Estimate of Mineralized Organic Nitrogen in Soil Using Nitrogen Balances and Determining Available Nitrogen by the Electro-ultrafiltration Technique. Application to Mediterranean Climate Soils

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To be able to optimize the nitrogenous fertilizer rate applied to agricultural crops, the soil's available N must be known, particularly that provided by the organic matter's N mineralization. The methodology proposed to achieve this aim is based on determining the soil's mineral N balance. Many parameters were controlled in this endeavor: mineral N content at three depths (0−30, 30−70, and 70−140 cm), crop absorbed N, leached N and the soil's moisture content. A mineral N balance was established for two types of crop with different cycles: winter cereal (wheat) and spring−summer cereal (maize). Two irrigation systems were also compared. This method enabled the mineralized N to be accurately estimated. It likewise enabled a formula for estimating available N based on the EUF technique.

Keywords: *N balance; EUF; N mineralization; available N; maize; wheat*

INTRODUCTION

The mass application of mineral fertilizers to soil has led to major increases in crop yield. Nitrogenous fertilizers are applied at the highest rates. Great concern is currently being shown for the environmental risks involved in their excessive application and, consequently, leaching of nitrates into groundwater; the efficiency of nitrogenous fertilizers must also be rationalized to minimize these processes and obtain higher crop profitability. These facts justify the intense research work being performed over the years (Wiklicky and Nemeth, 1981; Ziegler, 1989; Horn, 1990) with the aim of optimizing the rates of N applied.

The basis for this research work lies in determining the reserves of N available to the soil and what its degree of availability is as accurately as possible. Determining the reserves directly available at a given moment in time is relatively simple using any $N\text{-}NO_3^-$ + $N\text{-}NH_4^+$ (mineral N) extraction method. However, the problem lies in estimating what amount of organic N is going to be mineralized in the soil from that moment and up till the end of the growing cycle. N available (N_{av}) reflects the amount of mineral N available to the plant's root system or that will be so throughout the growing period.

Various methodologies have been proposed for estimating N_{av}, such as incubation (Stanford and Smith, 1972) or extraction, such as electro-ultrafiltration (EUF) (Nemeth, 1979) or the N_{min} method (Mengel, 1991). The first aim of this paper is to determine N_{av} by obtaining N balances applied to the soil profile. This methodology has also been used by other authors; nevertheless, the difficulty in field monitoring all of the parameters characterizing the balance has usually led to oversimplification so that its subsequent application is not always reliable. This paper's first aim is to characterize the N balance with the greatest possible number of field measurements, neglecting only those proving to be of scarce quantitative importance.

The second aim of this paper is to establish a new expression for estimating available N in the same form as proposed by Wiklicky and Nemeth (1981)

$$N_{av} = 30 \times \text{EUF-NO}_3^- + 50 \times \text{EUF-N}_{org} \quad (1)$$

but using the results of the N balance. Equation 1 is essentially an estimate of the N mineralized during the growing cycle. The EUF extraction method (Nemeth, 1979) stands out from all other methods since, apart from extracting NO_3^- -N and NH_4^+-N, it enables an organic N (EUF-N_{org}) to be determined. EUF-NO_3^- and EUF-NH_4^+ are, respectively, the NO_3^- -N and NH_4^+-N content of the EUF extracts; EUF-N_{org} relates to the EUF-extracted low molecular weight nitrogenous organic compounds that constitute a sign of easily mineralizable organic N. This fact has been demonstrated by various authors [Kohl and Werner (1986), Scherer et al. (1985) in incubation experiments; Appel and Steffens (1990) with cultivated ryegrass; Appel and Mengel (1990) in pot-grown rapeseed] on the basis of the high correlations found between EUF-N_{org} and N absorbed. This is why the EUF method has been proposed as an effective tool for determining N_{av}.

N_{av}, as an estimate of the N mineralized during the growing cycle, will depend on the soil's moisture and temperature conditions during this period which, in turn, will influence microbial flora and, therefore, the mineralization of organic N. This process will therefore be affected by the following factors: climate conditions, type of crop, and farming conditions. A new methodol-

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Table 1. Physical−Chemical Characterization of the Soil on the Experimental Plots

	av	std dev
sand (%)	37.7	5.6
silt (%)	45.5	9.0
clay (%)	13.1	5.2
apparent density (g cm^{-3})	1.49	0.1
OM[a] (%)	1.4	0.2
pH	8.1	0.1
$CaCO_3$ (%)	3.4	0.8
Ca^{2+} (mg kg^{-1})	3840	330
EUF K (20 °C) (mg kg^{-1})	122.5	21.5
EUF P (20 °C) (mg kg^{-1})	14.8	2.8

[a] Organic matter.

Table 2. Irrigation Schedule for Each Crop and both Irrigation Types and Rainfall during the Period

	conventional irrigation		efficient irrigation		
crop	no. of waterings	irrigation (mm)	no. of waterings	irrigation (mm)	rainfall (mm)
maize 1993	12	595	20	515	32
wheat 1994	5	120	5	120	12
maize 1995	10	554	10	464	25

ogy is therefore proposed for calibrating the N_{av} formula under these different conditions.

MATERIALS AND METHODS

Experimental Design. Experiments were carried out with two unfertilized crops (maize and wheat) having cycles that occur in different seasons of the year.

(1) Maize was sown in spring and maintained during the summer and part of the autumn, which is characterized by high summer temperatures coinciding with high moisture levels in the soil due to irrigation.

(2) Wheat (winter cereal) is characterized by its cycle developing mainly during the winter and spring. High temperatures are thus not reached during the crop's development, only at the end in the maturing period.

Two types of irrigation were also provided with the aim of observing the influence of cultivation practices on the N balance and, therefore, on the N_{av} formula's calibration.

The experiment was undertaken at La Poveda Field Station located in Arganda del Rey, 30 km southeast of Madrid, belonging to the CSIC. The experimental field displayed a sandy-loam texture in the first 0.5 m of soil depth and a sand-increasing rate as soil depth progressed below the surface. A dominant gravel layer appears at a varying soil depth (1.5−2.2 m) within the experimental field, and the water table at the site is located 4−4.5 m below the soil's surface. The soil's characteristics are shown in Table 1.

The experiment took place on six plots of 100 m^2 each. Three were irrigated at optimum rates [evapotranspiration (ET) = 1.03] and the other three used conventional irrigation (ET = 1.23), which represents three repetitions for both types of irrigation (Table 2).

Within the two sets of three plots, the central plot was provided with neutron access tubes (43 mm inside diameter) installed to a maximum depth of 2 m. Vertical tensiometers surrounding the neutron probe tubes were placed in the same plots. Tensiometers capable of measuring water pressures between 0 and 80 kPa were used (Diez et al., 1996). Soil water potential gradients were used to determine water movement in the soil profile. This was done by relating hydraulic head to soil depth. Samples of the soil water solution were taken with a ceramic candle extraction system with three tubes (63 mm inside diameter) per plot installed at 0.5, 0.9, and 1.4 m soil depth. These tubes were installed on each plot (Figure 1). Water samples from suction cups represent drainage water in the presence of drainage as the amount of drainage water at 140 cm soil depth, which is the same as at a lower depth

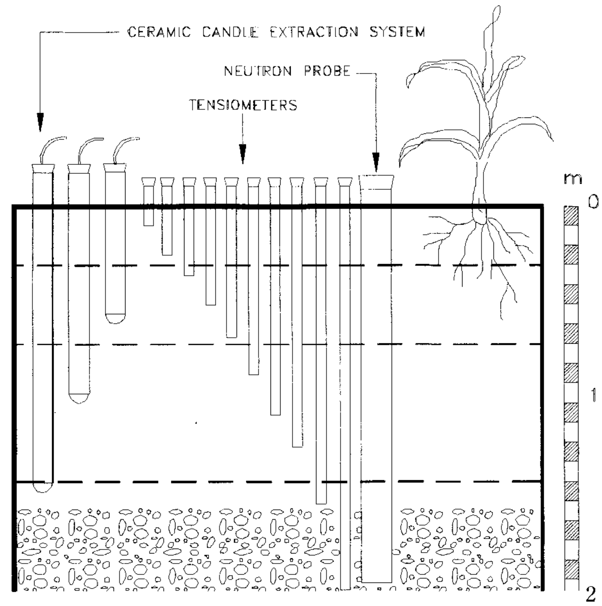

Figure 1. Metering equipment plot layout.

due to the textural characteristics of the soil profile. In the absence of drainage, suction cup samples may not represent soil water at lower depths, but in this case, leaching is absent.

Instrumentation of the experimental field and the methodology for determining seasonal water stored in the soil profile, water flow calculation, and the water balance partitioning scheme have been previously described (Roman et al., 1996). Water storage and hydraulic head controls were performed before and after irrigation during crop growing periods. In the course of bare land periods, at least one control per month was performed, depending on rainfall conditions. During the experiment (February 1993−December 1995), 82 and 102 controls were performed in conventionally and efficiently irrigated plots, respectively. Four water flow patterns were found, and the appropriate water balance partitioning scheme was applied, allowing seasonal evapotranspiration (ET) and drainage to be calculated.

Crops and Irrigation Management. The experiment lasted three years (1993−1995) in which the following maize−wheat−maize crop rotation was followed:

After plowing in a barley (*Hordeum vulgarum* L.) stubble, maize (*Zea mays* L.) cv. Juanita 700 (Pioneer) was planted on April 30, 1993, in rows spaced 0.75 m with a density of seven plants m^{-2}. At seedbed preparation, a compound fertilizer (0N−6.1P−5.8K) and K_2SO_4 were applied to the experimental field at the rates of 714 and 100 kg ha^{-1} respectively. A combination of atrazine [6-chloro-*N*-ethyl-*N*-(1-methylethyl)-1,3,5-triazine-2,4-diamine] at 0.9 kg ha^{-1} and metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide] at 1.5 kg ha^{-1} was applied pre-emergence for weed control. Maize was harvested in December 1993 at the maturing grain stage.

After plowing in the maize stubble, wheat (*Triticum aestivum* L.) cv. Yécora was planted on January 21, 1994, in rows spaced 0.17 m with a seeding rate of 150 kg ha^{-1}. An isobutyl ester formulation of 2,4-D [(2,4-dichlorophenoxy)acetic acid] at 0.6 kg ha^{-1} was applied after tilling for weed control. Wheat was harvested on July 21, 1994, at the maturing grain stage.

Wheat stubble was plowed in December 1994, and maize was planted on April 19, 1995, with similar planting methods as those recorded in 1993. This second maize within the cropping sequence was harvested on November 29, 1995.

A mobile-line overhead sprinkler irrigation system was used for watering the experimental field. Irrigation rates were adjusted by regulating the system's speed.

Plots under conventional irrigation were watered periodically at similar rates of 50 mm until the maize reached 0.5 m in height. Plots were watered 12 and 10 times in 1993 and 1995, respectively, according to rainfall during the maize growing seasons. The mean interval between water applications was 1 week. This irrigation method simulated the practice of most maize producers in the area (Table 2).

The efficient irrigation treatment was planned to match irrigation rates to the seasonal maize water consumption, thus avoiding drainage throughout both maize growing seasons. Plots under efficient irrigation were watered 20 times in 1993 (twice a week), bearing in mind seasonal ET and water storage and adjusting subsequent irrigation rates. It was apparent that such detailed control was not necessary, and in the 1995 maize cropping season, irrigation was performed only 10 times, but rates were always adjusted to seasonal ET.

Intercultivate wheat in 1994 was irrigated in a similar fashion in both sets of three plots and in accordance with the spring rainfall. Irrigation was performed five times with a total of 115 mm between March 24, 1995, and June 1, 1995 (Table 2).

A stream source of water from the River Jarama was used throughout the whole experiment. The amount of N provided to the soil through irrigation never exceeded 3 kg of N ha^{-1} for each crop.

Determining the Balance Parameters. *0−30 cm Mineral N Content (N_{0-30}).* Soil samples from the topsoil (0−30 cm) were taken before planting and after harvesting each crop. Nitrogen was determined using the EUF technique (Nemeth, 1979). NO_3^- in EUF extracts (EUF-NO_3) was determined colorimetrically using a Technicon AAII Autoanalyzer (Technicon Hispania, Madrid) with N1 naphthylethylenediamine. NH_4^+-N in EUF extracts (EUF-NH_4^+) was determined with selective electrodes for Orion gas model 95-12 (Banwart et al., 1972).

The mineral N content in kilograms of N per hectare in those 30 cm of soil (N_{0-30}) is obtained with (Nemeth, 1981)

$$N_{0-30} = 100 \times (\text{EUF-NO}_3 + \text{EUF-NH}_4{}^+)\rho\Delta d \qquad (2)$$

where EUF-NO_3 + EUF-NH_4^+ (EUF_m) is milligrams of N per 100 g of soil, ρ is the soil's apparent density (t m^{-3}), and Δd is the soil depth (0.3 m).

30−70 cm Mineral N Content (N_{30-70}). Soil water solution samples from the 50 cm depth ceramic candle were taken before planting and after harvesting each crop. The NO_3^- concentration was performed colorimetrically using a Technicon AAII Autoanalyzer (Technicon Hispania) with N1 naphthylethylenediamine.

The N content in kilograms of N per hectare between 30 and 70 cm soil depth (N_{30-70}) is given by (Kengni, 1993)

$$N_{30-70} = 2.25\theta[\text{NO}_3{}^-]\Delta d$$

where $[NO_3^-]$ is the concentration of NO_3^- in the sample in mg of NO_3^- L^{-1}, θ the moisture content at 50 cm depth on the sample-taking date in m^3 m^{-3}, and $\Delta d = 0.4$ m.

70−140 cm Mineral N Content (N_{70-140}). N_{70-140} is determined in the same way as N_{30-70} (Kengni, 1993) from soil water solution samples from the 90 cm depth suction cup, the moisture (θ) at 90 cm, and $\Delta d = 0.7$ m.

Mineral N Leached (N_l). Water flow measurements allowed for determining periods and amounts of water percolation. When a downward flow of water was detected from the deepest soil layer, the volume of drainage water was multiplied by a correspondent NO_3^- -N concentration at 140 cm. Seasonal integration of drainage periods allowed for an estimation of amounts of NO_3^- -N leached to the groundwater (Diez et al., 1996).

Plant N Uptake (N_{up}). Only N exportation by the crop has been considered to calculate N balances. This fraction is represented by the aboveground biomass; the resting fractions of the plant have been incorporated into the soil with plow.

For the maize crop, aboveground biomass was measured on plants harvested in 5 m of two adjacent rows in the middle of each plot. Of the plants harvested, 10 were randomly selected, and the plant parts (stalk, leaves, bracts, cob, and grain) were separated and weighed. Whole and fraction samples were oven-dried for 24 h at 60 °C and for 2 h at 80 °C for determining dry matter (DM). Grain yield was calculated by multiplying aboveground biomass by harvest index. Harvest index was calculated as the ratio of grain weight to aboveground biomass. Nitrogen concentration was determined in plant fractions by using the Kjeldhal method (AOAC, 1990); the plant fractions were pretreated with a solution of salicylic acid with sulfuric acid (Bremner, 1965).

For the wheat crop, aboveground biomass was controlled in 2 m × 5 m areas in the middle of each plot. Aboveground biomass was harvested to a stubble height of 0.10 m, and both grain and packed straw were removed from the experimental field. Dry matter and the N concentration of wheat fractions (grain and straw) were recorded in fashion similar to that used for the preceding maize.

Plant N uptake was calculated by multiplying fraction yields by their respective N concentrations.

Determining EUF-N_{org}. EUF-N_{org} is determined by difference between EUF-N and EUF-NO_3^- + EUF-NH_4^+. Total N in EUF extracts (EUF-N) from soil samples was determined by digestion with UV radiation and subsequent oxidation with potassium persulfate in an alkaline medium (Diez, 1988).

Mineral N Balance. The balance was determined in terms of mineral N (NO_3^- -N + NH_4^+-N) and in kg N ha^{-1}, although, below 30 cm depth, NH_4^+ contents are so low they have been deemed negligible. The balance is determined for a total 140 cm depth of profile since the NO_3^- reaching that depth is deemed to be leached.

The N balance is based on the equation

$$N_i + N_s - N_{lost} = N_f \qquad (3)$$

where N_i = initial N, N_s = N supplied, N_{lost} = N loss, and N_f = final N. N_i and N_f refer to the time prior to sowing and after harvesting, respectively. N_s and N_{lost} refer to the growing period.

RESULTS AND DISCUSSION

Mineral N Balance. The N gain (N_s) in eq 3 originates at various sources: atmospheric deposition (moist and dry), symbiotic fixation, and mineralization of the soil's organic matter. For the analysis in question, it was estimated that the organic matter's mineralized N (N_m) is of such a magnitude that N from atmospheric deposition can be neglected. Likewise, symbiotic fixation is not considered because of the type of crops alternating in rotation (cereals). As was said earlier, nitrogenous fertilizers were not applied in this experiment so that the N mineralized without external input could be assessed.

N loss (N_{lost}) refers to the N that came out of the profile considered and, therefore, finally stopped being crop available. Among them, we consider N leached (N_l) and crop uptaken N (N_{up}). NH_4^+ interlaminar fixation is deemed unimportant since, although the soil contains smectites and illites, its clay content is low and reduces with depth (Table 1). Tests prior to this experiment demonstrated that, under the area's climate conditions, volatilization losses do not occur in nonfertilized soils. It was also seen that, to occur, denitrification required high NO_3^- contents in the soil, moisture above field capacity, and moderate temperatures. These conditions were verified only at specific times when the measurements made gave insignificant values; therefore, it was estimated that denitrification is negligible compared to other balance items.

The equation representing the balance would be as follows:

$$N_i + N_m - N_l - N_{up} = N_f \qquad (4)$$

Table 3. N Balance in Maize Crop (1993)

Conventional Irrigation, Topsoil

	N_i				N_f				
depth (cm)	date	EUF_m (mg 100 g^{-1})	ρ (g cm^{-3})	N_i (kg ha^{-1})	date	EUF_m	ρ	N_f (kg ha^{-1})	ΔN
0−30	March 1993	2.30	1.49	102.81	Dec 1993	1.46	1.49	65.41	−37.40

Conventional Irrigation, Subsoil

	N_i				N_f				
depth (cm)	date	θ (× 100)	$[NO_3^-]$ (mg L^{-1})	N_i	date	θ (× 100)	$[NO_3^-]$	N_f	ΔN
30−70	March 1993	19.57 ± 3	298.00 ± 85	52.48	Dec 1993	25.17 ± 4	76.00 ± 38	17.22	−35.27
70−140	March 1993	23.25 ± 6	220.00[a]	80.56	Dec 1993	22.62 ± 5	55.00[a]	19.59	−60.97
total				235.85				102.22	−133.63

Efficient Irrigation, Topsoil

	N_i				N_f				
depth (cm)	date	EUF_m	ρ	N_i	date	EUF_m	ρ	N_f	ΔN
0−30	March 1993	2.21	1.49	98.79	Dec 1993	1.42	1.49	63.47	−35.31

Efficient Irrigation, Subsoil

	N_i				N_f				
depth (cm)	date	θ (× 100)	$[NO_3^-]$	N_i	date	θ (× 100)	$[NO_3^-]$	N_f	ΔN
30−70	March 1993	20.04 ± 4	100.00 ± 50	18.03	Dec 1993	24.31 ± 3	69.00 ± 26	15.10	−2.94
70−140	March 1993	8.88 ± 2	150.00[a]	20.97	Dec 1993	13.23 ± 5	125.00 ± 105	26.05	5.08
total				137.79				104.62	−33.17

[a] Only one sample.

In eq 4, all terms are found by measurement, except N_m. We can therefore rewrite eq 4 in another form

$$N_m = \Delta N + N_l + N_{up} \quad (5)$$

by replacing ($N_f - N_i$) with ΔN.

As described earlier, N contents are determined at three depths (0−30, 30−70, and 70−140 cm) of the profile; therefore, ΔN is made up of the following terms:

$$\Delta N = \Delta N_{0-30} + \Delta N_{30-70} + \Delta N_{70-140} \quad (6)$$

The balance equation would thus be represented by the expression

$$N_m = (\Delta N_{0-30} + \Delta N_{30-70} + \Delta N_{70-140}) + N_l + N_{up} \quad (7)$$

N_m is obtained as a result of the N balance over the whole profile; however, it is attributed to the top 30 cm since below this depth mineralization is accepted as negligible, bearing in mind the subsoil's lack of organic matter. That is to say, it is assumed that all of the N mineralized in the profile is mineralized in the first 30 cm.

The methodology for the balance expounded up to now has been illustrated with the experimental data from each of the three crops (maize−wheat−maize) and with each of the irrigation systems (conventional and efficient) (Tables 3−6).

Mineral N balances (ΔN) for the maize crop (1993 and 1995) were all negative, both in conventional irrigation (−133.63 kg ha^{-1} in 1993 and −37.1 kg ha^{-1} in 1995) and in the optimized (−33.17 kg ha^{-1} in 1993 and −65.63 kg ha^{-1} in 1995) (Tables 3 and 5, respectively) irrigation, which means that reserves of available N diminish in the soil's profile throughout the growing cycle. This is mainly due to the heavy nitrogen absorption of maize (Table 6), the average value of which was 238.26 ± 35.57 kg ha^{-1}, to which is added the N leached, the values of which were substantially different in relation to the irrigation system applied (Table 6).

On the other hand, the balance made for the wheat crop shows an accumulation of mineral N in the soil profile with both irrigation systems (5.24 kg ha^{-1} in conventional and 6.84 kg ha^{-1} in optimized) (Table 4). However, this accumulation is seen to originate only in the first 30 cm (17.43 kg ha^{-1} in conventional and 22.65 kg ha^{-1} in optimized), whereas in the soil's deeper layers, from 30 to 140 cm, N reserves diminish. This is explained by the temperature and moisture regime during this winter cereal's growing cycle, in which two periods are clearly differentiated: (1) During the early months, heavy precipitations and low temperatures coincide and nitrate leaching losses occur, whereas the organic matter's mineralization is very low. This finally leads to a reduction in the soil's N reserves. (2) During the growing cycle's last few months, nitrates stop leaching in the absence of rainfall, although maintenance irrigation is sometimes performed, and at the same time, temperature increases; this moderately activates the organic matter's mineralization. Considering both periods overall, the balance demonstrates a relatively small mineral N accumulation.

Nevertheless, we point out that the rainfall recorded during 1994 was low compared to the region's average. These results may thus vary from year to year, depending on the weather conditions during both the winter and spring (fairly irregular in the Mediterranean area).

Table 6 shows values of N_m; it can be seen that the balance figure obtained in maize (average of two years and two types of irrigation) was 186.82 ± 19.37 kg of N ha^{-1}; however, in wheat, this figure was 66.87 ± 8.89 kg of N ha^{-1}. The difference is a direct result of the different weather occurring in each growing period, as has been demonstrated. Thus, in the case of maize,

Table 4. N Balance in Wheat Crop (1994)

Conventional Irrigation, Topsoil

	N_i				N_f				
depth (cm)	date	EUF_m (mg 100 g^{-1})	ρ (g cm^{-3})	N_i (kg ha^{-1})	date	EUF_m	ρ	N_f (kg ha^{-1})	ΔN
0−30	Jan 1994	1.46 ± 0	1.49	65.41	July 1994	1.85 ± 1	1.49	82.84	17.43

Conventional Irrigation, Subsoil

	N_i				N_f				
depth (cm)	date	θ (× 100)	$[NO_3^-]$ (mg L^{-1})	N_i	date	θ (× 100)	$[NO_3^-]$	N_f	ΔN
30−70	Jan 1994	24.85 ± 4	90.00 ± 54	20.13	July 1994	20.85 ± 3	76.00 ± 72	14.26	−5.86
70−140	Jan 1994	21.99 ± 6	60.00[a]	20.78	July 1994	9.86 ± 3	93.00 ± 23	14.45	−6.33
total				106.32				111.55	5.24

Efficient Irrigation, Topsoil

	N_i				N_f				
depth (cm)	date	EUF_m	ρ	N_i	date	EUF_m	ρ	N_f	ΔN
0−30	Jan 1994	1.42 ± 0	1.49	63.47	July 1994	1.93 ± 1	1.49	86.12	22.65

Efficient Irrigation, Subsoil

	N_i				N_f				
depth (cm)	date	θ (× 100)	$[NO_3^-]$	N_i	date	θ (× 100)	$[NO_3^-]$	N_f	ΔN
30−70	Jan 1994	23.51 ± 2	72.00 ± 28	15.24	July 1994	23.31 ± 2	71.00 ± 29	14.89	−0.34
70−140	Jan 1994	17.04 ± 4	125.00 ± 110	33.6	July 1994	8.51 ± 5	135.00[a]	18.09	−15.46
total				112.26				119.10	6.84

[a] Only one sample.

Table 5. N Balance in Maize Crop (1995)

Conventional Irrigation, Topsoil

	N_i				N_f				
depth (cm)	date	EUF_m (mg 100 g^{-1})	ρ (g cm^{-3})	N_i (kg ha^{-1})	date	EUF_m	ρ	N_f (kg ha^{-1})	ΔN
0−30	April 1995	1.85 ± 1	1.49	82.84	Dec 1995	1.88 ± 1	1.49	83.89	1.04

Conventional Irrigation, Subsoil

	N_i				N_f				
depth (cm)	date	θ (× 100)	$[NO_3^-]$ (mg L^{-1})	N_i	date	θ (× 100)	$[NO_3^-]$	N_f	ΔN
30−70	April 1995	11.70 ± 5	110.00[a]	11.58	Dec 1995	12.68 ± 3	5.00[a]	0.57	−11.01
70−140	April 1995	9.77 ± 3	250.00 ± 70	38.46	Dec 1995	11.08 ± 4	65.00 ± 15	11.34	−27.13
total				132.88				95.8	−37.09

Efficient Irrigation, Topsoil

	N_i				N_f				
depth (cm)	date	EUF_m	ρ	N_i	date	EUF_m	ρ	N_f	ΔN
0−30	April 1995	1.9 ± 1	1.49	86.12	Dec 1995	1.79 ± 0	1.49	79.86	−6.26

Efficient Irrigation, Subsoil

	N_i				N_f				
depth (cm)	date	θ (× 100)	$[NO_3^-]$	N_i	date	θ (× 100)	$[NO_3^-]$	N_f	ΔN
30−70	April 1995	25.23 ± 6	298.00 ± 110	67.67	Dec 1995	19.77 ± 8	130.00[a]	23.14	−44.53
70−140	April 1995	8.51 ± 5	155.00[a]	20.77	Dec 1995	12.56 ± 7	30.0 ± 15	5.93	−14.84
total				112.26				119.10	−65.63

[a] Only one sample.

Table 6. N Mineralized to Each Crop Calculated by the Balance (Kilograms of N per Hectare)

	conventional irrigation				efficient irrigation			
crop	ΔN	N_l	N_{up}	N_m	ΔN	N_l	N_{up}	N_m
maize 1993	−133.63	49.08 ± 26	286.96 ± 34	201.41 ± 57	−33.17	1.76 ± 2	199.86 ± 14	168.45 ± 31
wheat 1994	5.24	9.58 ± 4	43.16 ± 10	57.98 ± 18.6	6.84	9.24 ± 9	59.66 ± 5	75.75 ± 22
maize 1995	−37.09	12.90 ± 6	234.61 ± 10	210.42 ± 65	−65.63	0.00 ± 0	232.60 ± 30	166.98 ± 56

optimum mineralization conditions occur, since temperatures are high and soil moisture is guaranteed through irrigation.

It was also seen in maize that the type of irrigation and, in particular, the rates applied, could influence the amount of mineralization and, hence, the equation's factors. Thus, it can be seen that N_m was greater in conventional (205.92 ± 4.51 kg of N ha^{-1}) than in optimized irrigation (167.72 ± 0.74 kg of N ha^{-1}) in the 2 years during which maize experiments were carried out. In the same way, rates of water applied were greater in conventional irrigation (595 mm in 1993 and 554 mm in 1995) (Table 2) than in optimized irrigation (515 mm in 1993 and 464 mm in 1995). Although the differences observed in N_m are not statistically significant, they could be due to the higher rates of water applied in the conventional system. In fact, the soil's moisture conditions could be the factor of greatest influence on the organic matter's mineralization in Mediterranean climates when the temperature is high.

As was said earlier, in irrigated Mediterranean spring–summer crops, optimum conditions coincide for rapid organic matter mineralization. This involves a major supply of mineral N to the crops. Thus, the EUF-obtained mineral N present in the soil at the beginning of maize growing (N_{0-30}) was, as an average of the whole experiment (2 years and two irrigation systems), 92.64 ± 8.36 kg of N ha^{-1}. On the other hand, the average organic matter's mineralized N (N_m) value for the maize crop was 186.82 ± 19.37 kg of N ha^{-1}. That is to say, organic matter's mineralized N (N_m) was two-thirds of the whole available N during the growing cycle, which is indicative of the enormous importance of assessing potentially minerizable N.

EUF Estimation of Available N (N_{av}). Various authors have found satisfactory relationships among the different determinations that can be made in EUF-obtained extracts (EUF-N, EUF-NO_3^-, EUF-NH_4^+, and EUF-N_{org}) and crop production or the N taken up by them under field conditions (Wiklicky et al., 1983; Fürstenfeld and Nemeth, 1984; Nemeth et al., 1987; Poletschny and Fabian, 1989; Ziegler, 1989; Ziegler et al., 1992). However, expression 1 as obtained by Wiklicky and Nemeth (1981) has been widely applied with highly positive results. In this relationship, soil samples are taken in the arable layer (0–30 cm deep), with N_{av} being in kg of N ha^{-1} and the EUF-obtained values of nitrogen being in mg of N 100 g^{-1} of soil. According to the authors, its main advantages lie in soil samples being taken only from the arable layer (30 cm) and the fact that the said samples can be taken in the summer or autumn before the crop is fertilized.

An N_{av} value will be established from the N_m value obtained by the methodology expounded, applying a similar equation

$$N_{av} = a \times \text{EUF-NO}_3^- + b \times \text{EUF-N}_{org} \qquad (8)$$

where N_{av} is in kg of N ha^{-1}, $a = 100 \times \rho\ (tm^{-3}) \times \Delta d$ (m), $b = N_m$ (kg of N ha^{-1})/EUF-N_{org} (mg of N 100 g^{-1}).

The values of b are calculated in Table 7 as a function of balance-obtained N_m, and the value of EUF-N_{org} has been calculated for each crop and with each irrigation rate. Two different N_{av} formulas have been established from these results, one for maize (spring crops) and the other for wheat (winter crops) according to the different moisture and temperature conditions in both cycles. Despite the point having been made, in the case of maize, that mineralization might have been more intense in conventional irrigation, only one formula has been established, since the differences found, both in N_m and in the b factor, were not statistically significant:

Table 7. Calibration of Coefficient *b* Relative to the EUF-N_{org} Parameter

		N_m[a]	EUF-N_{org}[b]	b
maize 1993	conventional irrigation	201.41	1.82	110.66
	efficient irrigation	168.45	1.91	88.19
wheat 1994	conventional irrigation	57.98	2.18	26.56
	efficient irrigation	75.75	1.96	38.65
maize 1995	conventional irrigation	210.42	2.59	81.14
	efficient irrigation	166.98	2.37	70.36

[a] Calculated by balance. [b] Sampling in the initial date of balance.

maize

$$N_{av} = 44.70\text{EUF-NO}_3^- + 87.59\text{EUF-N}_{org} \qquad (9)$$

wheat

$$N_{av} = 44.70\text{EUF-NO}_3^- + 32.61\text{EUF-N}_{org} \qquad (10)$$

These values contrast with those obtained by Wiklicky and Nemeth (1981). The factor affecting EUF-NO_3^- has been modified as a function of the specific conditions of the experimental soil (apparent density) in view of the fact that all nitrate initially present in the soil is deemed to be available to the crop.

However, the factor affecting EUF-N_{org} has been modified as a function of balance-determined organic N mineralization. The value obtained for maize (87.59 ± 17.04) proved to be appreciably higher than the 50 obtained by Wiklicky and Nemeth (1981). This result would seem more in keeping with Spain's weather conditions since the value as proposed by these authors is calculated for the sugar beet growing cycle in Central European climates (milder temperatures and no irrigation); in Spain, temperatures during the spring–summer growing cycle (maize) are much higher and irrigation is added so that, in the end, organic matter mineralization is much more intense.

On the other hand, in the case of winter cereals, the b value obtained in the experiment was 32.60 ± 8.55, which is a consequence of the crop developing at temperatures lower than those of maize and, in addition, of its cycle being shorter and with limited moisture. Consequently, the organic matter's mineralization will be less in relation to the sugar beet growing cycle in Central Europe, for the reasons given and, in addition, because the organic matter content here is lower.

Of the two formulas shown for evaluating N_{av}, eq 9 referring to maize is probably more reproducible due to part of the environmental conditions being controlled by irrigation, which removes part of the variability. The second (eq 10), referring to wheat, obviously depends on the weather prevailing in the winter–spring period, especially the temperature.

Soil Sampling Date. As several authors have demonstrated (Fürstenfeld and Nemeth, 1984; Diez et al., 1997), organic matter mineralization suffers various alternatives throughout the year, depending on prevailing weather conditions, which affect the predominance of some nitrogenous compounds over others. The work of Nemeth and Fürstenfeld, performed on soils in Lower Saxony in Germany, reveals an increase in N-NO_3^- and, simultaneously, a drop in EUF-N_{org} in the summer season and vice versa in winter. The work of Diez et al. (1997) carried out in the center of Spain on bare soil with summer irrigation, found an increase in EUF-N_{org} at the beginning of spring, which is followed by an increase in N-NO_3^- in summer, whereas both nitrogenous forms decrease in winter.

In the Mediterranean climate, rainfall is very irregular. In the case of maize, soil moisture can only be guaranteed from the time when irrigation commences, that is, weeks after sowing. If the sample were to be taken several months before, as Wiklicky and Nemeth propose for Central Europe (1981), a constant mineralization value as being proposed could not be accurately estimated. Likewise, the EUF-NO_3^- considered as available at the time of sample taking could be outside the scope of the crop when the latter needs it months later if the sampling date is much further away. It might well have been washed away by winter rainfall during that time.

As a result, it is imperative to properly choose sample-taking time to determine the fertilizer rate as a function of N_{av} value obtained. Given that N_{av} is essentially an estimate of the organic N field mineralization, the most suitable date would seem to be a little before the time when the plant begins to take N from the soil or the closest to crop sowing. At that time, the EUF-NO_3^- which is in available form as from that time is known and the N which will be becoming available to the plant during the growing cycle through the organic matter's mineralization can be estimated, through the duly calibrated EUF-N_{org} parameter.

For the N_{av} evaluation procedure to have practical effects, it is still recommended that a single sampling be made at the appropriate time. As the validity of the calibration procedure will be higher the more constant the environmental conditions are during the growing cycle, it is important to reduce the time elapsing between sample taking and the commencement of such cycle. This is why this paper proposes that the sample be taken as close as possible to the time when the plant activates its soil N uptake or, if not, immediately before the commencement of sowing.

CONCLUSIONS

The balance procedure for mineral N in the soil, determining all of the parameters significantly involved therein, enables the organic N that has been mineralized throughout growing to be accurately estimated. It is thus a useful tool for knowing a soil's organic N mineralization and rationalizing nitrogenous fertilization programs. Also, a study on the need and efficiency of N utilization by the plant is required.

The calibration procedure expounded enables the EUF technique to be adapted as an instrument for optimizing fertilization to different soil and climate conditions. This makes it useful for different geographical areas, although it requires calibration for different climate cycles.

The accuracy of the N_{av} evaluation is greater the less the environmental conditions vary between growing campaigns. In the two cases studied, it would seem to be clearly applicable, given that in the case of maize, summer irrigation reduces variability from year to year.

The sample-taking time should be as close as possible to the time when the crop commences to take up N or, if not possible, immediately before sowing.

Estimating organic N mineralization by this procedure demonstrated the importance of this biological process as a supplier of the N necessary for crops under Mediterranean conditions. In any event, bearing in mind the large amounts of N_m originating during a growing cycle, they should be considered when the fertilizer rate is calculated.

For maize in the center of Spain in irrigated land systems, the formula applicable for estimating N_{av} would be

$$N_{av} = 30 \times \rho\ (\text{t m}^{-3}) \times \text{EUF-NO}_3^-\ (\text{mg of N 100 g}^{-1}) + 87.59 \times \text{EUF-N}_{org}\ (\text{mg of N 100 g}^{-1})$$

and for winter wheat in dry land growing

$$N_{av} = 30 \times \rho\ (\text{t m}^{-3}) \times \text{EUF-NO}_3^-\ (\text{mg of N 100 g}^{-1}) + 32.60 \times \text{EUF-N}_{org}\ (\text{mg of N 100 g}^{-1})$$

ABBREVIATIONS USED

EUF, electro-ultrafiltration; N_{0-30}, 0−30 cm mineral N content; N_{30-70}, 30−70 cm mineral N content; N_{70-140}, 70−140 cm mineral N content; N_{av}, N available; N_f, final N; N_i, initial N; N_l, mineral N leached; N_{lost}, N loss; N_m, organic matter's mineralized N; N_s, N supplied; N_{up}, plant N uptake; Δd, soil depth.

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