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Research article

Bedding additives reduce ammonia emission and improve crop N uptake after soil application of solid cattle manure

Ghulam Abbas Shah [a, b], Ghulam Mustafa Shah [a, c], Muhammad Imtiaz Rashid [a, c, d, *], Jeroen C.J. Groot [a], Bouba Traore [e], Egbert A. Lantinga [a]

[a] Farming Systems Ecology Group, Wageningen University, Droevendaalsesteeg 1, 6708 PB, Wageningen, The Netherlands
[b] Department of Agronomy, PMAS-Arid Agriculture University Rawalpindi, Pakistan
[c] Department of Environmental Sciences, COMSATS Institute of Information Technology, Vehari, Pakistan
[d] Center of Excellence in Environmental Studies, King Abdulaziz University, P.O Box 80216, Jeddah 21589, Saudi Arabia
[e] International Crops Research Institute for the Semi-Arid and Tropics (ICRISAT), Mali

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ABSTRACT

This study examined the influences of three potential additives, i.e., lava meal, sandy soil top-layer and zeolite (used in animal bedding) amended solid cattle manures on (i) ammonia (NH_3), dinitrous oxide (N_2O), carbon dioxide (CO_2) and methane (CH_4) emissions and (ii) maize crop or grassland apparent N recovery (ANR). Diffusion samplers were installed at 20 cm height on grassland surface to measure the concentrations of NH_3 from the manures. A photoacoustic gas monitor was used to quantitate the fluxes of N_2O, CH_4 and CO_2 after manures' incorporation into the maize-field. Herbage ANR was calculated from dry matter yield and N uptake of three successive harvests, while maize crop ANR was determined at cusp of juvenile stage, outset of grain filling as well as physiological maturity stages. Use of additives decreased the NH_3 emission rates by about two-third from the manures applied on grassland surface than control untreated-manure. Total herbage ANR was more than doubled in treated manures and was 25% from manure amended with farm soil, 26% and 28% from zeolite and lava meal, respectively compared to 11% from control manure. In maize experiment, mean N_2O and CO_2 emission rates were the highest from the latter treatment but these rates were not differed from zero control in case of manures amended with farm soil or zeolite. However, mean CH_4 emissions was not differed among all treatments during the whole measuring period. The highest maize crop ANR was obtained at the beginning of grain filling stage (11–40%), however ample lower crop recoveries (8–14%) were achieved at the final physiological maturity stage. This phenomenon was occurred due to leaf senescence N losses from maize crop during the period of grains filling. The lowest losses were observed from control manure at this stage. Hence, all additives decreased the N losses from animal manure and enhanced crop N uptake thus improved the agro-environmental worth of animal manure.

1. Introduction

Management of livestock is becoming crucial in many European countries. At current, this sector is mainly accountable for emitting approximately 80% of the European ammonia (NH_3) and 10–17% of nitrous oxide (N_2O), methane (CH_4) and carbon dioxide (CO_2), in to the atmosphere (Leip et al., 2015). Around the globe, the sector estimated to contribute 5.6–7.5 $GtCO_2eq\ yr^{-1}$ of greenhouse gases (GHG) emissions during 1995–2005 (Herrero et al., 2016) whereas N_2O alone from manure management and manure after soil application was responsible for 0.21 and 0.49 $GtCO_2eq\ yr^{-1}$, respectively (Herrero et al., 2013). Likewise, in a very recent global meta-analysis study, it is found that soil applied animal manure was accountable for 32.7% increment in N_2O emission compared to the use of chemical fertilizer N alone (Zhou et al., 2017). Global warming potential of N_2O emission was 265–298 times higher compared to CO_2 up to a time scale of 100 years (EPA, 2017) and CH_4 emission from dairy manure was 8–10 times higher than CO_2 (Grant et al., 2015). Both of aforementioned gases play an imperative part in destroying stratospheric ozone layer (Akiyama and

* Corresponding author. Department of Environmental Sciences, COMSATS Institute of Information Technology, P.O Box 61100, Vehari, Pakistan.
E-mail address: muhammadimtiazrashid@ciitvehari.edu.pk (M.I. Rashid).

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Tsuruta, 2003). In addition to this, NH_3 emitted to the atmosphere can be deposited in dry or wet form to the soil or waterways and caused acidification or eutrophication of nitrogen (N) in terrestrial or aquatic ecosystems (Amon et al., 2001; Pearson and Stewart, 1993). These nitrogenous losses to the atmosphere or in the water bodies are the principle barriers of animal manure usage as fertilizer in modern climate smart agriculture. Consequently, innovative management strategies are required that may be helpful in the reduction of environmental pollution from animal manure after its application to soil for crop production and therefore help in sustaining its usage as recyclable environmental friendly fertilizer (Shah et al., 2016b; Yitbarek et al., 2017).

The NH_3 emission can be up to 100% of the ammoniacal N applied through solid cattle manure (SCM) (Huijsmans et al., 2001) to grassland. To date, only few attempts have been made for developing the practices that can reduce NH_3 emission after land application of SCM (Shah et al., 2012, 2016a, 2016b; Sommer and Hutchings, 2001; Webb et al., 2014). Immediate SCM incorporation in to the soil by plough as well as combine use of irrigation or lava meal after its surface application are well-known practices to reduce NH_3 emission (Shah et al., 2012; Webb et al., 2004, 2014). Incorporation of SCM cannot be practiced in (i) stony soils, (ii) permanent grassland, (iii) farms without powerful machines and (iv) soils that are vulnerable to erosion because of ploughing. The use of irrigation, lava meal or their combination (Shah et al., 2012) cannot be practiced in water scarce region. Besides, the above measures are only effective after soil application of SCM. So, there is a great need to design, evolve and/or evaluate effective measures that can reduce the gaseous emission or nutrient losses throughout manure management chain at farm scale (Loyon et al., 2016) to enhance overall crop N utilization.

Recently, mixing of zeolite (clinoptilolite), sandy farm soil and lava meal in animal bedding decreased the total N emission losses by 85 and 45% from animal housing and during manure storage, respectively than control manure without additives (Shah, 2013). The lava meal is rich source of Mg and P compounds while zeolite containing negative binding sites, and organic matter (SOM), silt and clay particles present in farm soil may act as absorbent of NH_4^+−N or NH_3 and thus could have potential to decrease N losses and especially NH_3 from SCM. Wightman et al. (1982) proposed the mechanisms of reducing NH_3 emission rate from the soil. They explained that clay/silt particles and SOM have negative charges in their surfaces and these complexes exchanged cations thus play an important role in NH_4^+ adsorption or fixation in clay minerals. Also, soils with pH below 6 (acidic soils) are not prone to NH_3 volatilization since at this pH mineral nitrogen is primarily found in NH_4^+−N or ionic form therefore N losses through NH_3 volatilization will be very low. Besides, crystalline-hydrated features resultant from three-dimensional zeolite structures make it a very unique and durable adsorbent of many cations (Mumpton and Fishman, 1977; Ndegwa et al., 2008). So, in the animal manure solution, NH_4^+ adsorption lessens the aqueous NH_3 (water) concentrations and thus emission of NH_3 gas (Ndegwa et al., 2008). This phenomenon will also retard the processes of nitrification as well as denitrification in manure (Zaman and Nguyen, 2010). Likewise, lava meal containing Mg and PO_4 will possibly react with NH_4^+ ions and form precipitation of struvite salt thereby reducing its availability for conversion into NH_3 gas (Ali et al., 2013; Zhang and Lau, 2007). Nevertheless, in our best of the information, no single study was found in the literature for elucidating the subsequent influences of bedding additives on reducing NH_3 or N_2O emission and improving crop N uptake after soil application of SCM. Therefore, the aims of this follow-up research were: (i) exploring the mitigative potential of animal bedding additives like lava meal, sandy farm soil and zeolite on NH_3 emission when SCM was surface-spread on grassland and the aforementioned gas as well as N_2O, CH_4 and CO_2 emissions after field incorporation of SCM before sowing of maize crop in an arable field, (ii) to calculate the apparent herbage and maize crop N recovery (ANR) from the manures, and (iii) to understand and explain the N dynamics in maize through crop N uptake or ANR with time from the commencement of grain filling phase to the stage when physiological maturity of maize was reached.

2. Materials and methods

The study was executed at Droevendaal organic Farm (55°99′N latitude and 5°66′E longitude). This is an experimental and training farm of the Wageningen University and Research Centre, located very close to the university's main campus in Wageningen, the Netherlands.

2.1. Production of animal manure and its storage

The animal housing system of the farm was consisted of different sloping-floor barn units. It was a naturally ventilated and normally wheat straw was being used as bedding material. In this housing systems, we used four bedding treatments, i.e. i) control treatment with only straw application ii) straw + zeolite, iii) straw + local farm sand soil, iv) straw + lava meal. A barn unit was consisted of a 42 m^2 bedding area and 21 m^2 of manure alley where young bulls (beef) were kept in a group of eight. The treatments were applied on surface of bedding in barn units three times in a week. These amounts were proportional to 5 kg straw dosage daily per livestock unit (LU), i.e. zeolite 10% (0.5 kg LU^{-1}), 20% of lava meal (1 kg LU^{-1}) and 33% of local farm sand soil (1.7 kg LU^{-1}) that was collected from the top soil layer. Table 1 presents chemical composition of zeolite, lava meal and sand soil used as bedding additives in this study. From manure alley, SCM was collected manually two times, early morning and late afternoon. The manure collection was carried out using a hand scraper during a collection period of 80 days. After weighing, the manure from each treatment was stockpiled inside a roofed building as a separate heap. At the end of collection, the manure was further stored for 80 days at the same place. The complete details with respect to housing and storage phases can be consulted from Shah (2013). Chemical composition of SCM at the time of field application is presented in Table 2.

2.2. Solid cattle manure application

2.2.1. Experimental grassland field (Expt. 1)

At grassland site, circular plots were selected on 16 June 2010 that were previously mown through motorized mower. Each plot diameter was 3 m (Fig. 1a), where 400 kg N ha^{-1} untreated and additive amended SCMs were spread on the surface. The treatments were applied in triplicates in a completely randomized block design. These treatments include i.e., negative control (unfertilized plot), positive control (untreated SCM), lava meal amended SCM, zeolite amended SCM and local farm sandy soil amended SCM.

After treatments application, the grass was harvested three times during 5 months of herbage growth period. The first harvest was done on 5th August, followed by second at 30 September and the last on 18 November 2010. A motorized mower with 0.9 m width of cutting bar was used to cut the herbage sward of each circular plot from an area of 0.9 m × 2 m at 4 cm stubble height from the soil surface during each grass harvest. Border effects were avoided by harvesting all plots from the inner side. Grass was weighed in field and the herbage weight of each field was recorded to calculate fresh herbage yield. After mixing the whole grass, an

Table 1
Chemical characteristics and application rate of the additives used in animal bedding.

Additive	Application rate	Total N	Inorganic N	[b]OM	P_2O_5	MgO	[c]CEC	pH- $CaCl_2$
	(kg [a]LU^{-1} day^{-1})	(g kg^{-1} DM)					(cmol kg^{-1})	
Zeolite	0.5	0.001	0	0	0.2	0.9	90	7.8
Farm topsoil	1.7	1.2	0.13	29	0.4	n.d.	2	4.9
Lava meal	1.0	0.002	0	0	10.0	85.0	12	7.9

n.d., Not determined.
[a] Livestock unit.
[b] Organic matter.
[c] Cation exchange capacity.

Table 2
Chemical characteristics of the untreated control and additives amended solid cattle manures used for application in grassland and arable field.

Treatment	DM[a]	OM[b]	Ash	N_{total}	N_{inorg}	N_{inorg}/N_{total}	C/N ratio	pH-$CaCl_2$
	(g kg^{-1})	(g kg^{-1} DM)				(%)		
Control	197	828	172	27	1.7	6	15	8.1
Zeolite	196	739	261	30	2.8	9	12	8.6
Farm topsoil	217	620	380	21	2.6	10	15	8.6
Lava meal	205	705	295	25	1.7	7	14	8.3

[a] Dry matter.
[b] Organic matter.

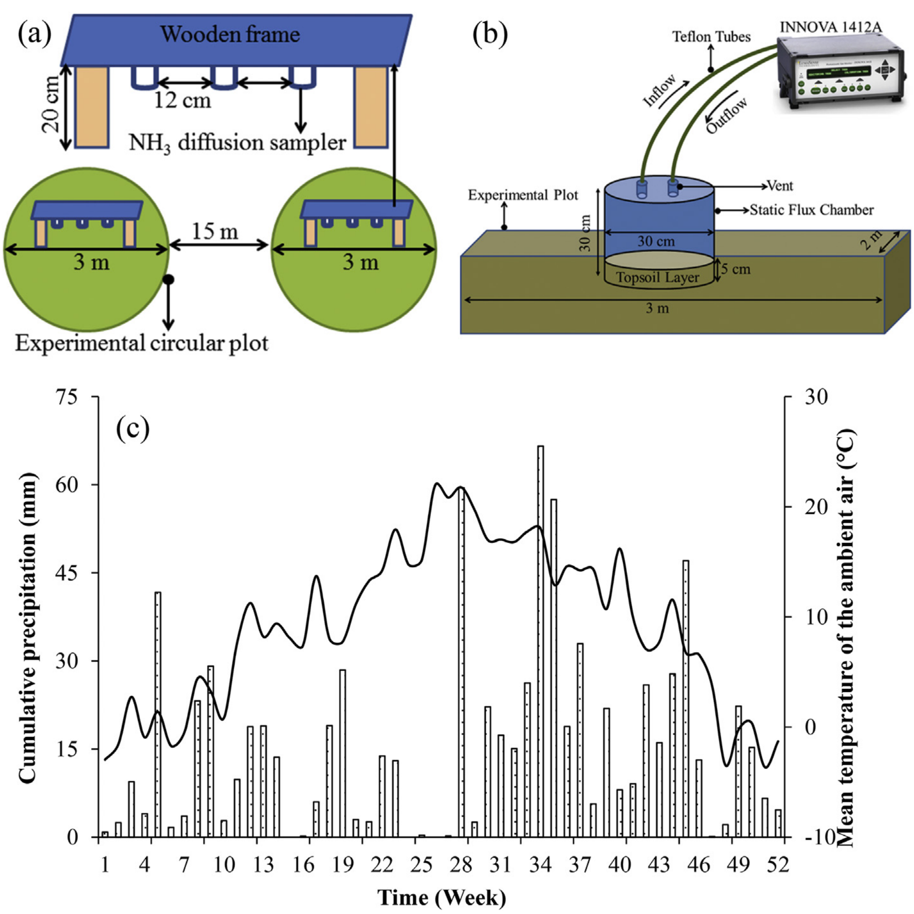

Fig. 1. Schematic diagram of experimental setup showing NH_3 gas collection through passive flux samplers in grassland (a) and greenhouse gaseous emissions measurement using INNOVA gas monitor in maize land experiment (b). Mean weekly temperature (solid line) as well as cumulative rainfall (bars) during experimental year 2010 (c).

auger was used to take a representative herbage sub-sample of ~200 g. Herbage DM yield was determined by oven drying all samples at 70 °C for two days (Sharkey, 1970). Subsequently, the grinding mill was used to grind the samples by passing them through 1 mm mesh screen. Afterward, the ground materials were subjected to N total analysis through Kjeldahl digestion method

(MAFF, 1986). Leftover grass in each circular plot was cut at same stubble height and removed from the study area after each harvest.

2.2.2. SCM application to arable land (Expt. 2)

The recommended dose 170 kg N ha^{-1} of untreated and additive amended manures were mechanically incorporated at above 10 cm soil layer of an arable field at the same farm. Each plot had an area of 15 m × 4.5 m where same treatments of Exp. 1 were applied in four replicates by using a completely randomised block design. After one week of manure application and seedbed preparation, silage maize (cv. Lapriora) seeds at the rate of 11 plants m^{-2} crop density were manually sown at 6 cm soil depth. Each plot consisted of six rows and the distance between two rows was 75 cm. Manual weeding was carried out at regular intervals and weeds were mixed in the soil to avoid nutrient loss from the field throughout the vegetative crop growth period.

We studied the N dynamics of the maize crop with time by determining N uptake or ANR from the manure treatments. For this purpose, randomly selected ten maize plants from the inner rows (2 and 5) were harvested manually with sharp knife at ground level after 55 days (juvenile stage) and at the beginning of grain filling (after 98 days) of the treatment application. After 131 days, at crop growth physiological maturity stage during final harvest, the remaining all plants in rows 3 and 4 were mechanically harvested by maize harvester who cuts plants at a height of 10 cm from the ground surface. Thereafter, the total remaining plants per plot were counted. The time duration of these crop growth phases were adapted from Gungula et al. (2003). A difference in DM or N uptake yields due to change in stubble height (4 vs. 10 cm) for the plant cuttings was corrected by ~4% of their respective yields (Shah et al., 2016b). To eliminate the border effects, 1 and 6 rows were not utilised for the determination of plant growth and yield parameters.

The harvested aboveground biomass of maize crop from each plot was weighed in the field to determine the fresh yield for each harvest. Afterward, all plants were cut into small pieces then crop biomass chopped parts were mixed thoroughly to make a representative sample and from this approximately 500 g material was sampled and taken into laboratory for further analyses. Crop DM yield was measured by drying each sample in oven at 70 °C for 48 h, subsequently the samples were passed through grinding mill with 1 mm mesh screen and total N content in plant was determined by Kjeldahl digestion (MAFF, 1986).

2.3. NH_3 measurement from surface applied manure on grassland (Expt. 1)

Passive diffusion flux samplers were used to measure NH_3 air concentration in the grassland. These samplers were vertically installed in the centre of each plot at a height of 20 cm above grassland surface (Fig. 1a) immediately after application of manure and remained there for a time period of consecutive three days (Kirchner et al., 1999). Diffusion samplers (three) were arranged in a wooden frame (self-designed) in such a way that open side of each sampler was kept downward towards the soil surface and the distance between two samplers was 12 cm (Fig. 1a). In akin experimental setup, Shah et al. (2012) assumed that NH_3 emission from the applied manure would be proportional to the mean NH_3 concentration measured in air present at 20 cm height from each plot (Fig. 1a). This assumption was made after correcting background concentration (Shah et al., 2012). A distance of 15 m was kept between two adjacent plots to avoid the mixing of NH_3 among experimental units (Malgeryd, 1998). The trapping of NH_3 was carried out in sampler steel grids that were coated with 60 μL sulphuric acid (10% (w/v)). After 3 days of installation, the samplers were removed from each plot and taken to the lab, since most of the NH_3 emission occurs during this time span of animal manure application on soil surface (McGinn and Sommer, 2007). The stainless steel grids capturing NH_3 were removed from each sampler and rinsed by 5 ml milli-Q water. Subsequently, solution from the grids was subjected to the analysis of NH_4^+–N content (Houba et al., 1989). Then, the mean concentration (μg m^{-3}) of NH_3 was estimated from the formula of Hofschreuder and Heeres (2002) after some modifications:

$$CN_{NH3} = \frac{Q_{NH4^+} \times Z_{lt}}{D_{co.} \times A_t \times T} \times \frac{17}{18} \quad (1)$$

$$D_{co.} = \left(\frac{Temp^{1.75}}{Pres}\right)\left(1.1265 \times 10^{-9}\right) \quad (2)$$

where CN_{NH3} represents concentration (μg m^{-3}) of NH_3, QNH_4^+ indicates the NH_4^+–N amount (μg) measured in washed water, Z_{lt} is tube length of $4.1*10^{-2}$ m, $D_{co.}$ denotes diffusion coefficient which is $2.28*10^{-5}$ m^2 s^{-1}, A_t representing the internal tube area ($7.85*10^{-5}$ m^2), T denotes the time of sampling taken in s (seconds), Temp representing the temperature of air in Kelvin and Pres denotes air pressure in bar.

2.4. Gaseous fluxes measurement (Expt. 2)

The fluxes of CO_2, CH_4 and N_2O were quantified after incorporation of untreated and treated animal manures in maize field. For this purpose, a flux chamber (static) where gas is internally circulated in a system that was connected through two Teflon tubes with 3 mm inner diameter to INNOVA (Fig. 1b), a photoacoustic gas monitor (1412A, Denmark). The poly vinyl chloride (PVC) flux chamber had 0.3 m internal diameter with a sharp edged bottom and is also known for its very low capacity of NH_3 adsorption (Shah et al., 2006). The sharp edge help us to press down the flux chamber 4–5 cm deep into the soil at each measurement event to avoid any gaseous leakage (Fig. 1b). The gases concentrations were recorded for 5–10 min at two or three random locations from each plot after incorporation of manure into the soil. The instrument has certain detection limits for NH_3 (200 ppb), N_2O (30 ppb), CH_4 (100 ppb) and CO_2 (5100 ppb). The gas-monitoring instrument was calibrated twice during experimental period. Firstly, in April 2009 and second calibration was carried out in May 2010 by ENMO services (Belgium). According to the company, the instrument was performing well at both occasions. The built-in compensation in the instrument will help to avoid CO_2 and water vapour cross interferences with other gases such as CH_4, NH_3 and N_2O. The average errors during validation measurements for CO_2, CH_4, NH_3 and N_2O was 5, -2, -13, and −12, respectively (Predotova et al., 2010) in a similar setup as installed in our study. Therefore, these errors may also led to underestimation of gaseous N losses during our measurement.

In arable cropping experiment (Expt. 2), dense rain falling happened immediately after animal manure was incorporated into the soil (Fig. 1c), which also continue later on. Such instantaneous weather events after fertilizer application expected to decrease the gaseous emissions from animal manure, which possibly led to eliminate the effect of bedding additives. To avoid this happening, measurement of gases were carried out in the same field one week later in a parallel experiment where same treatments were applied in 2 m × 3 m area plots in a completely randomised blocks design in triplicates. Using INNOVA, concentrations of gases were measured from each plot, immediately after animal manure incorporation in to the soil, that start at 9:00 a.m. in a similar setup as described above for three consecutive days.

2.4.1. Gaseous fluxes calculation (Expt. 2)

Biochemical processes in organic matter derive CO_2, CH_4 and N_2O production (Laguë, 2003) that resulted in linear increase of gaseous concentrations in the flux chamber (Expt. 2). Consequently, a linear slope, which is defined as S_2, fitted between the data set of concentration (mg m^{-3}) of gases (CO_2, CH_4 or N_2O) and time (min) signifies the instant rate of gases emission.

The following equation was used to calculate the emissions rates (R) of CO_2, CH_4, NH_3 or N_2O in mg m^{-2} day^{-1}:

$$R = S_{i=1,2} \times \frac{V_{TA}}{A_f} \times 1440 \quad (3)$$

where, a conversion factor of 1440 was used for up-scaling time in a minute into a day. S_1 represents an estimated instant rate of NH_3 emission in mg m^{-3} min^{-1}. S_2 indicates a linear slope fitted among concentration (mg m^{-3}) data set of CO_2, CH_4 or N_2O and time (min^{-1}). V_{TA} shows air volume (total) inside whole monitoring system ($1.82*10^{-2}$ m^3) during measurement period and A_f signifies the covering surface area ($7.07*10^{-2}$ m^2) of the flux chamber. V_{TA} is flux chamber reduced volume ($3.18*10^{-3}$ m^3) after soil insertion in the chamber minus internal total volume ($2.12*10^{-2}$ m^3), afterward the resultant value was added to the PVC tubes internal volume ($1.41*10^{-5}$ m^3) and volume of air present inside gas monitor ($1.4*10^{-4}$ m^3).

2.5. Crop apparent N recovery (Expts. 1 and 2)

Both crops ANR was calculated by using following equation:

$$ANR\,(\%) = \frac{(N_c \times DM_c) - (N_{C0} \times DM_{C0})}{N_{app}} \times 100 \quad (4)$$

where N_c representing the N content in kg N per Mg DM found in crops (maize or herbage) biomass in fertilized plots. DM_c signifies DM yield (Mg ha^{-1}) of the maize or grassland in the plots fertilized by animal manure. N_{C0} and DM_{C0} are the N content (kg N (Mg $DM)^{-1}$) or DM yield (Mg ha^{-1}), respectively of maize or grassland biomass in unfertilized plots, moreover N_{app} is applied N (total) in kg ha^{-1} through animal manure in maize or grassland fields.

2.6. Soil, plant and manure analysis

From the top 30 cm of each heap, a small amount of the animal manure was sampled from random twenty-five diverse positions and laterally a composite sample was made by mixing them thoroughly. In total three composite samples were taken from each manure heap just before its field application to grassland or maize crop. These samples were taken into the lab and frozen at −18 °C to avoid N transformations until further use. Afterwards, these samples were defrosted at ~20 °C (room temperature) before performing any analysis and then an automated machine was used for chopping (≤2 cm pieces) the manure containing straw particles (Sommer and Dahl, 1999). Laterally, DM content of all these manure samples were determined at 105 °C after drying in oven for 24 h. Immediately, raw ash content in these samples were determined after placing them in muffle furnace at 525 °C for 6 h by using loss on an ignition method. Kjeldahl digestion method was carried out for determining N content in all manure samples (MAFF, 1986). NH_4^+–N and NO_3^--N content was determined by extracting these nutrients from the animal manure samples with 0.01 M $CaCl_2$ at a ratio of 1:10 by using segmented-flow method (Houba et al., 1989) and pH through inoLab pH meter (WTW GmbH & Co. KG, Germany).

A ball-mill (Restech, Germany) was used for grinding the dried samples of maize crop that were laterally extracted with 5 mL ethanol (80%) at 80 °C for 20 min. After centrifuging, the supernatant was removed to get pellets of residues that were subsequently washed with 80% ethanol thrice before vacuum drying. This procedure was carried out to remove soluble sugars, already present in the $CaCl_2$ extracted plant material. The latter helps in accurately analysing starch content that was converted to glucose. During this process, enzymes were extracted in water with thermostable α-amylase (Serva 13452) at 90 °C and afterward the extraction was carried out in a mixture of 50 mM citrate buffer (pH = 4.6) and amyloglucosidase (Fluka 10115) at 60 °C for the conversion of starch to glucose. The extracts were put in CarboPac1 (250 × 2 mm) column and subjected to HPLC (Dionex ICS5000). Before the starch analysis, NaOH (100 mM) and sodium acetate (12.5 mM) solutions were used to elute HPLC column. The dried crop samples were extracted with H_2SO_4 to gravimetrically determine cellulose, hemicellulose or lignin content in the cell wall of maize crop samples by using NDF/ADF method as described in Dence (1992).

Soil in maize experiment (Expt. 2) was sampled from each treatment to determine NH_4^+–N and NO_3^--N content, collectively called as mineral N, on five occasions. The first sampling was carried out just before the incorporation of animal manures into the soil, and then at 2, 55, 98 and 131 days of sowing of maize. Soil was sampled at ten random locations from each plot at a depth of 0–30 and 30–60 cm with soil auger during each sampling. Afterward, these samples were oven dried at 40 °C for 2 days and 1 mm mesh of grinding mill was used to grind them. Then, soil samples were subjected to mineral N measurement through segmented-flow analysis (Houba et al., 1989) as described above for the determination of this parameter in manure samples.

2.7. Statistical analysis

The NH_3 concentrations, all gaseous fluxes, DM yield, N uptake and ANR measured from grassland (Expt. 1) and maize land (Expt. 2) were statistically evaluated by analysis of variance (ANOVA) with a statistical software package for social sciences (SPSS 17.0, IBM, USA). Multiple comparisons among treatment were statistically analysed by Duncan's multiple range tests. The significance of these tests were performed at 5% probability.

Similarly, the significance difference among all manure treatments for starch or cell wall consisted of cellulose, hemicellulose or lignin content at various maize crop growth stages (Expt. 2) were tested statistically by SPSS as described above. Linear regression was carried out to test the relationship between mineral N content in 0–30 cm soil depth and maize N uptake after 55 and 98 days of crop growth.

3. Results

3.1. Measurement of gaseous emissions (Expts. 1 and 2)

Fig. 2 presents the average NH_3 concentrations after correcting mean backgorud value from manured grassland plots (Expt. 1). The mean NH_3 concnetrations in all additive treated manures were 69% lower as compared to the control (untreated-manure).

The concentration of NH_3–N or N_2O–N that were emitted from the treatments to the atmosphere restricted to only <1% or ~1% of the applied mineral N content in the manures, respectively (data not presented). The highest rates of N_2O or CO_2 emission were observed from the untreated manure, while the emissions of these gases from the zeolite or sandy soil amended manures were similar to zero treatment, where no manure was applied (Table 3). All these

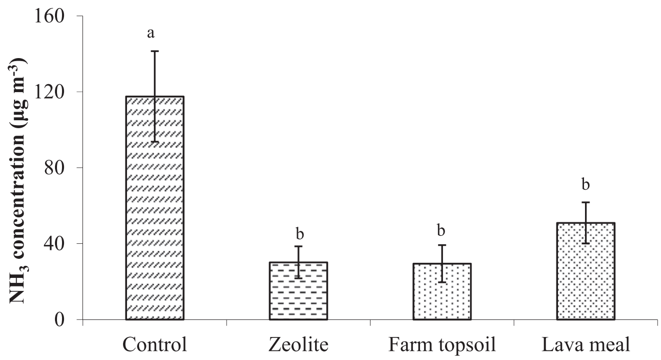

Fig. 2. Average concentration of NH_3 in air at 20 cm height from the soil surface of experimental plots after manure application during three consecutive days (Expt. 1). The data of this gas was corrected for the mean measured background concentration. Error bars represented mean's standard error (±). Small letters on bars represent the significant difference (P < .05) among treatments.

Table 3
Mean CO_2, CH_4, and N_2O emission rates after field incorporation of animal manures during three days measurement period (Maize crop Expt. 2).

Treatment	N_2O	CO_2	CH_4
	(mg m^{-2} day^{-1})		
Zero	$12^{a\dagger}$	15576^{a}	19^{a}
Control	17^{b}	22701^{c}	24^{a}
Zeolite	13^{ab}	17265^{ab}	26^{a}
Farm topsoil	15^{ab}	16354^{ab}	17^{a}
Lava meal	16^{ab}	20531^{bc}	18^{a}

†indicates the significant difference among the mean values in the same column (P < .05).

effects were only observed on day 1 during three days measurement period (Fig. 3a and b). Besides, no difference in average rates of CH_4 emission among all treatments were observe during the whole measurement period, indicating that any treatment did not significantly influence emission of this gas (Table 3; Fig. 3c).

3.2. Crop yield and N content parameters (Expts. 1 and 2)

Table 4 presents DM yield and N parameters such as crop uptake or apparent recovery (ANR) from three cuts of grassland (Expt. 1) as well as from three growth stages of maize crop (Expt. 2). Additives amended manure ~42% increased the total DM yield, ~68% of N taken up by crop and 139% of ANR than untreated manure in grassland (Table 4; Expt. 1), however multiple comparisons showed that these parameters were not significantly differed among the additive amended manure treatments (P > .05). The herbage ANR was 11% from control manure, while more than twofold increment in this parameter was observed in additives (ranged 25–28%) amended manures (Table 4).

In Expt. 2, additives amended manures enhanced maize crop ANR by 3–4 times at beginning of grain filling stage (Table 4). During this 33 days' time interval, the respective loss in NDF and N from the DM of their aboveground biomass in additive amended manure treatments was 1500 and 25 kg ha^{-1} (Fig. 4a and b; Tables 5a and b). So, no difference was observed in maize ANR among the additive amended and untreated manures at physiological maturity stage (Expt. 2; Table 4). Therefore, there was a very small difference among manure treatments in starch content at this stage. At grain filling phase, aboveground biomass DM content were increased in the zero, untreated control manure and lava meal

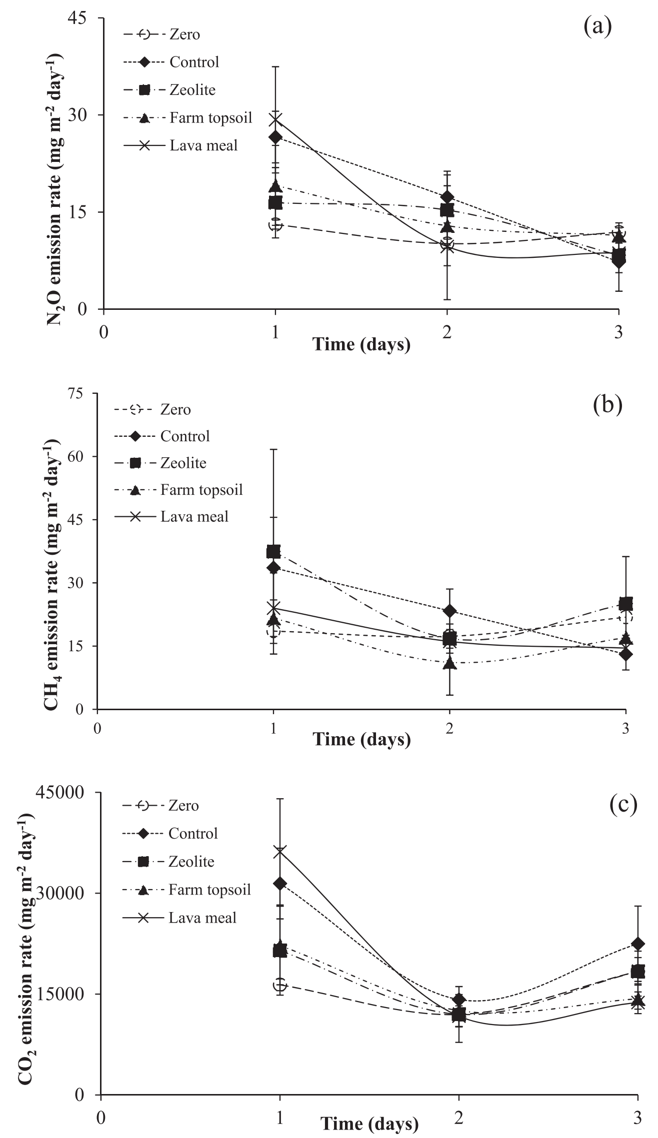

Fig. 3. Mean (a) N_2O, (b) CH_4 and (c) CO_2 emissions rates (mg m^{-2} day^{-1}) measured after manure incorporation to soil during three consecutive days (Expt. 2). Error bars represented mean standard error (±).

amended manure treatments, this parameter was decreased in zeolite-amended manure, and remained unchanged in sandy soil-amended manure treatment (Fig. 4c and d).

3.3. Mineral N dynamics in maize cropped soil (Expt. 2)

Mineral N content of 0–30 cm top soil and 30–60 cm sub soil layers of maize crop were presented in Fig. 5 after 2, 55, 98 and 131 days of sowing of maize. All treatments increased mineral N content in the top soil until day 55 after end of juvenile phase. Subsequently, a strong decrement in the mineral N content was observed (~63%) until grain filling phase during 55–98 days that was followed by partially no change in the soil mineral N status up to 131 days at physiological maturity. Therefore, the increment in N content in maize crop was positively correlated with net decline in soil mineral N content from the 0–30 cm depth during a period of 43 days. This correlation was occurred during termination of juvenile and beginning of grain filling stage (Fig. 6).

Table 4
Total herbage (three harvests, Expt. 1) and maize (three growth stages, Expt. 2) dry matter (DM) yield, N uptake and apparent N recovery (ANR) from negative (Zero) and positive (untretned manure) control and additives amended solid cattle manure.

Treatment	Herbage			Maize								
	Total of 3 cuts			End of the juvenile			Start of the grain filling			Physiological maturity		
	DM yield	N uptake	ANR	DM yield	N uptake	ANR	DM yield	N uptake	ANR	DM yield	N uptake	ANR
	(Mg ha^{-1})	(kg ha^{-1})	(%)	(Mg ha^{-1})	(kg ha^{-1})	(%)	(Mg ha^{-1})	(kg ha^{-1})	(%)	(Mg ha^{-1})	(kg ha^{-1})	(%)
Zero	2.2^{a}†	43^{a}	–	2.2^{a}	68^{a}	–	11.2^{a}	156^{a}		13.9^{a}	166^{a}	
Control	3.6^{b}	88^{b}	11^{a}	2.3^{a}	70^{a}	2^{a}	12.6^{a}	174^{b}	11^{a}	14.8^{ab}	179^{b}	8^{a}
Zeolite	5.1^{c}	148^{c}	26^{b}	3.2^{c}	101^{c}	21^{c}	16.3^{b}	230^{d}	44^{c}	15.1^{b}	189^{b}	12^{a}
Farm topsoil	4.9^{c}	142^{c}	25^{b}	2.9^{b}	89^{b}	13^{b}	15.5^{b}	206^{c}	30^{b}	15.5^{b}	189^{b}	14^{a}
Lava meal	5.3^{c}	154^{c}	28^{b}	3.0^{bc}	92^{b}	14^{b}	14.8^{b}	208^{c}	30^{b}	15.9^{b}	188^{b}	13^{a}

†indicates the significant difference among the mean values in the same column (P < .05).

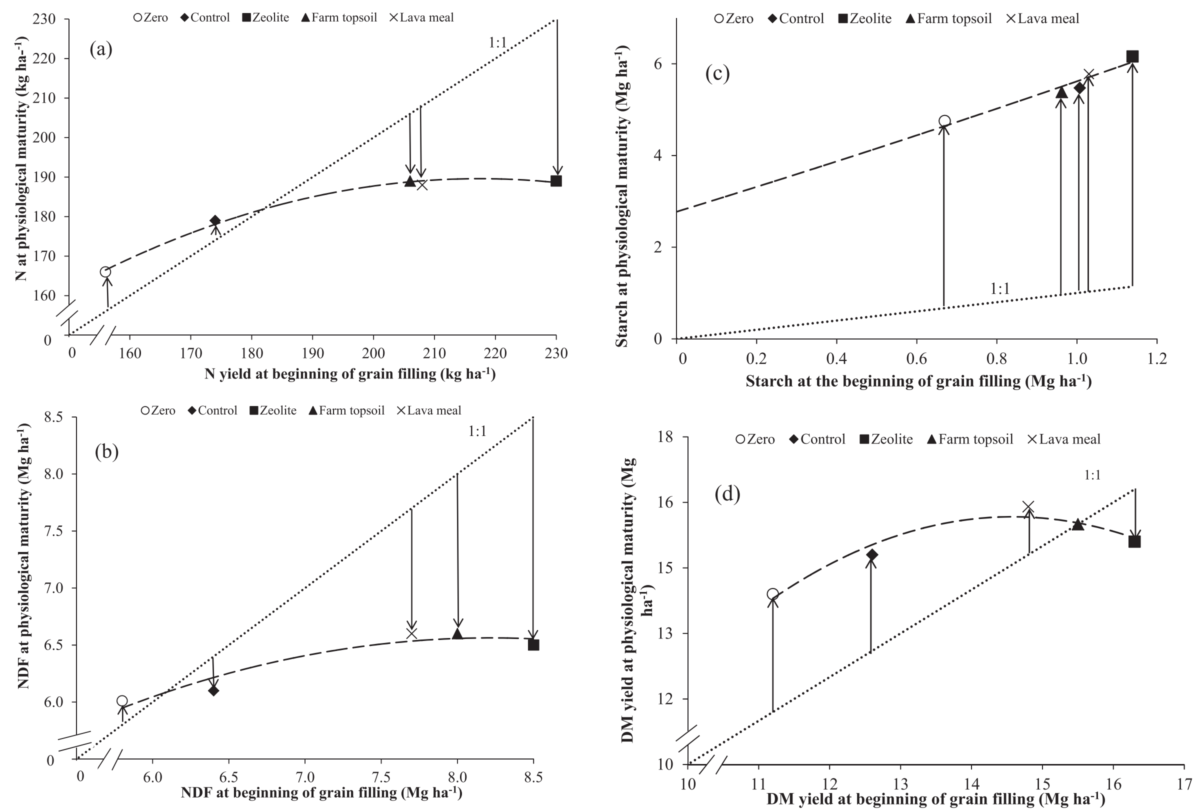

Fig. 4. Variation in (a) Nitrogen (N), (b) Neutral detergent fibre (NDF), (c) starch and (d) dry matter (DM) yields of maize crop between beginning of grain filling growth phase and physiological maturity (Expt. 2). 1:1 relationship and trend is represented by dotted and dashed lines, respectively. A decline in yields indicated by downward arrows and increment by upward arrows.

Table 5a
Silage maize starch, dry matter (DM) yields and nitrogen (N) uptake at different growth stages (Expt. 2).

Growth stage	Zero			Control			Zeolite			Farm topsoil			Lava meal		
	DM yield	N uptake	Starch yield	DM yield	N uptake	Starch yield	DM yield	N uptake	Starch yield	DM yield	N uptake	Starch yield	DM yield	N uptake	Starch yield
	(Mg ha^{-1})	(kg ha^{-1})		(Mg ha^{-1})	(kg ha^{-1})		(Mg ha^{-1})	(kg ha^{-1})		(Mg ha^{-1})	(kg ha^{-1})		(Mg ha^{-1})	(kg ha^{-1})	
End of juvenile	2.2^{a}†	68^{a}	5^{a}	2.3^{a}	70^{a}	6^{a}	3.2^{a}	101^{a}	7^{a}	2.9^{a}	89^{a}	6^{a}	3.0^{a}	92^{a}	7^{a}
Grain filling	11.2^{b}	155^{b}	670^{b}	12.6^{b}	174^{b}	1007^{b}	16.3^{b}	230^{c}	1139^{b}	15.5^{b}	206^{c}	962^{b}	14.8^{b}	208^{c}	1031^{b}
Physiological maturity	13.9^{c}	166^{b}	4753^{c}	14.8^{c}	179^{b}	5474^{c}	15.1^{b}	189^{b}	6160^{c}	15.5^{b}	189^{b}	5386^{c}	15.9^{c}	188^{b}	5777^{c}

†indicates the significant difference among the mean values in the same column (P < .05).

Table 5b
Neutral detergent fibre (NDF) yield of silage maize at different growth stages (Expt. 2).

Growth stage	Zero			Control			Zeolite			Farm topsoil			Lava meal		
	NDF			NDF			NDF			NDF			NDF		
	Cellulose	Hemicellulose	Lignin	Cellulose	Hemicellulose	Lignin	Cellulose	Hemicellulose	Lignin	Cellulose	Hemicellulose	Lignin	Cellulose	Hemicellulose	Lignin
	(kg ha^{-1})														
End of juvenile	563^{a}†	605^{a}	99^{a}	577^{a}	634^{a}	107^{a}	837^{a}	923^{a}	118^{a}	746^{a}	810^{a}	137^{a}	771^{a}	826^{a}	112^{a}
Grain filling	2712^{b}	2738^{b}	340^{b}	3041^{c}	3190^{b}	213^{b}	3980^{c}	4017^{c}	523^{c}	3802^{c}	3627^{c}	591^{c}	3622^{c}	3547^{c}	510^{c}
Physiological maturity	2713^{b}	2948^{c}	349^{b}	2767^{b}	3063^{b}	308^{c}	3003^{b}	3173^{b}	317^{b}	3050^{b}	3127^{b}	378^{b}	3069^{b}	3149^{b}	388^{b}

†indicates the significant difference among the mean values in the same column ($P < .05$).

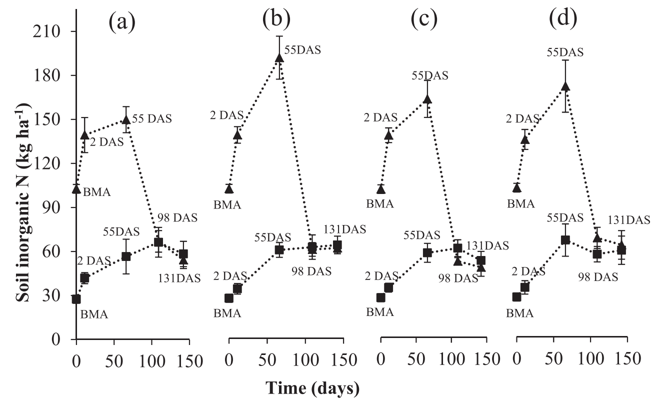

Fig. 5. Mineral N content at soil depths of 0–30 cm (triangles) as well as 30–60 cm (squares) after animal manure incorporation to the soil (Expt. 2) (a) untreated (control) and (b) amended with zeolite, (c) sandy soil or (d) lava meal at five time intervals before application of animal manure (BMA), and after 2, 55, 98 and 131 days of sowing (DAS). Error bars represented mean's standard error (±).

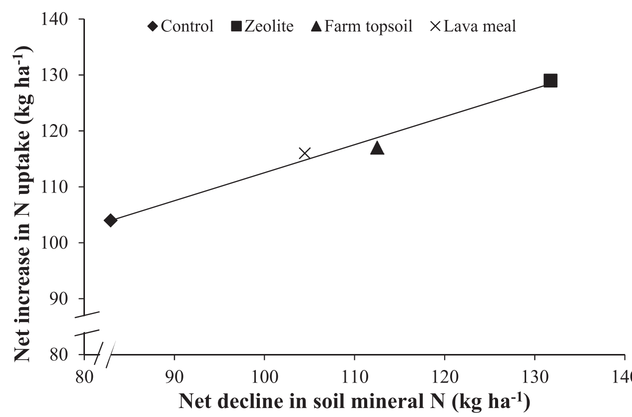

Fig. 6. Correlation between decline in mineral N content at soil layer 0–30 cm and upsurge in maize N uptake from the end of juvenile stage (55 day) to the beginning of grain filling (98 day) stage ($P < .05$; $y = 0.50x + 62.41$; $R^2 = 0.98$).

4. Discussion

4.1. Gaseous emissions

As expected, additives amended manures decreased the NH_3, CO_2, CH_4 and N_2O emissions after their soil application. According to our best of the knowledge only Shah et al. (2012) reported the influence of lava meal mixing in cattle manure to NH_3 emission reduction. They found that lava meal reduced this gas from the soil by 46%. However, these authors did not study the effect of this treatment on GHG emission. Therefore, this is the first study in its kind showing the effects of bedding additives as a mean of reducing GHG emissions in addition to NH_3 from the manure after its soil application. The emitted concentration of NH_3–N and N_2O–N were limited to ~1% of applied mineral N from all treated manures after their incorporation into the soil, respectively (Expt. 2). Reduction of various forms of nitrogen emission due to different additives may be ascribed to adsorption of NH_4^+ on their exchange sites as these have high cation exchange capacity (Table 1). This phenomenon may decrease the concentration of aqueous NH_3 (water) in the manure solution and hence reduce the NH_3 gas production from animal manure (Ndegwa et al., 2008). Moreover, all these additives and especially zeolite may also retard the occurrence of nitrification and denitrification processes in the soil that can also help in the reduction of N_2O emission (Zaman and Nguyen, 2010). Further decrement in N losses pathways may possibly be attributed to the physical barriers in soil for mass transport of gases throughout the matrix (Webb et al., 2004). Nevertheless, this could not be the case for the treatment where manure was treated with lava meal, since CO_2 emission on day 1 in this treatment was tended to be higher than control (Fig. 3). Alternatively, animal manure mixing in the soil may potentially change the N losses pathways over a long period. For example, Powell et al. (2011) found an increment in leaching of N when cattle manure was incorporated into the soil. However, in current study, adsorption of NH_4^+–N in additive amended manure may restrict the N leaching from soil. Also, animal manure was incorporated at ~10 cm soil depth in our study that may led to denitrification process (chemical and/or biological) and conversion of N_2O to N_2. This process is mainly influenced by the increment in gases diffusion pathway length in soil matrix, as well as carbon content, pore space filled by water and nitrate availability. In our study, latter soil parameter, amount of carbon content applied through manure and soil moisture content was similar in all treatments. Therefore only gaseous diffusion pathways would affect the denitrification process and hence less N_2O emission from the manures was occurred (Thorman et al., 2007). However, gaseous measurements in our study was carried out for consecutive three days, so long term influence of manure incorporation or additives amended manures on N losses through denitrification processes were not under the scope of this study.

4.2. Soil mineral N in maize crop (Expt. 2)

The increment in soil mineral N content up to day 55 after manure incorporation to soil indicates that OM mineralization in animal manure was occurred leading to high soil mineral N availability (Fig. 5). This indicated that N mineralization rate of OM present in manure was much higher compared to crop N uptake in course of initial growth stage. However, during 55–98 days, at peak growth period, a net decrement in mineral N content indicated that most of the plant available N was utilized/taken up by crop (Fig. 5) indicating higher plant N demand than supply. Consequently at this stage, there was a linear relationship between net decline in mineral N in the soil layer of 0–30 cm and increment in crop net N uptake ($P < .05$; $R^2 = 0.98$; Fig. 6). However, at the end of experiment, initial (BMA) or final mineral N content at day 131 in the soil at 0–30 cm soil depth was not differed significantly among all treatments (Fig. 5) but N taken up by crop in additive amended manure was higher than control during this time interval (Table 4). Besides, the crop N uptake was not differed among untreated or bedding additive amended manures at physiological maturity (Table 4).

4.3. Herbage and maize apparent N recovery

All additive amended manures increased both herbage and maize crops ANR when compared to untreated manure ($P < .05$) (Table 4). The increment in crop ANR in both crops due to additive amended manures was mainly ascribed to reduction in N losses from animal manure through the whole management chain (Shah, 2013). The additives used in animal bedding lessen the losses of N during housing as well as storage, and henceforth retained most of the excreted N in animal manure till its final application in the soil (Shah, 2013). Moreover, these amendments possibly prevented the nitrification, denitrification or N leaching from the manure by adsorbing most of the available NH_4^+–N on the exchange site of zeolite or lava meal therefore much of the retained N was ended up as crop uptake.

The economic analysis was carried out to determine cost benefit ratio of the additives used in our experiment. The costs of zeolite and lava meal was calculated by multiplying their purchase cost (0.25 € per kg when bought in bulk quantities) with the amounts needed (315 and 523 kg, respectively) to reduce 1 kg of NH_3–N emission. According to our estimate the costs for reducing 1 kg of NH_3–N losses through animal housing by using the sandy textured soil as bedding additive was only 10 € compared to 79 € for zeolite and 131 € for lava meal. Based on this analysis, it is concluded that sandy soil is a readily available and cost-effective resource to mitigate NH_3–N emissions through manure management chain.

5. Conclusions

Field application of additive amended manure remarkably reduced NH_3 emissions. The reduction in N losses were resulted in 2 and 3 times higher ANR of herbage and maize crops (at the beginning of grain filling), respectively. In maize crop, the decrement of ANR between beginning of grain filling phase and physiological maturity stage was ascribed to enhanced losses of N by leaves senescence (death) which mainly occurred during these stages in heaviest crops. Hence, our study successfully demonstrated that using additives during animal bedding have great potential for improving cattle manure agro-environmental value through reduction of gaseous N losses and improvement in crops N uptake. Among additives, sandy soil estimated to be an economical and more practical option for mitigating ammonia emission at farm level.

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