large enough to minimise spatial variation and allow management practices almost as normal.

Size of the SON and DON pools

Smith (1987) measured SON pools as large as, or larger than, mineral N pools in air-dried agricultural soils. He suggested that this reflected the presence of freshly de-

composed plant material and/or organic matter components disrupted during sample preparation. Recent studies with fresh soil have confirmed that as much SON as mineral N can exist in soil under agricultural cropping systems (Jensen et al. 1997; McNeill et al. 1998; Bhogal et al. 2000). Jensen et al. (1997) showed that 0.5 M K₂SO₄-extractable SON varied seasonally between 8–20 kg SON-N ha⁻¹ in a coarse sand and 15–30 kg SON-N ha⁻¹ in a sandy loam (0–15 cm); the minimum occurred during winter and the maximum in late summer. McNeill et al. (1998) showed that SON comprised 55–66% of the TSN under wheat (18 kg SON-N ha⁻¹) and pasture (28 kg SON-N ha⁻¹) on a loamy sand (0–10 cm) of low organic matter content. Assuming a bulk density of 1.5 g cm⁻³ for the 0 to 30-cm layer, Mengel et al. (1999) removed a CaCl₂-extractable SON pool (fraction 1, 20 °C) of approximately 30–45 kg N ha⁻¹ from 17 arable soils. Our data (Table 1) show, for a wide range of soil types (0 to 30-cm layer), a KCl-extractable SON-N content of generally 20–30 kg SON-N ha⁻¹ and a very constant ratio between mineral N and SON in arable soils, with SON comprising about 40–50% TSN. Both data sets were collected in spring, although our measurements were made on field-moist soil while those of Mengel et al. (1999) were conducted on air-dried sieved (<1 mm) soil.

On the sandy loam soil of the long-term Woburn ley-arable experiment (described by Johnston 1973) we measured SON contents in the 0 to 25-cm layer ranging from 7 kg SON-N ha⁻¹ under continuous arable cropping to 18 kg SON-N ha⁻¹ after 8 years of grass ley. These accounted for between 33% and 60% of the TSN. Our measurements of SON in the 0 to 25-cm layer of a range of soils on an organic farm showed that it accounted for 80% of TSN and ranged from 24 to 46 kg SON-N ha⁻¹, increasing with the number of previous years under grass/clover ley. Figure 2 shows mineral N and SON pool sizes in the plough layer (0–23 cm) under continuous arable (under wheat dur-

Table 1 Mineral and soluble organic N pools (kg N ha⁻¹) extracted in 2 M KCl for 12 soils (0–30 cm) under arable cropping in spring 1999. Values in parentheses are SEMs (*n*=3). *BD* Bulk density, *SON* soil organic N

Soil	Soil subgroup (SSLRC)	USDA great group	Texture	Previous crop	BD (g cm ⁻³)	Mineral N	SON
1	Typical brown earth	Dystrochrept	Sandy loam	Winter wheat	1.01	26 (6)	29 (8)
2	Typical argillic brown earth	Hapludalf	Silty loam	Winter wheat	1.44	35 (3)	33 (3)
3	Stagnogleyic argillic brown earth	Hapludalf	Sandy clay loam	Winter oilseed rape	1.42	37 (3)	22 (4)
4	Stagnogleyic argillic brown earth	Hapludalf	Sandy clay loam	Winter wheat	1.27	81 (8)	30 (1)
5	Gleyic argillic brown earth	Hapludalf	Silty clay loam	Celery	1.31	26 (1)	34 (1)
6	Typical humic-alluvial gley soils	Haplaquoll	Clay loam	Winter wheat	1.41	32 (2)	28 (3)
7	Brown rendzina	Eutrochrept	Clay loam	Field peas	1.31	21 (3)	33 (1)
8	Brown rendzina	Eutrochrept	Clay loam	Winter wheat	1.13	25 (1)	24 (2)
9	Pelo-stagnogley soil	Haplaquept	Clay	Winter wheat	0.97	33 (6)	24 (3)
10	Typical calcareous pelosol	Haplaquept	Clay	Winter wheat	1.26	33 (2)	27 (2)
11	Typical calcareous pelosol	Haplaquept	Clay	Winter wheat	1.36	27 (2)	33 (3)
12	Typical calcareous pelosol	Haplaquept	Clay	Winter barley	1.08	27 (2)	23 (3)

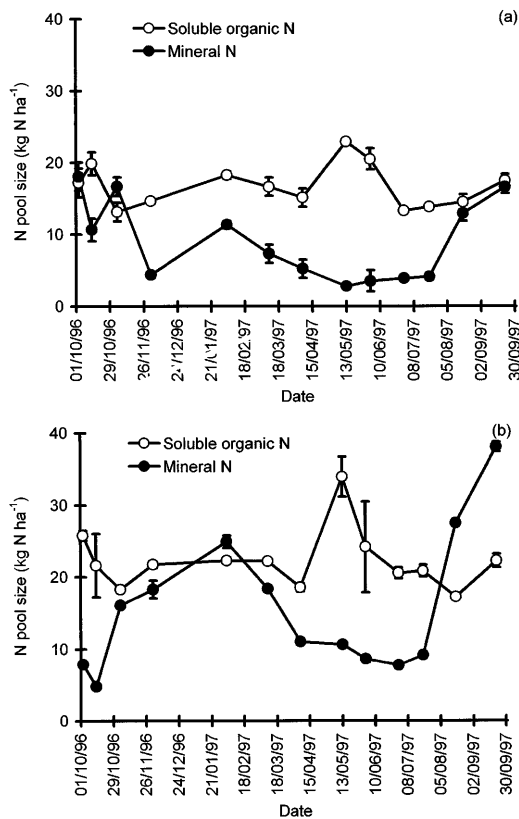


Fig. 2 The dynamics through a year (1 October 1996–30 September 1997) of the mineral N and soluble organic N (SON) pools (extracted in 2 M KCl) in the surface soil (0–23 cm) under a continuous arable plot (a) and a short-term ley ploughed up immediately after the first sampling and planted with wheat (b). Capped bars are SEM

ing year of sampling; Fig. 2a) and an 8-year ley ploughed up immediately after the first sampling and sown to wheat (Fig. 2b) in the Woburn ley-arable experiment. More SON and mineral N were found under the ploughed up grass, as was expected. Even larger SON pool sizes (70–500 kg SON-N ha⁻¹) have been measured in the soil profile (0–90 cm) after ploughing and reseeding long-term (>50 years) grasslands (Bhoggal et al. 1999). Clearly SON is a significant pool within agricultural soils.

Composition of SON

Dissolved organic matter leaching from forest floor litter is dominantly composed of decay-resistant organic acids formed by partial decomposition of plant, microbial and animal tissues (Currie et al. 1996). It is often fractionated by polarity and charge using resins and/or the optical absorbance of solutions determined at 340 nm (Raber et al. 1998; Scott et al. 1998; Tipping et al. 1999). In organic-rich layers, such as leaf litter or

peat, hydrophobic and hydrophilic acids occur in equal concentrations. However, hydrophobic compounds are retained by adsorption and aggregation in mineral horizons, and the relative concentration of hydrophilic acids increases in drainage from upland soils as the thickness of the mineral horizons increases (Tipping et al. 1999). Ligand exchange between the dissolved organic matter and carboxyl (Kaiser et al. 1997) or hydroxyl groups (Shen 1999) on the surface of soil minerals is thought to be an important mechanism for sorption, although a number of other mechanisms have also been proposed (see Chiou et al. 1983). Adsorption isotherms for interactions between dissolved organic C and arable agricultural soils can be represented by linear isotherms, where the different adsorption capacities of different soils are related to the clay content (Riffaldi et al. 1998). Shen (1999) found the sorption capacity of the soil to be influenced by pH (maximal at pH 4–5 and decreasing with pH > 5), clay content (through its relationship with the amount of mineral surface), the ionic strength of the soil solution and the ion species present in soil solution (e.g. Ca²⁺ binding to mineral sites or complexing with dissolved organic matter). Thus management practices in agricultural systems, such as manure application and liming, will change the sorption capacity of soil and the resulting composition of the dissolved organic matter in solution.

Dissolved organic matter from arable agricultural soils has a higher proportion of hydrophobic compounds when compared with extracts from grassland and forest soils (Raber et al. 1998). Total amounts of SON are usually higher under grassland and forest and the proportion of amino compounds is greater than in arable soils (Németh et al. 1988; Mengel et al. 1999). In arable soils, 23–55% of SON is hydrolysable. Free amino acids only make up 3% of DON, amino sugars and heterocyclic-N bases, on average, 15%; the remainder of the hydrolysable fraction is present in amino compounds.

The availability of suitable analytical techniques has restricted progress in determining the composition of SON/DON. However, new developments in techniques such as fluorescence spectroscopy (Senesi et al. 1991; Tam and Spósito 1993; Erich and Trusty 1997), Fourier-transform infrared spectroscopy (Candler et al. 1988; Gressel et al. 1995a; Kaiser et al. 1997), ¹³C-nuclear magnetic resonance spectra (Candler et al. 1988; Novak et al. 1992; Kaiser et al. 1997) and ultraviolet-visible spectra (Candler and Van Cleve 1982; Cronan et al. 1992) are now being employed to characterise dissolved organic matter into functional or structural groups. Most progress has been made from the analysis of humic substances (Gressel et al. 1995a) but research into dissolved organic matter (Gressel et al. 1995b) suggests that progress will be rapid. We need to further characterise specific components of SON rather than considering it as a single pool. Only then will we quantify the size of SON fractions that are actually involved in N cycling and loss processes.

Role of SON in N transformations

Mineralisation

The SON pool and its transformations have been largely overlooked in research into mineralisation, which has usually concentrated on changes in the size of the soil mineral N pool. However, the form of N determines which micro-organisms and plants can utilise it, and so the distinction between the mineralisation of organic matter through to NH_4^+ -N or only to SON is important.

Appel and Mengel (1993) have suggested that CaCl_2 -extractable SON is a reliable indicator of the pool of organic N available for mineralisation in sandy soils because the size of this pool correlates with net N mineralisation (Appel and Mengel 1992, 1993; Groot and Houba 1995). However, Appel and Xu (1995) attempted to relate the mineralisation of EUF- N_{org} to the appearance of mineral N by using ^{15}N -labelled rape residue as a tracer. They found that, while EUF was able to selectively extract organic N derived from the rape, the decline in the size of the EUF- N_{org} fraction was not sufficient to account for all of the production of ^{15}N -labelled mineral N. The authors also found that a large (but unknown) fraction of the EUF- N_{org} derived from the rape was not easily mineralisable.

Murphy et al. (1998b) found that changes in the size of the KCl-extractable SON pool in a loamy sand under pasture and wheat paralleled gross N mineralisation rates. We have recently found that the production of KCl-extractable SON during aerobic incubation is significantly correlated to gross ($r=0.73$, $P<0.001$) and net N mineralisation rates ($r=0.68$, $P<0.01$) in agricultural soils ranging in texture from sandy loam to clay loam. However, no direct link between SON turnover and gross N mineralisation rates has yet been established.

Smith (1987) showed that, during the long-term aerobic incubation of soil with periodic leaching [using the method of Stanford and Smith (1972)] DON was produced between leaching episodes, although the majority of leached N was removed as NO_3^- -N. Smith (1987) determined the mineralisation potential of the leachates in the absence of soil and concluded that the leached DON was not "exceptionally susceptible" to mineralisation. This may imply that DON is stable in soil and, after leaching, in streams and rivers. However, since the mineralisation potential was determined *outside* of the soil, the findings of Smith (1987) cannot be used to indicate an in situ rate of turnover for this pool.

Since the breakdown of soil organic matter can result in the production of organic compounds that are soluble but recalcitrant to further microbial decomposition (Smolander et al. 1995), it is likely that only a fraction of the SON pool will be mineralised. Better relationships may exist between N mineralisation and the labile fractions of SON. DeLuca and Keeney (1994)

measured a decline in the size of the soluble amino-N pool in soil under tallgrass prairie that coincided with an increase in SMB and N mineralisation. Kielland (1995) has suggested that the rapid turnover of amino acids in arctic tundra soil results in high rates of gross N mineralisation. Recently, Mengel et al. (1999) examined the relationship between net N mineralisation and fractions of SON (amino-N, amino sugars, heterocyclic-N of nucleic acids). They found a significant correlation between amino-N and net N mineralisation across 17 arable, 1 forest and 2 grassland soils. However, this relationship was not significant when the arable soils were examined independently: the range of amino acid contents of the arable soils was narrow compared to the variation in net N mineralisation rates, suggesting that N pool size does not necessarily reflect N process rates. Jones (1999) showed that the degradation of amino acids is extremely rapid with half-lives, for a range of amino acids, being only 1–12 h in a range of soils.

One difficulty with interpreting net N mineralisation rates is the confounding problem of immobilisation (Barraclough 1991; Davidson et al. 1991; Mary and Recous 1994; Murphy et al. 1998b; Recous et al. 1999). We have found that gross N mineralisation rates (i.e. ammonification) vary less than net N mineralisation across arable soils (unpublished data), highlighting the importance of immobilisation in the cycling of N in agricultural soils (Gaunt et al. 1998). Similarly, Barraclough et al. (1998) found that gross N mineralisation rates, associated with the decomposition of plant residues, were more constant than net N mineralisation rates. This suggests that, if the amino-N and amino sugar fractions are the direct sources from which inorganic N is produced (Mengel et al. 1999), then their pool size may be better related to total soil N supply (i.e. gross N mineralisation) than the net product of mineralisation-immobilisation turnover. However, fluxes in and out of the amino-N and amino sugar pools may still mask the relationship between N fraction and N transformation.

Immobilisation

NH_4^+ is the dominant form of N assimilated and immobilised by soil micro-organisms (Jansson and Person 1982; Recous et al. 1988; Shen et al. 1989), although NO_3^- -N can also be assimilated when C is available (Azam et al. 1986; Recous et al. 1988). Mineralisation-immobilisation theory (MIT) assumes that all N uptake is from the mineral pool. However, micro-organisms can also utilise low molecular weight SON compounds (Molina et al. 1983; Barak et al. 1990; Barraclough 1997), suggesting that classic MIT theory may be incorrect. Hart et al. (1994) found that the C:N ratio of the substrate utilised by heterotrophic micro-organisms in a forest soil was similar to that of the K_2SO_4 -extractable organic pool in that soil. They also showed that the K_2SO_4 -extractable SON pool declined when the chloroform-labile N pool (i.e. SMB-N) increased, and suggested that extractable SON is a major source of N for

micro-organisms in forest soil (Hart and Firestone 1991; Hart et al. 1994). In a soil under winter wheat, only 44% of added leucine-N and 82% of glycine-N was mineralised through to $\text{NH}_4^+\text{-N}$, while all of the amino-N disappeared from the soil, presumably due to direct assimilation by the SMB (Barraclough 1997). Thus conventional views of N transformation within soil may be an over-simplification.

Plant residues contain significant amounts of water-soluble C and N (Mengel and Kirkby 1978), and water-soluble fractions of straw have been shown to be relatively rich in N (Jensen et al. 1997). N from plant residues is rapidly assimilated by the SMB, and Jensen et al. (1997) found no significant increase in the amount of SON in soil after amendment with 4 and 8 t ha^{-1} oil-seed rape straw compared to unamended soil. By contrast, both SON and DON were larger in the FYM plot of the Broadbalk wheat experiment than in the other plots receiving fertiliser (Table 2). Clearly the quality of the organic material has a major impact on SON/DON. This is further supported by studies of nutrient dynamics on tropical soil amended with green manures, which showed the concentration of SON to increase substantially at the same time as immobilisation of mineral N (Mulongoy and Gasser 1993).

Figure 3 shows mineral N and SON pools in soil into which three contrasting crop residues had been incorporated. Both SON and mineral N pools were smaller in the soil to which maize residues had been added than in the control soil. Maize residues have a C:N ratio of 108:1, and it is probable that both mineral N and SON were immobilised in this treatment. By contrast, forage rape and rye have C:N residues of 11:1 and 14:1, and both the mineral N and SON contents of the soil to which these residues were applied increased greatly. During the residue incubation, rain fell after day 50. The SON content of the soil in the residue treatments returned to a value similar to that of the control after rainfall, perhaps because the organic N released from the residues was leached below the layer from which samples were taken. If this was the case, it indicates a difference in leachability and thus chemical composition between SON derived from newly incorporated residue and older SON.

Table 2 Mineral N, soluble organic N SON or dissolved organic N (DON) contents (kg N ha^{-1}) in the soil profile (0–75 cm) and drainage solution collected from tile drains (September–November 1998) located at a soil depth of 65 cm under plots of the

Method	Measurement	N0	N144	N288	FYM
Soil extraction ^a	Mineral N	19.3 (1.3)	35.9 (1.3)	49.3 (2.2)	82.9 (3.0)
	SON	46.9 (8.9)	23.7 (8.7)	55.3 (11.7)	60.5 (11.9)
Total drainage ^b	Mineral N	9.9	6.3	29.0	52.0
	DON	1.2	1.1	2.5	7.0

^a Soil profiles (0–75 cm) sampled on 7 December 1998 and extracted using 2 M KCl

^b Assumes that 200 mm of total drainage (tile drains plus leaching through to chalk) occurs over the total leaching period (Septem-

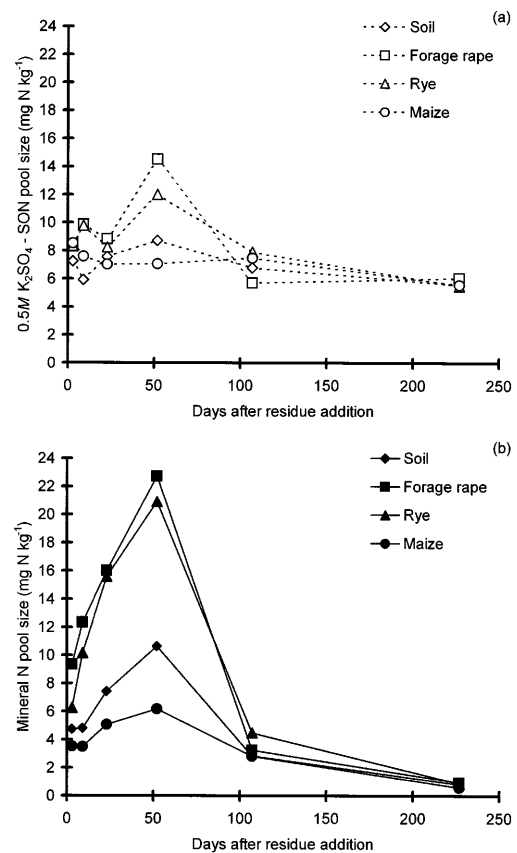


Fig. 3 The dynamics of the SON pool (a) and the mineral N pool (b) in soils into which forage rape, rye and maize residues had been incorporated

Leaching

Concentrations of DON in forest floor leachates exceed concentrations of mineral N (Yu et al. 1994), and DON has been found to be a dominant source of N leached into lakes in forested watersheds (Wissmar 1991). Stevens and Wannop (1987) studied the composition of TSN in leachate from lysimeters under the organic horizon, and from ceramic cup samples in the soil mineral layers, after the clearfelling of Sitka spruce in north

Broadbalk wheat experiment. Values in parentheses are SEMs ($n=4$) N0 No N applied, N144 144 $\text{kg (NH}_4)_2\text{NO}_3\text{-N ha}^{-1}$ year⁻¹, N288 288 $\text{kg (NH}_4)_2\text{NO}_3\text{-N ha}^{-1}$ year⁻¹, FYM farmyard manure with a N content equivalent to ca. 240 kg N ha^{-1} year⁻¹

ber–March). Values calculated using an average concentration of mineral N and DON concentration from the tile drains over the period September–November 1998

Wales. They found that, within the organic horizons, DON was >90% of TSN, but that deeper in the soil profile NO_3^- -N predominated, suggesting the transformation of DON to NO_3^- -N during percolation.

The current perception is that, in agricultural soils in temperate climates, NO_3^- -N is the main source of N in drainage water. It now seems that DON may also be a vehicle for significant loss of N from the soil. Table 2 shows some data recently collected from the Broadbalk continuous wheat experiment at Rothamsted [described by Dyke et al. (1983)]. This 156-year-old experiment compares the effects of different amounts and types of fertiliser and manures on wheat grown continuously and in rotation. Each plot is drained and samples collected from the drains and suction cups. DON in drain waters is compared with SON measured in KCl soil extracts. The data show that the SON pool in the soil is much larger than the amount of N leached as DON; the latter being equivalent to only 2–10% of the SON pool. However, approximately 10% of the N leached from drains is still lost in an organic form. Thus the amount of N that is likely to be leached in organic form is significant but much less than the amount that remains within the soil.

It is apparent that more total N and DON is leached from plots receiving farmyard manure (FYM) compared to inorganic N. Loss of DON increased in the order nil-N plot < N-fertiliser plots < FYM (Table 2). The increase in DON under FYM is related to the greater amount of N in the soil ($\text{N}_0 = 0.104\%$ N, $\text{N}_{144} = 0.127\%$ N, $\text{N}_{288} = 0.129\%$ N, $\text{FYM} = 0.297\%$ N) but may also be due to the reduced sorption of DON onto soil in the FYM plot. Soil organic matter blocks active sites on soil minerals, reducing the sorption of dissolved organic matter.

Very large amounts of DON (up to 20% of total N lost) have been found in drainage waters leaving grassland lysimeters in Devon, UK (Hawkins et al. 1997). Certainly the potential exists for large leaching losses of DON: substantial amounts of SON have been found at depth (0–90 cm) when extracted from soil under wheat and especially permanent pasture (Fig. 4; Bhogal et al. 1999). To date it is unclear whether SON is mineralised before leaving the surface soil, thus leaching as NO_3^- -N, or whether it is retained in the soil. It is also unclear whether DON leaving soils can be transformed to NO_3^- -N in surface- or groundwaters. If SON is being mineralised during percolation through soil then it is included in measured losses (as NH_4^+ -N, always small, and NO_3^- -N) and accounted for in the N balance. However, SON sorbed in lower soil horizons may not be accounted for in measurements. Losses of N from soil may therefore be greater than previously considered from NO_3^- leaching studies, and leached DON may partially explain the imbalance that is sometimes calculated in experiments tracing the fate and recovery of ^{15}N -labelled fertiliser (Glendinning et al. 1997). This is supported by findings of Németh (1985), who found that fertiliser N was recovered in both EUF- NO_3 and EUF- N_{org} fractions, and

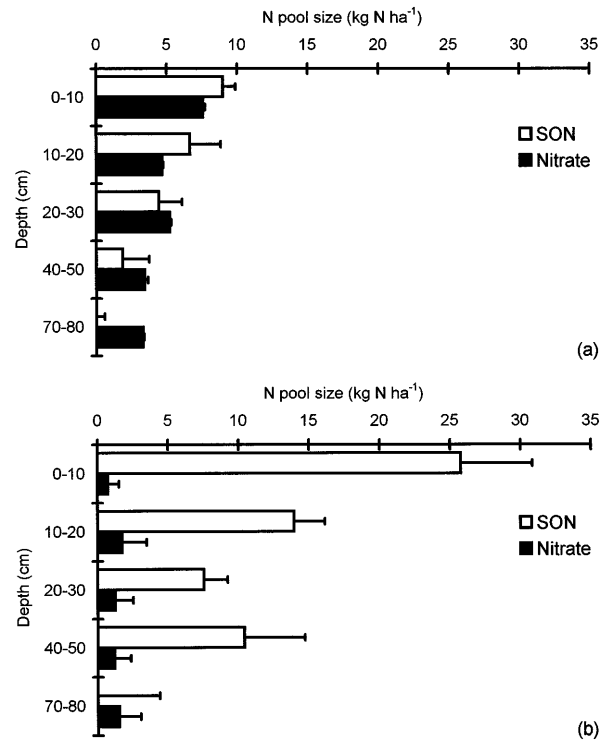


Fig. 4 Distribution of 2 M KCl-extractable SON and NO_3^- -N within the soil profile under continuous arable cropping (a) and permanent unimproved grassland (b) on a sandy loam soil. *Cap-ped bars* are the SEM

concluded that it is necessary to measure the easily mineralisable EUF- N_{org} fraction in fertiliser-recovery studies. However, Appel and Mengel (1992) did not measure an increase in the size of the EUF- N_{org} fraction following fertiliser addition.

Plant uptake

The release of N through the mineralisation of SOM and plant residues has long been identified as an important source for plant uptake (Scarsbrook 1965; Paul and Voroney 1980). Plants are usually thought to take up NH_4^+ -N and NO_3^- -N, with NO_3^- -N being favoured when it is available in abundance (Streeter and Barta 1988). Plants are able to take up urea directly in the absence of hydrolysis (Harper 1984), but more slowly than mineral N. Bollard (1959) demonstrated that many plants are able to use SON compounds as their sole N source. In some natural environments (e.g. temperate and arctic heathlands) mineralisation rates are too slow to supply all of the N required by plants as NO_3^- -N or NH_4^+ -N (Chapin et al. 1988; Nadelhoffer et al. 1991; Jonasson et al. 1999; Schmidt et al. 1999), and soluble forms of organic N are a major source of plant-available N (Chapin et al. 1993; Kielland 1994). Schmidt and Stewart (1997) found that, over 1 year of measurements, NH_4^+ -N and amino acids were the dominant

forms of N under subtropical heathland. It is well established that some plants are capable of utilising SON either directly (Chapin et al. 1993; Kielland 1994) or in association with mycorrhiza and ectomycorrhizae (Atkin 1996; Kielland 1994; Michelsen et al. 1996). Mycorrhizal roots may transport amino acids from the bulk soil via the extracellular mycelium, thus preventing their rapid degradation in the rhizosphere. This may be the main route for the direct uptake of SON by plants (Jones 1999). However, there is still little information on the contribution of SON to the total intake of N by mycorrhizal plants.

Within agricultural soils, the availability of organic N compounds to plant roots is usually assumed to be minimal (Harper 1984). It is not clear whether agricultural crops benefit from SON either by direct uptake or via microbial immobilisation of organic molecules and then re-mineralisation of $\text{NH}_4^+\text{-N}$. Appel and Mengel (1990, 1992) found that the size of the organic N pool extracted by EUF or CaCl_2 did not decline in sandy soils during the growth of rape plants, although this lack of change in the size of the SON pool does not indicate that the fraction is not turning over and supplying N to plants. Jones and Darrah (1994) demonstrated the presence of amino-acid-specific transporters in the cell membranes of plant roots capable of operating at low solution concentrations, and established that maize roots possess a highly efficient mechanism for scavenging SON. Further studies using ^{15}N as a tracer are required to determine what proportion of the extractable SON is used by plants.

Mercik and Németh (1985) showed that long-term (since 1923) annual applications of inorganic N (90 kg N ha^{-1}) increased both the EUF- NO_3 and EUF- N_{org} fractions compared to soils given no N. Mercik and Németh (1985) also found that leaching of EUF- NO_3 was greater under potato monoculture compared to rye monoculture. On the Broadbalk experiment at Rothamsted, less SON was present where wheat followed potatoes compared to continuous wheat. At present we are unsure whether this was related to: (1) a difference in the quality and quantity of residue inputs to soil under potatoes compared to wheat, or (2) a difference in the utilisation of SON between plant species.

Seasonal dynamics of SON

Seasonal variations in dissolved organic matter fluxes have been measured in the seepage water from forest soil and drainage from upland peat soils, with maximum fluxes occurring during summer (Tegen and Dörr 1996; Scott et al. 1998). The Woburn dynamic study (Fig. 2) was an attempt to measure the dynamics of all the major pools and transfer processes of N through an agricultural year. Figure 2 shows the dynamics of the mineral N and SON pools. Clearly the SON responds to periods of plant uptake and mineralisation/immobilisation, but it is not as dynamic as the mineral N pool.

Under continuous arable cultivation, the size of the SON pool was relatively constant at ca. $15\text{--}20 \text{ kg SON-N ha}^{-1}$ (0–23 cm), decreasing with leaching in early winter and increasing markedly during the period of rapid root growth in spring. Under ploughed-out grass, the SON pool size was larger at ca. $20\text{--}25 \text{ kg SON-N ha}^{-1}$ (0–23 cm), and the changes were larger than under continuous arable, but occurred at the same times of the year and in the same way. The dynamics of the SON and mineral N pool in the plough layer (0–23 cm) were reflected in subsoil down to 90 cm. The period of rapid plant growth (April to June) both above and below-ground (root growth/turnover and exudates) appeared to play an important role in SON dynamics. We hypothesise that in this soil there is a relatively constant pool of SON (related to soil organic matter content and soil texture) and a more dynamic pool of SON, which reflects current plant dynamics. Presumably these two fractions of SON vary greatly in their chemical composition, stability and transformation rates.

Transport of pollutants with DON

Early work appreciated that dissolved organic matter leached from soil could carry with it nutrient cations such as Ca^{2+} and Mg^{2+} and pollutants such as toxic metals (low affinity for DON – Cd, Zn; high affinity for DON – Cu, Cr, Hg) and pesticides (Chiou et al. 1986; Berggren et al. 1990; Wissmar 1991; Liu and Gary 1993). It is the concentration of a heavy metal in soil solution that is of importance in determining its environmental impact, not the total metal content (Temminghoff et al. 1998). This makes the study of dissolved organic matter/heavy metal relations even more important. Many of the functional groups of dissolved organic matter are acidic and deprotonated, resulting in anionic charged matter which facilitates its solubility and ability to complex with metals (Shen 1999). The availability and mobility of heavy metals in soils is dependent on their chemical speciation and relative distribution in soil solution. Heavy metals such as Cu that complex with dissolved organic matter are potentially highly mobile (Temminghoff et al. 1997; Kalbitz and Wennrich 1998; Romkens and Dolfing 1998). Reddy et al. (1995) showed that Cu was predominately complexed with dissolved organic matter at neutral pH, while under acidic conditions free ionic forms dominated. Animal manure is a source of Cu in agricultural systems (Romkens and Dolfing 1998) and we have measured a higher concentration of Cu in the drainage solution from the Broadbalk wheat experiment under FYM compared to mineral N plots.

The use of SON in fertiliser recommendations

To predict the availability of N to crops from soil it is necessary to determine both mineral N and N which is

easily mineralisable and likely to be released during crop growth. Many methods and models have been developed for measuring or predicting N released by mineralisation. These were reviewed by Jarvis et al. (1996) and Shepherd et al. (1996). Very little research has concentrated on SON. Smith et al. (1980) recognised the need to measure what they described as “organic N leached” when using extractants to estimate mineralisable N. Németh (1985) and Recke and Németh (1985) also concluded that it is necessary to measure both the EUF-NO₃ and EUF-N_{org} fractions of soil N when predicting N fertiliser requirements. The EUF method has been used to predict fertiliser requirements for sugar beet (Wiklicky 1982; Recke and Németh 1985; Sheehan 1985), grapes (Eifert et al. 1982) and other agricultural crops (Appel and Mengel 1990; Saint Fort et al. 1990; Linden et al. 1993). Rex et al. (1985) found a highly significant correlation between the grain yield of winter wheat and EUF-N (EUF-NO₃ plus EUF-N_{org}) content of the soil.

We found no strong relationship between the size of the KCl-extractable SON pool and the amount of potentially mineralisable N (PMN; determined by anaerobic incubation) in soil collected from a range of soil types and land uses (Fig. 5). Both the mineral N and SON pool size increased after anaerobic incubation, with the ratio between mineral N and SON being identical at the beginning and at the end of the incubation. The absence of any change in this ratio did not indicate

that SON was not the source of mineral N production, since input and output fluxes through this pool may have been in balance during the incubation. As an index, PMN would rank soils in the same order whether SON was included as a component of the total pool or not. However, if the size of the PMN pool released during incubation is thought to reflect the amount of the N that will become available in the short-term to plant uptake, then inclusion of SON within the PMN pool may be warranted. Measurement of both mineral N plus SON (i.e. TSN) may improve subsequent fertiliser recommendations but, with the exception of EUF recommendations, few attempts have been made to incorporate measurements of SON into decision support systems. This may be because the processes and conditions which promote and consume SON are not, as yet, well defined.

Conclusions

Concerns over the environmental and health impacts of NO₃-N leached from agricultural soils, as well as the importance of NH₄⁺-N and NO₃⁻-N in crop nutrition, have focused attention on the study of mineral N in agricultural soils. In contrast, SON in soil, its transformations, and losses by leaching of DON have received relatively little attention. Recent research suggests that the SON pool is as large as the mineral N pool, with at least a proportion of it leaching either untransformed as DON or transformed into NO₃⁻-N. DON carries with it nutrients and pollutants into surface- and groundwaters. It is very likely that SON plays an important role in mineralisation/immobilisation. However, the absence of a relationship between SON and other indices of N availability suggest that merely measuring SON will not indicate the size of the mineralisable N pool. Information on the role of SON in N transformations is sparse and often contradictory. Until the many questions surrounding SON are answered we will be limited in our ability to incorporate it into N-cycle models and decision support systems. We need to quantify the size and composition of SON pools in different systems, identify those fractions of SON that are involved in N mineralisation, microbial assimilation and plant uptake, and determine the ultimate fate of SON. The recent development of simple methods to measure SON and improved techniques to characterise SON will stimulate research and enable workers to begin to answer these questions.

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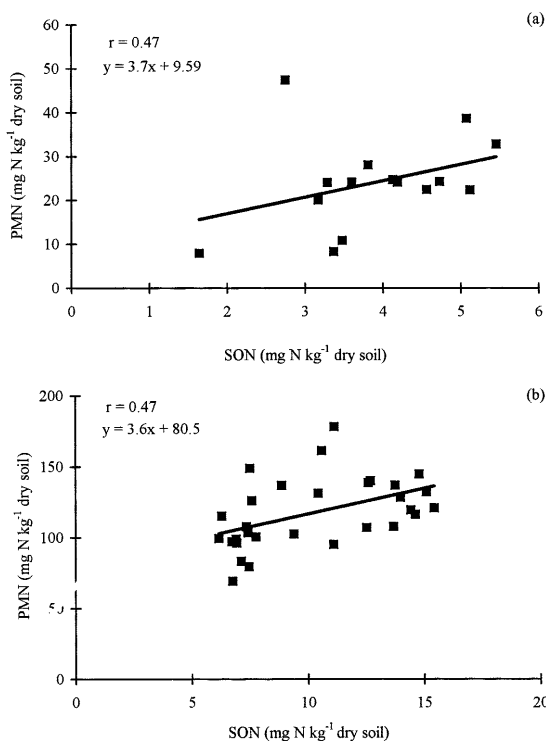


Fig. 5 Correlation between the amount of SON extracted in 2 M KCl (*x* axis) and potentially mineralisable N (PMN; *y* axis) in soil collected from the Woburn ley-arable experiments (a) and ley-arable plots on Duchy home farm (b)

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