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Rate of soil acidification under wheat in a semi-arid environment

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Abstract

The rate of acidification under wheat in south-eastern Australia was examined by measuring the fluxes of protons entering and leaving the soil, using the theoretical framework of Helyar and Porter (1989). Monthly proton budgets were estimated for the root zone (0–90 cm layer) and for the 0–25 and 25–90 cm layers. After an annual cycle, the root zone was alkalinized by 0.5 to 3.1 kmol OH^- ha^{-1}. The alkalinity originated from the mineralization of the organic anions contained in the organic matter. The budget was near neutrality in the 0–25 cm layer (range: -1.0 to 1.4 kmol H^+ ha^{-1}), whereas there was net alkalinization in the 25–90 cm layer (1.7 to 2.3 kmol OH^- ha^{-1}). In the 0–25 cm layer, the acidity produced in autumn by mineralization of organic nitrogen was counterbalanced by the alkalinity released from crop residues. The main acidifying factor in this layer was leaching of NO_3^- during early winter (2.4 kmol H^+ ha^{-1}). Nitrate added through leaching was the main alkalinizing factor in the 25–90 cm layer, as added NO_3^- was taken up by the roots or denitrified in this layer. Urea fertilization had almost no effect on the rate of acidification, as little NO_3^- was leached out of the root zone. The factors acidifying the soil under wheat were limited in this environment because of the small amount of NO_3^- leached and the retention of the crop residues.

Introduction

Soil acidity is an increasing limitation to agricultural production in many regions of the world where rainfall exceeds evapo-transpiration during the rainy season (van Breemen et al., 1984; Bolan et al., 1991). It is a natural process, accelerated by agriculture, which is generally more pronounced in higher rainfall areas and on soil with a low buffering capacity (Ulrich, 1980). The area of low pH soil extends into the low-rainfall zones of south-eastern Australia and into the Mediterranean climatic zone of the Western Australia wheat belt where there are periods of the year when rainfall significantly exceeds evaporation (Carr and Ritchie, 1993; Chartres et al., 1990; Coventry et al., 1987; Helyar et al., 1990).

The rate of acidification can either be hastened by the activity of plants, animals and agricultural enterprises or minimised by careful management practices that restrict the export of alkaline products from the soil-plant system. Previous estimates of the rates of acidification of different agricultural systems have been determined from fenceline comparisons between unimproved and adjacent cultivated fields, using the pH buffer capacity measurements in association with pH measurements (Chartres et al., 1990; Helyar et al., 1990; Ridley et al., 1990a,b). The rate of net acid addition ranges from near zero to 3–5 kmoles H^+ ha^{-1} yr^{-1}. Maximum rates of 10–20 kmoles H^+ ha^{-1} yr^{-1} have been measured in some exploitative systems. Information on the processes leading to net acid accumulation is useful to develop management strategies that minimize acid addition. Several authors (Bolan et al., 1991; Helyar and Porter, 1989; Williams, 1980) have shown that much of the accelerated acidification is associated with nitrogen inputs into the farming system in excess of the needs of the plant. There appears to

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be a growing acceptance that acidification in legume-grass pasture systems is essentially the outcome of the leaching of NO_3^- formed from the excessive N inputs into the soil (Helyar and Porter, 1989). To date this process has not been quantified in the field.

Agricultural systems in the semi-arid regions of Australia are often rotations between a legume and annual grass pasture and a cereal crop. Comparing on long term changes in soil pH between cultivated and adjacent unimproved areas is inappropriate to discriminate the proton balance between the two phases of the rotation. Detailed knowledge of the fluxes during each of the phases is thus important in devising management strategies that minimize soil acidification.

When measuring rates of acidification, budgets have been compiled for the entire root-zone generally without provision for differential rate of acidification within the profile. Recent research has indicated acidification in the surface soil and alkalization in the subsoil in both repacked soil columns (Black, 1992) and under field conditions (McLaughlin et al., 1990). In these cases and that of Conyers and Scott (1989), the bulk assessment had masked the tendency for the surface soil to become acid and the lower soil layers to become more alkaline.

The objective of this study was to determine the components of the proton budget and the net acidification rate that occur under wheat cultivation in a ley-farming system. We used the theoretical framework of Helyar and Porter (1989) to measure the monthly proton budget in the field. To discriminate between horizons, the fluxes were monitored both at the surface and at depth. By establishing a monthly budget for each depth, the contribution of the different factors to soil acidity can be discussed with respect to both the time of the year and the soil layer.

Theoretical background

The approach of Helyar and Porter (1989) assesses the rate of acidification of soils as the balance of inputs and outputs of protons to the soil. The proton pool (H^+) represents all protons in the soil, namely the exchange complex and soil solution. Inputs and outputs of protons change the proton pool of the soil by an amount equal to the amount of H^+ added or removed. The pH change is the product of the change in H^+ and the pH buffering capacity of the soil. The system considered was the entire soil profile, or individual soil layers. Root uptake was considered to be an export from the system and crop residue an input.

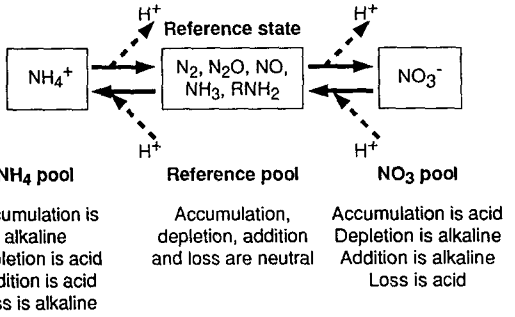

Fig. 1. Input and outflow of protons (H^+) in the ecosystem as the result of N-cycling (adapted from Helyar and Porter, 1989).

Protons are added to or removed from the soil, or are produced or consumed in reactions within the soil. The dissociation of water and carbonic acid is the only mechanism of direct input or output of protons whenever acid added by rain is negligible. In contrast, there are many processes that indirectly add or remove H^+ from the proton pool of the soil and these can be described in terms of the biochemical cycles of several elements.

Protons are either produced or consumed by biochemical association/dissociation reactions (Fig. 1). The contribution of different sources of acid (H^+) or alkali (OH^-) can be assessed by considering a reference group of compounds. Transformations between the compounds in the reference group do not involve production or consumption of H^+ or OH^-. Formation of products from the reference group result in either acid (H^+) or alkali production (H^+ consumption) thus causing a change in soil acidity. Addition or accumulation of products that are not in the reference group similarly affect soil acidity.

For example, N_2, N_2O, NO, NH_3 and RNH_2 constitute the reference group for nitrogen. The production of ammonium (NH_4^+) from the reference group consumes one H^+. The accumulation of NH_4^+ ($NH_4^+{}_{ac}$) from the reference group is an alkaline reaction and the export of NH_4^+ ($NH_4^+{}_{ex}$) is likewise an alkaline reaction.

The carbon cycle can be interpreted in the same way. In the carbon cycle the reference compounds are neutral carbon compounds such as sugars and starch and undissociated carbonic acid. The production of organic anions (OA) and bicarbonate (HCO_3^-) add protons to the ecosystem. The accumulation of organic anions (OA_{ac}) and export of organic anions (OA_{ex}) is acidifying with respect to the reference source. The addition of organic anions (OA_{ad}) is alkaline on the assumption of conversion to undissociated acid or oxidation to carbon dioxide in the system. Similarly, the leaching of bicarbonate ($HCO_3^-{}_{ex}$) and the accumulation of bicarbonate ($HCO_3^-{}_{ac}$) produces H^+ whereas the addition of bicarbonate ($HCO_3^-{}_{ad}$) produces alkali (consumes H^+).

Redox and hydrolytic reactions concerning aluminium (Al^{3+}) and manganese (Mn^{2+}) were also considered, as they may affect seasonal variations of soil pH potentially important to plant growth.

The rate of acidification in any layer of the soil can be calculated by adding the effects of the different components involved:

Acid addition (kmol H^+ ha^{-1} $period^{-1}$) = (nitrogen cycle effects) + (carbon cycle effects) + (manganese cycle effects) 4 + (aluminium cycle effects) + (addition of acids)

$$\text{Acid addition} = (NH_4^+{}_{ad} - NO_3^-{}_{ad} - NH_4^+{}_{ac} + NO_3^-{}_{ac} + NO_3^-{}_{ex} - NH_4^+{}_{ex}) + (HCO_3^-{}_{ex} + HCO_3^-{}_{ac} - HCO_3^-{}_{ad} + OA_{ac} + OA_{ex} - OA_{ad}) + (-Mn^{2+}_{ac} - Mn^{2+}_{ex}) + (-Al^{3+}_{ac} - Al^{3+}_{ex}) + (H^+_{ad} - H^+_{ex})$$

Where the subscripts $_{ad}$, $_{ex}$ and $_{ac}$ denote the addition, export and accumulation of material in the soil layer, respectively.

The assumptions made in evaluating the different terms of the equation are detailed in the calculation section.

Materials and methods

Experiment

Site and experimental design

The study was conducted in 1993 at Charles Sturt University near Wagga Wagga, New South Wales (35° 4′ S., 147° 21′ E., alt. 219 m). The climate is semi-arid, with mean annual precipitation of 539 mm, a mean class A pan evaporation of 1660 mm. For 5 months of the year precipitation exceeds evaporation. Cool and moist conditions tend to prevail between autumn and spring and the summer months (December to February) are typically hot and dry. The near average rainfall of 543 mm for 1993, with above average rainfall in July, September and October maintained high soil water contents during the growing season. Total rainfall from June to November was equivalent to the wettest 6% of years (1911–1993). This augmented the initially high subsoil water content which had resulted from the heavy rains in December 1992.

The soil was classified as a red kandosol (previously known as a red earth, Isbell (1993); Rhodoxeralf, Soil Survey Staff (1992); chromic Luvisol, FAO-UNESCO (1980)). The soil lacks strong textural contrast, has a weakly structured B horizon and is not calcareous. The profile was never saturated with water in 1993. The 0–90 cm layer was intensively colonised by roots. The soil was limed in 1991 (2.5 t ha^{-1}) to correct soil acidity (pH_{CaCl_2} in the 0–10 cm layer was 4.5 before liming). Selected chemical properties of the soil are given in Table 1. Kaolin was the dominant clay mineral.

The field (15 ha) had a cropping history of cereal and grain legume crops for the last 9 years and included stubble grazing during the fallow periods. Peas had been sown in 1988 and 1991, to provide the ley-farming component of the rotation. Stubble of the previous wheat crop was burnt on March 31, 1993. Ashes and unburnt straw were incorporated into the soil by tine cultivation to a depth of 10 cm on April 15. Wheat (*Triticium aestivum* L. cv. Janz) was sown on June 6 at the rate of 78 kg seed ha^{-1}. Diammonium phosphate (DAP;17 kg N ha^{-1} and 25 kg P ha^{-1}) was drilled with the seed. Two adjacent 5 ha areas were designated as the study plots within the field. Urea was broadcast at 140 kg N ha^{-1} on August 6, 1993 at the start of stem elongation (decimal code 30; Zadoks et al., 1974) to the northern plot. The crop was harvested on December 9, 1993.

Soil water balance and drainage

The drainage at 25 and 90 cm was calculated as the difference between rainfall, evapotranspiration and the change in soil water content. Evapotranspiration was continuously recorded on each plot both with weighing lysimeters (1.1 × 1.3 m, 1.8 m deep) and micrometeorological measurements for flux determinations by the energy balance or Bowen-ratio technique (Dunin et al., 1989). Soil water content was measured gravimetrically (oven dry at 105 °C) on cores (5.4 cm i.d.) taken generally at 2 week intervals throughout the year. Eight cores were taken in the surface 10 cm and four cores in the 10 to 90 cm layer of each plot. Cores were separated into 0–5, 5–10, 10–15, 15–25, 25–50, 50–70, and 70–90 cm depths and then bulked to give a composite sample representing each layer. At one sampling date, the individual samples were analysed to determine the variability of the results. There were few roots below 90 cm and the water content below this depth remained

Table 1. Selected chemical and physical properties of the soil

Depth (cm)	pH[a]	C (%)	N (%)	Clay (%)	CEC[b] (cmol$_c$ kg^{-1})	pH Buffer capacity[c] (cmol$_c$ kg^{-1})
0–5	5.8	1.42	0.12	23	6.7	1.48
10–15	4.5	0.59	0.04	33	4.7	1.63
15–25	5.1	0.46	0.04	37	5.9	1.19
70–90	5.8	0.15	0.02	55	7.2	0.74

[a] pH measured on 1:5 soil to 0.01 *M* $CaCl_2$ extract.
[b] CEC determined with 0.002 *M* $BaCl_2$.
[c] See materials and methods.

almost unchanged with time, therefore root extraction below 90 cm was not considered in the water balance. Drainage at 25 cm was calculated by assuming that plant water uptake came entirely from the 0–25 cm layer. The effect of this assumption will be discussed later. Run-off was considered to be negligible because the maximum rainfall intensity during the year was less than 5 mm h^{-1} which was considerably less than the saturated hydraulic conductivity of surface soil.

Concentration of ions in soil solution

Addition of ions to the soil through rainfall was evaluated by collecting one sample of rainwater each month from June to November 1993.

Soil solution at 25 and 90 cm was extracted using ceramic suction cups (Coinda Ceramics, PO Box 156, Bayswater 3153 Australia). Eight suction samplers were installed at each depth in each plot (Poss et al., 1994) and soil solution samples were collected at two week intervals between June and November. The samplers were evacuated overnight to a pressure of −70 kPa for sampling the soil solution. The pH was measured on sub-samples within 2 days of collection and the remaining soil solution was stored frozen until analysed. Concentrations of NH_4^+-N and NO_2^- plus NO_3^--N were determined on an autoanalyser, Al by pyrocatechol violet (Bartlett et al., 1987) and Mn by atomic absorption spectroscopy. Ammonium was measured by reacting with hypochlorite liberated from dichlor-isocyanurate under alkaline conditions. The chloramine formed reacts under catalysis of nitroprusside with salicylate at a temperature of 37 °C to form indophenol blue in an amount that is proportional to the ammonia concentration. The absorbance was measured at 660 nm. Nitrate was determined by quantitative reduction to nitrite by cadmium metal in a packed bed cadmium column.

Soil inorganic nitrogen

After thorough mixing of the composite soil sample representing each layer, NH_4^+ and NO_3^- (including NO_2^-) was extracted by shaking the equivalent of 5 g of dry soil with 25 cm^3 of 2 *M* KCl for 1 hour. The suspensions were filtered and the filtrate stored frozen until analysed using the same methods as used for the soil solutions.

Nitrogen mineralization

Before sowing, the N mineralization rates in each layer were calculated from the temporal change in soil inorganic N and field measured bulk densities. Post sowing estimates of mineralization were made in the non-fertilized plot in the 0–10 cm layer using a modification of the coring method described by Raison et al. (1987). At 2 week intervals, eight PVC tubes (5 cm i.d.) were forced in the soil to a depth of 10 cm. Four tubes were immediately removed (t_0), whereas the remaining 4 tubes were covered and incubated in situ for 14 days (t_1). The rate of mineralization was calculated from the increase in inorganic N between t_0 and t_1.

Mineralization rates in the deeper soil layers was calculated from the values of the 0–10 cm layer, assuming that the ratio between the mineralization in this layer and the deeper layers remained constant with time. The ratio between the rate of mineralization in the different layers was calculated from the changes in soil inorganic N before sowing and after harvesting. Furthermore, the mineralization of soil N in the plot top-dressed with urea was assumed to be the same as that measured in the non-fertilized plot.

Aluminium and manganese in the soil

Exchangeable aluminium and manganese were determined during the first five months of the experiment on composite samples from each layer after extraction with 0.01 *M* $CaCl_2$ using a 1:5 soil : solution ratio. Al and Mn were determined using the same methods as used for the soil solutions.

Residues from the previous crop

Residue input from the previous wheat crop was measured by taking five samples (0.32 m^2) along two transects across the field. At each sampling point, all the residue was removed, dried at 70 °C and weighed. Ash alkalinity of the residue was determined by titration using the procedure of Pierre and Banwart (1973) as modified by Jarvis and Robson (1983).

Crop growth and nutrient accumulation

Four samples of wheat were taken at 2 week intervals from quadrats (0.85 m^2) in both plots. Plant tops were cut at ground level, the material was dried at 70 °C, weighed and ground to pass a 0.42 mm sieve. The plant material was analysed for P, Cl, S, K, Ca, Mg, and Na by X-ray fluorescence (Norrish and Hutton, 1977). Total N content was determined on an autoanalyser after micro-Kjeldahl digestion.

pH and pH buffer capacity of the soil

Soil pH was determined throughout the year. Air dry soil (5 g) was mixed with 25 cm^3 of 0.01 *M* $CaCl_2$ and shaken, end-over-end, at room temperature for 1 hour. The suspensions were centrifuged, the glass electrode positioned in the supernatant and the pH value recorded when the meter reading appeared steady.

The soil pH buffering capacity ($cmol_c\ kg^{-1}\ pH^{-1}$) was determined by shaking soil for 1, 4 and 24 hours with varying amounts of acid or alkali. Acid (0.01 *M* H_2SO_4) or alkali (0.01 *M* $Ca(OH)_2$) was added to 4 g of air dry soil at rates equivalent to 0, 0.5, 1, 1.5, 2, 2.5, 5, and 10 $cmol_c\ kg^{-1}$ of soil. The ionic strength of added solution was kept constant at 0.03 by adding 0.01 *M* $CaCl_2$ and a 1:5 soil : solution ratio was maintained. The pH was measured in the supernatant of centrifuged samples using the procedure given above. There was no difference ($<p$ 0.05) in pH values measured at 1, 4 and 24 hours. The buffering capacity was approximately constant within the pH range 4.5 – 6.0, and was calculated by dividing the amount of H^+ ($cmol_c\ kg^{-1}$) required to change the pH from 6.0 to 4.5.

Calculations

Calculations were made on a monthly basis from March 1, 1993 to February 28, 1994 for the 0–25 and the 25–90 cm soil layers. The calculations involved an evaluation of the fluxes at 25 and 90 cm and an evaluation of the depletion of the products not in the reference groups in both layers. We use the term depletion ($_{dep}$) rather than accumulation ($_{ac}$) because in this study both NH_4^+ and NO_3^- were observed to decrease with time. The accumulation terms in the acidity equation must be changed from minus (accumulation) to plus (depletion). For example, $- NH_4^+{}_{ac}$ in the acidity equation becomes $+ NH_4^+{}_{dep}$.

Nitrogen cycle

Ammonium and nitrate added

$NH_4^+{}_{ad}$ in the diammonium phosphate was calculated from the amount applied to the crop. The addition of urea fertilizer was neutral.

The terms $NO_3^-{}_{ad}$ and $NH_4^+{}_{ad}$ from rain were evaluated by multiplying the amount of rainfall by the average NO_3^- and NH_4^+ concentration in the rainwater. The average NH_4^+ and NO_3^- concentrations were 0.014 and 0.010 mmol L^{-1}, respectively, and did not change significantly throughout the season. The annual additions of NH_4^+ and NO_3^- were 0.08 kmol ha^{-1} and 0.05 kmol ha^{-1} respectively, which were considered to be insignificant.

Ammonium and nitrate changes

The changes in NH_4^+ and NO_3^- content with time in each layer were calculated from the soil inorganic N values and the bulk density of the soil.

Ammonium and nitrate export

Leaching of NO_3^- and NH_4^+ was calculated at 2 week intervals by multiplying the drainage flux (mm) by the average concentration in the soil solution. Ammonium concentration in the soil solution was less than 0.008 mmol L^{-1} at 25 cm and less than 0.003 mmol L^{-1} at 90 cm. The total amount of NH_4^+ leached ($NH_4^+{}_{ex}$) was 0.004 kmol ha^{-1} at 25 cm and 0.001 kmol ha^{-1} at 90 cm, and was considered to be insignificant.

Root uptake of nitrogen in each layer was estimated as outlined below. Prior to sowing, KCl extractable NH_4^+ was low and the average value was 12 kg N ha^{-1} in the 0–90 cm layer. Later on in the season, two months after the wheat was sown, the value had decreased to 5 kg N ha^{-1} in both plots and remained at this low value throughout the season. We assumed that N assimilated by the crop occurred mainly from the NO_3^- pool, except for the 7 kg NH_4^+-N ha^{-1} decrease.

Plant N accumulation was calculated from above-ground biomass and nitrogen concentration. When the root system developed below 25 cm, the contribution of the different soil layers to plant N was calculated by assuming that uptake was proportional to the change in NO_3^- content in each layer after correction for any loss of NO_3^--N by leaching.

Carbon cycle

The reference group is made up of the neutral carbon compounds (e.g. sugar, starch), undissociated carbonic acid and CO_2.

Organic anions changes

Organic anions consumed by mineralization of the organic matter were estimated from the amount of carbon mineralized, using the organic matter/carbon ratio of 1.8, and the average cation exchange capacity of the organic matter (CEC_{om}) proposed by Helyar and Porter (1989):

$$CEC_{om} = 32\ (pH_{soil} - 1.5) \quad \text{unit} = cmol_c kg^{-1} \quad (1)$$

The amount of organic carbon mineralized was calculated at monthly intervals from the soil N mineralization data (i.e. calculated from the change in inorganic nitrogen before sowing, and from the incubation tubes after sowing) and the C/N ratio of the soil.

On a yearly basis, carbon release was concurrently estimated from the carbon content of the soil and a rate of mineralization of the organic matter of 2%, corresponding to the regional average for the wheat phase of the rotation (D P Heenan, pers. commun.).

Organic anions export

Organic anions in the soil solution were measured by titration of some samples. The values were less than 0.3 $mmol_c\ L^{-1}$, and the annual export of organic anion in the leachate was considered to be insignificant.

Organic anions addition

Organic anions added to the system in the crop residues were calculated from the ash alkalinity value of the residues and the dry weight. The crop residue was assumed to decompose within 1 month of burning and incorporation.

Bicarbonate export

Bicarbonate was exported from the system through leaching. The bicarbonate concentration in the soil solution was calculated with the relationship (Lindsay, 1979):

$$pHCO_3^- = pCO_2 - pH + 7.82 \qquad (2)$$

where $pHCO_3^-$ is the negative logarithm (base 10) of the HCO_3^- concentration (moles L^{-1}) and pCO_2 is the negative logarithm (base 10) of the partial pressure of CO_2 (atm). The partial pressure of CO_2 in the soil air was assumed to be 0.003 atm.

Bicarbonate added

Bicarbonate added through rainfall was calculated from Equation (2), using 0.0003 atm. as the partial pressure of CO_2 and the average pH of the rain (5.75). The average HCO_3^- concentration in the rainwater was 0.002 mmol L^{-1}. The addition of HCO_3^- in rainfall was considered to be negligible.

The net excretion of bicarbonate or protons from roots was calculated from the charge balance equation where we assumed that any excess in the uptake of anions to cations was compensated by the excretion of HCO_3^- and vice versa (Kennedy, 1992):

$$\begin{aligned} \text{Net}\,HCO_3^- &= (NO_3^- + H_2PO_3^- + Cl^- + SO_4^{2-}) \\ &\quad -(K^+ + Ca^{2+} + Mg^{2+} + Na^+ + NH_4^+) \quad (3) \end{aligned}$$

where the ions are expressed as their charge equivalent, phosphorus being taken up as monovalent ion and sulphur as a divalent ion.

Uptake of NO_3^- was calculated from the total N content of the crop after correction for the uptake of NH_4^+ (cf. nitrogen cycle). The uptake of the other nutrients was estimated from their concentration in the plant material and total above-ground biomass.

The partitioning of nutrient uptake between the two layers was assumed to be the same as for nitrogen. Little HCO_3^-, if any, would be fixed in this soil. Therefore, change in soil HCO_3^- content was ignored.

Manganese and aluminium cycles

Manganese and aluminium changes

Changes in Mn and Al content of the soil were calculated from the $CaCl_2$ extractable values and the bulk densities of each layer. Although the exchangeable Al is underestimated in 0.01 *M* $CaCl_2$ extracts, the values were very low in this soil, and thus the error caused by not extracting exchangeable Al with 1 *M* KCl is insignificant.

Manganese and aluminium export

At 25 cm, the concentration of Mn in the soil solution was less than 0.004 mmol L^{-1} and Al was less than 0.002 mmol L^{-1}. No Mn and Al was detected in soil solution at 90 cm, which is consistent with the high pH (> 6.5) of the soil solution. Manganese and Al export were considered to be insignificant.

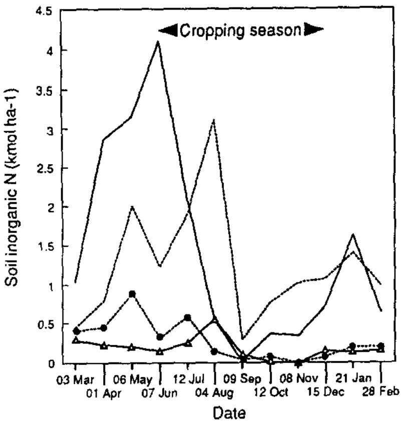

Fig. 2. Changes in inorganic nitrogen with time in the soil under the unfertilized wheat. NO_3^- (0–25 cm), — NO_3^- (25–90 cm), - - - - -; NH_4^+ (0–25 cm), Δ; NH_4^+ (25–90 cm), ●.

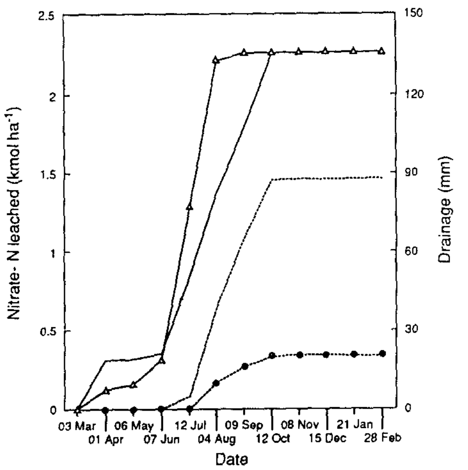

Fig. 3. Cumulative drainage and leaching in the soil of the unfertilized wheat treatment. Drainage (25 cm), —; Drainage (90 cm), - - - -; NO_3^- (25 cm), Δ; NO_3^- (90 cm), ●.

Addition of acids

The concentration of protons (H^+) in rainfall and in the leachates at 25 and 90 cm were calculated from the average pH of the rain water and the soil solutions. The H^+ concentrations were 0.002 mmol L^{-1} in the rainwater and less than 0.001 mmol L^{-1} in the leachate. Proton addition by rainfall and removal by leaching were neglected.

Results

Monthly proton budget

The monthly proton budget for the 0–25 and 25–90 cm layer of soil sown to wheat in the unfertilized treatment is given in Table 2. The differences between the unfertilized and fertilized wheat are indicated in the text.

Nitrogen cycle

Ammonium and nitrate added
Ammonium added in the DAP was equivalent to 1.2 kmol ha^{-1}.

Ammonium and nitrate changes
In the 0–25 cm layer, mineralization of organic matter increased soil NO_3^- by 3 kmol ha^{-1} in the autumn before sowing (Fig. 2). The soil NO_3^- content decreased by 4 kmol ha^{-1} during the first part of the cropping season, and reached its minimal value at stem elongation (9 September). Thereafter soil NO_3^- values increased. Nitrate values in February were slightly lower than the values measured in the previous year. The standard error ($p < 0.05$) was 0.6 kmol ha^{-1} in autumn after the first rain and 0.7 kmol ha^{-1} at the beginning of winter (peak concentration). In the 25–90 cm layer, NO_3^- values increased until May 6 and then declined possibly due to immobilization or denitrification reactions. Nitrate values increased after June 6, and reached a maximum on August 4. The increase in NO_3^- values in the 25–90 cm layer was accompanied by a decrease in the surface 25 cm and we attribute this increase to the leaching of NO_3^- from the 0–25 cm layer during July. Approximately 3 kmol ha^{-1} of NO_3^- was assimilated by the roots in August. After September 9, soil NO_3^- values in the 25–90 cm layer also increased and the final value measured in February was slightly greater than that measured in March of the previous year. The standard error ($p < 0.05$) was 0.2 kmol ha^{-1} after the first rain in autumn.

Ammonium values in the soil remained low (<1.0 kmol ha^{-1}) in both layers. The addition of DAP in June and urea in August to one plot had no effect on either the NO_3^- or the NH_4^+ content of the soil one month later.

Ammonium and nitrate exported
Total drainage was 134 mm at 25 cm and 94 mm at 90 cm, irrespective of urea fertilization. Drainage occurred mainly between July and September (Fig. 3). On both plots, NO_3^- concentration in the soil solution at 25 cm decreased from 4.4 mmol L^{-1} on July 13 to

Table 2. Monthly proton (kmol H^+ ha^{-1}) budgets in the 0–25 and 25–90 cm layers of the soil of the unfertilized wheat

Period		3 Mar 1Apr	1 Apr 6 May	6 May 7 Jun	7 Jun 12 Jul	12 Jul 4 Aug	4 Aug 9 Sep	9 Sep 12 Oct	12 Oct 8 Nov	8 Nov 15 Dec	15 Dec 21 Jan	21 Jan 28 Feb	Total year
0–25 cm													
N cycling													
$-NO_{3ad}$	Rainfall	−0.01			−0.01	−0.01	−0.01		−0.01				−0.06
$+NH_{4ad}$	DAP				1.2								1.2
$-NO_{3dep}$	Soil	1.9	0.2	0.9	−2.0	−1.6	−0.5	0.4	−0.0	0.4	0.9	−1.0	−0.4
$+NO_{3ex}$	Leaching	0.1	0.0	0.2	1.0	0.9	0.0	0.1	0.0	0.0	0.0	0.0	2.3
$+NO_{3ex}$	Root uptake				0.2	0.9	0.7	0.7	−0.2	0.7			3.0
C cycling													
$+HCO_{3ex}$	Leaching	0.03	0.00	0.00	0.04	0.05	0.04	0.04	0.00	0.00	0.00	0.00	0.20
$-HCO_{3ad}$	Root excretion				−0.2	−0.6	−0.3	0.1	0.3	−1.0			−1.7
$-OA_{ad}$	Crop residues		−1.8										−1.8
$-OA_{dep}$	Mineralization	−0.7	−0.1	−0.4	−0.4	−0.2	−0.3	−0.5	−0.3	−0.4	−0.3	−0.1	−3.7
Net C and N cycle acid addition		1.3	−1.7	0.7	−0.1	−0.6	−0.3	0.8	−0.2	−0.4	0.6	−1.1	−1.0
Al and Mn cycling													
$+Mn_{dep}$	Soil	−0.6	0.5	0.2	0.6	−0.1							
$+Al_{dep}$	Soil	0.0	−0.2	0.0	0.1	−0.1							
Al and Mn cycle acid addition		−0.6	0.3	0.2	0.7	−0.2							
25–90 cm													
N cycling													
$-NO_{3ad}$	Leaching	−0.1	0.0	−0.2	−1.0	−1.0	0.0	0.0	0.0	0.0	0.0	0.0	−2.3
$+NH_{4dep}$	Soil	0.0	0.0	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.5
$-NO_{3dep}$	Soil	0.3	1.2	−0.8	0.7	1.2	−2.8	0.5	0.2	0.1	0.3	−0.4	0.5
$+NO_{3ex}$	Leaching	0.0	0.0	0.0	0.0	0.2	0.1	0.1	0.0	0.0	0.0	0.0	0.4
$+NO_{3ex}$	Root uptake				0.0	0.0	1.2	0.0	0.0	0.4			1.6
$-NH_{4ex}$	Root uptake						−0.5						−0.5
C cycling													
$+HCO_{3ex}$	Leaching	0.0	0.0	0.0	0.0	0.2	0.2	0.1	0.0	0.0	0.0	0.0	0.5
$-HCO_{3ad}$	Leaching	−0.03	0.00	0.00	−0.04	−0.05	−0.04	−0.04	0.00	0.00	0.00	0.0	−0.20
$-HCO_{3ad}$	Root excretion				0.0	0.0	0.1	0.0	0.0	−0.5			−0.4
$-OA_{dep}$	Mineralization	−0.1	−0.0	−0.2	−0.2	−0.1	−0.2	−0.2	−0.1	−0.2	−0.1	−0.1	−1.5
Net C and N cycle acid addition		0.1	1.2	−1.2	−0.4	0.4	−1.4	0.4	0.1	−0.2	0.2	−0.5	−1.4
Al and Mn cycling													
$+Mn_{dep}$	Soil	0.0	−0.1	0.0									

0.7 mmol L^{-1} on August 4 and remained below 0.01 mmol L^{-1} after September 22, as crop N accumulation increased. The low concentration of NO_3^- in the soil solution after August 4 was responsible for the fact that little leaching of NO_3^- occurred at 25 cm after July. Nitrate leaching at 90 cm was concomitant with drainage, as NO_3^- content in the soil solution remained between 0.2 and 0.5 mmol L^{-1}. The total NO_3^- leaching flux was 2.2 kmol ha^{-1} at 25 cm and 0.3 kmol ha^{-1} at 90 cm (Fig. 3).

On the unfertilized plot, 71 kg N ha^{-1} accumulated in the above-ground biomass of the crop. Nitrogen accumulation with time and the allocation of the N between the 0–25 and 25–90 cm layer are given in Table 3. In August, the soil NO_3^- budget decreased by 18 kg N ha^{-1} in the 0–25 cm layer and by 45 kg N ha^{-1} in the 25–90 cm layer. Therefore the N accumulation of 33 kg ha^{-1} was distributed in proportion to the decrease in soil NO_3^-; that is, 10 kg N ha^{-1} in the 0–25 cm layer and 23 kg N ha^{-1} in the 25–90 cm layer. For the fertilized plot, total nitrogen accumulation was 184 kg N ha^{-1}. As there was no leaching of nitrogen below 25 cm after the application of urea (August 6, 1993; Fig. 3), we assumed that the same amount of nitrogen (23 kg N ha^{-1}) was accumulated in August from the 25–90 cm layer as estimated for the unfertilized plot. Nitrogen accumulation from the 0–25 cm layer was calculated by difference and was estimated to be 161 kg N ha^{-1}.

Carbon cycle

Organic anions depletion

Total organic anion depletion was estimated to be 5.2 kmol ha^{-1} (Table 4). As these values were derived from the rate of mineralization of the organic nitrogen, they were greatest in autumn when mineralization rates were the highest.

Organic anions addition

The amount of the crop residues was 9700 kg ha^{-1} and the ash alkalinity of the residues was 18 $cmol_c$ kg^{-1}. The amount of organic anions added to the soil in April was equivalent to 1.8 kmol (OH^-) ha^{-1} (Table 4).

Bicarbonate export

The average pH of the soil solution was 6.5 at 25 cm and 7.1 at 90 cm. The bicarbonate concentrations, calculated from Equation 2, were 0.14 mmol L^{-1} at 25 cm and 0.57 mmol L^{-1} at 90 cm. Bicarbonate leaching on both plots was estimated to be 0.2 kmol ha^{-1} at 25 cm and 0.5 kmol ha^{-1} at 90 cm; most leaching occurred between July and September (Table 2).

Bicarbonate addition

Bicarbonate was mainly excreted by the roots in July, August and November (Fig. 4a and b). In September and October, the uptake of cations was greater than the uptake of anions therefore we assumed that protons were excreted from the roots to balance the charge.

Manganese and aluminium cycles

The monthly changes in Mn concentration varied between 0.1 and 0.6 kmol ha^{-1} and Al concentration between 0 to 0.2 kmol ha^{-1} in the 0–25 cm layer. Manganese values were less than 0.1 kmol ha^{-1} in the 25–90 cm layer. Changes in Al were not considered in the 25–90 cm layer because soil pH was greater than 5.5. Others (Aitken, 1992; Little, 1993) have shown that exchangeable Al values are extremely low when the soil pH is greater than 5.0.

Monthly proton budget

The cumulative change of acidity with time was calculated for each period from the rate of acidification (Fig. 5a and b). Manganese and aluminium were not included, because they were not measured throughout the entire experiment.

In the unfertilized plot, the changes in acidity in the 0–25 cm layer remained low throughout the year. The increase in acidity due to the mineralization of the organic nitrogen in autumn was compensated for in the following month by the incorporation of the alkaline crop residues (−1.8 kmol H^+ ha^{-1}). In the fertilized plot, acid addition occurred in September and October, due to plant accumulation of NO_3^- formed in the same layer without excretion of the equivalent amount of bicarbonate.

The rate of acid addition in the 25–90 cm layer followed the same pattern in both plots, because the acidifying reactions were the same. Acidity generated in April by the mineralization of the organic nitrogen was neutralised one month later when the NO_3^- content of the soil decreased either by denitrification or immobilization reactions. Net alkalization of 2 kmol ha^{-1} occurred in August, when the NO_3^- formed in the surface 25 cm was leached to the 25–90 cm layer and assimilated by the crop.

Table 3. Nitrogen uptake (kg N ha^{-1}) by the wheat

Interval (months)	June 6 July 12	July 12 Aug. 4	Aug. 4 Sept. 9	Sept. 9 Oct. 12	Oct. 12 Nov. 8	Nov. 8 Dec. 15
Unfertilized wheat						
Soil budget						
0–25 cm			−18	−14	−11	−8
25–90 cm			−45	−1	−1	−6
Plant uptake	3	13	33	10	−3	15
Partition 0–25 cm	3	13	10	10	−3	9
25–90 cm	0	0	23	0	0	6
Fertilized wheat						
Plant uptake	3	9	106	22	−21	65
Partition 0–25 cm	3	9	83	22	−21	60
25–90 cm	0	0	23	0	0	5

Table 4. Proton balance (kmol H^+ ha^{-1}) under wheat

Acid processes					**Alkaline processes**				
	0–25 cm		25–90 cm			0–25 cm		25–90cm	
	Unfert.	Fert.	Unfert.	Fert.		Unfert.	Fert.	Unfert.	Fert.
$-NO_3^-{}_{dep}$	−0. 4	−0.2	0.5	0.4	OA_{dep}	−3.7	−3.7	−1.5	−1.5
					(2%/yr)	(−1.6)	(−1.6)	(−1.1)	(−1.1)
$NO_3^-{}_{ex}$									
Leaching	2.3	2.2	0.4	0.3	OA_{ad}	−1.8	−1.8		
Plant	3.0	10.7	1.6	1.6	$NO_3^-{}_{ad}$	−0.1	−0.1	−2.3	−2.2
$NH_4^+{}_{ad}$	1.2	1.2	-	-	$NH_4^-{}_{ex}$			−0.5	−0.5
$NH_4^-{}_{dep}$	-	-	0.5	0.5	$HCO_3^-{}_{ad}$				
$HCO_3^-{}_{ex}$	0.2	0.2	0.5	0.5	Leaching			−0.2	−0.2
					Plant	−1.7	−6.6	−0.4	−0.4

Balance

	0–25 cm	25–90 cm	Total
Unfertilized	−1.0(1.1)[a]	−1.4(−1.0)	−2.4(0.1)
Fertilized	1.8(3.9)	−0.9(−0.5)	0.9(3.4)

[a] Values in parenthesis were calculated assuming that 2% of the organic matter decomposed each year instead of 3.5% estimated using mineralization tubes.

The pH of the soil remained between 5.0 and 5.5 in the 0–25 cm layer in both plots, except in November and January when the pH was higher in the fertilized plot. At depth, the pH fluctuated between 5.6 and 6.1 (Fig. 5b) in both plots, except in January where it was lower. There was no consistent relationship between changes in acid addition to the system and measured change in soil pH.

Annual proton budget

The annual proton budget was calculated by summing the monthly figures and assuming that there was no net change in exchangeable Mn and Al over the year (Table 4). During 1993, the net acidification was 0.9 kmol H^+ ha^{-1} for the fertilized plot and −2.4 kmol H^+ ha^{-1} for the unfertilized plot, when the estimates are based on

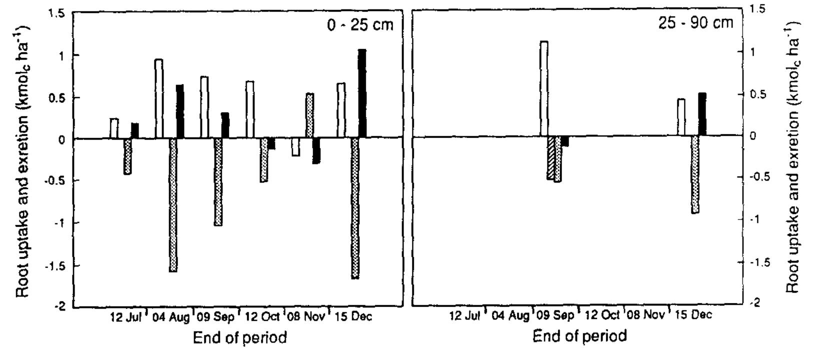

Fig. 4. Nitrogen assimilation, bicarbonate and proton excretion resulting from root activity. NO_3^- -N uptake, □ ; NH_4^+-N uptake, ▨ ; Non N cation-anion uptake, ▩ ; HCO_3^--protons excreted, ■ .

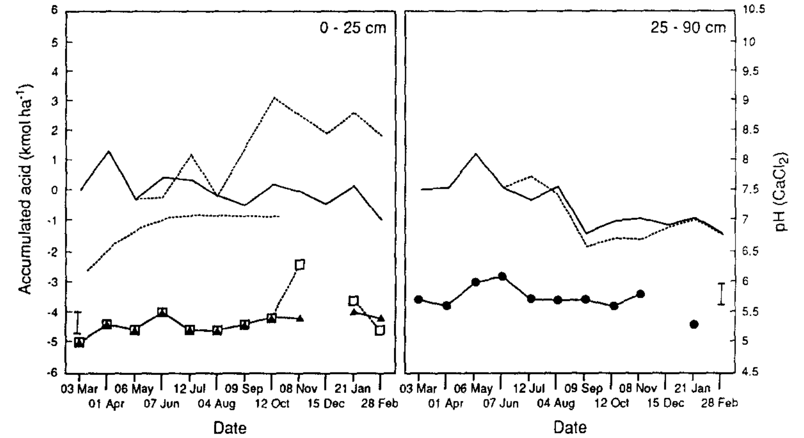

Fig. 5. Cumulative changes in acid addition with time and the corresponding soil pH. The vertical bar represents the confidence interval (p <0.05) for the data. Accumulated acid in the unfertilized treatment, —; accumulated acid in the fertilized treatment, - - - - -; pH (0–10 cm) in the unfertilized treatment, ▲; pH (0–10 cm) in the fertilized treatment, □; pH (25–50 cm) ●.

measured nitrogen mineralization rates. However, the rates were 3.4 and −0.1 kmol H^+ ha^{-1}, respectively, when we assume that 2% of the organic matter is mineralized each year. The 0–25 cm layer was acidified by 1.8 kmol H^+ ha^{-1} for the fertilized treatment, but alkalized by 1.0 kmol OH^- ha^{-1} in the unfertilized treatment. The 25–90 cm layer became more alkaline (+0.9 to +1.4 kmol OH^- ha^{-1}). The greater acidification of the 0–25 cm layer on the fertilized plot was mainly due to increased crop N uptake. The excretion of bicarbonate to compensate for excess anion uptake by the plant only partially neutralized the acidity generated through the formation of NO_3^- by mineralization. In the 25–90 cm soil layer, most of the alkalinity arose from the addition of NO_3^- through leaching and from the mineralization of the organic anions. Net acid addition due to leaching of NO_3^- below 90 cm was unimportant compared to other factors.

Annual acidification rate under wheat

When discussing the effect of a crop on soil acidity, the components of the budget resulting from particular experimental conditions have to be removed. In the case studied, soil NO_3^- values were different at the end of the cropping phase than at the beginning. Furthermore, ash alkalinity of the crop residues added to the soil at the beginning of the current cropping year was different from the ash alkalinity that remained in the stubble at the end of the experiment.

An annual acidity balance sheet independent of the experimental conditions was calculated assuming that there was no change in soil inorganic N and that the alkalinity added to the soil in the crop residues was equivalent to the alkalinity of the stubble at harvest. The grain contained 0.1 kmol of alkalinity (OH^-) per hectare and consequently 0.1 kmol H^+ ha^{-1} is added to

Table 5. Estimated annual rate of acidification (kmol H^+ ha^{-1}) for a red kandosol under a wheat crop following wheat, peas and wheat in the previous 3 years

	Non-fertilized			Fertilized		
	0–25 cm	25–90 cm	0–90 cm	0–25 cm	25–90 cm	0–90 cm
Mineralization OA	−3.7	−1.5	−5.2	−3.7	−1.5	−5.2
(2% a year)	(−1.6)	(−1.1)	(−2.7)	(−1.6)	(−1.1)	(−2.7)
Mineral input						
(DAP)	1.2		1.2	1.2		1.2
Leaching						
$HCO_3^-{}_{ex}$	0.2	0.5		0.2	0.5	
$NO_3^-{}_{ex}$	2.3	0.4		2.2	0.3	
$HCO_3^-{}_{ad}$		−0.2			−0.2	
$NO_3^-{}_{ad}$		−2.3			−2.2	
Subtotal	**2.5**	**−1.6**	**0.9**	**2.4**	**−1.6**	**0.8**
Plant						
OA_{ad} (residues)	−1.7			−5.1		
$NO_3^-{}_{ex}$ (uptake)	3.0	2.1		10.7	2.1	
$HCO_3^-{}_{ad}$ (excretion)	−2.0	−1.3		−6.4	−1.2	
Subtotal	**−0.7**	**0.8**	**0.1**	**−0.8**	**0.9**	**0.1**
Total	**−0.7**	**−2.3**	**−3.0**	**−0.9**	**−2.2**	**−3.1**
	(+1.4)[a]	**(−1.9)**	**(−0.5)**	**(+1.2)**	**(−1.8)**	**(−0.6)**

[a] Values in parenthesis were calculated assuming that 2% of the organic matter decomposed each year.

the system by exporting the grain. Furthermore, calculations were made using the in situ mineralization rate or assuming that 2% of the organic matter is mineralized each year. The proton fluxes were apportioned to the mineralization of the organic matter, fertiliser inputs, leaching and plant related effects (Table 5).

Discussion

Processes of acidification and alkalinisation

The net effect of a wheat crop on soil acidity was a net alkalinization of 0.5 to 3.1 kmol OH^- ha^{-1}. The alkalinity was mainly produced by the mineralization of organic anions. The highest rate of alkalization occurred in the 25–90 cm layer, and was due to the combined effects of mineralization of the organic anions and the addition of NO_3^- leached from the 0–25 cm layer. In the surface 25 cm, it was not possible to determine whether there was net acidification or alkalization, because of uncertainties in the rate of mineralization of organic matter.

Addition of DAP, leaching and the removal of grain produced acidity. Addition of urea did not produce acidity, because there was no leaching of NO_3^- after the urea was applied nor did it increase the total amount of NO_3^- or NH_4^+ in the soil. Unlike most agricultural systems, the acidity generated by leaching below 90 cm was limited (0. 8 to 0. 9 kmol H^+ ha^{-1}), because most NO_3^- leached from the surface was either assimilated by the wheat or lost from the soil by denitrification. Stomer (1965) suggested that NO_3^- is likely to be leached further into the root-zone during periods of high rainfall in the autumn and winter, but most of the N is likely to be assimilated by the wheat later in the growing season. However, any leaching of NO_3^- away from its site of production (that is, decoupling of NO_3^- production and consumption reactions) generates acidity that may lead to the development of low pH zones in the surface section of the root-zone.

Acidity originating from the crop was very low (0.1 kmol H^+ ha^{-1}) because only the grain was exported from the field. The export of the stubble, either as straw for animals or as ash in the wind after burning, has the potential to produce an acidification between 1.7 and 5.1 kmol H^+ ha^{-1}. However, the crop did produce a transfer of acidity between the soil layers. The result of the root activity (NO_3^- uptake not fully matched by bicarbonate excretion) was net acidification of the soil; 1.8 kmol H^+ ha^{-1} in the unfertilized plot and 5.2 kmol H^+ ha^{-1} in the fertilized plot. This acidity, however, was counterbalanced by the alkalinity stored in the crop residue. The effect of the crop was to remove alkalinity from the bulk of the soil during the cropping season and to recycle the alkalinity to the soil surface when the crop residues were incorporated. The only difference between the unfertilized and fertilized plots was the magnitude of the transfer. The fertilized system produced more acidity in the 0–25 cm layer, but there was a commensurate amount of alkaline producing organic anions returned to the soil surface in the stubble.

The changes in exchangeable Mn and Al with time were not negligible on a monthly basis in the 0–25 cm layer (Table 2). However, they produced a negligible change in soil pH, as the pH buffer capacity of the soil is about 100 fold greater than the largest observed change (Table 1).

The monthly variations in soil pH (Fig. 5a and b) did not correspond to the calculated rate of acid addition. Calculation based on the pH buffer capacity of the soil suggest that the measured rate of mineralization should have produced monthly changes of less than 0.1 pH units. The variations in soil pH was possibly due to the poor repeatability of the measurements. This variability was higher than the confidence interval reported on the graph, as the confidence interval was calculated from a group of samples taken at a particular date.

Reliability of the results

When discussing the reliability of the values, the overall rate of acidification (0–90 cm layer) must be distinguished from the rate of acidification in each layer.

In the 0–90 cm layer the three acidifying factors were fertilizer input, plant outputs and leaching. Acid addition through fertilizer is known accurately, and this acidifying factor could be removed by using a neutral product as urea instead of ammonium. As long as the grain alone is exported, the acidifying effect of the crop is limited to the ash alkalinity of the grain. This alkalinity is always less than 0.1 kmol OH^- ha^{-1} with yields less than 10 t ha^{-1}. Leaching is a sensitive parameter in the budget as leaching of 14 kg N ha^{-1} as NO_3^- produces an addition of 1 kmol H^+ ha^{-1}. The accuracy of drainage flux values was estimated by making the calculations for several two week periods before drainage occurred at the bottom of the profile and was found to be around 5 mm (5% of the annual drainage). The confidence interval of the quantity of NO_3^- leached below 90 cm was evaluated to be less than 1 kg N ha^{-1} (< 0.1 kmol H^+ ha^{-1}; Poss et al., 1994). Thus the uncertainty on NO_3^- leaching was trivial on the overall proton budget.

The major uncertainty in the acidifying process relates to the amount of bicarbonate leached. This term was estimated from the pH of the soil solution and the partial pressure of CO_2 in the soil air. If we assume the partial pressure of CO_2 in the soil air to be 0.03 atm, tenfold higher than the value used for the calculations, the rate of acidification would be increased by 4. 5 kmol H^+ ha^{-1}. Such a value may be unrealistic, as it represents 100 times the partial pressure in the atmosphere. Moreover, the year studied was exceptional in the drainage at 90 cm; an outflow of 20% of annual average rainfall would rank it as a 1 in 20 year occurrence in the region (M Stapper, pers. commun.). Consequently, we estimate an average acid addition by leaching of 0.8–0.9 kmol H^+ ha^{-1} with a confidence interval of +0.5 kmol H^+ ha^{-1}. In this system, average acid addition arising from grain removal, and the leaching of NO_3^- and bicarbonate ions is about 1 kmol H^+ ha^{-1}.

The only alkalinising process was the mineralisation of the organic anions in the organic matter. The calculations were based on the rate of mineralisation of the organic matter, the C/N ratio of the soil and cation exchange capacity of the organic matter. The C/N ratio of the soil was around 12 in the upper section of the profile (0–25 cm; Table 1). The rate of mineralisation of the organic matter estimated from the incubation tubes (3.5% $year^{-1}$) was probably a maximum, as the method tends to overestimate the rate of mineralisation due to the inclusion of fresh root material cut off as the tubes were inserted into the soil. The minimum rate of mineralisation would be around 1.0% $year^{-1}$, given the warm autumns and the wet springs in the region. The cation exchange capacity of the organic matter lies between 7 $cmol_c$ kg^{-1} for plant litter and 83 $cmol_c$ kg^{-1} for humic acids (Helyar and Porter, 1989), the calculations having been made with the mean value of 32 $cmol_c$ kg^{-1}. Using the extreme values, the mineralisation of the organic anions produced between 0.3

and 13.5 kmol OH^- ha^{-1}. The value of 2.7 kmol OH^- ha^{-1}, resulting from a mineralisation rate of 2% and a cation exchange capacity of the organic matter of 32 $cmol_c$ kg^{-1} is considered to be the best estimate of alkalisation associated with the consumption of organic anions. However, this value has a large error term due to uncertainty in estimating the cation exchange capacity of the organic matter.

When calculating the proton budget in each layer, we have to address the reliability of the values for NO_3^- and bicarbonate transfer and the partitioning of root uptake between layers. The calculations of drainage at 25 cm were made assuming that the roots tapped water only from the 0–25 cm layer. This assumption was valid up to 2 months after sowing, as the roots were only found in this layer. Later in the season the calculated values were minimal, as some water was extracted from the lower layer. Maximum values can be estimated considering that all the water transpired by the crop originated from the 25–90 cm layer after the wheat roots had reached 25 cm. The difference in drainage at 25 cm between extreme values was 70 mm, but the difference in NO_3^- leaching was only 3 kg N ha^{-1} (0.2 kmol H^+ ha^{-1}) as the NO_3^- content in the soil solution was less than 0.05 m*M* in both plots by stem elongation because of crop uptake. The value of bicarbonate transfer is also reliable, as the bicarbonate content of the soil solution at 25 cm remained low because of low soil pH. The values of bicarbonate and NO_3^- transfer in Table 5 are thus reliable within 0.2 kmol H^+ ha^{-1}.

We assumed that the nitrogen assimilated by the crop was in the NO_3^- form. This assumption may be questioned for the fertilized plot, when about 50% of the urea-N was recovered in the crop within the first month. However, the form of N taken up by the crop has no effect on the rate of acidification when the nitrogen originates from a product in the reference group and no transfer occurs between the soil layers. The transformation of one mole of nitrogen from the reference group to the ammonium pool consumes one mole of protons. When wheat assimilates one mole of ammonium, a mole of protons is released, thereby counterbalancing the protons previously consumed. Similarly, the formation of NO_3^- releases protons which are later neutralized by the excretion of bicarbonate when the NO_3^- is taken up by the wheat.

The partitioning of NO_3^-, PO_4^{2-} and SO_4^{2-} uptake between the surface and subsurface layers introduces uncertainties in the rate of acidification of the individual layers, although it does not change the total budget. Nitrate uptake in the 25–90 cm layer was limited by the amount of NO_3^- present in this layer (Table 3). Maximum NO_3^- uptake from the 25–90 cm layer may have been 10 kg N ha^{-1} greater that the estimated value. This value was however an overestimate, as it presumes that no NO_3^- is taken up from the 0–25 cm layer during August. This seems to be an unlikely scenario given that there was 18 kg NO_3^--N ha^{-1} available in the 0–25 cm layer. If all of the NO_3^- had been taken up by the wheat from the 25–90 cm layer, alkalinization for both plots would have increased by 0.8 kmol ha^{-1} in this layer.

If PO_4^{2-} and SO_4^{2-} uptake had occurred only in the 0–25 cm, the rate of alkalinisation in the 25–90 cm layer would have been 0.2 and 0.5 kmol ha^{-1} lower in the unfertilized and fertilized plots, respectively. In both cases, acidification in the surface layer would have been lower accordingly. Consequently, the uncertainty in the values for NO_3^- uptake and bicarbonate excretion per layer in Table 5 are 0.8 and 0.5 kmol ha^{-1}, respectively.

The rate of mineralisation of the organic matter in the 25–90 cm layer was calculated from the increase in NO_3^- in this layer at the beginning of autumn and a proportionality of the rate of mineralisation with the surface layer later in the season. A value higher than 1.5 kmol H^+ ha^{-1} would be unlikely, because of the low carbon content of the layer and the low temperature during the wettest months of the year. Taking into account the uncertainty in NO_3^- and bicarbonate leaching below 90 cm, the confidence interval for the proton budget in the 25–90 cm layer is around 1 kmol H^+ ha^{-1}. However the values refer to a year with drainage well above the average. In a drier year with limited drainage below 25 cm and no root uptake at depth, change in acidity in the 25–90 cm layer would be negligible.

Conclusions

Soil acidifying under wheat in this season in south-eastern Australia was limited because of low NO_3^- concentration in the soil solution when water drained below the root zone. The return of organic anions to the surface balanced and acidifying effects. This crop year was balanced with respect to acid addition because the amount of N cycling matched the capacity of the wheat and microbial communities to assimilate the mineralized N and convert it to protein. The turnover of products within the system was high, but very few products escaped from the system.

Mineralization of organic matter and release of organic anions were the only source of alkalinity in the system. The critical determinants are the rate of oxidation of organic matter and the proportion that occurs as organic anions. The latter factor can be estimated from the cation exchange capacity of the organic matter, which is derived from knowledge of the soil organic matter content, the initial soil pH, and the *a* values (slope) in Equation (1). The mean slope (*a*) lies between 7 and 83 cmol($^+$) kg^{-1} (Helyar and Porter, 1989). Only estimates of these data can be provided at the present. Given the importance of organic matter oxidation to the proton budget, the measurement of the change in soil organic anions is critical if annual budgets are to be estimated accurately.

The study, carried out during a year with high drainage, permits the generalization that the leaching potential for NO_3^--N under wheat is low on the gradational clay soils in the Riverina plains of south-eastern Australia. The implication that wheat contributes little to the observed acidification of the region is subject to the qualifications that the stubble remains on the field and root development is sufficient to take up any NO_3^- leached to depth in the soil profile. This suggests that the ley-phase (either crop or pasture) in combination with fallow breaks between growing seasons are implicated in the acidification widespread throughout the region.

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