Replacing organic with mineral N fertilization does not reduce nitrate leaching in double crop forage systems under Mediterranean conditions

Elsevier Editorial System(tm) for Agriculture, Ecosystems and Environment
Manuscript Draft

Manuscript Number: AGEE13437R3

Title: Replacing organic with mineral N fertilization does not reduce nitrate leaching in double crop forage systems under Mediterranean conditions

Article Type: Research Paper

Keywords: Disc lysimeter; Silage maize; Italian ryegrass; Cattle slurry; Manure; Nitrate Vulnerable Zone.

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Manuscript Region of Origin: ITALY

Abstract: This research evaluated the impact of four nitrogen (N) fertilizer management systems on nitrate losses in an irrigated forage system under Mediterranean conditions within a Nitrate Vulnerable Zone (NVZ). The experiment was conducted from June 2009 to May 2012 in an intensive dairy cattle farm that produces silage maize and Italian ryegrass in a double cropping system. A monthly monitoring of the nitrate concentrations in the soil solution was carried out using 10 cm diameter disc lysimeters. The N fertilization systems had a target N application of 316 and 130 kg ha-1 for maize and Italian ryegrass, respectively. Four systems were compared: cattle manure (MA); cattle slurry (SL); cattle slurry + mineral N fertilizer (SM); mineral N fertilization (MI). A clear seasonal dynamics of nitrate concentration was observed in the three years and was similar among treatments, with maximum occurring in autumn-winter. On average, at soil depths between 50 and 90 cm, nitrate concentrations in the soil solution were intermediate for the MI treatment (146 ± 10.4 mg L-1), in between those of SL or SM (202 ± 11.3 and 164 ± 9.4 mg L-1 respectively) and MA (78 ± 4.9 mg L-1). Despite the high average concentrations, only in some sampling dates the nitrate concentration was significantly higher than 50 mg L-1. The estimated annual N leaching losses below 90 cm soil depth ranged from 42 (MA) to 110 (SL) kg N ha-1.
These findings highlighted that, under Mediterranean conditions and with the N input rates, nitrate leaching in autumn-winter cannot be easily controlled through N fertilizer management because it is mainly associated to the natural water surplus and the low N uptake from the winter crop. The cattle manure has proved to be the most conservative in terms of N leaching, while replacing organic with mineral sources of N did not reduce nitrate leaching.

Highlights

- The impact of mineral and organic fertilizers on nitrate leaching was assessed
- Disc lysimeters were used for the nitrate content monitoring in the soil solution
- Cattle manure proved to be the most conservative in terms of nitrate content
- The replacement of organic with mineral fertilizer did not reduce nitrate leaching
- Autumn-winter soil water nitrates were almost independent from fertilizer systems

Replacing organic with mineral N fertilization does not reduce nitrate leaching in double crop forage systems under Mediterranean conditions

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Abstract

This research evaluated the impact of four nitrogen (N) fertilizer management systems on nitrate losses in an irrigated forage system under Mediterranean conditions within a Nitrate Vulnerable Zone (NVZ). The experiment was conducted from June 2009 to May 2012 in an intensive dairy cattle farm that produces silage maize and Italian ryegrass in a double cropping system. A monthly monitoring of the nitrate concentrations in the soil solution was carried out using 10 cm diameter disc lysimeters. The N fertilization systems had a target N application of 316 and 130 kg ha^{-1} for maize and Italian ryegrass, respectively. Four systems were compared: cattle manure (MA); cattle slurry (SL); cattle slurry + mineral N fertilizer (SM); mineral N fertilization (MI). A clear seasonal dynamics of nitrate concentration was observed in the three years and was similar among treatments, with maximum occurring in autumn-winter. On average, at soil depths between 50 and 90 cm, nitrate concentrations in the soil solution were intermediate for the MI treatment (146 ± 10.4 mg L^{-1}), in between those of SL or SM (202 ± 11.3 and 164 ± 9.4 mg L^{-1} respectively) and MA (78 ± 4.9 mg L^{-1}). Despite the high average concentrations, only in some sampling dates the nitrate concentration was significantly higher than 50 mg L^{-1}. The estimated annual N leaching losses below 90 cm soil depth ranged from 42 (MA) to 110 (SL) kg N ha^{-1}. These findings highlighted that, under Mediterranean conditions and with the N input rates, nitrate leaching in autumn-winter cannot be easily controlled through N fertilizer management because it is mainly associated to the natural water surplus and the low N uptake from the winter crop. The cattle manure has proved to be the most conservative in terms of N leaching, while replacing organic with mineral sources of N did not reduce nitrate leaching.

Key words: disc lysimeter, silage maize, Italian ryegrass, cattle slurry, manure, Nitrate Vulnerable Zone.

Introduction

Intensive, grain-fed livestock production systems are considered a major source of nitrate (NO_3^-) leaching and pollution. The mitigation of NO_3^- leaching from agricultural soils has become of global outstanding relevance (Hooda et al., 2000). The European Nitrate Directive (ND, 1991/676/EEC) intends to reduce diffuse NO_3^- pollution of water bodies by designating Nitrate Vulnerable Zones (NVZs) that need to be managed in a way that prevent NO_3^- buildup. The ND established a 50 mg L^{-1} threshold for NO_3^- concentration in ground and surface water (European Union, 1998). In NVZs, the use of organic fertilizers is restricted to 170 kg N ha^{-1} with a restricted time window for its application (e.g. between November and February in the Mediterranean area). The only restriction for the mineral fertilizer supply is that of not exceeding crop requirements. This is because mineral fertilization is assumed to have higher efficiency than organic fertilizers (Hernández et al., 2013). Moreover, the ND does not make any distinction in terms of amount or timing between different types of organic fertilizers, assuming that the amount of leached N is not influenced by the organic N source and management.

The implementation of ND prescriptions has also often resulted in increased costs for crop fertilization and particularly for disposing the excess N from the farm effluents out of the NVZ (de Roest et al., 2007).

The impact of different N fertilization sources on NO_3^- leaching is not clearly established since NO_3^- dynamics are controlled mainly by a complex set of interrelationships between rainfall patterns (Fang et al., 2013), irrigation (Jamali et al., 2015) and fertilization management practices, as well as by soil type and cropping systems (Jabloun et al., 2015; Barros et al., 2012).

In many NVZs, the increased demand for high-quality milk has led to an evolution of the dairy cattle housing from the bedded-pack to the cubicle housing system. This resulted in a higher production of slurry than farmyard manure (Phillips, 2010), even though the bedded pack system was recognized to be compatible with high quality milk and better animal welfare (Atzori et al., 2009 a).

The development of site-specific sustainable fertilization management options for mitigating NO_3^- pollution is therefore a key priority for policy decision makers and land managers (Zavattaro et al., 2012).

The NO_3^- pollution is an issue in Mediterranean semi-arid countries (Daudén et al., 2004). In the Mediterranean regions of the northern hemisphere, 50-90% of total NO_3^- losses by leaching were found to occur particularly between October and February (De Paz et al., 2009; Trindade et al., 1997; Goss et al., 1988). The application of N fertilizers in autumn reinforces the natural accumulation of NO_3^- in the soil at the start of the rainy period (Trindade et al., 2009), thus promoting significant N leaching (Trindade et al., 1997). The dynamic of these processes relates to both the N source and application scheme.

Experiments in Mediterranean conditions showed that the NO_3^- leaching potential from the application of slurries could be lower than those from N mineral fertilizer application (Trindade et al., 2009; Daudén and Quílez, 2004). However, it was also recognized that NO_3^- leaching can be a serious problem when organic effluents are used (Giola et al., 2012; Daudén et al., 2004; Chambers et al., 2000; Trindade et al., 1997). Hence it is still an open question whether the replacement of organic with mineral N fertilizers can effectively mitigate NO_3^- leaching in NVZ and if the type of organic effluent can make a difference in improving the environmental sustainability of intensive dairy farming under Mediterranean conditions. This issue is particularly relevant for intensive livestock farming areas under Mediterranean conditions, like the district of Arborea (Sardinia, Italy). This farming district is characterized by very high stocking rate and high productivity of its dairy cattle system, one of the highest in Europe (Manca, 2009), with a stocking rate of some 5 livestock unit ha^{-1}. In these conditions, the annual animal effluent production is somehow double than the maximum applicable to farmland according to the ND (Nguyen et al, 2014). This study showed that to comply with the ND, Arborea farmers must buy additional mineral N fertilizer to meet the total N crop requirements and must also rent additional land or pay to dispose the cattle effluents outside the NVZ, thus increasing the production costs. This situation is clearly unsustainable and has given rise to controversy about the effectiveness of the ND measures to mitigate NO_3^- pollution while maintaining the profitability of the dairy farming.

The objective of this study was to compare a range of N fertilization options for dairy farming systems in NVZ under Mediterranean conditions, to support the development of sustainable fertilization strategies by exploiting the recycling of the farm N resources.

In this paper, we tested two hypotheses: i) in the Mediterranean intensive forage systems, the seasonal dynamics of the NO_3^-concentrations in the soil solution is very wide and can be effectively controlled by the fertilization management systems; ii) the mineral fertilizers are less impacting on NO_3^- losses than organic fertilizers in NVZ.

We measured the dynamics of the NO_3^- concentration in the soil solution and assessed the potential N leaching as influenced by four N fertilization management systems for an irrigated double forage cropping system in sandy soil under Mediterranean conditions.

1. **Material and methods**

1.1. Site and crop management

The field experiment was conducted from June 2009 until May 2012 in a private farm located in the NVZ of Arborea, Italy (39°47’ N, 8°33’ E, 3 m asl). In the district of Arborea, some 28,000 Bovine Livestock Units are reared by 160 farms on a 5,000 ha irrigated plain. This plain was drained in the 1930’s from wetlands and salt marshes. The groundwater table dynamics is somehow regulated by the local Water User Association dewatering pump system, which controls the drainage of the whole area. The groundwater table depth was monitored during the three year of experiment through 12 piezometers installed in the experimental field.

In this area, about two thirds of the livestock effluent volume is represented by slurry and one third by manure. Considering the N content of the two effluents, the N load from manure and slurry in this NVZ is approximately 38 % and 62 %, respectively.

The climate is Mediterranean and the mean annual temperature and precipitation are 16.7 °C and 568 mm, respectively (1959-2012). Some 73 % of the annual rainfall occurs between October and March and the average annual aridity index (rainfall/reference evapotranspiration) is 0.49 (semi-arid area). The soil was classified as Psammentic Palexeralfs (USDA, 2006) and the soil slope was less than 0.5 %. The soil properties are reported in Table 1. The field capacity of soil profile was determined according to Romano and Santini (2002). The water balance dynamic from May 2009 to June is shown in Figure 1. The common forage cropping system is based on the double-crop rotation of silage maize (*Zea mays* L.) grown from June to September and Italian ryegrass (*Lolium multiflorum* Lam.), grown from October to May. In this cropping system, organic fertilizers (slurry and manure) are applied regularly prior to sowing of each crop and combined with mineral fertilization. During the Italian ryegrass cycle, mineral fertilizers are often applied at the end of the winter to compensate for insufficient soil mineral N availability, while maize is fertilized in summer either at seeding or at the 4-6 leaves stage.

We compared four fertilization systems at the same target N rate (316 and 130 kg ha^{-1} for maize and ryegrass respectively), set on the basis of the N fertilization prescriptions for NVZs, and of the business as usual local fertilization practices, which should correspond to the expected N uptakes of silage maize and Italian ryegrass. The experimental design was a randomized complete block design with four replicates and a plot size of 12 m × 60 m. The treatments were:

i) manure (MA): cattle farmyard manure applied before the sowing of each crop with a conventional spreader and followed by rotary tillage. About 70 % of the total amount was spread to maize at the end of May and 30 % to ryegrass in October;

ii) slurry (SL): cattle slurry applied before sowing with a conventional spreader and immediately incorporated into the soil through rotary tillage using the same proportions as the MA treatment for maize and ryegrass;

iii) slurry+mineral (SM): following the NVZs prescriptions, slurry was applied at a corresponding target rate of 100 and 70 kg ha^{-1} of N for maize and ryegrass respectively and mineral fertilizer (ENTEC 26®) at a rate of 216 and 60 kg ha^{-1} of N applied before sowing for maize and at the end of ryegrass tillering respectively;

iv) mineral (MI): mineral fertilizer (ENTEC 26®) applied before sowing for maize and at the end of ryegrass tillering (mid February - beginning of March).

The amount of total N rate actually supplied with organic fertilizers (Table 2) was calculated *ex post* on the basis of the volume of fertilizer distributed and its actual nutrient concentration. The fertilizer was sampled from the field spreader at each distribution event, for a total of six sampling dates. Four and eight samples per sampling date were collected respectively for manure and slurry and stored frozen until the determination of total N content. The cattle slurry was stored in concrete storage pits at the farm and was homogenized prior to surface application using a vacuum-tank spreader. The cattle manure was stored for five months before spreading and it was sampled just before application.

A mixture of four varieties and hybrids of Italian ryegrass (cultivars Meritra, Ivan, Littorio and Mowester) was sown around mid-October each year. Seedbed was prepared by harrowing and milling. Auxiliary sprinkler irrigation was provided to ryegrass when necessary to minimize crop water stress (a total of about 80 mm per cycle). Ryegrass hay was harvested in mid-May at early earing stage. The Calcio hybrid (FAO 700) of maize was sown during the first ten days of June and it was harvested between the 15th and the 20th of September at the dough stage (target of 33 % DM for the whole plant). The maize seedbed was prepared using a rotavator, ripper and harrow. The sprinkler irrigation for maize started at seeding in June until one week before harvest. The total water volumes were on average 4600 m^3 ha^{-1}. Weeds were controlled with the pre-emergence herbicide Lumax®.

1.2. Soil solution sampling and analysis

Two tension disc lysimeters (10 cm diameter, PRENART®) were installed in each plot below the Ap soil horizons, at soil depths between 50 and 90 cm (average depth 68 cm). A total of 32 disc lysimeters were installed. Special care was taken in repacking the soil from different layers in the original position. The disc lysimeters were connected to aboveground with plastic pipes at the border of each plot. Near the soil surface a 20 cm rubber collar was put around the plastic pipe to prevent water from seeping from the surface down through the pipe. The soil solution was sampled through the disc lysimeters at monthly intervals by applying a suction of −70 kPa for about 45 minutes using an electric pump. Before collecting the sample to be analyzed, pipes were cleaned out of the water left from the previous sampling in the connecting pipe and disc lysimeter. Collected samples were stored under cooled conditions (4 °C) and filtered in the lab through a 0.2 μm membrane filter. The NO_3^- concentration was determined by ion chromatography (anion column Alltech model allsep anion 7 μm, 100 mm).

1.3. Water balance

The water balance of the maize-Italian ryegrass cropping system was estimated using the EPIC model (Williams, 1995). The model was set using local soil and weather data, information about the actual management, including irrigation volumes and amount of fertilizers distributed, and crop related data such as plants density and crop growing period. EPIC simulated actual evapotranspiration from the Penman Monteith equation considering the actual crop management. Daily weather data were collected from a weather station located about 5 km away from the experimental field (39°45’ N; 8°34’ E. 13 m asl, OR, Italy). Soil characteristics were obtained analyzing soil samples collected in the experimental field and water holding capacity was measured in the field through systematic gravimetric and tensiometric measurements between saturation and field capacity. The actual physical and chemical soil characteristic (including the hydraulic properties) were used as inputs in the EPIC model. Because the groundwater table depth is controlled by the local Water Use Association (WUA), part of the subroutine that simulates the groundwater table dynamics in EPIC was modified considering a deeper groundwater table in spring and summer and a shallower groundwater table in autumn and winter. The modification in EPIC allowed to overwrite the initial maximum and minimum depth for the groundwater table fluctuation and to use different maximum and minimum depths in different periods of the year. The model was calibrated for the crops yield and ground water table dynamics. For each crop a total of 12 yield observations (3 years × 4 replicates) were available. Six observations were used for the calibration and the remaining six observations were used for the validation. For the groundwater table depth, a total of 24 observations were available from November 2009 to May 2012. The first 12 observations were used for the calibration and the last 12 observations were used for the validation. The calibration and validation were evaluated using relative root mean square error (RRMSE; Bellocchi et al., 2002), modeling efficiency (EF; Loague and Green, 1991), slope and intercept of the regression line and coefficient of determination (R^2). After the calibration and validation, the EPIC model was used to estimate the percolation below the average lysimeters depth. The calculation of the total percolation, including groundwater table fluctuations, was performed for those days in which a water surplus (Precipitation + Irrigation > ET) occurred.

1.4. Nitrate leaching and N balance

Assuming that the soil water percolation between two soil water sampling dates had the average NO_3^- concentration of the sampled soil water, the amount of NO_3^- leached (kg N ha^{-1}) was calculated using the average NO_3^- concentration between two subsequent sampling dates times and the volume of percolation between the two dates as estimated with EPIC.

The cumulative N leaching was estimated on the basis of average NO_3^- concentration and the soil water percolation (as simulated by the EPIC model) for each sampling date.

Crop yield, aboveground biomass at harvest and N removal were measured every year but in this paper we report only the data on crop N removal. The entire plots were harvested using farm machineries and the removed products (fresh aboveground maize or ryegrass hay) were weighed immediately using electronic weighing cells positioned in a flat place under the tractor cart. The biomass dry matter content at harvest was assessed by sampling 1 kg of ryegrass hay or fresh chopped maize that was immediately cooled in plastic bags and hence dried in a forced-air oven at 65 °C for 72 h. The crop N removal was estimated by multiplying the crop yield and N concentration determined on harvested biomass samples by the Kjeldahl method (Mipaaf, 2006). N surplus was defined as the difference between N fertilizer input at plot scale and crop N removal (Grignani and Zavattaro, 2000). While, combining the data on crop N removal and leached N we also estimated by difference the residual soil N pools available for N immobilization, volatilization or denitrification.

1.5. Statistical analysis

The NO_3^- concentration and yearly cumulative N (removal, leaching and residual) were analyzed with the PROC MIXED procedure in SAS (SAS institute, 1999), suitable for analyzing mixed effects and repeated measures with non-constant variance and any covariance structure models. The independence assumption on the error terms required for the ANOVA of a factorial model (Montgomery, 1997) was likely not met. Therefore, the appropriate assumption on the error terms for this experiment was the non normal distribution with heterogeneous (non-constant) variance by sampling date and a given covariance structure. The appropriate covariance structure for this particular experiment was determined using −2 Log Likelihood (−2RLL), Akaike's Information Criterion (AIC), Corrected Akaike's Information Criterion (AICC) and Schwarz's Bayesian Criterion (BIC), which are essentially log likelihood values penalized for the number of parameters estimated (Littell et al., 1996). Also, according to the fit statistic −2RLL, AIC AICC and BIC, the best covariance structure was determined to be the Compound Symmetry covariance type. The statistical test results given in the following section are based on the transformation of original NO_3^- concentration data as reported Shen et al. (2006).

A one-tailed t test was performed on data from each sampling date to determine whether treatments significantly exceed the EU threshold of 50 mg L^{-1} of NO_3^- concentration using the pooled error variances when appropriate.

All data analyses were performed using Microsoft Excel® and SAS Statistical Package (SAS institute, 1999).

2. Results

2.1. Nitrate concentration in the soil solution

The average concentration of NO_3^- in the investigated soil depths showed a high variability and it fluctuated from 0.8 ± 0.3 (mean ± SE, June 2010) to 586 ± 122 (November 2011) mg L^{-1} in MA, from 6 ± 3 (May 2010) to 593± 104 (January 2012) mg L^{-1} in SL, from 13 ± 3 (June 2009) to 460 ± 54 (December 2011) mg L^{-1} in SM and from 2.6 ± 0.4 (June 2009) to 390 ± 25 (December 2010) mg L^{-1} in MI (Figs. 2-4).

The dynamics of NO_3^- concentration (mg L^{-1}) in the soil solution showed a strong seasonal pattern for all treatments, characterized by two maximum values, one in the winter, during the ryegrass crop phase, and one in the summer, during the maize crop phase (Figs. 2-4). Minimum values were typically observed at ryegrass and maize harvest, in late spring and September. In all treatments, the NO_3^- concentrations decreased to reach a minimum in April and May, with the exception of spring 2012 (Fig. 4), when the observed NO_3^- concentrations remained high until the end of April in all treatments. Plots receiving the MI treatment showed high NO_3^- concentration in all autumns, even though N fertilizer was not applied until February.

In the three years, the mean NO_3^- concentration significantly exceeded the 50 mg L^{-1} on 5, 14, 15 and 8 dates out of the total 33 sampling dates in MA, SL, SM and MI respectively (Figs. 2-4). Of these dates, 5/5, 8/14, 7/15 and 7/8 respectively in MA, SL, SM and MI occurred in the November-February period and the remaining occurred in the spring 2012.

Of the 33 sampling dates, only 6 showed a significant difference between treatments. In particular, 4 dates in the third year (Jan-Mar-Apr-May) had higher NO_3^- concentration in SL with respect to MI and MA, while SM was not significantly different from all the other treatments. In December 2010 the NO_3^- concentration was lower in MA treatment than in SL and MI treatments, despite the mineral fertilizer was not applied yet.

The lowest average NO_3^- concentration was observed in MA. In 2009 and 2010 MA showed an average annual NO_3^- concentration of about 46 ± 16 mg L^{-1}, but in 2012 the NO_3^- dynamics of MA was similar to that observed in the other treatments (Fig. 4).

2.2. EPIC model calibration and validation

Model performance for crop yields and groundwater table dynamics were satisfactory for all the data considered and for both the calibration and validation phases (Table 3). For silage maize the RRMSE values indicate small deviations of the simulated values from the observed ones and the EF > 0 indicates that the model is a good predictor of the observed values. For Italian ryegrass the deviations of the model results from the observed values were acceptable in terms of RRMSE and good for EF values. The model was also able to reasonably simulate the variation during time of the groundwater table depth. The deviation of the simulated data from the observed data was about 26 % and 20 % during the calibration and validation process respectively and the EF value was of 0.37 for the calibration and 0.54 for the validation. Moreover, the slope and intercept of the regression line were close to the optimal values.

2.3. Soil water percolation

The estimated average annual percolation simulated by EPIC was 252 mm, 292 mm and 268 mm during June-May in 2009-2010, 2010-2011 and 2011-2012, respectively. In all years, percolation events occurred almost exclusively from October to February with an influence of cumulative monthly precipitation (y) on estimated cumulative monthly percolation (x), as evidenced by the significant linear regression between these two variables ($y = 0{,}327x + 4{,}891$; R^2=0.66**). The average soil water percolation in October-January was about 130 mm and it represented 1/2 of the total annual percolation (60 % between Oct-Feb). The rainfall in autumn 2010 (392 mm in Nov-Dec) was considerably higher than the long term average recorded for the study area (158 mm) and this was mirrored by the calculated drainage volumes (Fig. 3). From April to September no relevant drainage was estimated, the percolation was on average about 60 mm as the total water supply (730 mm = 194 mm rain and 536 mm irrigation) rarely exceeded crop transpiration demands (670 mm). The groundwater table depth ranged between 0.25m (in January-February) and 1.80 m in July-August. Groundwater table depth reached the highest values from June to September, while the water table was the shallowest during the autumn from November to February in coincidence with rainfall events.

2.4. Nitrate leaching and N balance

The average N concentration of slurry was 0.26 % but ranged between 0.09 and 0.47, while that of manure was 0.71 % (0.45 – 0.83). The average ammonia N concentration was 0.12 % in slurry and 0.17 % in farmyard manure. The nitric nitrogen was 0.002 % in slurry and 0.01 % in manure.

The N input of organic fertilizers varied widely (Tab. 2) according to the variable N concentration of the animal effluent.

The C:N ratio and the organic N concentration in the animal effluents were respectively 8.01 ± 0.85 (mean ± SE) - 0.14 ± 0.01 % for slurry and 13.02 ± 1.17 - 0.51 ± 0.04 % for manure.

The estimated N leaching and residual N were significantly influenced by the fertilization treatment ($P < 0.05$) and no significant year × treatment interaction was observed (data not shown). The estimated residual N was variable among years, particularly for SL. The exception was the MI treatment, in which residual N variability was much lower than all other treatments, likely due to a lower and more constant rate of N inputs relative to that observed for organic fertilizers ($r = 0.47$, ns). For this reason, N inputs on SL and SM explained as much as 97 % of the variability of the residual N ($P < 0.01$), while there was no linear correlation between N input and N leaching considering all treatments ($r = 0.42$) or between N surplus and N leaching ($r = 0.30$, ns). The estimated annual N leaching losses below 90 cm soil depth were reported in Table 4. The relative proportion of the N surplus lost with leaching was high (62 %) just for MI while it represented less than about 17 % of the surplus when organic fertilizers were used.

On average, N removal roughly represented between 1/3 (SL) and 1/2 (SM) of the N input in all treatments with organic fertilizers, while it reached 2/3 of the total N input in MI (Tab. 4). N leaching in MA was 32 % lower than the average of the other fertilization systems.

The dynamics of the cumulated N leaching showed the same pattern in the three years of experiment (Fig.5). On average, 78 % of the total N leaching was in autumn (44 %) and winter (34 %). Almost no soil water percolation and hence no leaching was recorded during the maize crop phase, despite the relatively high NO_3^- concentration in soil solution, but we estimated a high percolation in April.

The total cumulated annual water drainage simulated by EPIC was reported in previous paragraph. If the NO_3^- losses were expressed as a function of the cumulative drainage (data not shown), the loss of NO_3^- corresponding to a drainage concentration of 50 mg L^{-1} of NO_3^- was 28.4, 33.1 and 25.9 kg ha^{-1} in year 1, 2 and 3 respectively. The estimated NO_3^- losses reached these thresholds between 125 mm and 170 mm of drainage in MI and MA respectively in the first year; between 60 mm and 125 mm in SL and MA in the second year and about 35 mm for all treatments in the third year.

3. Discussion

The NO_3^- concentration dynamics in the soil solution was very variable during the year and was influenced by weather and crop N uptake. This was consistent with our first hypothesis. About 68 % of the average total annual NO_3^- leaching occurred between October and February, which corresponds to the period in which 57 % of the annual percolation occurred, as a consequence of the unbalance between rainfall and evapotranspiration, as usual under Mediterranean conditions (Carneiro et al., 2012; Arregui and Quemada, 2006). In this period, N uptake of Italian ryegrass is very low as the crop is in the establishment-tillering phase (Carneiro et al., 2012; De Paz et al., 2009).

A wide variation in N concentrations in soil water collected using the same methodology under similar agro-environmental conditions of this study was also observed by Carneiro et al.(2012)

and Trindade et al. (1997). The wide variation in the soil water NO_3^- concentration at a given sampling time was attributed to the heterogeneous distribution of fertilizers into the soil, to the soil composition variability and the corresponding expected uneven infiltration pattern (Cuttle et al., 1992). However, the wide variability of soil water NO_3^- concentration may also be related to microbiological processes (Liang et al., 2010). Moreover, the high N content variability of manure and slurry determined *a posteriori* in our study, led to application of a higher N supply than the amount planned, and, hence, higher than crop requirements. This unintentional over-application led to a high N surplus, as similarly reported also by Trindade et al. (2009), generating a source of difficulty for the accurate comparison of NO_3^- concentration data in the soil solution among the four N fertilization systems. The N input from SL and SM treatments was significantly higher than that from MI treatment, while the nitrate leaching rates for SL, SM and MI were similar. This was interpreted as possibly due to the ammonium Nimmobilization through microbial decomposition of organic matter in the slurry after application, that plays a significant role in the organic N retention in soil (Sørensen, 2004). This immobilised N is stabilised and slowly released a few months after application (Sørensen, 2004). We can then assume that much more N was immobilized after slurry or manure incorporation than after mineral fertilizer application. Moreover, the significantly lower N leaching achieved from MA treatment could be associated to the higher C:N ration of farmyard manure than slurry. However, neither the N input nor the N surplus showed a significant linear correlation with N leaching considering all treatments, similarly to what reported by Morari et al. (2012) and Zavattaro et al. (2012). In contrast to our results, Silgram et al. (2001) reported that the leaching losses are linearly related to N inputs, over-simplifying a complex N loss function which depends on the interactions between over-winter rainfall, soil type, cropping, and the rate/timing of fertilizer/manure applications. Since in our study the NO_3^- leaching was estimated considering only losses associated to percolation in the days when water surplus occurred (i.e. Rain+Irrigation-ET), it is likely that the total N losses were underestimated. However, the rate of estimated N leaching was not affected neither by the N input or N surplus and the percolation was not very high, on average 271 mm per year. The shallow groundwater in autumn-winter could have contributed with washing away to the N leaching rate, in particular under the winter crop as shown by the drop of NO_3^- concentration at the end of the winter, while the contribution of the deep groundwater table to NO_3^- leaching and maize water requirements was assumed to be negligible.

The average monthly NO_3^- concentration was lower in April and May, except for the third year, when we observed low winter rainfall (and percolation) and higher NO_3^- concentrations from December to February and in July, as found for other irrigated Mediterranean cropping systems (Ibrikci et al., 2015). In particular, the high NO_3^- concentrations were recorded after fertilization and precipitation/irrigation events, in agreement with what found by Perego et al. (2012) in summer on maize.

In the present study, the observed high soil water NO_3^- concentration in the autumn was independent of the fertilization system, hence the NO_3^- concentrations in the soil solution were not effectively controlled by the fertilization management. The potential impact of the presence of the nitrification inhibitor under MI was assumed to be negligible below a soil depth of 40 cm as reported Yu et al. (2007). In this period, the MI treatment had not been fertilized yet, but showed high NO_3^- concentration. This could be interpreted hypothesizing that the maximum NO_3^- concentrations observed in autumn were the outcome of the accumulation of NO_3^- in the soil after the maize harvest, in a period in which soil temperature and water content were not limiting for microbial activity (Liang et al., 2010), crop uptake was zero and the maize crop residues were incorporated into the soil before ryegrass seeding. Although the residual amount of soil NO_3^- after maize harvest was not measured in this experiment, we estimated it from the NO_3^- concentration between two subsequent sampling dates (September and November) across maize harvest dates and the soil water percolation volume estimated by EPIC. The outcomes of this estimate showed that on average the estimated NO_3^- at maize harvest ranged from 10 kg N

ha^{-1} to 30 kg N ha^{-1} and this is in accordance to the results obtained from the application of the linear relationship proposed by Andrasky et al. (2000) for 1.3-1.5 m soil depth. Several studies reported that silage maize often shows high residual mineral soil N amounts ranging from 48 kg N ha^{-1} under low N input up to 278 kg N ha^{-1} under high fertilized treatments (Morari et al., 2012; Kayser et al., 2011) leading to high over-winter NO_3^- leaching (Trindade et al., 2009; Le Gall et al., 1997; Simon and Le Corre, 1988).

The estimated N leaching loss is within the range reported by Carneiro et al. (2012), while sometimes we found that the mean annual leaching was lower than that reported by Perego et al. (2012) in Northern Italy, where the annual drainage (about 350 mm $year^{-1}$) was higher than that observed in our experiment (about 271 mm $year^{-1}$). The magnitude of the losses was mainly determined by the NO_3^- concentration in the soil solution in November and December.

The N mineralized between October and March may also have represented an important NO_3^- source. Vertes and Decau (1992) estimated that 90 % of N leaching losses were originated from N mineralization. Therefore, these authors recommended for preventing high soil NO_3^- concentration in the autumn to apply conservative fertilization and cropping practices for the summer crop to avoid high residual-NO_3^- values, in order to favour the early establishment of the autumn–winter crops or to minimize the amount of N supplied at the winter crop, particularly when sown late (Carneiro et al., 2012). The same authors suggested that the mineral N should be applied only through top-dressing applications. This may explain why in similar agro-environmental conditions, it was observed that N applied at tillering was recovered more efficiently than that applied at emergence (López-Bellido et al., 2005; Kirda et al., 2001). In agreement with this study, Trindade et al. (2009) reported that the treatments where mineral-N fertilizer was applied had higher soil NO_3^--leaching potential after the maize crop. Moreover, Smith and Chambers (1993) suggested that wherever cool and wet winters prevail, N leaching can be reduced using organic fertilizers with a low mineral to organic N ratio, as farmyard manure. On the contrary, Shepherd and Newell-Price (2013) reported that annual applications of farmyard manure increased NO_3^- leaching by 39 % more than the inorganic fertilizer, under a 7-yr rotation (wheat-potatoes, wheat-winter barley, sugar beet- wheat). This could be related to the site-specific dynamics of the soil organic matter: in this study, the soil organic matter accumulated over the years from long-term organic fertilization may have acted as a buffer of organic N available for mineralization (Indraratne et al., 2009; Kaur et al., 2008; Gutser et al., 2005; Schröder et al., 2005; Hao et al., 2003).

The findings of this study suggest that under Mediterranean conditions N fertilization in autumn could be omitted to mitigate the leaching of NO_3^- in the autumn-winter period without affecting crop yields. López-Bellido et al. (2012) showed that the postponing of the N fertilizer application to tillering-stem elongation phases for winter crops is usually more efficient in terms of plant N uptake. Besides, this is confirmed by the findings of Trindade et al. (2009) who reported no significant effects on Italian ryegrass annual dry matter yields of the N application in October compared to no N fertilization using similar total N inputs to our study. Moreover, despite the ND prescriptions are forbidding the supply of organic or mineral fertilization from November to February , this practice did not mitigate the NO_3^- leaching.

Studies conducted in the Netherlands under maize and grassland crops reported that about 25 % of the total N input applied as cattle slurry was lost by leaching and it was independent of its rate application (Schröder and Dilz, 1987). So that the N losses depends on the source as well. An investigation by Worrall et al. (2009) showed the lack of objective success in the majority of the 32 NVZs studied in the United Kingdom. This has called into doubt the use of input management as a means of limiting NO_3^- pollution, especially when the areas designated are small. The lack of objective success for NVZ designation suggests that NO_3^- pollution control strategies based only on input management need to be rethought.

The residual N input that is not uptaken by the crop or leached, can be subjected to various processes such as volatilization (Atzori et al, 2009), immobilization (Divito et al., 2011; Kaur et al., 2008) or denitrification (Morari et al., 2012). However the assessment of the relative contribution of these processes to the fate of the residual N was not the object of this study and is worthy of further studies.

The lowest average NO_3^- concentration was observed in MA and this was associated to the higher C:N ratio and proportion of organic N in farmyard manure than in slurry. Similar findings were reported by several scholars under a range of agro-environmental conditions (Sänger et al., 2010; Bertora et al., 2008; Moral et al., 2005). Ever more frequently the amount of manure produced in this farming livestock system decreases when cattle management shifts from a bed-pack system to cubicle housing as occurred in this study area. In fact the production of manure instead of slurry is related to structural changes of the livestock housing system, which in turn is indirectly related to farming targets of milk quality and animal welfare.

However, the bed-pack management and particularly the straw availability are key components for achieving good milk quality (Wenz et al., 2007) and animal welfare standards (ADAS, 1994; Singh et al., 1994) that can be compatible with the production of manure, which proved to be much more sustainable in terms of environmental impacts of intensive dairy farming under Mediterranean conditions.

4. Conclusions

The study supported the hypothesis that the NO_3^- dynamics in the soil water in a maize-ryegrass double cropping forage system under Mediterranean conditions are variable, independently of the fertilization system. This implies that the NO_3^- losses can be only partially controlled by the fertilization system, while the complex interactions between the winter rainfall, the crop sequence and the soil organic N buffer are far more important.

Among the fertilization systems under comparison, the cattle manure proved to be the most conservative, while the replacement of organic with mineral N fertilization systems was not effective in mitigating NO_3^- leaching, despite the lower yearly residual N estimated.

The maximum soil water NO_3^- concentrations observed in the autumn-winter were almost independent from the type of fertilizer and actual N input rate. This was explained by the impossibility of controlling effectively the leaching associated to the natural water surplus in winter and the observed soil water NO_3^- concentration dynamics in autumn-winter. It seems that the autumn-winter NO_3^- leaching in the maize-ryegrass double cropping is unavoidable in highly fertilized systems. The fertilization with mineral N instead of organic N does not reduce N leaching in winter. The average annual NO_3^- losses and soil water NO_3^- concentrations were significantly lower using 100% farmyard manure as N fertilizer. This may have relevant implications on the livestock effluent management system at the farm scale (e.g. from cubicle housing to straw bedded-pack), that could be addressed to obtain fertilizers with higher C:N ratio in order to minimize the release of NO_3^- during the leaching period. However the organic fertilizers must be carefully managed to prevent over- or under-application and to account for the cumulative environmental effects of application as well as storage.

Acknowledgements

This study was carried out within the Agroscenari project (2008–2013) funded by the Italian Ministry of Agricultural, Food and Forestry Policies and the PRIN-ZVN project (2008–10). We are grateful to Azienda Sardo farm for hosting our experimental activities and the Arborea Farmers' Cooperative for their fruitful collaboration during this study. A special thanks is provided to Dr. Armen Kemanian, Penn State University for his valuable comments on the early stage of the manuscript. This research formed a part of a PhD program on "Crop productivity " carried out at the Dipartimento di Agraria of the, University of Sassari, Italy. Furthermore, we thank Dr. Giulia Urracci and Dr. Laura Mula for their collaboration in the design of the experiment and for the support in the field activities. Authors are also grateful to Alberto Stanislao Atzori for his support on the calculations of the N loads from livestock effluents at case study scale.

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Figure 1. Water balance dynamic from May 2009 to June 2012 under Maize-Italian Ryegrass system.

Figure 2. Dynamics of the NO_3^- concentration (mg L^{-1}, transformed by Shen et al., 2006) in the soil solution and soil water percolation as simulated by EPIC model during the silage maize – Italian ryegrass rotation (2009–2010) for the different treatments (MA = Cattle Manure; SL = Cattle Slurry; SM = Cattle Slurry+ Mineral; MI = Mineral). Vertical black arrows indicate the dates of fertilizers distribution. The horizontal black line indicates the legal threshold of 50 mg L^{-1} for drinkable water and the rectangles indicate the duration of cropping cycle. The asterisks indicate the sampling dates when the NO_3^- concentration significantly exceeded 50 mg L^{-1}.

Figure 3. Dynamics of the NO_3^- concentration (mg L^{-1}, transformed by Shen et al., 2006) in the soil solution and soil water percolation as simulated by EPIC model during the silage maize – Italian ryegrass rotation (2010–2011) for the different treatments (MA = Cattle Manure; SL = Cattle Slurry; SM = Cattle Slurry+ Mineral; MI = Mineral). Vertical black arrows indicate the dates of fertilizers distribution. The horizontal black line indicates the legal threshold of 50 mg L^{-1} for drinkable water and the rectangles indicate the duration of cropping cycle. The asterisks indicate the sampling dates when the NO_3^-concentration significantly exceeded 50 mg L^{-1}.

Figure 4. Dynamics of the NO_3^- concentration (mg L^{-1}, transformed by Shen et al., 2006) in the soil solution and soil water percolation as simulated by EPIC model during the silage maize – Italian ryegrass rotation (2011–2012) for the different treatments (MA = Cattle Manure; SL = Cattle Slurry; SM = Cattle Slurry+ Mineral; MI = Mineral). Vertical black arrows indicate the dates of fertilizers distribution. The horizontal black dotted line indicates the legal threshold of 50 mg L^{-1} for drinkable water and the rectangles indicate the duration of cropping cycle. The

asterisks indicate the sampling dates when the NO_3^- concentration significantly exceeded 50 mg L^{-1}.

Figure 5. Distribution of cumulated N leaching (kg N ha^{-1}) from June 2009 to May 2012 for the different treatments.

Table 1. Physical and chemical characteristics of the soil at the beginning of the experiment (2009).

	Soil depth (cm)			
Trait	**0-45**	**46-70**	**71-100**	**>100**
Clay, g kg^{-1}	25 ±0.16	20 ±0.15	28 ±0.48	66 ±1.04
Sand, g kg^{-1}	953 ±0.20	940 ±1.44	954 ±0.47	912 ±1.01
Silt, g kg^{-1}	21 ±0.14	19 ±0.13	22 ±0.22	22 ±0.31
Bulk density, g cm^{-3}	1.55 ±0.02	1.35 ±0.11	1.22 ±0.17	1.25 ±0.18
Water holding capacity, %Vol 0 kPa	41.6	49.2	52.5	52.3
Field capacity, %Vol 33kPa	6.6	7.8	8.8	9.7
Field capacity, %Vol 23kPa	17.7	20.5	22.3	23.2
Wilting point, %Vol 1500 kPa	3.8	3.2	3.8	3.8
Soil Organic Matter, g kg^{-1}	23.4 ±0.10	8.0 ±0.19	4.7 ±0.14	4.1 ±0.10
Tot N, g kg^{-1}	1.3 ±0.04	0.4 ±0.08	0.3 ±0.05	0.4 ±0.07

Table 2. N inputs (kg N ha^{-1}) from organic and mineral fertilizers (three-years average ± std error) for Italian ryegrass and maize (MA = Cattle Manure; SL = Cattle Slurry; SM = Cattle Slurry + Mineral; MI = Mineral).

	Italian ryegrass	**Maize**
Treatments	**2009-12**	**2009-2011**
MA	151 ±24	379 ±38
SL	317 ±115	469 ±213
SM	231 ±53	374 ±60
MI	130 ±0	316 ±0

Table 3. Indices used for the evaluation of the model performances (RRMSE= relative root mean square error; EF=modeling efficiency) for calibration and validation in Italian ryegrass, maize and ground water table depth.

		RRMSE	**EF**	**Slope**	**Intercept**	**R^2**
	Best	0.0	1.0	1.0	0.0	1.0
	Min	0.0	$-\infty$	$-\infty$	$-\infty$	$-\infty$
	Max	$+\infty$	1.0	$+\infty$	$+\infty$	$+\infty$
Silage maize yield	Calibration	5.90	0.50	0.70	6.95	0.57
	Validation	8.02	0.24	0.46	12.00	0.31
It. ryegrass yield	Calibration	17.55	0.55	0.65	2.68	0.64
	Validation	19.40	0.25	0.75	2.21	0.57
Groundwater table depth	Calibration	25.75	0.37	1.13	-0.01	0.72
	Validation	19.50	0.54	0.89	0.17	0.67

Table 4. Average three years N balance estimated from N input, removal and leaching as influenced by the treatments (MA = Cattle Manure; SL = Cattle Slurry; SM = Cattle Slurry+ Mineral; MI = Mineral). The residual N is calculated by difference. Means followed by the same letter were not significantly different (P<0.05). Means followed by standard errors refer to variables with heteroschedastic error variances.

Treatments	**N input**		**N removal**		**N leaching**		**Residual N**	
	(kg N ha^{-1}± err std)	**(%)**	**(kg N ha^{-1})**	**(%)**	**(kg N ha^{-1})**	**(%)**	**(kg N ha^{-1}± err std)**	**(%)**
MA	530 ± 64	100	216 b	41	42 b	8	272 ± 41 c	51
SL	813 ± 249	100	255 ab	31	110 a	14	447 ± 246 a	55
SM	602 ± 88	100	281 a	47	94 a	16	226 ± 95 b	38
MI	446 ± 0	100	301 a	68	89 a	20	56 ± 44 c	12
Mean	599	100	264	47	84	15	250	39
CV (%)	20	-	14	-	29	-	83	-

Figure 1
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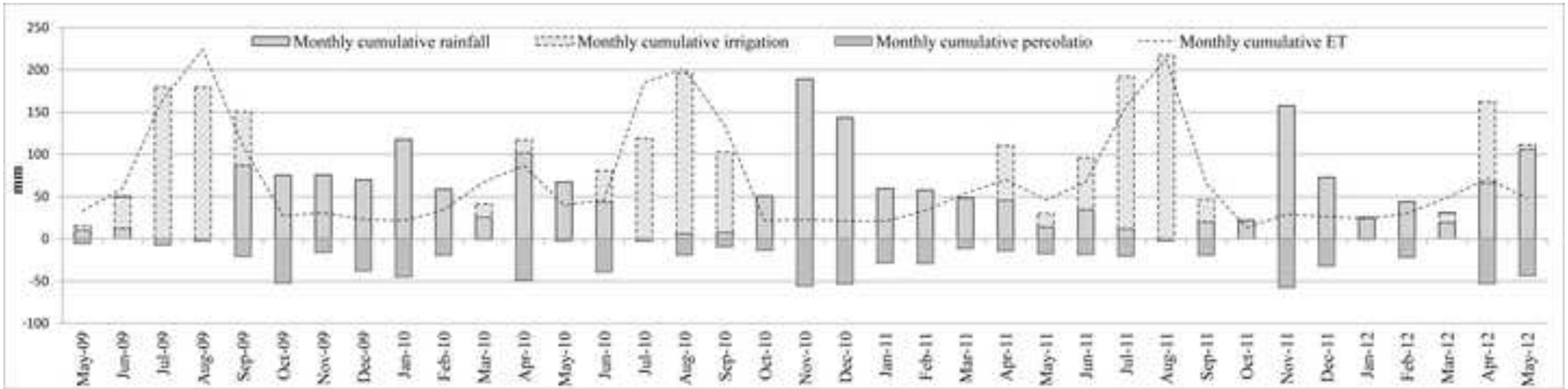

Figure 2

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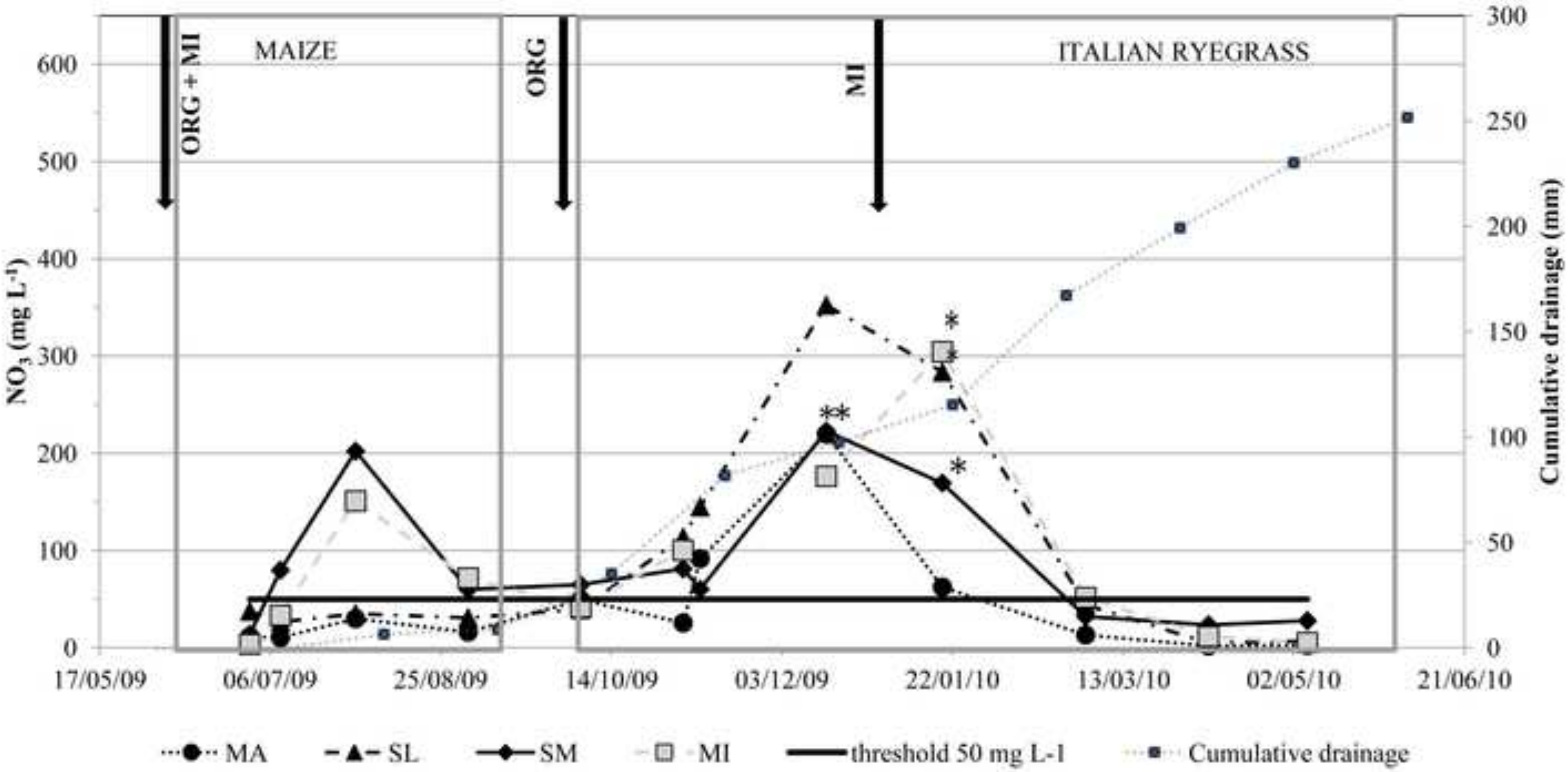

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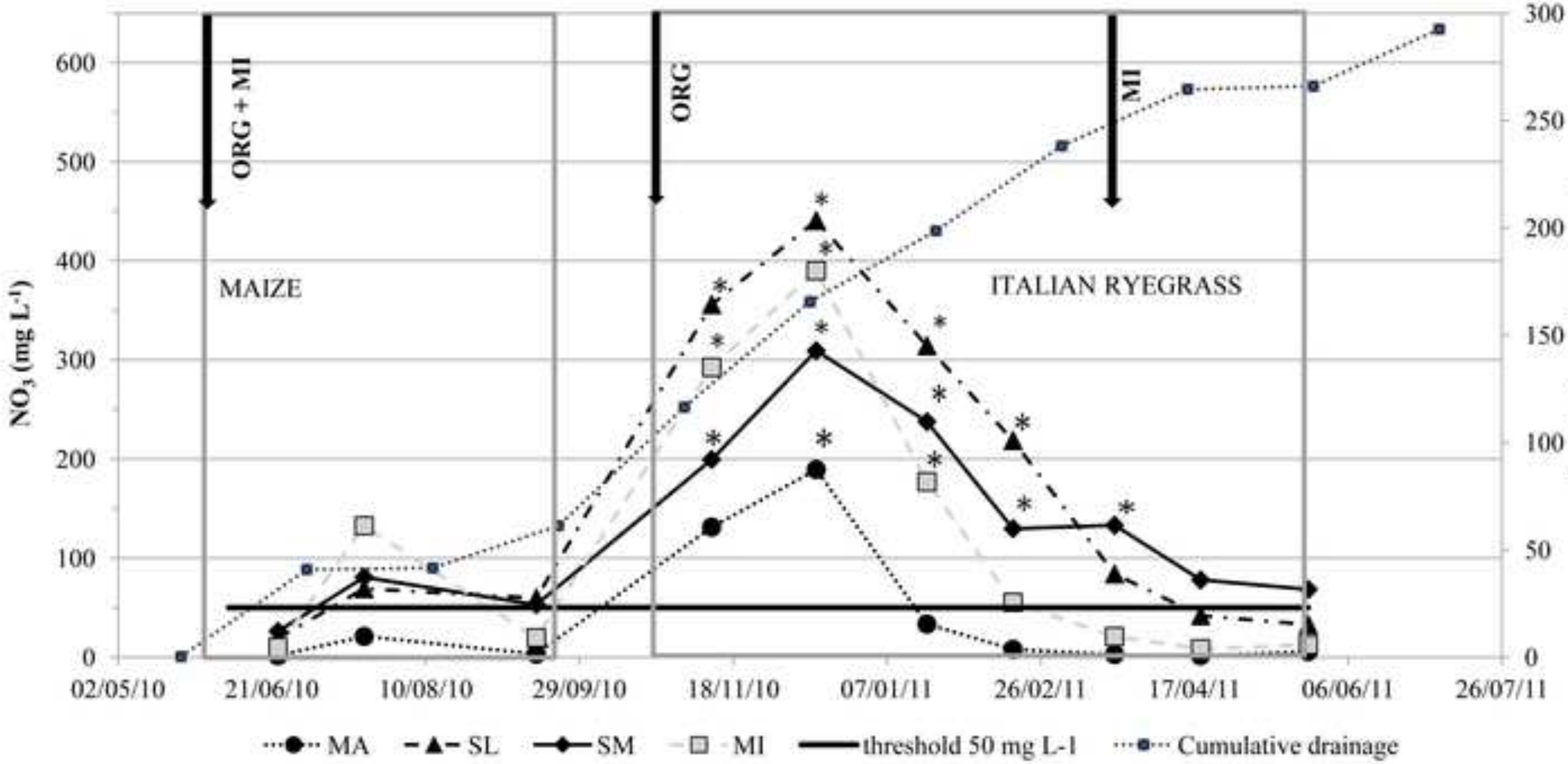

Figure 4

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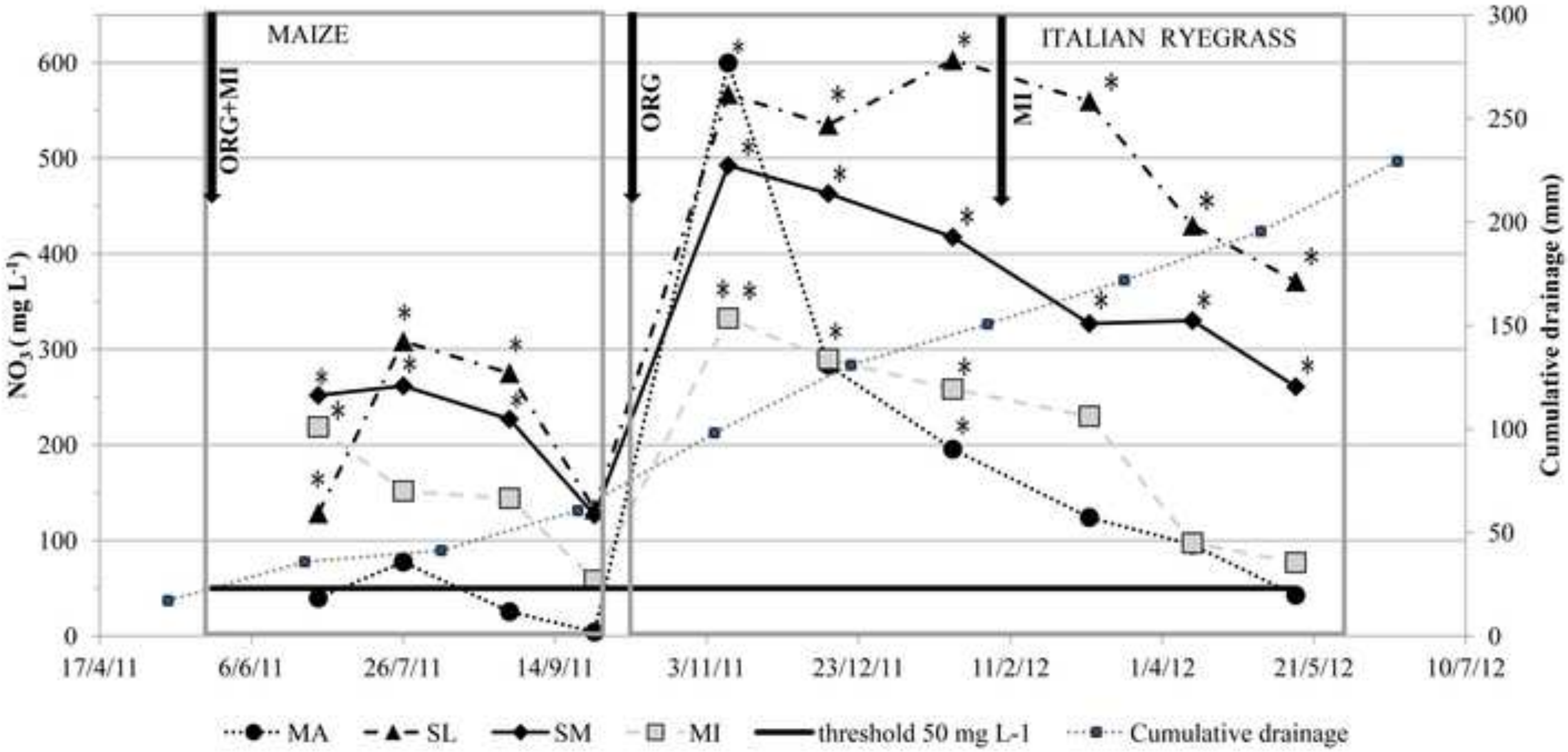

Figure 5
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