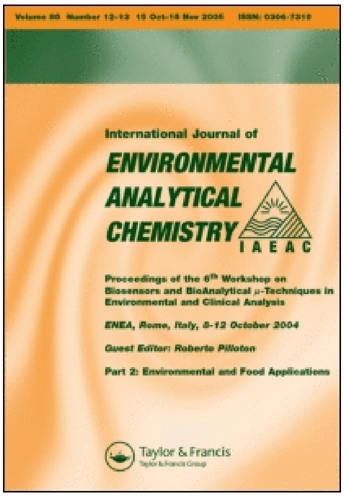

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MONITORING OF SOIL NITRATE RESIDUES BY ELECTRO-ULTRAFILTRATION (EUF)

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An investigation on nitrate residues in a nitrogen fertilized silty-clay soil of Southern Italy was carried out using the Electro-ultrafiltration method (EUF). The method, previously employed to determine several nutrient fractions of different plant availability, allowed us to evaluate periodically the amounts of nitrate ion in soil during the growth of *Brassica campestris L.*

The availability of nitrates was evaluated as two different ion fractions released from soil: (1) Soluble-NO_3^-, i.e., an easily available and quickly released fraction, and (2) Reserve-NO_3^-, i.e., a more firmly retained and slowly released form.

Results showed that nitrate concentration was influenced by the source of fertilizer used. The increase of nitrate concentration in soil also influenced the level of the ion in the edible part of the plants, suggesting a potential toxicity for human health.

KEY WORDS: Nitrates, residues, soil, electro-ultrafiltration, *Brassica campestris L.*

INTRODUCTION

The increased use of inorganic fertilizers has given rise to increases of crop yields and, also, increased levels of phosphorus and potassium in soils.

It has been shown that nitrogen in the soil could not be increased by the use of inorganic fertilizers alone.[1] The rate of the nitrogen loss from the soil rises, however, with the increasing use of nitrogen fertilizers.[2]

A particular portion of the nitrogen loss occurs through the leaching of nitrates, thus polluting ground water.[3] It was also shown that it is very difficult to prevent water pollution by nitrates if their level in the soil markedly exceeds the uptake by plants.[4] On the other hand, owing to nitrate excess in soil, this ion can also accumulate in plants,[5] and the possible reduction of nitrate to nitrite may be responsible for adverse effects on human and animal health.[6]

These considerations suggest the need for further investigations on nitrate levels in soil and methods to extract and analyse it.

Recently, a new extraction technique has been developed based on Electro-

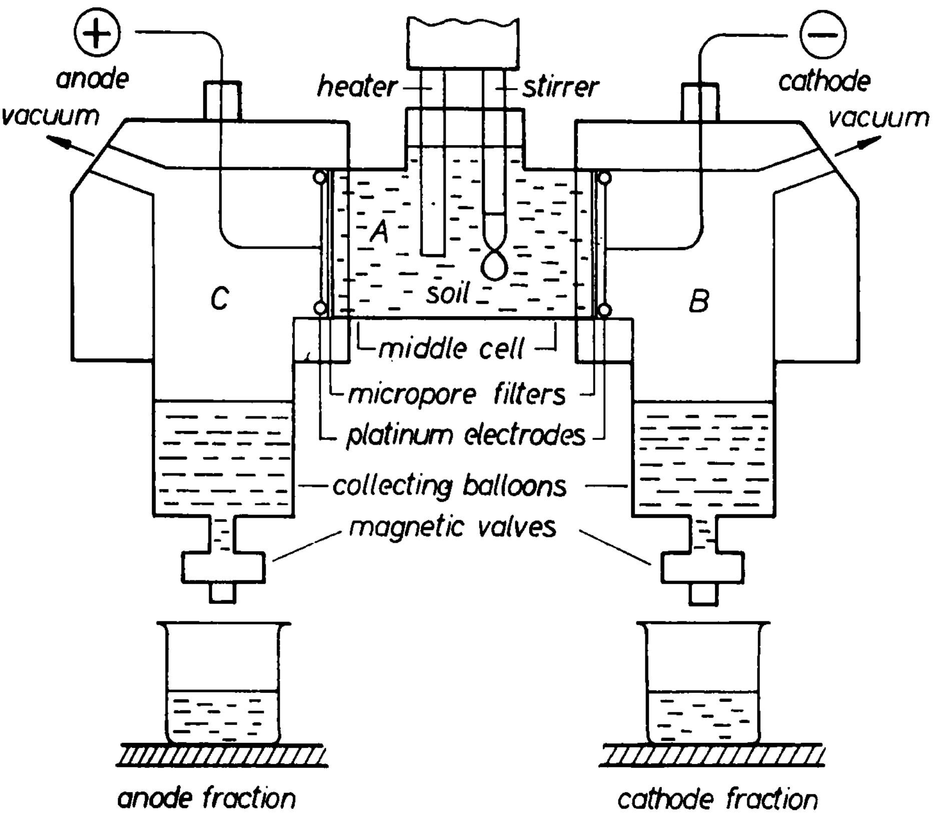

Figure 1 EUF apparatus according to Németh.

ultrafiltration (EUF) to assess fertilizer requirements for plant growth using the results of soil analysis.[7-11]

The EUF procedure has also been used to extract soil nitrate, obtaining concentrations of this ion as high as those found using traditional methods based on chemical extractants.[12,13]

The method is based on a combination of ultrafiltration with electrodialysis (Figure 1). An electric field (44 V/cm) is applied to a soil water suspension; consequently, cations migrate to the cathode and anions to the anode. Therefore the electric field continually disturbs the equilibria established in the soil-water system. As a result the soil tends to replenish the concentration of ions displaced during the extraction.

The apparatus is also equipped with a sensor to regulate the opening of an electrovalve which automatically governs the introduction of water into the cell so that the suspension volume remains constant during the whole extraction period.

In this work, the EUF has been employed to investigate nitrate release from a silty-clay soil during the growth cycle of broccoli raab (or rapini), which has been used as a plant test for nitrate accumulation.

Table 1 Physical and chemical characteristics of the soil

Sand	23.8%
Silt	44.3%
Clay	31.9%
Organic carbon	1.9%
$CaCO_3$	7.7%
Total N	0.19%
Total K	1.5%
Total P	546 ppm
Exchangeable K[18]	216 ppm
Olsen-P[18]	26.6 ppm
pH(H_2O)	7.1
Density	1.2 g/cm^3
C/N	10

MATERIALS AND METHODS

Crop

Broccoli raab or rapini (*Brassica campestris L. ruvo group*)[14] is a vegetable commodity in Southern Italy where it is mostly preferred to broccoli. The edible part of the plant is made up by the inflorescence and the uppermost leaves. Rapini plants are characterized by a high accumulation of nitrates[15,16] and a nitrogen uptake averaging about 450 kg/ha N (V. Magnifico, unpublished data).

The crop (cv. Di Marzo) was fertilized at two nitrogen regimes (0 and 300 kg/ha N, the optimized one), using four different nitrogen sources (urea, calcium nitrate, ammonium nitrate, and ammonium sulphate). In the previous year, on the same site non-nitrogen fertilized vetch (*Vicia sativa L.*) had been grown.

The highest rate of nitrogen was split (150 + 150 kg/ha N) and broadcast on Nov. 19, and Dec. 19, 1987, respectively. The edible part of the plant was sampled on Jan. 22, 1988, dried in a forced-draft oven at 65 °C, and ground in a mill. Nitrate ions were extracted by shaking 1 g of the ground material for 30 min in 100 ml of a buffer solution of $NaHCO_3/Na_2CO_3$ (0.25 M/0.85 M) at pH 11.

Soil

Soils were sampled (0–40 cm) for nitrate evaluation 0, 14, 28, 56, 70 and 98 days after the first nitrogen application. Main characteristics of the soil are listed in Table 1.

To extract nitrates from soil, the EUF procedure suggested by Németh was used but modified keeping the voltage at constant value during the whole extraction period.

An aliquot (5 g) of soil from each sample, sieved at 1 mm, was suspended in 50 ml of water in the EUF cell; six extracts were collected one every 5 min applying an electric field of 44 V/cm at 15 mA and 25 °C for a duration of 30 min (EUF_1), after which current was increased to 150 mA and temperature to 80 °C

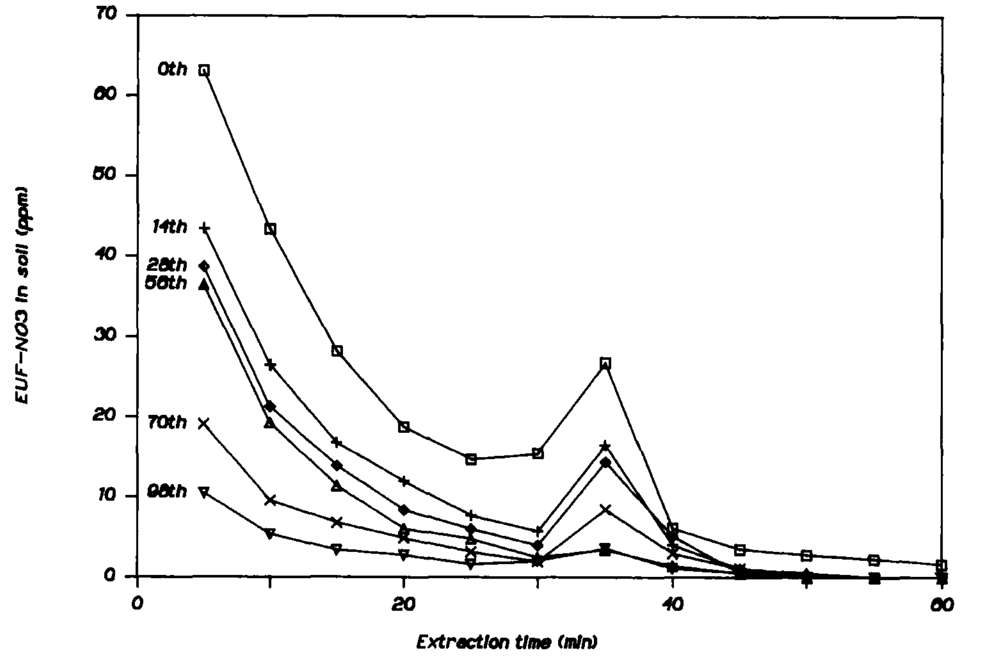

Figure 2 EUF-NO_3^- curves of untreated soil, sampled during the crop growth.

and another six extracts were collected once every 5 min for another 30 min (EUF_2).

Ion chromatography (IC) was used to analyse nitrates both in plant and soil extracts. An aliquot of each extract, purified using a C-18 disposable cartridge, was injected into a Dionex QIC analyzer. This instrument is a low pressure liquid chromatograph that employs an analytical column packed with low capacity anion agglomerate resin and a suppressor column packed with a high capacity cation exchange resin. A precolumn containing the same resin as the analytical column, was used to protect the separator column by removing potentially poisonous substances from the eluent stream. The eluent was 0.25 M $NaHCO_3$ + 0.85 M Na_2CO_3 pumped at a flow rate of 120 ml/h and a pump pressure of 800 psi. The components and theory of operation of IC are described in detail by Dick and Tabatai.[17]

RESULTS

Figure 2 shows typical extraction curves obtained from the EUF data and referred to untreated soil samples during the growth of the crop. The results shown in Figure 2 suggest the existence of two fractions with different availability of nitrate in untreated soil at beginning of the growth cycle. The stronger extraction conditions used in EUF_2, resulted in the release of large amounts of nitrate ions

Table 2 EUF-NO_3^- values in soil during cropping period (ppm)

Days	*Fraction*	*Untreated*	*Fertilizer*			
			$CO(NH_2)_2$	$Ca(NO_3)_2$	NH_4NO_3	$(NH_4)_2SO_4$
0	1st fertilization rate					
	EUF_1	184	—	—	—	—
	EUF_2	43	—	—	—	—
	Total EUF	227	—	—	—	—
14	EUF_1	112	329	370	245	185
	EUF_2	22	102	78	64	42
	Total EUF	134	431	448	309	227
28	EUF_1	86	258	213	276	246
	EUF_2	24	100	41	67	75
	Total EUF	110	350	254	343	321
30	2nd fertilization rate					
56	EUF_1	81	332	397	168	118
	EUF_2	5	89	105	37	52
	Total EUF	86	421	502	205	170
70	EUF_1	46	256	244	209	169
	EUF_2	13	53	54	31	57
	Total EUF	58	309	298	240	226
98	EUF_1	26	110	135	97	31
	EUF_2	5	24	26	23	23
	Total EUF	31	134	161	120	54

which were more firmly retained by soil components, inorganic or organic, and could not be extracted during the EUF_1 procedure.

In agreement with Németh *et al.*,[7,13] we have assessed as the Soluble-NO_3^- the total amount of nitrate extracted using EUF_1, the less vigorous procedure. This NO_3^- is the easily available or quickly released fraction of this ion from soil. We assessed as the Reserve-NO_3^- the total amount extracted using EUF_2, the more vigorous procedure. This NO_3^- is the more firmly retained or slowly released nitrate fraction.

From the Figure 2 it can also be observed that, during plant growth, the Reserve-NO_3^- level decreases so that this fraction declines to almost negligible amounts at the end of the growth cycle.

Table 2 lists nitrate concentrations in soil as total amounts obtained by EUF_1 and EUF_2 procedures during plant growth. These data show that all N-dressings increased both Soluble-NO_3^- and Reserve-NO_3^- fractions in soil. At the end of the growing cycle (98th day) soils treated with urea, and calcium and ammonium nitrate, contained very similar amounts of total EUF nitrate, with an average of 138 ppm which was 2.5 times as high as that in the ammonium suphate treated soil and 4.4 times as high as in the untreated one. The ammonium sulphate treated soil showed a similar quantity of Soluble-NO_3^- (EUF_1) to the untreated soil and almost the same amount of Reserve-NO_3^- (EUF_2) as the soil treated with the other three fertilizers.

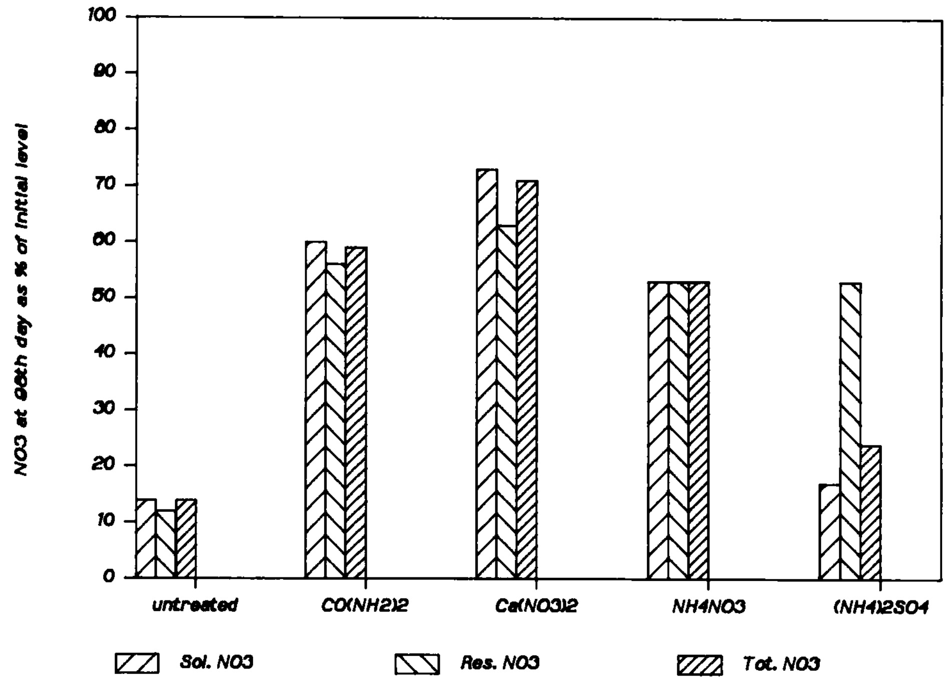

Figure 3 EUF-NO_3^- levels at the 98th day as percentage of the background level at 0th day of both Soluble-NO_3^- and Reserve-NO_3^-.

Figure 3 shows the EUF-NO_3^- levels at the 98th day calculated as percentage of the background level at 0th day of both Soluble-NO_3^- and Reserve-NO_3^-. The calcium nitrate-treated soil retained the higher amount of both fractions followed by the urea treated one. As occurred in the untreated soil, the Soluble-NO_3^- fraction persisted longer than the Reserve-NO_3^- fraction for the first two fertilizers. The two values were the same where ammonium nitrate has been used, but Reserve-NO_3^- was more firmly retained than Soluble-NO_3^- in the soil treated with ammonium sulphate.

In all cases the total level of nitrate decreased with plant uptake and, at the end of growth, only 14% of the background content of the ion was retained in the untreated soil, with 24%, 53%, 59% and 71% retained in the ammonium sulphate, ammonium nitrate, urea and calcium nitrate treated soils, respectively.

Results of nitrate determinations on the edible part of plants showed that $(NH_4)_2SO_4$ dressing gave the lowest NO_3^- concentration (6.5 mg/g d.m.); $Ca(NO_3)_2$ and NH_4NO_3 gave the highest values (14.2 and 18.4 mg/g d.m., respectively), while urea produced almost the same quantity of nitrate as the untreated plants (10.2 and 9.4 mg/g d.m.).

CONCLUSIONS

In conclusion the results showed that using EUF it is possible to characterize two fractions of nitrate in soil, if the total content of the ion is appreciable. The use of N-fertilizers increases the level of nitrate in soil, but, if the fertilization rate is optimized, the amount of the ion concentration, at the end of plant growth, is lower than the background. The Reserve-NO_3^- level at the end of the growing period is almost the same quite apart from the N-source used, while the Soluble-NO_3^- concentration is strictly dependent on the form of the N-dressing used.

The N-source also influences the level of the ion in the edible part of the crop which may affect potential toxicity for human health.

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