High resolution short-term investigation of soil CO_2, N_2O, NO_x and NH_3 emissions after different chabazite zeolite amendments

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Abstract

Reducing the effects of climate change is a key-point to achieve sustainable development. It is known that fertilizer application stimulates soil gaseous N losses, especially immediately after their application. In this short-term incubation experiment, the effects of different chabazite zeolite amendments on soil gaseous emissions (CO_2, N_2O, NO_x and NH_3) were evaluated in high resolution as potential mitigation strategy for agricultural soils. Different soil-zeolite mixtures, including both natural and NH_4^+-enriched chabazite zeolites, were incubated for 24 h both immediately after the application of urea fertilizer and without a further N input in order to carry out a high resolution investigation of soil CO_2, N_2O, NO_x and NH_3 fluxes, in comparison to an unamended soil. Immediate CO_2, N_2O, NO_x and especially NH_3 emissions after fertilizer application were generally reduced in soils amended with zeolites at natural state, indicating a potential valuable material for reducing soil C-N gaseous losses. On the other hand, the application of NH_4^+-enriched zeolites lowered CO_2 and N_2O emissions, but very high NO_x fluxes occurred during the first 24 h even without applying any further N input. NH_3 emissions were higher in NH_4^+-enriched zeolites amended soil, but if the amendment is performed without further N inputs, the emissions can be significantly lowered with respect to a conventional urea fertilization.

Keywords: *natural zeolites; NH_3; CO_2; N_2O; NO_x; soil emissions.*

1.0 Introduction

Notwithstanding the increasing number of climate change mitigation policies, the annual emissions of greenhouse gases (GHGs) keeps rising, leading to high costs in terms of environmental quality (Edenhofer et al., 2014). In particular, the agricultural sector accounts for an estimated emission of 10-12 % of the total global anthropogenic GHGs production (Smith et al., 2007).

CO_2 and N_2O are potent GHGs whereby N_2O has a 298-fold global warming potential "GWP" of CO_2 (Edenhofer et al., 2014). In addition, nitrogen oxides (NO_x) and ammonia (NH_3), even if not considered GHGs, can cause indirect N_2O emissions, increase acidity of precipitations and strongly influence tropospheric O_3 formation (Akiyama et al., 2004; Schindlbacher and Zechmeister-Boltenstern, 2004). Moreover, all N gaseous losses cause remarkable reductions in fertilization efficiency, representing thus an economic loss for the farmers (Smil, 1999).

It is known that the great majority of gaseous N losses occurs during the first days after fertilizer application and these "immediate" direct flux rates are not completely known, in particular, NH_3 emission have been found to account up to 75 % of the applied N within the first 24 h (Stevens and Logan, 1987). For this reason, finding new methodologies that

62 can delay immediate gaseous N-losses may lead to an increase of fertilizer use efficiency and thus to a reduction of their

63 environmental impacts.

64 Since many years, natural zeolites have been recognized as valuable soil conditioners that can positively affect the soil-

65 plant system. These aluminosilicates are characterized by a high and selective cation exchange capacity (CEC),

66 reversible dehydration and molecular sieving that can strongly influence soil physico-chemical characteristics and N

67 cycling by reducing N leaching, increasing nitrogen use efficiency and crop yield (Colombani et al., 2014; De Campos

68 Bernardi et al., 2013; Gholamhoseini et al., 2013; Malferrari et al., 2013; Reháková et al., 2004). Zeolites can be easily

69 modified from their natural state by enrichment processes which cause the adsorption of specific cations (i.e., NH_4^+,

70 Na^+) (Barbarick et al., 1990; Campisi et al., 2016; Dwairi, 1998; Leggo, 2000), for this reason, the use of NH_4^+-enriched

71 zeolite has been proposed as "slow release fertilizer" (Barbarick and Pirela 1984; Dwairi, 1998; Faccini et al., 2015;

72 Lewis et al. 1984). Up to now, however, very few studies exist on the effects of zeolite amendments on soil gaseous

73 emission especially concerning natural zeolite of the chabazite type. Natural clinoptilolite zeolite as amendment to soils

74 have been described to reduce respiratory activity probably because of the adsorption capacity of zeolites for CO_2

75 (Mühlbachová and Šimon, 2003). Kučić et al. (2013) showed that natural clinoptilolite zeolite adsorption potential for

76 CO_2 and NH_3 evolved during co-composting of grape and tobacco waste was 31% and 100%, respectively. In addition,

77 pasture and wetland soils amended with clinoptilolite zeolite showed a reduction in daily and total N_2O emissions

78 during a 90-day incubation compared to unamended soils (Zaman et al., 2007). These reductions are due to the sorption

79 of NH_4^+ by zeolite, lowering the available substrate for microbial nitrification and hence potential losses of N_2O from

80 nitrification and denitrification. The literature about the mitigation potential of zeolite application for NH_3 emissions is

81 more consistent (Bundan et al., 2011; De Campos Bernardi et al., 2013; Haruna Ahmed et al., 2008; He et al., 2002;

82 Kučić et al., 2013), however, the majority of these studies has been conducted on surface applied zeolite in combination

83 with fertilizer and not as amendment well homogenized in the soil profile. Yet, to our best knowledge, the effects of

84 zeolite as soil amendments on NO_x emissions have not been reported. Besides, the majority of studies were conducted

85 employing clinoptilolite zeolites, with so far unknown effects of the less abundant chabazite zeolite, the main natural

86 zeolite occurring in the Italian peninsula (Malferrari et al., 2013). Moreover, the effects of NH_4^+-enriched zeolites on

87 soil gaseous emissions are completely unknown and usually the N input added with this material is very high (Ferretti et

88 al., 2017). Finally, there is a lack of studies applying different type of zeolites as soil amendment that simultaneously

89 investigate a wide range of gaseous species focusing on a high resolution investigation of the immediate emission after

90 fertilizer applications.

91 To this end, the present study aims at elucidating the effects of different chabazite zeolites amendments on soil CO_2,

92 N_2O, NO_x and NH_3 emissions evolved during the first 24 h after fertilizer application from an agricultural soil in high

93 resolution. The experimentation was designed in order to mimic the same treatment and condition of the ZeoLIFE

94 experimental field, which consist in an EU funded project that is testing different chabazite zeolite amendment at the

95 field scale in an Italian nitrate vulnerable zone (NVZ) (Nitrate Directive 91/676/EEC).

96 For this reason, we decided to test chabazite zeolites amendments both at natural and NH_4^+-enriched state in comparison

97 to an unamended soil both under an N input from urea of 170 kg N ha^{-1} (maximum amount of N applicable in a NVZ)

98 and without any further N input (unfertilized conditions). Considering the actual knowledge about zeolite amendments,

99 we built our experiment in order to test the following hypotheses:

100   1) The zeolite-derived effects on the dynamics of NH_4^+ ions (Leyva-Ramos et al., 2010) are expected to decrease

101   short-term N_2O, NO_x and NH_3 emissions after fertilizer application especially in soil amended with zeolites at

102   natural states;

103   2) The controlled slow NH_4^+ release behavior of NH_4^+-enriched chabazite zeolites is expected to not influence

104   significantly soil N fluxes in the first 24 h, if no further fertilizer is applied notwithstanding its high N content;

105   3) The possibility of a CO_2 sorption and the probable influence on microbial activity (Bonenfant et al., 2008;

106   Kučić et al., 2013; Mühlbachová and Šimon, 2003; Reháková et al., 2004; Ridha and Webley, 2009) are

107   expected to decrease the short-term soil CO_2 emissions.

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110   **2.0 Material and Methods**

111 Soil samples (Clayey-Silt Calcaric Gleyic Cambisol) were taken from the ZeoLIFE project experimental field (Ferrara

112 province, Italy, 44°50′33″ N and 12°05′40″E) where both natural chabazite zeolites (NZ) and NH_4^+-enriched chabazite

113 zeolites (CZ) (created following the method proposed by Faccini et al., 2015) were added to the soil as amendments at

114 the field scale (www.zeolife.it) (see Electronic Supplementary Material "ESM1" for the main soil properties and

115 additional information on zeolites characteristics). Soil samples were taken from an unamended plot and zeolites were

116 added in the laboratory immediately before the begin of the experiment, in order to reproduce the same conditions

117 immediately after the amendment. NZ and CZ were added to air dry sieved soil ($\leq$ 5 mm) in different proportions, in

118 order to obtain various soil-zeolite mixtures (see Table 1 for the experimental set up) as in the ZeoLIFE experimental

119 field.

120 60 g of each treatment were incubated at 20°C (well representative of average field temperatures) for 24 h in three

121 replicates. Water filled pore space (WFPS) level was adjusted according to Haney and Haney (2010) to 65 %

122 accounting for changes in bulk density after the amendment. This WFPS level is considered a threshold between the

123 relative prevalence of nitrification/denitrification processes (Bateman and Baggs, 2005). In order to check the moisture

124 level reached, soil water content was also measured by oven-drying soils at 105°C overnight and the difference between

125 the adjusted and measured WFPS was < 5 %. No rewetting operations were performed during the incubation.

126 The experiment was conducted with and without urea input equivalent to 170 kg-N ha^{-1}, (in liquid form, maintaining 65

127 % WFPS) representing fertilized and unfertilized conditions, respectively. The employed fertilizer rate was the same as

128 in the ZeoLIFE experimental field. These high application rates are common in countries such as Italy (in which

129 fertilization can reach more than 340 kg ha^{-1} in non-nitrate vulnerable zones) or even lower in comparison to some

130 studies available in the scientific literature (e.g. Min et al., 2011; Ju et al., 2006) in which more than 600 kg N ha^{-1} have

131 been applied. We choose to reproduce the maximum admissible rates of the nitrate vulnerable zone where the ZeoLIFE

132 experimental field site is located in order to get insights on the amounts of N losses immediately after the application of

133 chemical fertilizers like urea with and without the use of zeolites as soil amendment in this particular area.

134 The 10CZ treatment that was applied in the ZeoLIFE field experiment was also reproduced in the present study

135 providing an N input equivalent to approximately 497 kg N ha^{-1}. Although, the applied N is unbalanced if compared to

136 the other treatments, this allowed to test the behaviour in presence of an excess of N above the recommendation.

137 This N input from CZ was mainly constituted by exchangeable NH_4^+-N and by a little fraction of residual NO_3^--N from

138 the enrichment process (ESM 1). The 10CZ treatment was tested with and without urea fertilizer, consequently it is

139 further termed as "unfertilized" when no urea was added, while it is further termed "fertilized" when it received the

140 additional 170 kg N ha^{-1} from urea as all the other treatments.

141 CO_2 and NO_x (NO + NO_2) were measured in a fully automated continuous flow laboratory system, well described in the

142 work of Schindlbacher and Zechmeister-Boltenstern (2004), with doubled acquisition time of each chamber. N_2O was

143 sampled by closing the chambers and taking samples with a gas tight syringe after 0, 15, 30 and 45 minutes of the

144 closure of the chamber. Samples were injected in a pre-evacuated 10 ml glass vials (Agilent Technologies) and then

145 analysed with a GC-System (Agilent Technologies) equipped with a headspace auto-sampler and an electron capture

146 detector (ECD), for more information see also Leitner et al. (2016). N_2O measurements were performed once after

147 approx. 4 hours of incubations and fluxes were calculated according to Metcalfe et al. (2007).

148 NH_3 measurements were conducted with a fully automated device composed of an incubation system with 6 chambers

149 (ø 7.8 cm and 7.8 cm height) connected to a Cavity Ring-Down Spectrometer (CRDS, Picarro G2103). Chambers and

tubes of the incubation device are built of Polytetrafluoroethylene (PTFE) in order to avoid any NH_3 retention. Dried compressed air was used as carrier gas with a constant flow of 1 l min^{-1}. One chamber was used as blank in order to measure NH_3 background air concentrations (Haller, 2015).

CO_2, NO_x and NH_3 fluxes were calculated according to Schindlbacher and Zechmeister-Boltenstern (2004) and represented as cumulative emissions by integrating over the 24 h of incubation. Moreover, we considered also the emissions per unit of N added by calculating the ratio between the amount of gas emitted divided by the total N added.

NO_3^--N was extracted with Milly-Q (Millipore USA) water in a 1:10 (w/v) ratio, the solution was shaken for 1 h and then filtered. NO_3^--N 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; quality control (QC) samples were run every ten samples. pH was measured on the same extracts with an Orion 9102BNWP pH-meter connected to an Orion 4star pH – ISE benchtop (Thermo Fisher).

Exchangeable NH_4^+-N was extracted with 1 M KCl in a 1:10 (w/v) ratio, the solution was shaken for 1 h and then filtered. The solution was diluted and analysed with an Ion Selective Electrode (ISE) Orion 95-12 connected to an Orion 4star pH – ISE benchtop (Thermo Fisher).

Shapiro-Wilk and Levene's Test were performed for testing data normality and homogeneity of variance. One-way ANOVA (or Kruskal-Wallis test if ANOVA assumption were not met) and Fisher (LSD) tests were then employed for evaluating significant differences between the treatments at p=0.05 level. SigmaPlot 12.0 was used for statistical analysis.

3.0 Results and discussions

Cumulative CO_2, NO_x and NH_3 emissions over the 24 h are presented in Fig 1. Soil pH, exchangeable NH_4^+-N, NO_3^--N mean values and N_2O-N fluxes are visible in Table 2, while the total amounts of volatilized gaseous species (expressed in kg N ha^{-1}), the reduction/increment % with respect to the CNTR and the effects of the fertilization rates on cumulative gaseous losses are shown in Table 3. The total amounts of volatilized gaseous species (expressed in kg N ha^{-1}), the reduction/increment % with respect to the CNTR of the treatments with no N added from fertilization (or from CZ) are visible in the Electronic Supplementary Material "ESM2".

All zeolite amended soils (see Table 1 for treatments description) resulted in significantly lower (p<0.05) CO_2 emissions compared to the unamended soil (CNTR) under fertilized conditions (Fig 1a). These preliminary results show a reduction in CO_2 emissions with the addition of zeolites regardless of zeolite type and application rate, and may

180 indicate a CO_2 sorption effect by zeolites after the fertilization (Kučić et al., 2013; Mühlbachová and Šimon, 2003) or,

181 alternatively, to a higher Carbon Use Efficiency (CUE) (Blagodatskaya et al., 2014; Keiblinger et al., 2010). On the

182 other hand, regarding CO_2 emissions under unfertilized conditions (Fig 1b), the fluxes were not significantly different

183 between the various treatments (p>0.05).

184 It is possible that, without the addition of urea, the substrate C:N ratio was higher, resulting in a higher amount of

185 respired CO_2 to meet metabolic requirements (Russell and Cook, 1995; Schimel and Weintraub, 2003) and hence a

186 lower CUE (Keiblinger et al., 2010). In the present work, it has to be noticed that cumulative CO_2 emissions were

187 similar between fertilized and unfertilized conditions, highlighting that microbial activity was high in this agricultural

188 soil even without adding a fresh N-C input. Concerning this aspect, contrasting effects were reported in the scientific

189 literature; while urea fertilization was found to increase soil CO_2 emissions because of increased mineralization of soil

190 organic carbon by heterotrophic bacteria (Choi et al., 2011), the opposite effect was reported by Wilson and Al-Kaisi

191 (2008) after fertilization with NH_4NO_3. However, the reason why no significant differences in CO_2 emissions were

192 observed under unfertilized conditions is hard to explain without a more detailed investigation on treatment specific

193 microbial CUE and CO_2 adsorption mechanisms. Concomitantly, also the cation exchange processes between the soil

194 solution and zeolite minerals were probably different without and with the addition of fertilizers. It is in fact widely

195 known that the CO_2 adsorption capacity of zeolites depends on many factors including also the distribution and the

196 number of exchangeable cations presents in their cavities (Bonenfant et al., 2008).

197 The cumulative soil CO_2 emissions evolved in 24 h have been reduced by ~21 % to approximately ~30 % with respect

198 to the CNTR soil in presence of urea fertilizer, coherently, the CNTR showed the highest emissions in relation to the

199 total amount of N added (Table 3), even if compared to the very high amount of N supplied by CZ.

200 N_2O fluxes of fertilized soils were significantly lower (p<0.05) in both 5NZ (soil plus 5% in weight of NZ) and 10CZ

201 (soil plus 10 % in weight of CZ) treatments with respect to CNTR, while 15NZ treatment (soil plus 15% in weight of

202 NZ) tended to be slightly lower albeit not statistically different (Table 2). N_2O is produced by both nitrification and

203 denitrification processes, where the main substrate for nitrification is NH_4^+ while for denitrification is NO_3^-. However,

204 these processes are strongly influenced by WFPS level, substrate and oxygen availability (Akiyama et al., 2004;

205 Schindlbacher and Zechmeister-Boltenstern, 2004; Stevens et al., 1997). The WFPS used in this experiment should be

206 the critical threshold between these two processes (Bateman and Baggs, 2005). Since WFPS and oxygen availability are

207 closely related, the observed differences regarding N_2O emissions can be mainly attributed to a change in soil physical

208 properties operated by zeolite amendments. Zeolite amendment (in a 3-5 mm size) has probably increased soil aeration

209 and thus reduced the presence of anaerobic microsites in which denitrification can occur at 65 % WFPS, consequently

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reducing total N_2O emissions with respect to CNTR. Another explanation can be that the NH_4^+ adsorption from soil solution, managed especially by the initially N-devoid NZ, might have reduced the immediate availability of the substrate required for nitrification, thus reducing N_2O emissions (Zaman et al., 2007). The latter hypothesis is supported by our results from NZ amendments were in fact NO_3^--N was generally lower, but not for CZ amendment, where on the contrary NO_3^--N was strongly higher than in CNTR (Table 2).

NO_x are intermediate reactive volatile compounds of both nitrification and denitrification processes and mainly produced after the addition of fertilizers (Skiba et al., 1997). Coherently, the amount of N lost as NO_X was considerably higher after urea application compared to unfertilized conditions (Fig 1c,d). Cumulative NO_x emissions after fertilization were significantly lower ($p<0.05$) in 5NZ and 15NZ treatments compared to CNTR (Fig 1c). This evidence can be partially explained by the lower NO_3^--N contents in both 5NZ and 15NZ treatments, which suggests that some NH_4^+ ions were probably protected from nitrification (Table 2) in this time frame (Zaman et al., 2007). The entity of the reduction of the 5NZ and 15NZ with respect to the CNTR soil under fertilized conditions ranged from ~ 25 - 31 % (Table 3).

Generally, urea fertilization caused an equal increase of the NO_3^--N level of around 40 mg kg^{-1} in all the treatments. However, the NO_3^--N content of 10CZ soil was extremely high both with and without the addition of urea fertilizer, meaning that probably part of the N supplied with CZ has been subjected to immediate nitrification after the application to the soil. These high NO_3^--N levels in the short-term period needs to be taken into account for potential immediate effects on N leaching from the soil system. However, concerning NO_x emissions, it has to be noticed that notwithstanding the excessive N level of this treatment (CZ + urea), the cumulative emissions were not significantly different from CNTR and both NZ treatments ($p>0.05$), thus the total amounts of NO_X emitted per unit of N added result considerably lower (Table 3). On the other hand, 10CZ NO_x emissions of the unfertilized soils (Fig 1d) were comparable to the fertilized one and not statistically different from the fertilized CNTR although a 3-fold N amount was applied to the same soil (Table 3). While for the other unfertilized treatments, NO_x emissions were very low as expected. These higher emissions in 10CZ can be attributed to an immediate transformation of the N supplied by the already N-enriched CZ. In fact, the extremely high NO_3^--N contents suggests strongly enhanced nitrification (biotic or abiotic) in this particular treatment. Commonly, NH_4-enriched zeolites are considered as "slow release" fertilizers (Barbarick and Pirela 1984; Dwairi, 1998; Lewis et al. 1984) but Leggo (2000) found a strong increase in NO_3^--N content immediately after the amendment with NH_4-enriched zeolites (starting from the first week). In that work, the increase in NO_3^--N was attributed to an exchange reaction with soil cations (which have substituted the NH_4^+ inside the mineral lattice) and subsequently NH_4^+ oxidation by nitrifying bacteria. This may have occurred also in the present

240   study since the soil is characterized by a high natural salinity (Di Giuseppe et al., 2014) and a high CEC, which has

241   been further increased by the zeolite amendment (Ferretti et al., 2017; Gholamhoseini et al., 2013).

242   Considering the fact that without addition of urea NO_3^--N levels and NO_x emissions increased significantly with CZ

243   application to the soil with respect to the CNTR, this material likely supplied an immediate available N source so that

244   CZ should be considered as a fertilizer. However, considering the extremely higher N input from CZ (~ 3 times more

245   than the N added from urea), the emission evolved from CZ treated soil in relation to the amount of N added were

246   always lower with respect to an untreated soil (Table 3).

247   In the present study, NH_3 emissions evolved within the first 24 h were comparable with those observed by other authors

248   in the literature (Bundan et al., 2011). Soil NH_3 emissions are known to be highly variable and dependent by many

249   factors such as soil pH, wind speed, soil moisture and CEC (Bundan et al., 2011). Notwithstanding the soil pH was sub-

250   alkaline in all the treatments (Table 2) and thus favourable to NH_3 volatilization, the relatively low NH_3 losses occurred

251   in all the incubated soils may be due to the high soil CEC that, even without the addition of zeolites, can act a good

252   retention of NH_4^+ ions reducing NH_3 volatilization phenomena (Bundan et al., 2011).

253   In both fertilized and unfertilized conditions, a clear reduction in NH_3 emissions was found (Fig. 1e-f) in NZ treatments

254   with respect to CNTR (p<0.05). The entity of reduction after fertilization was of -24 and -55% in 5NZ and 15NZ,

255   respectively, while in unfertilized conditions the reduction was of -40 and -60 % respectively (Table 3). This behaviour

256   is attributable to the NH_4^+ ions adsorption inside NZ, which can physically protect NH_4^+ from NH_3 volatilization (De

257   Campos Bernardi et al., 2013) and it is related to the amount of NZ added in the substrate. However, 10CZ treatment

258   showed high NH_3 emissions in both fertilized and unfertilized conditions, suggesting that some residual NH_4^+ ions from

259   the enrichment process were available for volatilization. In is interesting to note that for all the other gaseous species,

260   10CZ (without further N input from urea), showed higher or similar emissions with respect to the urea-fertilized CNTR

261   (Fig 1a,c), while regarding cumulative NH_3 emissions, those of urea-fertilized CNTR were about twice of unfertilized

262   10CZ (Fig 1e-f, Table 3) notwithstanding a three times lower application rate. This means that urea-N contribute much

263   more to NH_3 emissions than CZ-N and that even applying a considerably higher N input, the losses by NH_3

264   volatilization can be reduced by the half.

265   Finally, it has to be noticed that generally, the ratio between total emissions of each gaseous species and the amounts of

266   N added was always higher in the CNTR soil, meaning that zeolite addition (even in presence of a great excess of N

267   from fertilization) may have important positive effects on gaseous N (and C) losses and consequently also on

268   fertilization efficiency.

269

4.0 Conclusions

The outcomes of this high-resolution short-term incubation experiment highlighted the potential of zeolite application as soil amendment for the reduction of immediate gaseous N (and C) emissions. Results revealed that after 24 h of monitoring, NZ amendments seemed to reduce the immediate production of CO_2, N_2O, NO_x, and especially NH_3 emissions after the application of urea fertilizer, constituting thus a potential valuable material for reducing short-term soil gaseous C and N losses. The amount of NZ applied (5 % or 15 % in weight) had no influences on CO_2, N_2O and NO_x emissions, while the cumulative emissions of NH_3 were inversely related to the amount of NZ in the substrate.

On the other hand, the outcomes of this study revealed that NH_4^+-enriched zeolites, created following the ZeoLIFE project protocol, supplied a fraction of N that was immediately subjected to gaseous losses. CZ amendment lowered CO_2 and N_2O emissions evolved during the first 24 h after fertilizer application, however, nitrification was stimulated and NO_x emission were significantly high even without the addition of urea fertilizer, indicating that part of the N supplied with CZ was immediately transformed biotically or abiotically. The emissions per unit of N added were generally higher in the CNTR soil, meaning that zeolite addition (even in presence of a great excess of N from fertilization) may play an important role in GHG and non-GHG mitigation in agricultural context and consequently also on fertilization efficiency.

We are aware of the fact that our short-term, high resolution experiment is limiting the potential to draw conclusions on long-term mitigation strategies, in terms of immediate gaseous N losses, for this reason, further long-term investigations are required.

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409 **Figure Captions** *(created with SigmaPlot 12.0 and Canvas 11)* <u>**ONLINE COLOR ONLY**</u>

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411 **Fig 1** Cumulative emissions with standard error (error bars) over the incubation of both fertilized and unfertilized

412 treatments. Graphs "a" and "b" refers to soil CO_2 emissions, graphs "c" and "d" to soil NO_x emissions and graphs "e"

413 and "f" to soil NH_3 emissions. Different lowercase letters next to the legend indicate significant differences between the

414 treatments while different capital letters indicate significant differences between fertilized and unfertilized conditions of

415 each gas species, as results of statistical analysis (ANOVA and multi-comparison Fisher LSD test at p=0.05)

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418 **Table 1**: Experimental set-up. CNTR refer to the unamended soil, 5NZ mixture is created by adding 5% in weight of

419 natural zeolite (NZ) to the untreated soil, 15NZ mixture is created by adding 15% in weight of NZ to the untreated soil

420 while 10CZ mixture is created adding 10% in weight of NH_4^+-enriched zeolites (CZ) to the untreated soil.

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	Treatments	Zeolite amount (wt%)	Zeolite type	N input from zeolites (kg N ha⁻¹)	N input from urea (kg N ha⁻¹)	Total N input to soil (kg N ha⁻¹)
	CNTR	0	/	/	170	170
Fertilized with Urea	5NZ	5	NZ	0	170	170
	15NZ	15	NZ	0	170	170
	10CZ	10	CZ	497	170	667
	CNTR	0	/	/	0	0
Unfertilized (no Urea added)	5NZ	5	NZ	0	0	0
	15NZ	15	NZ	0	0	0
	10CZ	10	CZ	497	0	497

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Table 2: Soil pH, exchangeable NH_4^+-N, NO_3^--N mean values (measured at the end of the incubation) and N_2O-N fluxes (measured after 4 h of incubation) with the associated standard errors between brackets. Different upper case letters indicate significant differences (p<0.05) as results of statistical analysis (ANOVA and multi-comparison Fisher LSD test at p=0.05). The presence of "n.m" indicate not measured values.

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	Treatments	pH	NH_4^+-N $(mg\ kg^{-1})$	NO_3^--N $(mg\ kg^{-1})$	N_2O-N $(\mu g\ m^{-2}\ h^{-1})$
Unfertilized	CNTR	7.73 (0.04)[a]	10.1 (0.4)[a]	54.3 (0.7)[b]	n.m
	5NZ	7.80 (0.04)[a]	9.7 (0.3)[a]	47.9 (0.4)[a]	n.m
	15NZ	7.93 (0.06)[a]	9.5 (0.2)[a]	53.7 (0.9)[b]	n.m
	10CZ	7.79 (0.04)[a]	79.6 (6.9)[b]	309 (6.4)[c]	n.m
Fertilized with Urea (170 kg-N ha^{-1})	CNTR	7.94 (0.02)[a]	9.7 (0.3)[a]	97.4 (0.9)[b]	358 (69)[b]
	5NZ	7.99 (0.06)[a]	10.1 (0.2)[a]	84.7 (0.5)[a]	165 (37)[a]
	15NZ	8.12 (0.09)[a]	9.9 (0.4)[a]	83.6 (1.0)[a]	281 (21)[ab]
	10CZ	8.11 (0.10)[a]	81.6 (8.3)[b]	347 (12)[c]	155 (11)[a]

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446 **Table 3:** Cumulative NO_x, NH_3 and CO_2 emissions over 24 h, % of reduction or increment with respect to the CNTR soil and ratio between cumulative emissions and N added.

447 For treatments with no N added see ESM 2. Different upper case letters indicate significant differences ($p<0.05$) as results of statistical analysis (ANOVA and multi-comparison

448 Fisher LSD test at $p=0.05$).

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	N input from zeolites *(kg N ha^{-1})*	N input from Urea *(kg N ha^{-1})*	24 h cumul. CO$_2$-C *(kg C ha^{-1})*	Reduction %	CO$_2$-C/N added	24 h cumul. NO$_x$-N *(kg N ha^{-1})*	Reduction %	NO$_x$-N/N added	24 h cumul. NH$_3$-N *(kg N ha^{-1})*	Reduction %	NH$_3$-N/N added
CNTR	0	170	425 (60)^b	-	2.5	1.11 (0.06)^b	-	0.007	0.42 (0.05)^c	-	0.003
5NZ	0	170	334 (10)^a	-21	2.0	0.77 (0.06)^a	-31	0.005	0.32 (0.02)^b	-24	0.002
15NZ	0	170	323 (51)^a	-24	1.9	0.83 (0.17)^a	-25	0.006	0.19 (0.01)^a	-55	0.001
10CZ	497	0	457 (85)^b	-	0.9	1.29 (0.15)^b	-	0.003	0.18 (0.04)^a	-57	0.0004
10CZ	497	170	298 (34)^a	-30	0.4	1.01 (0.16)^{ab}	-	0.002	0.52 (0.06)^b	+24	0.001

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