Natural and NH_4^+-enriched zeolitite amendment effects on nitrate leaching from a reclaimed agricultural soil (Ferrara Province, Italy)

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Abstract

In this paper we report an overview of the main outcomes of a three-years experimental cultivation carried out in an Italian reclaimed agricultural field amended with different types of zeolitites (rock containing > 50% of zeolites), under cereals cultivation (*Sorghum vulgare Pers*, *Zea mais* and *Triticum durum*). The aim of the experiment was to exploit the properties of zeolite-rich volcanic rocks (zeolitites) for reducing the excessively high NO_3^- content in the soil and in waters flowing out the sub-surface drainage system (SSDS) of the field and flushing into the surface water system, reducing concomitantly also chemical fertilization application rates (up to 50 %). Zeolitites were tested both in their natural state and in a NH_4^+-enriched form, obtained through an enrichment process with NH_4^+-rich zoo-technical effluents (pig slurry).

NO_3^- content in soils and in waters discharged through SSDS were periodically monitored during the experimentation and crop yield quantified. Results showed that, for three consecutive cultivation cycles, the overall NO_3^- concentrations in water extracts was reduced by 45 % in the zeolitite treated soils, while in SSDS waters the reduction reached the 64 %. Notwithstanding the lower N input from chemical fertilizers, crop yield was not negatively affected in the zeolitite amended soils with respect to the control. Zeolitite addition increased thus soil NH_4^+ retention and probably influenced several pathways of N losses, allowing a better fertilizer use efficiency by plants and a reduction of the overall NO_3^- concentrations in the surface waters.

Keywords: nitrate, natural and NH_4^+-enriched zeolitite, sustainable agriculture, tile drains, water extractable NO_3^-

1.0 Introduction

The impact of agriculture on water quality is a worldwide recognized problem (Bouraoui and Grizzetti 2014; Smith and Siciliano 2015) and has become a matter of concern for the European Union (EU) since the early nineties. According to the Food and Agriculture Organization (FAO) of the United Nation, it is necessary to summarize and disseminate good water management practices in order to reduce agricultural runoff and chemical inputs and, at the same time, to strengthen the protection of the water resource (FAO 2013).

Fertilizer-N inputs are generally inefficiently exploited by crops, resulting in widespread nitrogen (N) losses in the environment (Peng et al. 2006; Dawson et al. 2008; Wu and Liu 2008). Agricultural systems characterized by low fertilizer use efficiency (FUE) are responsible for altering the equilibrium of natural ecosystems (Bijay-Singh et al. 1995) and to cause important economic losses to the farmers (Buczko and Kuchenbuch 2010). Despite NO_3^- being a fundamental nutrient for crops, it is well recognized that the excessive use of N-based fertilizers (organic or synthetic) increases the risk of NO_3^- leaching through the ground and superficial water bodies, reflecting in the deterioration of their quality. NO_3^- concentration in water systems is normally low (0 - 18 mg L^{-1}), but inadequate agricultural practices can easily increase it to several hundred mg L^{-1} (WHO 1985). Freshwater affected by NO_3^- pollution cannot be destined for human consumption because of severe toxic health effects, such as methemoglobinemia, stomach cancer, and non-Hodgkin Lymphoma (WHO 2011). Moreover, high NO_3^- and P levels lead to eutrophication phenomena due to the proliferation of Harmful and Nuisance Algal Blooms (HNABs) (Hudnell 2010). Recent studies showed that, in order to make modern agriculture a sustainable activity, fertilization reductions must be combined with FUE improvements (Van Groenigen et al. 2010). To this end, with the implementation of Nitrates Directive (91/676/EC) and the Water Framework Directive (2000/60/EC) the EU aimed at preventing the negative effects linked to the excess of NO_3^- in some areas (for e.g. the Ferrara Province in Italy, declared as Nitrate Vulnerable Zone “NVZ” in 2006) by promoting the use of good and innovative farming practices. It established protocols for water protection and management, reporting measures that must be taken by each Member State to reduce dumping and toxic substance emissions, favouring the restoration of the hydrologic resources and reaching a good chemical and ecological state of waters.

N species distribution in the pore-waters can be indicative of the potential leaching losses (Foster et al. 1982) and, in agricultural areas characterized by a poor-drainage, the presence of subsurface drainage systems (SSDS) may constitute a preferential way of pollution. The SSDS is a drainage technology that avoids waterlogged conditions by lowering the water table to a specific depth, employing a series of pipes buried below the root zone (Mastrocicco et al. 2013; Di Giuseppe et al. 2014). This system allows the direct discharge of water from the upper soil layer to superficial water bodies, increasing their vulnerability to contamination due to the compounds used in agriculture (e.g fertilizers, pesticides and organic contaminants) (Skaggs et al. 1994).

Several new environmental-friendly agricultural management practices, including the use of rocks and minerals as soil conditioners, have been recently proposed (Valente et al. 1982; Reháková et al. 2004; Galli and Passaglia 2011; Campisi et al. 2016). Zeolitites, i. e. rocks containing more than 50 % of minerals belonging to the zeolite group (Galli and Passaglia 2011) are geo-materials suitable for agronomic purposes and environmental protection, thanks to their peculiar physical-chemical properties (Reháková et al. 2004; Campisi et al. 2016). Zeolites are aluminosilicates with an open, three-dimensional and negatively charged framework characterized by the presence of channels and cages of nanometric dimensions where different kind of polar and non-polar molecules (including both inorganic and organic compounds) can be adsorbed and exchanged, with particular affinity to ammonium ions (NH_4^+) (Reháková et al. 2004; Leyva-Ramos et al. 2010). NH_4^+, the main product of synthetic urea fertilizer hydrolysis, is held by the negative sites of soil clay minerals and humus. It is generally retained in the top soil layer where oxic condition are usually present, thus quickly converted into NO_2^- and/or NO_3^- by nitrification processes (Ruiz et al. 2003). NH_4^+ is also the main mineral N form contained in livestock effluents commonly used as fertilizers (with concentrations often exceeding 1,000 mg L^{-1}; Faccini et al. 2015) and it is known that intensive livestock breeding is one of the major sources of N groundwater pollution (Widory et al. 2004). Zeolitites have a wide range of environmental applications (Misaelides et al. 2011), including the agricultural context where their very high NH_4^+ adsorption/desorption capacity proved to be extremely useful for reducing N leaching as well as increasing N use efficiency (NUE) and crop yield (Reháková et al. 2004; Passaglia 2008; Sepaskhah and Barzegar 2010**;** Gholamhoseini et al. 2013; De Campos Bernardi et al. 2013; Li et al. 2013; Colombani et al. 2015; Di Giuseppe et al. 2015; Ozbahce et al., 2015).

On the basis of previous studies, we hypothesized that the addition of both natural and NH_4^+-enriched zeolitite to the agricultural soil would have positively influenced NUE and decreased N losses, allowing significant reduction of N input from fertilizer and thus decreasing the amount of nitrate flushed into the surface water system. With this paper, we review the main outcomes of an experimental cultivation carried out in an Italian NVZ, where a reclaimed agricultural field was amended with different types of zeolitites as inorganic soil amendment, in order to evaluate the effects of this practice on the NO_3^- leaching and crop growth. The main objective of the experiment was the testing of an innovative "integrated" (at farm level) zeolitite cycle aimed at i) reducing N fertilization in agriculture while leaving unaltered or even increasing the yield; ii) reducing NO_3^- leaching from the agricultural soil. For three consecutive years of cereal cultivation (*Sorghum vulgare Pers*, *Zea mais* and *Triticum durum*) different zeolitite amendments in open-field conditions were tested, under high fertilizer-N input reductions. During the experimentation, NO_3^-concentration in the soil and in the water discharged through the SSDS system was periodically monitored, as well as crop yield quantified. The experimental cultivation was performed in a real agricultural context (managed by a private local farm) and the results have been compared with the company's agronomic programs, planned according to the regional Maximum Application Standard (MAS) of fertilizer-N input.

2 Material and methods

2.1 Description of the employed zeolitites

The zeolitite used in this study is a by-product of a quarry located near Sorano village (central Italy) that is mainly exploited to obtain blocks and bricks for construction and gardening. The quarried rock is a zeolitized pyroclastic deposit belonging to the Lithic Yellow Tuff body of the Sorano formation, Làtera Volcanic Complex (Vezzoli et al. 1987) ; according to Malferrari et al. (2013), the total cation exchange capacity (CEC) of the employed zeolitite was 217 cmol (+) kg^{-1} while the main zeolite species present in the rocks are K-rich, Na-poor chabazite (~ 68 %), phillipsite (~ 1.8 %) and analcime (~ 0.6 %).

In this experiment, the zeolitite was employed in its natural state (NZ), i.e. without any processing after the excavation, and enriched with NH_4^+ ions (CZ). The enrichment method, based on a static mixing procedure of pig slurry and natural zeolitite in a specifically conceived prototype, has been widely described by Faccini et al. (2015). It is in fact known that zeolites can be easily modified from their natural state by exchange processes based on the absorption of specific cations (i.e. NH_4^+) (Eberl et al. 1995; Dwairi et al. 1998; Leggo 2000; Passaglia 2008; Passaglia and Laurora 2013).

The production of CZ in the prototype plant occurred in two cycles: one before sorghum cultivation (April-October 2012) and one before maize cultivation (April-October 2013). Due to prototype design and operational characteristics, the zeolitite was not brought to full saturation; the amount of NH_4^+ adsorbed by CZ after the enrichment process was on average ~ 8 mg g^{-1} and ~ 5 mg g^{-1} in the material produced in the 2012 and 2013 cycles, respectively. The slight difference could be ascribed to different climatic conditions that may have slowed down the exchange process (the prototype worked in open-air) and/or different NH_4^+ concentration in the manure storage basin (Faccini et al., 2015). CZ production rate was limited by the prototype dimensions to a maximum of 500 kg d^{-1}.The reason for the employment of two different types of zeolitites resides on the different interactions that NZ or CZ develop within the soil system with respect to N cycles and plant nutrition. Both kinds of zeolitite increase the physical-chemical properties of the soil, like CEC andwater retention and reduce surface dryness (Colombani et al. 2014). Because of the absence of nitrogen in NZ, the aim of this zeolitite was to adsorb NH_4^+ from the fertilizer added to the soil, enhancing its retention time and reducing N leaching during the growing season. On the other hand, the use of CZ had the double aim of reducing the NH_4^+ content of pig slurry during the enrichment process (thus lowering manure environmental impact) and of supplying a slow-release pool of N to plants when applied to the soil. Once the N pool is completely exploited, CZ will behave as a NZ. Both practices allow a strong reduction in the application of synthetic fertilizers. A grain size of 3-6 mm for the zeolitite was selected and used in the experimentation; this grain size was directly available at the quarry plants and no further raw material manufacturing was needed, thus no additional costs were required beside purchase and transport to the test site. Raw natural zeolitite price including transport was 36 € ton^{-1}.

2.2 Experimental field description and setting

The tests were carried out during 2012/2013, 2013/2014 and 2014/2015 agronomic years in a ~6 ha agricultural field located 40 km east of Ferrara city (44°50'33'' N and 12°05'40'' E, Italy) and 15 km inland from the Adriatic Sea. In this area the average rainfall is between 500 and 800 mm per year (Supplementary Table_S1), with peaks in autumn and summer (sub-continental climate); in the last case precipitation almost exclusively occurs as short-lived thunderstorms, with possible flash floods (Supplementary Table_S2). Average daytime temperatures range from 4 °C in January to 27 °C in July (Supplementary Table_S1); maximum temperatures often reach or even trespass 36 °C in summer (Fig 1a, b). Marine thermoregulation helps to maintain minimum temperatures over zero, reducing the number of night frosts (Mastrocicco et al. 2013).

The experimental field lays at an average altitude of 3 m below sea level and consists of clayey-silt soils reclaimed in the period 1860-1890, defined as Calcaric Gleyic Cambisol according to the World Reference Base for Soil Resources (IUSS 2007; Mastrocicco et al. 2013; Di Giuseppe et al. 2014). Soil mineralogical composition is characterized by quartz, feldspar, calcite and clay minerals (illite, kaolinite and chlorite), with occasional presence of small amounts of serpentine and dolomite (Malferrari et al. 2013). The field is equipped with a SSDS, consisting of a series of 90 mm diameter pipes of corrugated perforated PVC installed at approximately 1 m depth. More detailed information concerning the specific SSDS of the experimental field can be found in Mastrocicco et al. (2013). Colombani et al. (2016) carried out a detailed 2D density-dependent numerical modelling in order to quantify non-reactive solute transport within the aquifer-aquitard system and unravel the hydraulic interconnections between SSDS and superficial/ground waters in the same experimental field of this study. Results suggested that lateral fluxes were limited due to the low hydraulic conductivity of the sediments while water table fluctuation was significant, with SSDS augmenting the interactions between groundwater and surface water.

This work was funded by the EU LIFE+ instrument, requiring demonstrative projects to be carried out in direct collaboration with local public Bodies and private economic institutions, in order to facilitate the adoption/recommendation of good practices and environmental-friendly solutions by Municipal, Regional and National Entities. A local farm hosted the experimental cultivation and the field was divided into straight, hectare-sized parcels with the aim of conciliating farm requirements, research purposes and the availability of NH_4^+-enriched zeolitite. Maximization of production was the main concern for the farmer and working operations were subject to the limits of the available machines. In this framework, the experimental set-up had to be designed with single, large plots without replicates, making estimations on uncertainties and variance on the measurements not accomplishable. Similarly, the application of chemical fertilization reductions in the control parcels was not allowed, as the probable yield decrease would have been a problem for the host farm. Fertilization reductions were thus applied only to the zeolitite-added parcels.

In order to compare the different zeolitite treatments with respect to the host company's agricultural practices, the experimental field was parcelled at the beginning of the experiment. The linear and continuous design of the plots facilitated the movements of farm machines and the differentiation of the yield, avoiding time-consuming operations for the host farm. Preliminary greenhouse tests were carried out in order to determine both the adequate amount of the two different types of zeolitites (NZ and CZ) and the fertilization reductions applicable to each treatment. Based on doses used in previous open-field leaching tests (Passaglia, 2008), on the type of soil (Ming and Allen, 2001, Leggo et al., 2006; Malekian et al., 2011) and on cost/effectiveness of the treatment (Islam et al., 2011), different amounts of CZ and NZ (5-10 kg m^{-2}) were used for two series of pot experiments, aimed at verifying the suitability of zeolitite addition on maize growth, evaluating the reduction of NO_3^- concentration in the leachate and optimizing maize production in comparison to traditional agronomic practices (Campisi et al. 2016). Greenhouse test results showed that the application of 5 kg m^{-2} of CZ and of 5-10 kg m^{-2} of NZ, respectively coupled with fertilization reductions up to 50 % and 30 % of the control, matched well the objectives of the trial.

Passing from laboratory to a real cultivation test on a clayey-silt agricultural soil, we decided to increase the zeolitite doses with respect to that used in the greenhouse tests, up to 7-10 kg m^{-2} (70-100 ton ha^{-1}) for CZ and to 15 kg m^{-2} (150 ton ha^{-1}) for NZ. The choice was made in order to i) verify if such high amounts of zeolitite could further reduce N leaching with respect to a dose of 5 kg m^{-2} (50 ton ha^{-1}) in open-field conditions where the rainfall variable was substantially unpredictable; ii) give such a fine-grained soil, prone to water-logged conditions, the maximum textural improvement, especially in terms of aeration and drainage.

One parcel (1st cultivation year, 3.5 ha; 2nd cultivation year, 3 ha) was cropped without the use of zeolitites and thus left unamended (UA). Two parcels (1 ha each) were amended with 50 and 150 tons ha^{-1} of natural zeolitites (NZ1 and NZ2) respectively. During the first cultivation year, one parcel of 0.5 ha was amended with 70 tons ha^{-1} of CZ (CZ1), while starting from the 2nd cultivation year, the zeolitite dose in CZ1 was increased to 100 tons ha^{-1} and another parcel of 0.5

ha each was amended with 100 tons ha^{-1} of CZ (CZ2). For a better readability, the experimental set up and the agricultural management will be described separately for each year of cultivation and are resumed in Table 1. Zeolitites were first distributed on the soil surface and then homogenised via ploughing in the first 0.35 m soil layer, in order to maximise the contact and exchanges between plant roots and zeolitite grains.

2.2.1 1st cultivation year (Sorghum)

During the first year of experimentation (November 2012 - September 2013) the field was subdivided in 4 treatments. Approximately 3.5 ha were left without any zeolitite addition (Unamended; UA), two plots of 1 ha each were amended with 5 and 15 kg m^{-2} of NZ, hereafter named NZ1 and NZ2, respectively, and one plot of 0.5 ha was amended with 7 kg^{-2} of CZ1 (Table 1). N input from CZ addition in CZ1 was about 436 kg N ha^{-1}, considering the average amount of NH_4^+ adsorbed by CZ during the enrichment process of 8 mg g^{-1}.

Sorghum (*Sorghum vulgare Pers*.) was sowed on May, 9th, and harvested on September, 23rd, 2013; a total of 190 kg-N ha^{-1} of synthetic fertilizers (of which 22 kg-N from Diammonium Phosphate and 168 kg-N from Urea) was applied in UA plot in two-steps, on May, 09th, and June, 03th, 2013 (Fig. 1a). A reduction of 30 % on the Urea input was applied to NZ1 and NZ2 (i.e. a total of 152 kg - N ha^{-1}) while a reduction of 50% on the Urea input was applied to CZ1 (i.e. 95 kg - N ha^{-1}) with respect to the UA plot.

2.2.2 2nd cultivation year (Maize)

At the beginning of the second experimentation year (October 2013 - November 2014), another plot (hereafter CZ2) was created by applying 10 kg m^{-2} of CZ to 0.5 ha of soil previously belonging to the UA plot (which was thus reduced to 3 ha). Further 15 tons of CZ were applied to CZ1 in order to reach the amount of 10 kg m^{-2}. Thus, during the second cultivation cycle, the experimental field included five treatments: UA (reduced to 3 ha), NZ1 and NZ2 (not modified), CZ1 and CZ2 (0.5 ha each). N inputs from CZ addition in CZ1 was about ~ 160 kg ha^{-1}, while in CZ2 it was of ~ 390 kg ha^{-1} since in the second cycle of production the amount of NH_4^+ adsorbed by CZ was lower (~ 5 mg g^{-1}) (Ferretti et al. 2017a).

Maize (*Zea mais*) was sowed on March, 28th, 2014 and harvested on September, 07th, 2014; a total of 240 kg - N ha^{-1} of synthetic fertilizers (of which 27 kg-N from Diammonium Phosphate and 213 kg-N from Urea) was applied in UA plot in three steps, on March 27th, April 18th and May 5th, 2014 (Fig. 1a). A reduction of 30 % on the Urea input was applied in NZ1 and NZ2 (i.e. 168 kg - N ha^{-1}) while a reduction of 50 % on the Urea input was applied in CZ1 and CZ2 (i.e. 120 kg - N ha^{-1}) with respect to the UA plot (Table 1).

2.2.3 3rd cultivation year (Durum Wheat)

During the third year of experimentation (November 2014-September 2015), no further zeolitite was applied and the treatments were not changed with respect to the previous year. Winter Durum Wheat (*Triticum durum*) was sowed on November, 3rd, 2014 (Fig. 1a) and harvested on June, 30th, 2015 (Fig. 1b). A total of 155 kg N ha^{-1} of synthetic fertilizers (of which 18 kg-N from Diammonium Phosphate and 137 kg-N from Ammonium Nitrate) was applied in the UA plot in three steps, on November, 3rd, March, 04th and April, 29th, 2015 (Fig. 1a, b). A reduction of 30% on the Ammonium Nitrate input was applied in all the zeolitite amended plots (i.e. 109 kg N ha^{-1}) with respect to the UA plot (Table 1).

2.3 Monitoring activities

During three years of monitoring activity, 11 soil sampling campaigns were conducted. A total of 418 soil samples from the 0 - 0.5 and 0.5 - 1 m soil layers were collected with an Ejielkamp Agrisearch auger and analysed for extractable NO_3^- in soil. We choose to investigate these two depths since the SSDS system is placed at 1m depth and previous studies carried out in the same location (e.g Mastrocicco et al., 2013) established that NO_3^- is concentrated in this layer. Since the activation of the SSDS, intended as the discharge of water from the drains into the lateral ditches, strongly depend on the natural conditions and anthropic activities related to the local Reclamation Consortium (Colombani et al. 2016), water samples for NO_3^- determination were collected once or twice for every episode of activation occurred during the monitoring period (see activation description below). In order to determine the annual NO_3^- flux, the water flow was measured during each activation for each reference tube during every sampling campaign. For each parcel, a flow meter was installed in the drain adjacent to that chosen as reference, in order to cross check the total amount of discharged water via different methods. The intrinsic variability of the system did not allow any statistical approach, as both drain water NO_3^- content and soil water extractable NO_3^- concentrations varied from season to season and with respect to the position within the field.

SSDS activated many times from January to May 2014, from December 2014 to March 2015 and from February 2015 to March 2016 (Fig. 1a, b), on the basis of the amount of rain and the fluctuations of the water table level. The activations can be divided into three periods: from January to May 2014, from December 2014 to March 2015 and from February to March 2016 (Table 2). The first period occurred after sorghum harvest; the second period occurred after maize cultivation and was concomitant with wheat growth, while the third took place more than 7 months after wheat harvest. The water discharge essentially may occur in two ways: winter activations and spring activations. Winter activations are more frequent and typically take place between the November and March, when the combination of prolonged rainfalls, low solar irradiation and low evapotranspiration are more likely to lead to soil saturation and increase of the water table level. This kind of activation may last between 3 and 15 days or even more, with variable flow rates but an almost continuous water output from the SSDS. Spring activations are much rare and may occur mainly between April and June, after thunderstorms with very high rainfall intensity. These activations generally last from few hours to a maximum of 2-3 days.

The amount of NO_3^- leached from the field by the SSDS was calculated considering the soil volume drained from each drain tube and the amount of water discharged from the field, rescaled to one ha. The drained volume was calculated considering the drain length (140 m) multiplied by the depth of the SSDS (1 m) and by a distance between the drain axes (8 m) empirically determined when the SSDS was designed, taking into account the high clay and silt contents of the soil and the average rainfall of the River Po plain area. Crop yield was evaluated separately for each plot and for each cultivation cycle using a combine harvester. Meteorological conditions (temperature, pressure, wind speed, wind direction, rain, humidity, solar energy, solar radiation, UV dose, ET) were monitored with a ventilated (i. e. equipped with a ventilation system to prevent temperature overestimation) DAVIS Vantage Pro2 Plus meteorological station installed in the proximity of the experimental field; data were acquired at one-hour intervals from April 2012 to June 2016 and sent weekly via GPRS.

2.4 Analytical techniques

Soil NO_3^- was extracted with Milly-Q (Millipore USA) water in a 1:10 (w/v) ratio. The solution was shaken for 1 hour and then filtered through 0.22 µm Dionex polypropylene filters prior to the analysis. Results of soil water extractable NO_3^- analyses are expressed in mg of NO_3^- for each kg of dry soil. For SSDS waters, samples were only filtered through 0.22 µm Dionex polypropylene filters prior to analysis. NO_3^- content was determined by ion chromatography with an isocratic dual pump (ICS-1000 Dionex) equipped with an AS9-HC 4×250 mm high-capacity column and an ASRS-Ultra 4-mm self-suppressor. An AS-40 Dionex auto-sampler was employed to run the analysis, while quality control (QC) samples were run every ten samples. NH_4^+ concentration was determined in both soil water extracts and in SSDS waters using an Ion Selective Electrode (ISE) Orion 95-12 connected to a Thermo Fisher Orion 4star pH – ISE benchtop. Soil bulk density was determined using Core Method following procedure of Miller and Donahue (1990).

3 RESULTS

3.1 Crop yields

For all the three cultivation cycles, crop yield in all zeolitite-amended plots was higher or comparable to that of the controls (Table 1), notwithstanding the consistent reductions in the applied synthetic N fertilization.

Concerning sorghum, the highest yield was obtained in CZ amended plot (6,630 kg ha^{-1}), while the lowest was recorded in the UA plot (5,800 kg ha^{-1}). The yield in NZ1 and NZ2 plots was equal or slightly higher than that the UA plot. The yields increments calculated with respect to the UA were of +3.7 % and +13.9 % for NZ and CZ amended plots, respectively (Table 1).

Concerning maize, the highest yield was recorded in NZ2 plot (11,800 kg ha^{-1}) while the lowest was recorded in the UA plot (9,490 kg ha^{-1}). NZ1, CZ1 and CZ2 obtained a yield of 10,300, 9,710 and 10,000 kg ha$^{-1,}$ respectively. The yield increments calculated with respect to the UA were + 0.1 %, + 6.3 %, + 3.1 %, +21.7 % for NZ1, CZ1, CZ2 and NZ2, respectively (Table 1).

Concerning wheat, the highest yield was obtained in NZ1 (7,200 kg ha^{-1}), while the lowest in CZ2 (6,530 kg ha^{-1}). UA obtained a yield of 6,600 kg ha^{-1}, while CZ1 and NZ2 showed the same yield (7,060 kg ha^{-1}). Wheat harvest was 1.1 % lower in CZ2 with respect to the UA, while in CZ1, NZ2 and NZ1 yield increased by +6.1%, +6.1% and +9.1%, respectively (Table 1).

3.2 Water extractable NO_3^-

During the first cultivation cycle, water extractable NO_3^- concentration in soil was generally higher in the first 0.5 m of depth than in the 0.5 - 1 m soil layer. In the first 0.5 m of soil, the average NO_3^- concentration in the UA plot was 151 mg kg^{-1}. With respect to this value NZ1 and NZ2 showed lower NO_3^- content, with 84 and 79 mg kg^{-1}, respectively, while the concentration in CZ1 was higher, with 169 mg kg^{-1} (Fig 2a). On the other hand, in the 0.5 - 1 m soil layer of all the zeolitite treated plots the NO_3^- concentrations were lower (76, 55 and 23 mg kg^{-1} in NZ1, NZ2 and CZ1, respectively) with respect to that of the UA plot (95 mg kg^{-1}), (Fig 2b).

During the second year of monitoring, water extractable NO_3^- concentration in the first 0.50 m of soil was on average lower in CZ2, NZ2 and CZ1 (73, 78 and 98 mg kg^{-1}, respectively) but higher in NZ1 (122 mg kg^{-1}) with respect to the UA plot (96 mg kg^{-1}), (Fig 2a). In the 0.5 - 1 m soil layer, UA and NZ1, showed very similar values (70 and 68 mg kg^{-1}, respectively) while NZ2, CZ2 and CZ1 were lower than UA (47, 49 and 67 mg kg^{-1}, respectively), (Fig 2b).

During the third year of monitoring, water extractable NO_3^- concentration in the first 0.5 m of soil was lower in NZ2, CZ1 and CZ2 (74, 63 and 50 mg kg^{-1}, respectively) and higher in NZ1 (112 mg kg^{-1}) with respect to UA (89 mg kg^{-1}) (Fig 2a). In the 0.5 - 1 m of soil, NO_3^- concentration where very similar between UA, NZ1, CZ1 and CZ2 (79, 84, 80 and 73 mg kg^{-1}, respectively) but very low in NZ2 (45 mg kg^{-1}) (Fig 2b).

On the whole, during the three cultivation cycles, the average concentration of water extractable NO_3^- in the first 0.5 m of soil in NZ1, NZ2 and CZ2 plots was lower (14, 39 and 45 %, respectively) with respect to the UA plot, while CZ1 showed a comparable concentration (Fig 2c). In the 0.5 - 1 m soil layer, the extent of NO_3^- reduction with respect to the UA plot was of 6, 23, 37 and 40 % for NZ1, CZ2, CZ1 and NZ2, respectively (Fig 2d).

The general overview of the three years of water extractable NO_3^- monitoring the first meter of soil is summarized in Figure 2e. Using an average bulk density of 1250 kg m^{-3}, the average NO_3^- content in the first soil meter was of 1237 kg-NO_3^- ha^{-1} in the UA plot, 1087 and 752 kg-NO_3 ha^{-1} in NZ1 and NZ2, respectively, while average NO_3^- contents were 1116 and 758 kg-NO_3^- ha^{-1} in CZ1 and CZ2, respectively. NZ1, NZ2, CZ1 and CZ2 amended plots decreased by 12, 39, 10 and 39 % with respect to the UA plot.

Average NH_4^+ concentration in the water extracts of both 0 - 0.5 m and 0.5 - 1 m soil layers was very low throughout the three years of experimental cultivation. In most of the cases it was below the instrumental detection limit; when detectable, it never exceeded 2 mg kg^{-1}.

3.2 SSDS waters

The total amount of NO_3^- ha^{-1} leached from each plot during the monitored period is showed in Figure 3. The total NO_3^- load discharged from the UA plot after sorghum cultivation was 57 kg-NO_3^- ha^{-1}; all the other treatments discharged less NO_3^-. In particular, CZ1, NZ1 and NZ2 discharged an amount of 55, 38 and 3 kg-NO_3^- ha^{-1}, respectively (Fig 3a). This correspond to a reduction of 4 %, 33 % and 94 % with respect to the UA plot.

After maize cultivation, the total NO_3^- content in SSDS water was generally lower if compared to the previous year. The amount discharged in the UA plot was approximately of 5.7 kg NO_3^- ha^{-1}, while in CZ1, CZ2, NZ1 and NZ2 was of 5.4, 5.0, 3.3 and 3.0 kg NO_3^- ha^{-1}, respectively (Fig 3a). The extent of reduction with respect to the UA plot was of 6 % for CZ1, 43% for CZ2, 11% for NZ1 and 48% for NZ2.

After wheat cultivation, the total amount of NO_3^- discharged through SSDS increased significantly. The UA plot discharged a total amount of 156 kg NO_3^- ha^{-1}, while CZ1, CZ2, NZ1 and NZ2 discharged a total amount of 117, 97, 126 and 75 kg NO_3^- ha^{-1}, respectively (Fig 3a). The extent of reduction with respect to the UA plot were of 27 % for CZ1, 40 % for CZ2, 22 % for NZ1 and 53 % for NZ2.

The general overview of the three years of SSDS monitoring is summarized in Figure 3b. The total amounts of NO_3^- discharged during the three years was of 223 kg NO_3^- ha^{-1} in the UA plot, 177 and 126 kg NO_3^- ha^{-1} in CZ1 and CZ2, 169 and 81 kg NO_3^- ha^{-1} in NZ1 and NZ2, respectively. The global reductions with respect to the UA plot over the three years of monitoring were 21 % for CZ1, 43 % for CZ2, 24 % for NZ1 and 64 % for NZ2. Being the NH_4^+ concentration in the SSDS water always < 1.7 mg L^{-1} and in most of the cases below instrumental detection limit, its contribution to the total amount of N discharged into the surface water system was negligible.

4 DISCUSSIONS

4.1 Relationships between NO_3^- concentrations, field setting and meteorological events

The long experimental period allowed the assessment of the potentiality of zeolitites application for reducing NO_3^- leaching from agricultural systems. In agricultural soils, the NO_3^- that is present in the upper layer is mainly related to the application of fertilizers and it is potentially subjected to many losses (e.g. leaching through water systems, NH_3 volatilization and other gaseous N losses). In the experimental field area, soils below 2 m are characterized by high amounts of organic matter and reducing conditions and host large amounts of NH_4^+ derived from organic N mineralization (Mastrocicco et al. 2013). Although a contribution from this "deep" N source cannot be ruled out (when the water table rises, NH_4^+ would be quickly nitrified in the upper oxic soil layers, according to Mastrocicco et al. (2013) the high NO_3^- contents found in the studied upper soil layers can be predominantly ascribed to agricultural practices; furthermore, the presence of SSDS may be able to change soil redox conditions, favouring nitrification processes at higher depth and thus increasing the vulnerability of the superficial water systems. High concentrations of NO_3^- in soil pore-water even at about 1 m depth confirms this evidence and implies that NO_3^- can be easily leached through SSDS in case of waterlogged conditions (prerequisite for their activation).

In the first and second year of experimental cultivation, the growing seasons of sorghum (May-September) and maize (April-September) largely coincided with the period of low precipitation (June-September) (Fig 1a), when rainfall events occur almost exclusively as quick (generally lasting less than 1 h), high precipitation rate thunderstorms (Supplementary Table S1) and SSDS activation is an exceptional and short-lived event linked to flash floods ("spring activations"). Beside an event in May 2014, SSDS activation for the first and second year of experimentation occurred indeed during the winter season, due to prolonged rainy periods that easily induced waterlogged conditions in the upper soil layer. As revealed by meteorological data, the periods between October 2012 and April 2013 and between October 2013 and April 2014 were rainier than average for this area (Supplementary Table S1). On the other hand, during the third cultivation cycle, winter wheat developed from November 2015 to June 2016 and the activation of the SSDS occurred during the growing season, from December 2014 to March 2015, one month after the addition of the 1st tranche of chemical fertilizers and close to the 2nd fertilization (Fig 1a, b). The average NO_3^- concentration in SSDS water for this period was lower if compared to the previous and the following SSDS activations (Fig 3), probably because of crop uptake.

4.2 Role of zeolitites in NO_3^- leaching reduction

Since the agricultural management (type of crop, fertilization amount and type of fertilizers, timing of field works) and meteorological conditions were different between the three years of experimental cultivation, soil water extractable

NO_3^- concentration and the total amount of NO_3^- discharged by SSDS were very different for each treatment. On the whole, all zeolitite-treated parcels were characterized by a generally lower NO_3^- content in both soil waters extracts and SSDS waters, regardless of the amount of N applied.

As far as NZ1 and NZ2 are concerned, the generally lower NO_3^- content can be mainly attributable to the lower N inputs from chemical fertilizers applied. Higher N inputs are expected to induce higher crop yields (Malhi and Lemke 2007) whereas in these parcels, by decreasing N inputs, higher or similar yields were obtained with respect to UA. This evidence, together with some other measurements performed (data not shown in this paper) such as leaves chlorophyll content and total N-C of the cultivated sorghum, maize and wheat plants (Campisi et al. 2016; Di Giuseppe et al. 2016; Ferretti et al. 2017a) indicates that none of the investigated plant suffered any N deficiency.

The possibility to trap cations inside zeolite extra-framework sites should allow a higher retention time of NH_4^+ in the soil and delay the immediate transformation into NO_3^- by nitrifying bacteria, thus lowering the potential N losses by leaching and volatilization (Ippolito et al, 2011), resulting in a higher FUE. Coherently, Gholamhoseini et al. (2013) observed both an increase in sunflower yield and a reduction of N leaching after the spreading of cattle manure composted with natural clinoptilolite zeolite to an agricultural soil. Combining Urea with natural zeolites leaded to an increase of the Urea-N efficiency, a reduction of the gaseous ammonia (NH_3) losses (Ahmed et al. 2008) and an increase of NH_4^+ retention in the soil with a delay in NO_3^- formation (Latifah et al. 2011). It is well known that chemical fertilizers (especially Urea and all NH_4^+ based fertilizers) are subjected to important N losses through NH_3 volatilization immediately after their application to the soil and, if conditions are favourable (sub-alkaline soil pH, moist soil, high wind speed and temperatures), these losses may be even more than 30 % of the applied N (Soares et al. 2012). For this reason, the possibility of decreasing NH_3 losses may have contributed to increase FUE during our experimentation. Ferretti et al. (2017a) found indeed evidences of a higher FUE in NZ-amended plots after performing an isotopic tracing in the soil-plant system of the experimental field and demonstrated that in similar conditions NH_3 emissions can be reduced up to 60 % (Ferretti et al., 2017c).

Concerning CZ amended parcels (both CZ1 and CZ2), it has to be highlighted that the total N input during the 1st and 2nd cultivation cycle was considerably higher with respect to the other treatments, if also the N added with CZ itself is considered (Table 1). This considerably high N input was justified by the fact that CZ generally should act as slow release fertilizer (Eberl et al. 1985; Dwairi 1998), thus allowing a stronger reduction of chemical fertilization (up to 50 %) and contemporaneously also reducing N leaching losses. However, several field analysis and short-term incubation experiments carried out contemporaneously to this experiment, showed that few days after the addition to the soil, CZ had a priming effect on soil microbial biomass (increase in mineralization and immobilization processes) (Ferretti 2017b). This behaviour can easily explain the higher NO_3^- levels found in water extracts of the first 0.50 m of soil layer (but not in SSDS water) during sorghum cultivation in CZ1 (Fig 2a). In this light, it is thus reasonable to think that part of the N added with CZ has been subjected to some short-term immediate losses (as NO_3^- and N gaseous emissions). Notwithstanding, Ferretti et al. (2017a) demonstrated that plants were able to uptake significant amounts of N from CZ minerals for at least two consecutive cultivation cycles. With the exception of the abovementioned high concentration encountered in CZ1 during sorghum cultivation in the upper soil layer and notwithstanding the high N input applied, the average NO_3^- concentration in soil water extracts and SSDS waters in both CZ1 and CZ2 were always similar or lower with respect to the unamended soil, resulting in an overall lower NO_3^- content in the soil for three cultivation cycles (Fig 2e and Fig 3b). These evidences indicate that CZ is an efficient N-rich amendment with also good potentiality concerning the reduction of NO_3^- pollution. However, it is important to pay attention in the timing of application to soil in order to avoid N losses before the beginning of the growing season. It is thus recommendable to apply CZ immediately before the sowing or, alternatively, to use it as component for greenhouse cultivation systems rather than in the open field where, generally, the timing of application is constrained by agricultural practices (e.g. ploughing, since CZ need to be mixed in the upper soil layer) and crop rotation.

A cost/benefit analysis of the adoption of an integrated (on-site production and use, for a circular economy) zeolitite cycle has been carried out (Blasi et al., 2015; CURSA Research Unit 2015). The cost of zeolitite varied from 36 € ton^{-1} for NZ to 63 € ton^{-1} for CZ in the perspective of a large-scale production. In the light of the results of the experimental cultivation, 50 ton ha^{-1} can be a sufficient dose to obtain a consistent mitigation of the N input into the surface water system and maintaining or even increasing the yield. The positive effects of zeolitite addition to the soil are permanent thanks to the long-term structural stability of chabazite (Gualtieri and Passaglia 2006), thus the amendment can be done once (or in several tranches until the optimal dose is reached) and a fertilization reduction of at least 30 % of the MAS can become the routine practice. Zeolitite addition to soils need to be considered a long-term land amelioration that should be partially (or totally) funded by National or Regional Entities in the framework of rural development plans. For the above-mentioned reasons and although initially relevant, the investment resulted convenient both in terms of fruitfulness and of capital over a period of 10 years.

5 CONCLUSIONS

The outcomes of this 3 years experimentation gave important insights on the environmental benefits of the employment of natural and NH_4^+-enriched zeolitites as soil conditioner in agricultural contexts. With the use of NZ or CZ, N inputs from chemical fertilizers can be significantly reduced (up to 50 % with respect to common practices) even for several consecutive cultivation cycles without affecting crop yield and with important positive implications. NZ and CZ application to soil in combination with high reductions in chemical fertilization lead to a general decrease of NO_3^-

concentration in soil water extracts and in the water discharged by the SSDS, thus reducing the potential N losses by leaching and the vulnerability of ground and superficial water bodies. Positive effects were also observed for the crop yield, probably as consequence of an increased FUE. This practice represents thus a potentially valid method for ameliorating the environmental and long-term economic sustainability of agricultural activities by reducing the N inputs from chemical fertilization without impairing productivity, as required by EU strategies and Directives.

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Figure Captions

Fig 1. Temperature and rainfall in the experimental field for years 2013, 2014 (a), 2015 and 2016 (b). Sowing and harvest of sorghum (S), maize (M) and durum wheat (DW) are also reported (black lines), together with fertilization applications (fert 1, 2, 3, dashed lines). Grey shaded boxes indicate the periods of SSDS activation. Blank periods in year 2013 are due to temporary meteorological station malfunction.

Fig 2. Average concentrations of NO_3^-: a) in the first 0.5 m of soil for each cultivation cycle; b) in the 0.5 - 1 m soil layer for each cultivation cycle; c) in the first 0.5 m of soil layer, during the three years of water extractable NO_3^- monitoring; d) in the 0.5 - 1 m soil layer, during the three years of water extractable NO_3^- monitoring; e) in the first m of soil, during the three years of water extractable NO_3^- monitoring.

Fig 3. Total amount of NO_3^- ha^{-1}: a) leached from each plot for each cultivation cycle; b) discharged by the different treatments during the whole monitoring period.