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C-N elemental and isotopic investigation in agricultural soils: Insights on the effects of zeolitite amendments

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ABSTRACT

In this paper we present an elemental and isotopic investigation of carbon and nitrogen in the soil-plant system. Plants grown in an unamended soil were compared to plants grown in a soil amended with natural and NH_4^+-enriched zeolitites. The aim was to verify that zeolitites at natural state increase the chemical fertilization efficiency and the nitrogen transfer from NH_4^+-enriched zeolitites to plants. Results showed that plants grown on plots amended with zeolitites have generally a $\delta^{15}N$ approaching that of chemical fertilizers, suggesting an enhanced nitrogen uptake from this specific N source with respect to the unamended plot. The $\delta^{15}N$ of plants grown on NH_4^+-enriched zeolitites was strongly influenced by pig-slurry $\delta^{15}N$ (employed for the enrichment process), confirming the nitrogen transfer from zeolitites to plants. The different agricultural practices are also reflected in the plant physiology as recorded by the carbon discrimination factor, which generally increases in plots amended with natural zeolitites, indicating better water/nutrient conditions.

1. Introduction

Intensive agricultural practices, which involve systematic use of chemical fertilizers, cause soil quality degradation, loss of soil organic matter, decrease of soil biological properties and widespread water pollution, particularly reflected by high concentration of dissolved nitrogen (N) compounds that contaminate the interacting surface and ground-water (Golchin et al., 1995; Sacchi et al., 2013; Marchina et al., 2015). Chemical fertilization implies significant N losses that may occur after their application (such as NO_3^- leaching/runoff, NO_x, N_2O and NH_3 volatilization), which have negative consequences from the economical, agronomical and environmental point of view (Smil, 1999). In this framework, the application of organic and inorganic amendments has been recognized as a valuable technique for increasing soil physico-chemical properties as well as soil fertility (Waltz and McCarty, 2003; Ferreras et al., 2006; Lima et al., 2009; Colombani et al., 2014). Among inorganic amendments, zeolitites are increasingly used. They are lithologies containing more than 50% of zeolite minerals (Galli and Passaglia, 2011), which are crystalline hydrated aluminosilicates constituted by a three-dimensional framework of linked tetrahedra and by open cavities in the form of channels and cages (Gottardi and Galli, 1985; Coombs et al., 1997). They are known to be suitable in a wide range of agricultural applications (Reháková et al., 2004) in relation to their high Cation Exchange Capacity (CEC). Their structure allows in fact a controlled retention/release of water and nutrients (e.g. NH_4^+), thus reducing N leaching and NH_3 volatilization from agricultural soils. As a consequence, the use of these amendments generally increase crop yield, water and N use efficiency (Bigelow et al., 2001; Reháková et al., 2004; Passaglia, 2008; Sepaskhah and Barzegar, 2010; Ippolito et al., 2011; Latifah et al., 2011; Bernardi et al., 2013; Gholamhoseini et al., 2013; Li et al., 2013; Malferrari et al., 2013; Colombani et al., 2014, 2015; Ozbahce et al., 2015; Di Giuseppe et al., 2016).

Among zeolitites, chabazite-bearing zeolitites (in which chabazite zeolite is prevalent) are recognized as one of the best zeolitites to be used for agronomical purposes, in relation to its very high CEC (2.0–2.1 meq g^{-1}), selective reversible NH_4^+ sorption and structure stability over long period (Baerlocher et al., 2001; Passaglia, 2008).

In this context, the ZeoLIFE project (LIFE10+ ENV/IT/00321) investigated the use of zeolitites amendments to minimize the nitrate pollution in agricultural soils and ground/superficial waters, increasing at the same time yield and fertilization efficiency in a

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nitrate vulnerable zone (Ferrara Province, Italy). Notwithstanding the high number of studies in which natural and NH_4^+-enriched zeolitites were employed in agricultural applications (Barbarick and Pirela, 1984; Lewis et al., 1984; Dwairi, 1998; Reháková et al., 2004 and reference therein), the use of stable isotopes has never been applied for evaluating the effects of this practice on plant N uptake and for tracing the N transfer from zeolitites to plants.

In this framework, we used an isotopic approach to evaluate the nutrient transfer from zeolitites to plants as well as to verify the increase in fertilizers N uptake with respect to an unamended soil.

A very powerful tool that allows a better understanding of the plant-soil N dynamics is the measurement of the $^{15}N/^{14}N$ isotopic ratio (expressed as $\delta^{15}N$) in soils and associated plants (Högberg, 1997; Szpak, 2014). It is well known that variations in the N isotopic ratio can give robust information about N fluxes and plant N sources in ecosystems. Many studies consider that no variation of the isotopic ratio occurs after the absorption of N by the plant, thus, foliar or stem $\delta^{15}N$ can act as tracer, reflecting the isotopic ratio of the N source in the soil (Handley and Raven, 1992; Högberg, 1997; Evans, 2001). This assumption is however not completely corrected due to possible fractionations during N uptake, intra-plant N re-allocation and physiological factors due to mycorrhizal associations (Evans, 2001; Szpak, 2014).

Zootechnical effluents, such as pig-slurry that is commonly used as organic fertilizer, are strongly enriched in the heavier ^{15}N isotope (>20‰) due to NH_3 volatilization that causes depletion in the lighter ^{14}N (Högberg, 1997; Dittert et al., 1998; Schmidt and Ostle, 1999; Lim et al., 2007). This in turn implies that plants grown on organic fertilizers have higher $\delta^{15}N$ with respect to plants grown under unfertilized or under chemical N-fertilizers (Choi et al., 2002; Choi et al., 2003; Bateman et al., 2005; Yun et al., 2006; Szpak et al., 2012; Szpak, 2014). It is also known that site specific conditions such as water and nutrients availability, soil salinity and soil compaction can cause important variation in the carbon (C) discrimination factor ($\Delta^{13}C$), giving information on the physiological status of plants (Lasa et al., 2011; Maxwell et al., 2014).

The goal of this paper is to verify if soil amendments with zeolitites at natural state can effectively increase chemical fertilization efficiency and to trace the N transfer from NH_4^+-enriched zeolitites to plants by taking into consideration the N and C elemental and isotopic distribution in the soil-plant system. The investigation has been carried out for two cultivation cycles (maize and wheat). During the experimentation, three different zeolitite amendments, one employing NH_4^+-enriched zeolitites and two employing zeolitites at natural state applied in various amount, were compared to an unamended soil.

Our hypothesis is that in soils amended with zeolitites at natural state, plants are more influenced by the chemical fertilizers isotopic signature with respect to plants grown on an unamended soil, since zeolitites should enhance the adsorption of NH_4^+ ions formed after the application of chemical fertilizers and allow a more efficient uptake of this specific N source. On the other hand, in soils amended with NH_4^+-enriched zeolitites (obtained by doping zeolitites with pig-slurry characterized by a very high ^{15}N natural abundance), plants are expected to show a higher isotopic signature, as a consequence of the N transfer from the mineral to the plants.

2. Materials and methods

2.1. Zeolitites used in the study

The natural zeolitite (NZ) used in this study is a byproduct from a quarry located near Sorano village (central Italy) that is mainly exploited to obtain blocks and bricks for construction and gardening.

The quarried material is a zeolitized tuff composed of more than 68% of K-chabazite constituting thus a “chabazite-bearing zeolitite” (Malferrari et al., 2013). A grain size of 3–6 mm was selected and used in the experimentation. After sieving, part of the NZ was subjected to an enrichment process which allowed the enrichment of the zeolitite with NH_4^+ ions, creating an NH_4^+-enriched zeolitite (CZ). The enrichment process, based on a mixing procedure of pig-slurry and natural zeolitite in a specifically conceived prototype, has been described by Faccini et al. (2015).

2.2. Experimental field setting

This study has been carried out during the agronomic years 2014 and 2015 in a 6 ha agricultural field located 40 km eastward of Ferrara city (45°50′33′′ N and 12°05′40′′ E, Italy) and 15 km from the Adriatic Sea. The average rainfall is between 500 and 700 mm per year with peaks in autumn and summer (sub-continental climate). Average daytime temperatures range from 5 °C in January to 25 °C in July. Marine thermoregulation helps to maintain minima 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 recently reclaimed (1860–1890) clayey-silt soils (Mastrocicco et al., 2013; Di Giuseppe et al., 2014a) defined as Calcaric Gleyic Cambisol, according to the World Reference Base for Soil Resources (IUSS Working Group, 2007) (see Table 1 for the main soil physico-chemical properties). These soils have been previously characterized from the geochemical point of view (Bianchini et al., 2012; Bianchini et al., 2013; Di Giuseppe et al., 2014b; Di Giuseppe et al., 2014c). The mineralogical composition is characterized by quartz, feldspar, calcite and clay minerals (illite, smectite, chlorite, serpentine and mixed-layer) (Malferrari et al., 2013).

The experimental field was parcelled at the begin of ZeoLIFE project (year 2012) in order to compare different zeolitite treatments with the traditional agricultural practices (Fig. 1).

Distinct parcels were linear and continuous in order to facilitate the movements of farm machines. One parcel of 1.5 ha was cultivated without the use of zeolitites and thus left unamended (UA). Two parcels of 1 ha each were amended with 5 and 15 kg m^{-2} of zeolitites (5NZ and 15NZ, respectively), and one parcel of 0.5 ha was amended with 10 kg m^{-2} of NH_4^+-enriched zeolitite (10CZ). The 10CZ plot was relatively smaller with respect to other NZ plots because of the limited CZ availability. The experimental set-up is summarized in Table 2.

Maize (*Zea mays*) was sowed on March 28th, 2014 and harvested on September 7th, 2014, while wheat (*Triticum durum*) was sowed on November 11th, 2014 and harvested on June 30th, 2015. The project developed in a real agricultural context (the field was managed by a local farm company) in order to demonstrate the possibility of reducing N pollution from fertilization by increas-

Table 1
Main properties of the ZeoLIFE experimental field soil (first 30 cm depth). EC refers to Electrical Conductivity, TN to Total Nitrogen and TOC to Total Organic Carbon. Standard deviation within brackets.

	Soil
pH	7.6 (0.2)
EC (mS cm^{-1})	1.0 (0.1)
$CaCO_3$ (g kg^{-1})	64.5 (3.5)
CEC (meq g^{-1})	0.45 (0.02)
TN (g kg^{-1})	2.33 (0.31)
TOC (g kg^{-1})	22.76 (3.2)
Soil TOC/TN ratio	9.76 (0.34)
Bulk Density (kg m^{-3})	1250