

**PERIODICO di MINERALOGIA**  
*established in 1930*

*An International Journal of  
MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY,  
ORE DEPOSITS, PETROLOGY, VOLCANOLOGY  
and applied topics on Environment, Archaeometry and Cultural Heritage*

## **Ammonium-exchanged zeolite preparation for agricultural uses: from laboratory tests to large-scale application in ZeoLIFE project prototype**

Barbara Faccini<sup>1,\*</sup>, Dario Di Giuseppe<sup>1</sup>, Daniele Malferrari<sup>2</sup>, Massimo Coltorti<sup>1</sup>,  
Federica Abbondanzi<sup>3</sup>, Tiziana Campisi<sup>3</sup>, Angela Laurora<sup>2</sup> and Elio Passaglia<sup>2</sup>

<sup>1</sup> Dipartimento di Fisica e Scienze della Terra, Università di Ferrara, Via Saragat 1, 44122, Ferrara, Italy

<sup>2</sup> Dipartimento di Scienze Chimiche e Geologiche, Università di Modena and Reggio Emilia,  
Via Giuseppe Campi 183, 41125, Modena, Italy

<sup>3</sup> Environmental Research and Service Center (CRSA-MED INGEGNERIA),  
Via Putinati 71/C, 44123, Ferrara, Italy

\* Corresponding author: [barbara.faccini@unife.it](mailto:barbara.faccini@unife.it)

### **Abstract**

Water nitrate pollution is one of the biggest environmental issues in all those Countries whose economy is largely based on agriculture. Limiting the nitrogen compound input in the soil-water-air system requires the development of innovative and sustainable farming practices, allowing the reduction of fertilizer amounts but assuring good yields. This study describes the optimization of the uptake of swine manure-derived ammonium by zeolite, as one of the first result of ZeoLIFE project (“Water pollution reduction and water saving using a natural zeolite cycle”, LIFE+10 ENV/IT/000321). Natural Italian chabazite-bearing zeolite has been mixed with swine manure at different zeolite/manure ratios and operative conditions, in a series of laboratory batch tests. The effective  $\text{NH}_4^+$ -uptake has been measured with different methods, in order to validate the best criteria to reproduce the cation exchange reaction at large scale in a prototype, specifically conceived and built for the industrial production of  $\text{NH}_4^+$ -charged zeolite.

Experimental results indicate that the best conditions for maximum ammonium uptake are matched using a zeolite/manure ratio of 25 g/L, a stirring time of 45 minutes and a resting time of 12 hours. These experimental conditions, when operatively applied at the prototype, always led to a good absorption of ammonium, although appreciably less than that obtained in laboratory tests. The obtained material has been spread into an agricultural field, where an increase of the yield has been obtained notwithstanding a significant reduction of the chemical fertilization.

*Key words:* Zeolite; Ammonium; CEC; Swine manure; Fertilizer; Prototype.

## Introduction

Agriculture remains one of the main source of water pollution, and farmers need to adopt more sustainable practices, as huge efforts are still required in order to restore optimal water quality across the European Union (EU). Generally, farming is responsible for the major N-compound discharges into surface waters and groundwater, and still nowadays agricultural practices in all Europe use a large amount of chemical fertilizers and animal manure, with large regional differences (Velthof et al., 2014). Of the total nitrogen input in the fields, a large amount is actually not absorbed by the crops and resides in the soil (Mastrocicco et al., 2013; Wang et al., 2013a; Sebilo et al., 2013), where it could be converted into highly soluble nitrates and flushed away into the water system (Arbat et al., 2012; Aschonitis et al., 2012; Wick et al., 2012; Wang et al., 2013b), triggering different degenerative processes and ultimately causing eutrophication phenomena (Del Amo et al. 1997; De Wit et al., 2005; Statham, 2012). Moreover, when denitrification processes occur in soils (Rivett et al., 2008), greenhouse gases are released into the atmosphere (Benbi, 2013; Skinner et al., 2014). Livestock effluents, whose  $\text{NH}_4^+$  concentration could exceed 1000 mg/L, are often used as fertilizers; it is known that intensive livestock breeding is one of the major sources of nitrogen pollution in water (Goldberg, 1989; Williams, 1995; Widory et al., 2004) and it heavily contributes to greenhouse gases (like  $\text{CO}_2$  and methane) emissions worldwide (FAO, 2006). With the Nitrates Directive (91/676/EC) and the Water Framework Directive (WFD 2000/60/EC) the EU aimed at preventing nitrate pollution by promoting the use of good farming practices and established a protocol for water protection and management, reporting measures that must be taken by each Member State to reduce dumping and toxic substance emissions, favor the restoration of hydrologic resources

and reach a good chemical and ecological state of waters. All EU States have drawn up action programs, and by 2010 about 40% of the territory is subject to their implementation.

Natural zeolites are rocks containing more than 50% of zeolites (Galli and Passaglia, 2011), a kind of minerals with peculiar physical and chemical properties, as high and selective cation exchange capacity (CEC), molecular absorption and reversible dehydration (Bish and Ming, 2001). Zeolites have a complex three-dimensional, negatively charged tecto-silicatic structure (framework) with large, cage-like cavities interconnected through channels, that are able to accommodate  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  or other cations, water and even small organic molecules. Cations are only weakly connected to the framework and can migrate in and out of the zeolite structure; they can be released partly or totally when the mineral comes in contact with a solution from which, in turn, the zeolite extracts an equivalent amount of other cations. Thanks to their high CEC and remarkable selectivity for cations characterized by low ionic potential ( $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Ba}^{2+}$ ; Passaglia, 2008), zeolites are capable to uptake ammonium from solutions in various environments (Passaglia and Laurora, 2013) and then to release it under proper conditions. Thus, the use of natural zeolites in environmental protection is progressively increasing, and they have been used for the treatment of sewage waters, to remove ammonium and to amend greenhouse substrates and agricultural soils (Ming and Allen, 2001; MO2013A000354). In this context, ZeoLIFE project (LIFE+10 ENV/IT/000321) has been conceived to test an innovative integrated zeolite cycle aiming at reducing the ammonium content in livestock effluents and correcting agricultural soils, with improvement of the yield and economization of fertilizers and water for irrigation, ultimately leading to a reduction of fresh and groundwater pollution and excessive exploitation of the water resource.

This study describes the optimization of swine

manure-derived ammonium uptake by zeolite, as the first result of ZeoLIFE project. Natural chabazite-bearing zeolite from a quarry in the Central Italy (Malferrari et al., 2013) has been mixed with swine manure at different zeolite/manure ratios and operative conditions, in a series of laboratory batch tests. The effective  $\text{NH}_4^+$ -uptake has been measured with different methods, in order to validate the best criteria for the reproduction of the charging process at large scale in a prototype, specifically conceived and built at the project pilot site for the industrial production of the  $\text{NH}_4^+$ -charged zeolite.

## Materials and Methods

### Materials

*Batch experiment apparatus.* The selected zeolite comes from a zeolitized pyroclastic deposit quarried in a particular lithostratigraphic unit of the Sorano Formation (the so-called Lithic Yellow Tuff body) where K-Chabazite is the overall prevalent zeolite specie. For its detailed mineralogical and chemical characterization see Malferrari et al. (2013). The Sorano Formation is part of phonolitic-tephritic ignimbrite with black pumices deposits, erupted during Quaternary by the volcanic complexes of Bolsena, Vico and Bracciano lakes (Passaglia et al., 1990). These rocks underwent extensive zeolitization in a sort of natural autoclave environment (“geoautoclave”; Passaglia and Vezzalini (1985), (and references therein), thanks to the activity of pore fluids heated by the thermal energy of the pyroclastic deposit itself. This peculiar phenomenon is at the base of the very fine grain size of the zeolites and their homogeneous distribution within the rock, as well as the prevalent mineral type and its composition reflect the low Na/K and Si/Al ratios of the original volcanic glass and the pH of the circulating pore waters (Passaglia and Vezzalini, 1985; Passaglia et al., 1990). The thickness of these pyroclastic deposits (up to 80 m), their widespread occurrence (the sole Sorano

quarry has an extension of 60,000 m<sup>2</sup>) and the high zeolitic content make them an exploitable resource from the economical point of view.

Exchange experiment between zeolite and manure were carried out using a granular ( $\varnothing = 0.2\text{-}3\text{ mm}$ ) byproduct of the quarrying activity, in static mode (Vassileva and Voikova, 2009), being this one the most suitable method for large-scale reproduction in a prototype.

The main goal was to determine the interaction conditions that allow the maximum ammonium uptake by the zeolite. This result does not necessarily coincide with the maximum reduction of ammonium in manure, as it is strictly related to the amount of added zeolite. Thus several exchanging experiments (Figure 1, in supplementary material) were performed varying the zeolite/manure ratio, the stirring and resting times (i.e., the amount of time during which the zeolite remains still in contact with the manure after stirring). Taking into account the potential operating capacity of the prototype for large-scale production, 25 and 75 grams per liter of manure have been respectively selected as the minimum and maximum amounts of zeolite used in the laboratory tests. Each exchange experiment was performed in triplicates at room conditions with a fixed volume (1 L) of manure. After stirring, during the resting period, small aliquots (i.e., 5 mL) of manure were sampled at increasing intervals of time, properly diluted, and characterized for residual ammonium content. At the end of the resting period, the zeolite has been separated from the slurry with a 250  $\mu\text{m}$  filter, washed with distilled water and air dried. Both manure and zeolite have been chemically characterized for main ions contents. An outline of manure and  $\text{NH}_4^+$ -charged zeolite (NH4CZ hereafter) samples prepared in laboratory is shown in Table 1.

### Prototype for large scale NH4CZ production

The prototype (Figure 1) is composed by a 2.2

Table 1. Manure and zeolite samples after laboratory experiments.

Zeolite / manure ratio (g/L)	Stirring times (min)	Resting time before manure sampling (hrs)	Last manure samples labels	NH <sub>4</sub> CZ samples labels
25			M-25-15-12	25-15-12
50	15		M-50-15-12	50-15-12
75			M-75-15-12	75-15-12
25			M-25-30-12	25-30-12
50	30	4, 8, and 12	M-50-30-12	50-30-12
75			M-75-30-12	75-30-12
25			M-25-45-12	25-45-12
50	45		M-50-45-12	50-45-12
75			M-75-45-12	75-45-12

Stirring times indicate times under which zeolite samples were kept in contact with manure under continuous stirring. Resting times indicate the lapses of time of static interaction before manure sampling for ammonium analysis and, in text and figures, is indicated by the last number of each label (for example, in Figures 2 and 3, label M-25-45-8 identifies a manure sample from a batch with zeolite/manure ratio of 25 g/L, stirred for 45 minutes and sampled after 8 hours of static contact with the zeolite). Last manure samples are those selected for main ions content determinations (see Table 2). NH<sub>4</sub>CZ are zeolite samples separated from manure after the highest resting time (i.e., 12 hours), washed with deionized water and air dried.

m (ø) x 5.3 m (h) main tank for the swine manure storage (about 10 m<sup>3</sup>), with 2 inflow and 2 outflow valves. The loading of swine manure is performed using a 30 m<sup>3</sup>/h pumps (Pmax = 1.5 bar) for the transport of the liquid fraction from the storage pool. Zeolite can be introduced from the top into the vessel by a motorized pulley. The tank is equipped with a vertical mixer (mechanical stirrer) regulated with a timer, with a top speed of 300 m<sup>3</sup>/h for the mixing of zeolite and manure. After interaction, the manure can be discharged into a

drain well. For recovery of the NH<sub>4</sub><sup>+</sup>-charged zeolite, the treated material is discharged opening the ball valve at the bottom of the tank. A 250 µm-sieving vibrating system may be, optionally, inserted at the bottom of the vessel to separate the different particle size of NH<sub>4</sub>CZ.

The prototype, that is located in Codigoro (Ferrara, Italy) near ZeoLIFE experimental field described in Malferrari et al. (2013), Mastrocicco et al. (2013) and Di Giuseppe et al. (2014), processes the same swine manure and zeolite

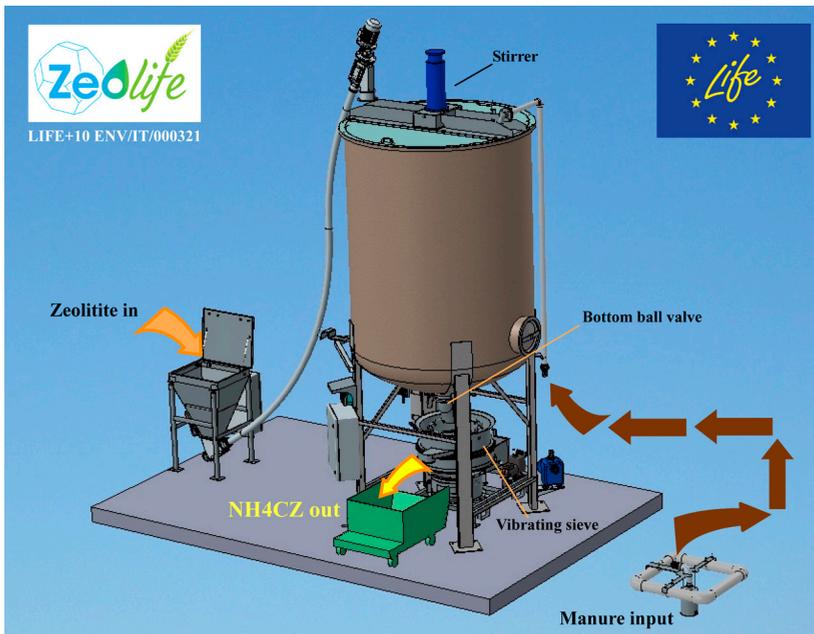


Figure 1. Sketch of the prototype® for zeolite treatment with swine manure.

used in batch experiments. Manure ammonium content has been regularly measured before and after each treating cycle with a gas-sensing electrode probe installed in situ, after conversion to ammonia. Anion and trace element contents have been analyzed on a sub set of representative samples collected during the whole length of prototype activity period.

The mechanical features of the prototype and the application of the operating conditions optimized with the laboratory test allowed to obtain, on average, up to 500 Kg/day of  $\text{NH}_4\text{CZ}$ . A selection of prototype  $\text{NH}_4\text{CZ}$  samples (labeled as PRT-1-PRT-9), collected weekly after appropriate quartering for a period of about two months, have been gathered for this study.

#### *Main anions and cations determination on manure*

The swine manure used in the batch experiments is a low density ( $1 \text{ gr/cm}^3$ ) liquid

with a solid fraction lesser than 1%. EC and pH are, on average, 21 mS/cm and 8.0, respectively. Main ions content for manure samples before and after treatment with zeolite used in each exchange experiments is reported in Table 2.  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $(\text{NO}_2)^-$ ,  $\text{Br}^-$ ,  $(\text{NO}_3)^-$ ,  $(\text{PO}_4)^{3-}$ , and  $(\text{SO}_4)^{2-}$  measurements have been carried out via a Dionex ICS-1000 ion chromatographer. Manure samples were conveniently diluted and put in 5 mL test tubes sealed with a cap equipped with a  $0.22 \mu\text{m}$  filter. The tubes are put in an AS-40 Dionex automatic sampler where an injection pump extracts the solution that passes through the filter and is conveyed to the mixing chamber. Quality Control (QC) samples were run every 10 samples and the standard deviation for all QC samples run was better than 4%.

$\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  have been measured using a X Series Thermo-Scientific ICP-MS spectrometer. Manure samples were diluted in

Table 2. Main ions concentration in manure before and after treatments with zeolite.

	Ions concentration (mmol/L)									
	MANURE (*)	M-25- 15-12	M-50- 15-12	M-75- 15-12	M-25- 30-12	M-50- 30-12	M-75- 30-12	M-25- 45-12	M-50- 45-12	M-75- 45-12
F <sup>-</sup>	2.71	2.55	2.25	1.17	1.39	1.56	1.57	1.40	1.40	1.49
Cl <sup>-</sup>	41.2	46.6	42.7	41.7	43.4	40.6	40.4	42.2	42.4	43.3
(NO <sub>2</sub> ) <sup>-</sup>	0.213	0.220	0.197	0.128	0.220	0.226	0.219	0.201	0.194	0.211
Br <sup>-</sup>	0.065	0.083	0.073	0.064	0.065	0.076	0.072	0.072	0.066	0.070
(NO <sub>3</sub> ) <sup>-</sup>	0.005	0.008	0.030	0.004	0.004	0.004	0.009	0.003	0.002	0.011
(PO <sub>4</sub> ) <sup>3-</sup>	1.37	1.09	0.918	0.778	0.823	0.499	0.265	0.816	0.637	0.535
(SO <sub>4</sub> ) <sup>2-</sup>	0.138	0.574	0.109	0.233	0.923	0.174	0.125	0.086	0.113	0.172
Na <sup>+</sup>	34.5	32.9	33.8	31.4	33.0	33.0	33.1	32.7	34.7	38.8
K <sup>+</sup>	42.0	43.4	40.3	36.1	41.0	39.6	41.6	41.2	40.3	46.2
Ca <sup>2+</sup>	3.53	6.05	11.65	4.61	4.35	7.02	7.02	6.14	5.90	5.85
Mg <sup>2+</sup>	0.75	0.86	1.16	0.71	0.89	1.20	0.84	1.06	1.34	1.08
NH <sub>4</sub> <sup>+</sup>	109	91.6	91.0	75.7	87.6	91.7	80.4	80.3	92.1	91.9

(\*) Average composition of ten manure analyses before treatment with zeolite.

deionized water at 1:50; 10 mL of the diluted solutions were put in test tubes for automatic sampling. Specific amounts of Rh, In and Re were added to the analyzed solutions as an internal standard, in order to correct for instrument drift. Accuracy and precision, based on replicated analyses of samples and standards, are better than 10% for all elements, well above the detection limit. Reference standards (ESL1, EUL1, ref) were also analyzed to cross-check and validate the results.

#### *Ammonium measurements*

Ammonium in manure was measured with an ORION 95-12 gas-sensing electrode after conversion to ammonia. Two mL of ISA (Ionic

Strenght Adjustor) were added to 100 mL of all manure samples (after proper dilution) and standards immediately before each measurement. Calibration was carried out by single meter reading of two standards bracketing the expected sample range and differing in concentration by a factor of ten (these standards are obtained properly diluting a 1000 mg/L certificated ammonium standard solution). Calibration was verified every hour by placing the electrode in a fresh aliquot of the standard solutions; errors for each measurement were in the order of  $\pm 2\%$ . Additional information on the adopted analytical techniques are reported in the supplementary information SI-1.

Ammonium absorbed by zeolite was

determined both in solution after proper selective chemical extraction, and directly on solid via thermogravimetric measurement coupled with evolved gases mass spectrometry.

*Chemical extraction and gas-sensing electrode (GSE) measurements.* Five grams of each NH<sub>4</sub>CZ sample were put in centrifuge tubes, added with 50 mL of a 1N NaCl solution, stirred at 640 rpm on orbital stirrer for 15 minutes, and then allowed to rest for other 15 minutes. The obtained suspension was subsequently centrifuged at 5000 rpm for 3 minutes. The supernatant was carefully poured off into a PVC container. The last bit of supernatant was removed with a pipet tip, and the container was properly sealed. This procedure was repeated three times, thus obtaining a total of 150 mL of supernatant for each starting NH<sub>4</sub>CZ sample. The sealed containers were stored in a refrigerator at 4 °C. Since a slight turbidity of suspension does not affect the ammonium measurement, samples needed neither distillation nor filtration. Ammonium measurements were done following the same procedure as previously described for manure.

The cation exchange capacity is usually measured employing cesium as exchange cation. In this research, however, we preferred to use sodium essentially for two reasons: i) chabazite has a high affinity for sodium; ii) a purpose of the project is to parallel as much as possible the reactions that could occur in the soil of ZeoLIFE project experimental field, where the porewater may have high sodium concentrations (Di Giuseppe et al., 2014).

*Thermogravimetric measurement (pyrolytic extraction).* Thermogravimetry (TGA) allows the determination of the mass as a function of temperature or time; this thermal technique provides information concerning thermal stability and composition of the sample and of any intermediate compound which may be

formed. When these measures are combined with chemical analysis of evolved gases, it is possible to determine the reactions that are at the base of each thermal effect. In particular, it is possible to estimate the amount of absorbed ammonium by evaluating the variation of mass in correspondence with the release of NO<sub>3</sub><sup>-</sup> derived from the oxidation of NH<sub>4</sub><sup>+</sup> by the oxygen present in the furnace atmosphere.

Pyrolytic extraction of absorbed ammonium is more far-reaching than a chemical extraction; however, as a result of a possible partial overlapping of contiguous thermal reactions, it cannot be excluded that the extraction via pyrolysis involves a small overestimation.

Before thermal measurement, zeolite samples have been powdered (grain size less than 2 micron). Thermo gravimetric curves were obtained using a Seiko SSC 5200 equipped with TG/DTA 320U Module and the gas mass spectrometer GeneSys Quadstar 422. The experimental conditions were: Heating rate: 10.0 °C/min; Heating range: 25-900 °C; Data measurement: every 0.5 sec; Purging gas: helium/oxygen (90/10) at a flow rate of 100µL/min; DTA reference: calcinated kaolinite; Mass analyses: in multiple ion detection mode scan on m/z=14, 16, 17, 18, 28, 30, 32, 44, 46, where m/z is the ratio between selected AMU and charge; AMU integration time: 1 sec; Detector current: 1100V both on SEM and FARADAY. Further information are reported in the supplementary information SI-2a.

#### *Chemical analyses of zeolites*

Chemical analysis of zeolite samples after treatment with manure was carried out on pressed pellets of powdered rock via a wavelength-dispersive Philips PW 1480 X-Ray Fluorescence (XRF) spectrometer, using the methods of Franzini et al. (1975) and Leoni and Saitta (1976) for the determination of element concentration. Fe was assumed to be in its trivalent oxide form. As Loss On Ignition (LOI),

the values determined via thermogravimetric measurements were considered. Chemical and mineralogical compositions of natural zeolite are reported in Malferrari et al. (2013).

### Results and Discussion

#### Batch experiments

*Ammonium measurements in manure.* Results of batch experiment are reported in Figures 2

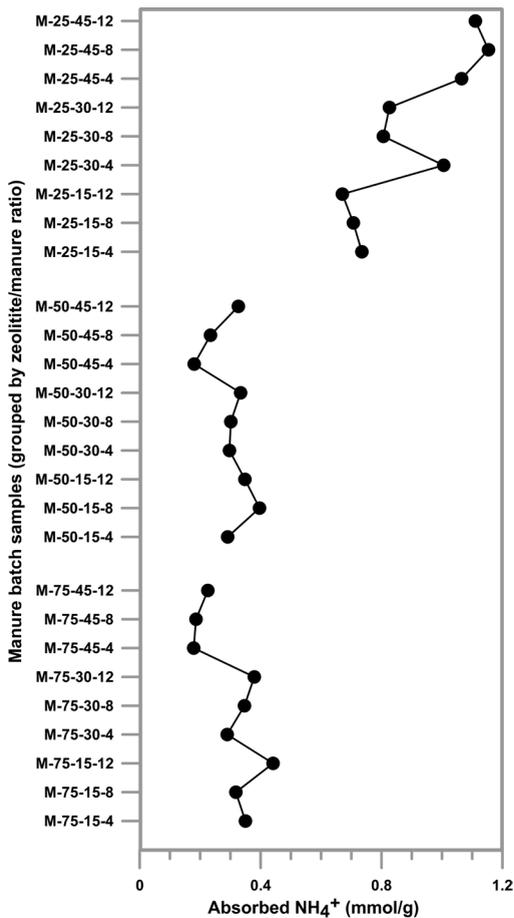


Figure 2. Absorbed ammonium in zeolite after batch experiments, as determined from the difference in ammonium content of swine manure before and after treatment. Samples are grouped by zeolite/manure ratio. The numerical code of sample labels indicates respectively zeolite/manure ratio, stirring time and resting time.

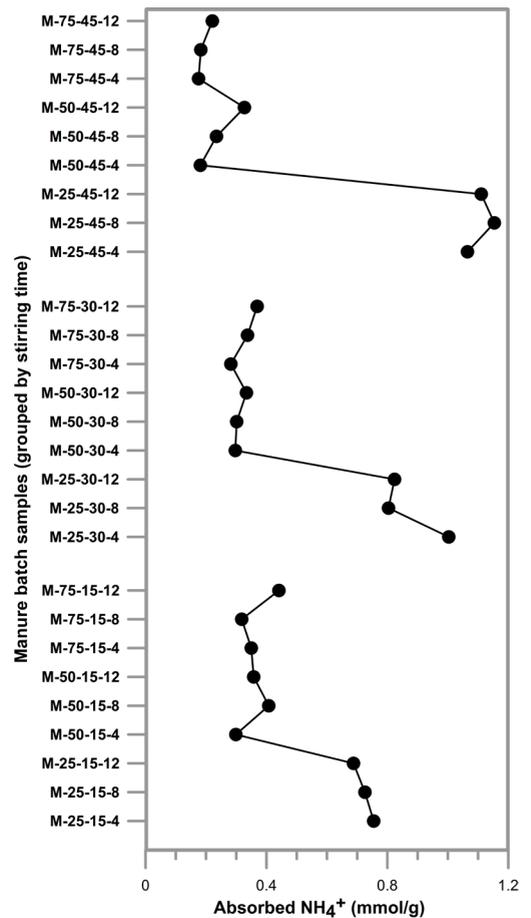


Figure 3. Absorbed ammonium in zeolite after batch experiments, as determined from the difference in ammonium content of swine manure before and after treatment. Samples are grouped by stirring time. The numerical code of sample labels indicates respectively zeolite/manure ratio, stirring time and resting time.

only in the case of 45 minutes of treatment, and, additionally, it seems to greatly facilitate the absorption only in the case of low zeolite/manure ratio (Figure 3), iii) the resting time does not really affect the absorption, since the measured variations frequently fall within the experimental error. The most relevant outcome, however, is that there is no linear relationship between zeolite/manure ratio and amount of absorbed ammonium: in fact, the use of 50 or 75 g/L of zeolite does not cause significant differences in absorption in spite of a greater reduction of ammonium concentration in manure when using 25 g/L.

*Main ions measurements in manure.* Main anions and potential exchangeable cations in manure before and after laboratory experiment are reported in Table 2. Noticeable variations in  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations in manure are in relation with the exchange reactions that occur between manure and zeolite; however, no correlation between their changes in concentration can be found, thus suggesting that exchange mechanisms are complex and not modelizable in this environment. A decrease in the most abundant cations in the manure, coupled with an increase in the less concentrated can overall be envisaged in the post-treatment liquid (Figure 4a).

Regarding the anions (Figure 4b), fluorides show a general decrease which is, generally, higher when longer stirring times are used; phosphate reduction is in close correlation with both stirring time and zeolite/manure ratio (Figure 5) and, in particular, it is favored by low zeolite/manure ratios. It is noteworthy that nitrites and nitrates concentrations are very low and similar at the beginning and at the end of the experiments, which means that all the ammonium missing in the liquid has been taken up by the zeolite and not been oxidized. No correlation can be found for chlorides and sulphates concentrations.

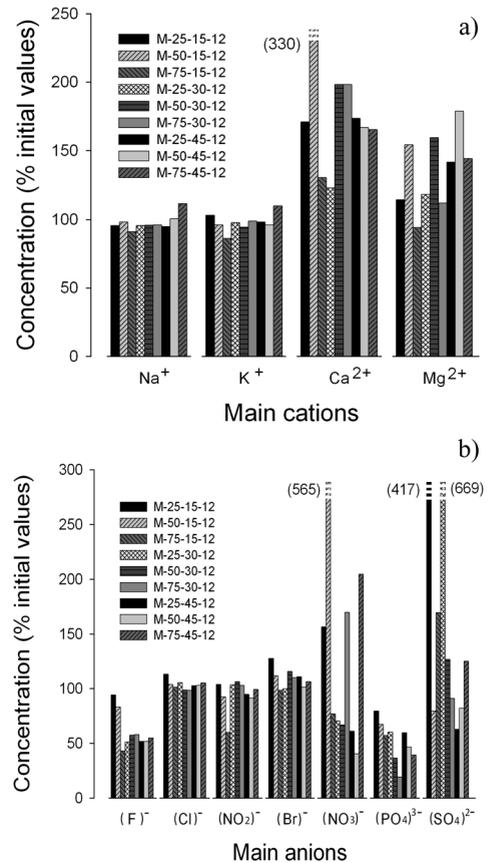


Figure 4. Main cations (a) and anions (b) concentration in manure samples from the laboratory batch experiments after the maximum resting time (12h).

*Ammonium measurements on  $\text{NH}_4\text{CZ}$  (chemical and pyrolytic extraction).* As already stated,  $\text{NH}_4^+$  absorbed by zeolite can be estimated both as the  $\text{NH}_4^+$  released when the  $\text{NH}_4\text{CZ}$  interacts with a solution containing cations (e.g.,  $\text{Na}^+$ ) that can substitute, via cation exchange mechanism, the absorbed  $\text{NH}_4^+$  in zeolite, and as the amount of ammonium released in a well-defined thermal range (see also supplementary information SI-1 and SI2b).

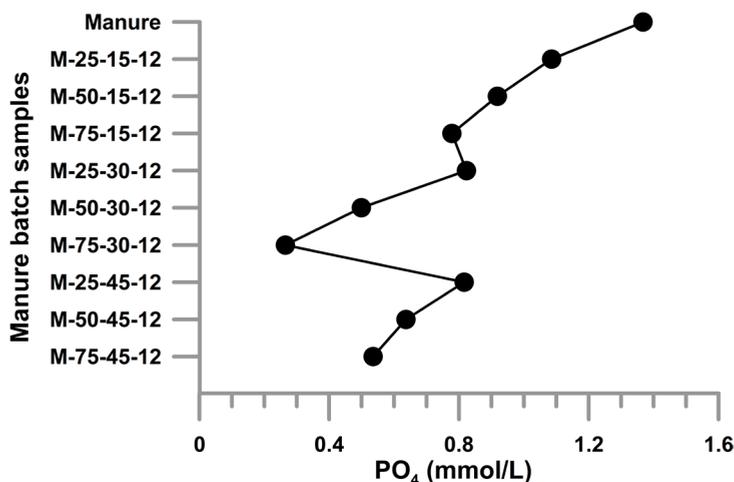


Figure 5.  $(\text{PO}_4)^{3-}$  concentration in manure samples from the laboratory batch experiments after the maximum resting time (12 h). Samples are grouped by stirring time.

Results of chemical and pyrolytic extraction are reported in Table 3.

The amount of ammonium determined via pyrolytic extraction is always greater than the amount detected via chemical extraction, as a result of both the partial overlap of the thermal decomposition reactions and the increased efficiency of the heating process with respect to the chemical extraction. Actually, an average of the two values can be considered a reliable result. In contrast, it is often found a mismatch between the measurements performed on manure after treatment with the zeolite and the measurements on the corresponding NH<sub>4</sub>CZ samples, in particular when referring to the samples obtained using a zeolite/manure ratio of 25 g/L.

*Chemical characterization of zeolite after treatment.* The results of chemical analysis via X-ray fluorescence on natural zeolite and after treatments are shown in Table 4. Variations measured on major elements fall within the variations ranges of natural zeolite, as also

documented in Malferrari et al. (2013), and therefore can be considered as negligible the effect of leaching during the exchange with manure. This conclusion is also supported by quantitative mineralogical analysis on zeolite after treatment, that does not detect substantial changes (supplementary information SI-3). A sensible variation of the exchangeable cations Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and, to a lesser extent, Mg<sup>2+</sup>, can be envisaged. In particular, all NH<sub>4</sub>CZ samples show a slight increase in Mg<sup>2+</sup> and a reduction of the others afore mentioned elements. In the manure, by contrast, a corresponding trend of variation of these cations cannot be found, with the only exception of Ca<sup>2+</sup> (Table 2, Figure 4a). Phosphorous content variations are concordant, as it decreases in manure and increases in zeolite. Since a direct interaction (e.g., absorption) between phosphorus and minerals contained in zeolite is not possible, the increase in the solid fraction is likely due to precipitation of compounds of this element, maybe induced by the interaction between manure and zeolite and/or by biologically

Table 3. NH<sub>4</sub> measurements (mmol/g) in NH<sub>4</sub>CZ samples determined via chemical (GSE) and pyrolytic (TGA) extraction.

SAMPLE	GSE	TGA	MANURE	AVG M/Z (S.D.)	% NomCEC
25-15-12_R1	0.37	0.39			
25-15-12_R2	0.40	0.51			
25-15-12_R3	0.39	0.43			
Average (R1-R3)	0.38	0.44	0.69	0.51	23.3
<i>ST. DEV (R1-R3)</i>	<i>0.01</i>	<i>0.05</i>		<i>0.16</i>	
50-15-12_R1	0.38	0.44			
50-15-12_R2	0.37	0.45			
50-15-12_R3	0.35	0.47			
Average (R1-R3)	0.37	0.45	0.36	0.39	18.0
<i>ST. DEV (R1-R3)</i>	<i>0.01</i>	<i>0.01</i>		<i>0.05</i>	
75-15-12_R1	0.31	0.38			
75-15-12_R2	0.29	0.38			
75-15-12_R3	0.28	0.32			
Average (R1-R3)	0.29	0.36	0.44	0.37	16.8
<i>ST. DEV (R1-R3)</i>	<i>0.01</i>	<i>0.03</i>		<i>0.07</i>	
25-30-12_R1	0.49	0.47			
25-30-12_R2	0.47	0.43			
25-30-12_R3	0.46	0.44			
Average (R1-R3)	0.47	0.45	0.85	0.59	27.2
<i>ST. DEV (R1-R3)</i>	<i>0.01</i>	<i>0.02</i>		<i>0.22</i>	
50-30-12_R1	0.45	0.57			
50-30-12_R2	0.41	0.53			
50-30-12_R3	0.41	0.55			
Average (R1-R3)	0.42	0.55	0.34	0.44	20.2
<i>ST. DEV (R1-R3)</i>	<i>0.02</i>	<i>0.02</i>		<i>0.10</i>	
75-30-12_R1	0.34	0.47			
75-30-12_R2	0.36	0.44			
75-30-12_R3	0.36	0.48			
Average (R1-R3)	0.35	0.46	0.38	0.40	18.4
<i>ST. DEV (R1-R3)</i>	<i>0.01</i>	<i>0.02</i>		<i>0.06</i>	
25-45-12_R1	0.47	0.62			
25-45-12_R2	0.43	0.58			
25-45-12_R3	0.53	0.66			
Average (R1-R3)	0.48	0.62	1.14	0.75	34.3
<i>ST. DEV (R1-R3)</i>	<i>0.04</i>	<i>0.03</i>		<i>0.35</i>	
50-45-12_R1	0.33	0.49			
50-45-12_R2	0.39	0.44			
50-45-12_R3	0.32	0.49			
Average (R1-R3)	0.35	0.47	0.33	0.38	17.7
<i>ST. DEV (R1-R3)</i>	<i>0.03</i>	<i>0.02</i>		<i>0.08</i>	
75-45-12_R1	0.28	0.39			
75-45-12_R2	0.28	0.38			
75-45-12_R3	0.36	0.46			
Average (R1-R3)	0.31	0.41	0.23	0.31	14.5
<i>ST. DEV (R1-R3)</i>	<i>0.04</i>	<i>0.04</i>		<i>0.09</i>	

MANURE reports the NH<sub>4</sub> concentration in zeolite determined as the amount of NH<sub>4</sub> subtracted from manure after 12 hours of resting time; AVG-M/Z is the average (with Standard Deviation in italic) of NH<sub>4</sub> concentrations measured via EGA, TGA and from manure; %NomCEC is the percentage of the nominal C.E.C. (i.e., 2.17 mmol/g -Malferrari et al. 2013) accomplished with the experiments and calculated with respect to AVG-M/Z values. R1-R3 are the three replicates.

Table 4. Major elements (oxide weight %) in NH<sub>4</sub>CZ samples obtained in the laboratory experiments. Each value is the arithmetic mean of three replicates; standard deviation (S.D.) is reported in italic.

OXIDE	Natural zeolite	<i>S.D.</i>	25-15-12	<i>S.D.</i>	25-30-12	<i>S.D.</i>	25-45-12	<i>S.D.</i>	50-15-12	<i>S.D.</i>
SiO <sub>2</sub>	51.60	<i>0.350</i>	53.30	<i>0.591</i>	54.00	<i>0.295</i>	54.00	<i>0.005</i>	53.90	<i>0.310</i>
Al <sub>2</sub> O <sub>3</sub>	16.60	<i>0.356</i>	17.30	<i>0.192</i>	17.60	<i>0.096</i>	17.60	<i>0.002</i>	17.50	<i>0.101</i>
Fe <sub>2</sub> O <sub>3</sub>	3.38	<i>0.095</i>	3.53	<i>0.039</i>	3.58	<i>0.020</i>	3.58	<i>0.000</i>	3.58	<i>0.021</i>
TiO <sub>2</sub>	0.48	<i>0.031</i>	0.47	<i>0.005</i>	0.47	<i>0.003</i>	0.47	<i>0.000</i>	0.47	<i>0.003</i>
P <sub>2</sub> O <sub>5</sub>	0.18	<i>0.012</i>	0.21	<i>0.014</i>	0.22	<i>0.013</i>	0.22	<i>0.012</i>	0.22	<i>0.012</i>
MnO	0.11	<i>0.006</i>	0.11	<i>0.001</i>	0.12	<i>0.001</i>	0.12	<i>0.000</i>	0.12	<i>0.001</i>
MgO	1.76	<i>0.184</i>	1.78	<i>0.026</i>	1.80	<i>0.019</i>	1.80	<i>0.012</i>	1.80	<i>0.021</i>
CaO	5.00	<i>0.151</i>	2.93	<i>0.037</i>	2.97	<i>0.019</i>	2.97	<i>0.010</i>	2.97	<i>0.016</i>
Na <sub>2</sub> O	0.79	<i>0.030</i>	0.27	<i>0.004</i>	0.27	<i>0.003</i>	0.27	<i>0.002</i>	0.27	<i>0.002</i>
K <sub>2</sub> O	5.84	<i>0.122</i>	4.94	<i>0.057</i>	5.01	<i>0.028</i>	5.01	<i>0.005</i>	5.01	<i>0.027</i>
LOI	14.30	<i>0.762</i>	15.20	<i>0.862</i>	14.00	<i>0.517</i>	14.00	<i>0.089</i>	14.10	<i>0.505</i>
SUM	100.00		100.00		100.00		100.00		100.00	

OXIDE	50-30-12	<i>S.D.</i>	50-45-12	<i>S.D.</i>	75-15-12	<i>S.D.</i>	75-30-12	<i>S.D.</i>	75-45-12	<i>S.D.</i>
SiO <sub>2</sub>	53.80	<i>0.176</i>	54.00	<i>0.249</i>	54.20	<i>0.297</i>	54.10	<i>0.310</i>	54.0	<i>0.239</i>
Al <sub>2</sub> O <sub>3</sub>	17.50	<i>0.057</i>	17.60	<i>0.081</i>	17.6	<i>0.097</i>	17.60	<i>0.101</i>	17.6	<i>0.078</i>
Fe <sub>2</sub> O <sub>3</sub>	3.57	<i>0.012</i>	3.58	<i>0.017</i>	3.59	<i>0.020</i>	3.59	<i>0.021</i>	3.58	<i>0.016</i>
TiO <sub>2</sub>	0.47	<i>0.002</i>	0.47	<i>0.002</i>	0.47	<i>0.003</i>	0.47	<i>0.003</i>	0.47	<i>0.002</i>
P <sub>2</sub> O <sub>5</sub>	0.22	<i>0.012</i>	0.22	<i>0.011</i>	0.22	<i>0.012</i>	0.22	<i>0.011</i>	0.22	<i>0.011</i>
MnO	0.12	<i>0.000</i>	0.12	<i>0.001</i>	0.12	<i>0.001</i>	0.12	<i>0.001</i>	0.12	<i>0.001</i>
MgO	1.80	<i>0.017</i>	1.80	<i>0.017</i>	1.81	<i>0.020</i>	1.81	<i>0.020</i>	1.80	<i>0.017</i>
CaO	2.96	<i>0.011</i>	2.97	<i>0.008</i>	2.98	<i>0.017</i>	2.97	<i>0.008</i>	2.97	<i>0.007</i>
Na <sub>2</sub> O	0.27	<i>0.002</i>	0.27	<i>0.002</i>	0.27	<i>0.002</i>	0.27	<i>0.001</i>	0.27	<i>0.002</i>
K <sub>2</sub> O	4.99	<i>0.015</i>	5.010	<i>0.019</i>	5.030	<i>0.027</i>	5.02	<i>0.024</i>	5.02	<i>0.018</i>
LOI	14.30	<i>0.321</i>	14.00	<i>0.352</i>	13.70	<i>0.434</i>	13.80	<i>0.464</i>	13.90	<i>0.378</i>
SUM	100.00		100.00		100.00		100.00		100.00	

induced chemical precipitation (Bortone et al., 1992) and variations in the oxidation-reduction potential (Obaja et al., 2003).

### *Prototype production*

The laboratory experiments were aimed at determining the interaction conditions between zeolite and manure leading to the maximum ammonium uptake by the zeolite. Absorbed ammonium measurements carried out both on manure and NH<sub>4</sub>CZ samples after laboratory treatments indicate that a zeolite/manure ratio of 25 g/L, a stirring time of 45 minutes and a rest time of 12 hours are the most suitable conditions to achieve the goal; thus these “optimized” parameters were paralleled at the prototype. Each cycle employed 250 Kg of zeolite and 1 x 10<sup>4</sup> L of manure; prototype activity started at the beginning of April and went on until October 20<sup>th</sup>, 2012, with an average of one cycle per day. Due to the cold temperatures and unfavorable weather, the production has been stopped during winter and resumed in the middle of April 2013. At the end of May, the in-situ gas-sensing electrode probe required maintenance and ammonium and nitrate measurements started again in July; the production went on until the middle of October 2013, for a total NH<sub>4</sub>CZ amount of 87 tons.

Ammonium content in manure before treatment can vary mainly in dependence of temperature, the amount of liquid stored in the basin, and the quantity of water used to wash the pigpens (in the operative period we found values ranging from 530 to 2560 mg/L, Figure 6), thus the ammonium decrease in manure after each treating cycle can vary a little. An average decrease of 203 mg/L and of 251 mg/L in the operative periods of 2012 and 2013 has been respectively obtained. Other variable affecting ammonium uptake can also be ascribed to operative conditions such as exact the correct weighting of zeolite (250 ± 5 Kg) as its relative humidity that can slightly vary in function of the

atmospheric conditions (the zeolite was stored in open-air conditions).

Nitrate contents in the manure used in the prototype are higher than those found in manure used in the batch experiments, being on average 41 mg/L in 2012 and 93.8 mg/L in 2013. Since the source is the same, the difference is most probably due to the suction method employed to transfer the liquid from the storage basin to the tank, which implies a partial oxygenation of the manure. NO<sub>3</sub><sup>-</sup>, however, cannot be exchanged with zeolite; in-situ denitrification processes (Bortone et al., 1992) can explain the average manure nitrate concentrations of 36.8 and 73.5 mg/L found after prototype treatment in 2012 and 2013, respectively.

Periodic measurements on NH<sub>4</sub>CZ samples obtained at the prototype are reported in Table 5. As anticipated, the measurement reported here are related to a selection of samples (PRT-1-PRT-9) produced in about two months of prototype activity. In order to make measurements as homogenous as possible, all the samples, before characterization, were air dried under the same conditions of humidity and temperature; washing with distilled water has not been performed.

The effective ammonium absorption in zeolite after treatment with manure (Table 5a) was lower than those registered during batch experiments at the same experimental conditions. It may also be noted that the difference between the measurements performed on NH<sub>4</sub>CZ samples via chemical and pyrolytic extraction is not only less marked than in batch experiments, but a reversal of the trend (on average) can be envisaged.

As far as major elements (Table 5b) are concerned, like in the case of laboratory experiment, an increase of phosphorus compared to the natural zeolite can be observed in NH<sub>4</sub>CZ samples, indicating the probable precipitation of phosphates. The differences concerning exchangeable cations

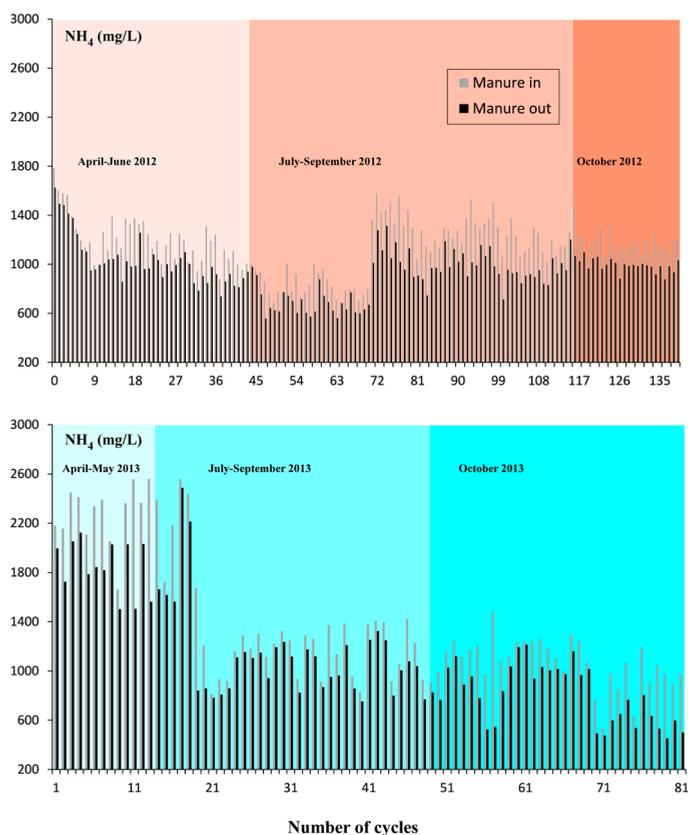


Figure 6.  $\text{NH}_4^+$  contents in manure before and after each treatment cycle in the prototype during 2012 and 2013 working period. Histograms refer to the data-log file of the in situ probe and, for ease of reading, are reported in mg/L.

Table 5a.  $\text{NH}_4^+$  measurements (mmol/g) in  $\text{NH}_4\text{CZ}$  samples obtained at the prototype determined via both chemical (GSE) and pyrolytic (TGA) extraction. Each value is the arithmetic mean of three replicates; standard deviation (S.D.) is reported in italic.

	PRT-1	PRT-2	PRT-3	PRT-4	PRT-5	PRT-6	PRT-7	PRT-8	PRT-9	AVERAGE	25-45-12
GSE	0.39	0.43	0.39	0.41	0.57	0.39	0.42	0.40	0.42	0.43	0.48
S.D.	0.042	0.025	0.038	0.020	0.042	0.043	0.029	0.018	0.063		0.04
TGA	0.37	0.38	0.40	0.49	0.37	0.56	0.38	0.33	0.37	0.40	0.62
S.D.	0.004	0.007	0.008	0.001	0.007	0.037	0.013	0.044	0.083		0.03
AVGVAL	0.38	0.41	0.40	0.45	0.47	0.48	0.40	0.36	0.40		

AVGVAL is the average value between GSE and TGA measurements. AVERAGE is the average value among all  $\text{NH}_4\text{CZ}$  samples here reported. For direct comparison is reported  $\text{NH}_4$  concentration of the laboratory sample 25-45-12 like in Table 3.

Table 5b. Major elements (oxide weight %) in NH<sub>4</sub>CZ samples obtained at the prototype. Each value is the arithmetic mean of three replicates; standard deviation (S.D.) is reported in italic.

	PRT-1	<i>S.D.</i>	PRT-2	<i>S.D.</i>	PRT-3	<i>S.D.</i>	PRT-4	<i>S.D.</i>	PRT-5	<i>S.D.</i>	PRT-6	<i>S.D.</i>
SiO <sub>2</sub>	53.80	<i>0.123</i>	53.80	<i>0.069</i>	53.70	<i>0.112</i>	53.90	<i>0.172</i>	53.10	<i>0.121</i>	53.40	<i>0.179</i>
Al <sub>2</sub> O <sub>3</sub>	17.50	<i>0.040</i>	17.50	<i>0.023</i>	17.50	<i>0.036</i>	17.50	<i>0.056</i>	17.30	<i>0.039</i>	17.40	<i>0.058</i>
Fe <sub>2</sub> O <sub>3</sub>	3.56	<i>0.008</i>	3.57	<i>0.005</i>	3.56	<i>0.007</i>	3.57	<i>0.011</i>	3.52	<i>0.008</i>	3.54	<i>0.012</i>
TiO <sub>2</sub>	0.47	<i>0.001</i>	0.47	<i>0.001</i>	0.47	<i>0.001</i>	0.47	<i>0.002</i>	0.47	<i>0.001</i>	0.47	<i>0.002</i>
P <sub>2</sub> O <sub>5</sub>	0.22	<i>0.012</i>	0.22	<i>0.012</i>	0.23	<i>0.012</i>	0.23	<i>0.005</i>	0.23	<i>0.009</i>	0.23	<i>0.010</i>
MnO	0.11	<i>0.000</i>	0.12	<i>0.000</i>	0.11	<i>0.000</i>	0.12	<i>0.000</i>	0.11	<i>0.000</i>	0.11	<i>0.000</i>
MgO	2.06	<i>0.129</i>	1.93	<i>0.071</i>	1.79	<i>0.047</i>	1.79	<i>0.026</i>	1.57	<i>0.048</i>	1.83	<i>0.039</i>
CaO	3.26	<i>0.011</i>	3.11	<i>0.011</i>	2.96	<i>0.015</i>	2.97	<i>0.012</i>	2.14	<i>0.011</i>	3.02	<i>0.014</i>
Na <sub>2</sub> O	0.27	<i>0.003</i>	0.27	<i>0.002</i>	0.27	<i>0.003</i>	0.27	<i>0.002</i>	0.19	<i>0.002</i>	0.27	<i>0.002</i>
K <sub>2</sub> O	4.99	<i>0.013</i>	4.99	<i>0.009</i>	4.99	<i>0.014</i>	5.00	<i>0.017</i>	3.96	<i>0.013</i>	4.96	<i>0.018</i>
LOI	13.80	<i>0.290</i>	14.10	<i>0.113</i>	14.50	<i>0.187</i>	14.20	<i>0.260</i>	17.40	<i>0.186</i>	14.80	<i>0.124</i>
SUM	100.00		100.00		100.00		100.00		100.00		100.00	
	PRT-7	<i>S.D.</i>	PRT-8	<i>S.D.</i>	PRT-9	<i>S.D.</i>	AV.	<i>S.D.</i>	25-45-12	<i>S.D.</i>	Nat. Zeo	<i>S.D.</i>
SiO <sub>2</sub>	53.70	<i>0.199</i>	53.80	<i>0.229</i>	54.20	<i>0.197</i>	53.70	<i>0.299</i>	54.00	<i>0.005</i>	51.60	<i>0.350</i>
Al <sub>2</sub> O <sub>3</sub>	17.50	<i>0.065</i>	17.50	<i>0.075</i>	17.60	<i>0.064</i>	17.47	<i>0.097</i>	17.60	<i>0.002</i>	16.60	<i>0.356</i>
Fe <sub>2</sub> O <sub>3</sub>	3.56	<i>0.013</i>	3.56	<i>0.015</i>	3.60	<i>0.013</i>	3.56	<i>0.020</i>	3.58	<i>0.000</i>	3.38	<i>0.095</i>
TiO <sub>2</sub>	0.47	<i>0.002</i>	0.47	<i>0.002</i>	0.47	<i>0.002</i>	0.47	<i>0.003</i>	0.47	<i>0.000</i>	0.48	<i>0.031</i>
P <sub>2</sub> O <sub>5</sub>	0.21	<i>0.011</i>	0.21	<i>0.012</i>	0.22	<i>0.009</i>	0.22	<i>0.009</i>	0.22	<i>0.012</i>	0.18	<i>0.012</i>
MnO	0.11	<i>0.000</i>	0.11	<i>0.000</i>	0.12	<i>0.000</i>	0.11	<i>0.001</i>	0.12	<i>0.000</i>	0.11	<i>0.006</i>
MgO	1.83	<i>0.040</i>	1.91	<i>0.045</i>	1.88	<i>0.033</i>	1.84	<i>0.133</i>	1.80	<i>0.012</i>	1.76	<i>0.184</i>
CaO	3.02	<i>0.012</i>	3.02	<i>0.015</i>	3.06	<i>0.014</i>	2.95	<i>0.316</i>	2.97	<i>0.010</i>	5.00	<i>0.151</i>
Na <sub>2</sub> O	0.27	<i>0.002</i>	0.27	<i>0.002</i>	0.27	<i>0.002</i>	0.26	<i>0.027</i>	0.27	<i>0.002</i>	0.79	<i>0.030</i>
K <sub>2</sub> O	4.98	<i>0.018</i>	4.98	<i>0.022</i>	5.03	<i>0.019</i>	4.88	<i>0.346</i>	5.01	<i>0.005</i>	5.84	<i>0.122</i>
LOI	14.4	<i>0.075</i>	14.20	<i>0.137</i>	13.50	<i>0.130</i>	14.54	<i>1.131</i>	14.00	<i>0.089</i>	14.30	<i>0.762</i>
SUM	100.00		100.00		100.00		100.00				100.00	

AVERAGE is the average value among all NH<sub>4</sub>CZ samples here reported. For direct comparison are reported elements concentrations both of the laboratory sample 25-45-12 and natural zeolite like in Table 4.

are less evident, with the exception of potassium that underwent a higher degree of exchange in comparison to the treatments at laboratory scale.

#### Main considerations

The main aim of batch experiments was to find the best parameters, in terms of zeolite/

manure ratio, stirring and resting time, to produce a zeolite as much as possible rich in ammonium. As already stated by Malferrari et al. (2013), the nominal CEC of the selected zeolite for ammonium is of 2.17 mmol/g. Since manure is a poly-cationic solution, a much lower operational CEC was expected,

due to the competition between ammonium and other cations (approximately, 1/5 of the nominal CEC, also in consideration of what reported in Hedström, 2001); despite this, in all the experiments where a zeolite/manure ratio equal to 25 g/L has been used, the amount of absorbed ammonium in manure indicated a CEC (Table 3) higher than the expected operative CEC (i.e., about 0.4 mmol/g). The apparent “extra-load” can be explained if a correction for the nitrogen loss by evaporation is supposed and applied. Nitrogen evaporation could have been enhanced during the experimental runs both by the stirring and the ventilation of the laminar flow hoods; however it can be roughly considered equal for each replicate and each run, due to the relatively small differences in the stirring time in comparison with the length of the resting, and being the flow hoods always working during all the experiments. This conclusion is supported also by measurements on NH<sub>4</sub>CZ samples, showing a smaller gap between measured and nominal CEC.

Treatment with slurry does not cause substantial variations in the quantitative mineralogical composition of the zeolite (supplementary information SI-3). By contrast, it affects significantly the zeolite chemical composition, especially concerning the exchangeable cations. However, it should be pointed out that, at least for calcium, the measurements may be influenced by the precipitation of calcium phosphates, and through XRF analysis it is not possible to discriminate the calcium fixed in the structural channels of the zeolite from that precipitated as “external” phase. We can suppose, in fact, that phosphorous in manure tends to combine with the Ca made available by the zeolite, to form either mono-, or di-, or more likely tri-calcium phosphates. Being mostly insoluble ( $21 < -\log(K_{ps}) < \sim 30$ ), these compounds precipitates together with the zeolite during the resting phase, as supposed by Lai and Eberl (1986) and recently reported by Karapınar (2009).

In consideration of our final purpose (soils amendment), this phenomenon, if verified, can be considered greatly promising since phosphate creates a pool of phosphorus for plants growth (Antoniadis et al., 2012).

Regarding the differences detected between the measurements of ammonium in zeolite, it is significant that there is a marked difference only when considering the two series (i.e., GSE and TGA) of measurements of batch experiment samples, whereas the differences between the prototype samples are less pronounced. Prototype samples differ from batch experiment samples because: i) after the treatment they were not washed and ii) they were left in air (i.e., accumulated in the storage box) for at least 24 hours before being selected. The lack of washing should have caused a greater mass variation (relative to the thermal extraction of ammonium) in the samples from the prototype, but (on average) the opposite have been observed. Although the differences involved are modest, these findings leave an uncertainty on the correct assessment of the actual amount of ammonium absorbed by the NH<sub>4</sub>CZ. As far as author’s knowledge is concerned, and with the exception of the NIST Ammonium ZSM-5 (which, however, is related to a synthetic zeolite), there is no certificated standard for natural zeolite exchanged with ammonium to be used to make a comparison.

Beside this, the overall analysis of the experimental results seems to indicate that, when operating conditions developed in the laboratory are paralleled at the prototype, the efficiency is lower (i.e., a minor amount of ammonium is absorbed by zeolite, Table 5a). This outcome, however, was expected since it was reasonable to assume that the physical interaction between manure and zeolite obtained in the batch experiments on small amounts of suspension can be paralleled at the prototype, but not exactly replicated.

The cation exchange capacity of the zeolite

largely depends on the content of zeolite added to the solution: a low value of zeolite/manure ratio determines a low daily production of zeolite with a high  $\text{NH}_4^+$  content; conversely a high value of the ratio allows a greater production of zeolite with low content of ammonium. The experiments optimized the best working conditions in order to allow  $\text{NH}_4\text{CZ}$  production at large scale. To achieve this goal it would have been counterproductive to test ratios lower than 25 g/L and greater than 75 g/L since in the first case, the operating potential of the prototype would have been underperformed, whereas, in the second case, a zeolite with an ammonium content too low for agricultural purposes would have been produced.

The differences between some of the measured parameters, in terms of exchanged cations, are not strictly relevant for the ultimate goal of manufacturing a zeolite enriched in ammonium to be used as a good soil conditioner. The  $\text{NH}_4\text{CZ}$  obtained through the prototype treatment bears 0.40-0.43 mmol/g of ammonium (Table 5a), which means an average of 9.6 g of nitrogen per each Kg of material; when added into an agricultural soil at an amount  $\geq 50$  ton/ha, it supplies 480 kg or more of nitrogen, allowing a considerable reduction of the fertilization (up to 70% depending on the kind of crop).  $\text{NH}_4\text{CZ}$  do not suffer ammonium leakage in consequence of rainfalls and/or irrigation (Colombani et al., 2014), so that the total amount of nitrogen input in an agricultural field thanks to the addition of  $\text{NH}_4\text{CZ}$  is theoretically at crop's disposal, as testified by several studies on greenhouse tests (Passaglia, 2008 and references therein), and by the results of the first year of experimental cultivation at ZeoLIFE experimental field (Faccini et al., 2014). Of course, the possible range of variation of ammonium content have to be taken into consideration when the mass balances between nitrogen added to the soil and nitrogen detected in porewater and groundwater will be carried out as a task of ZeoLIFE project.

## Conclusions

Laboratory batch experiments for ammonium exchange between natural chabazite-zeolite and swine manure resulted in a maximum uptake using a zeolite/manure ratio of 25 g/L, 45' of stirring time and a optimal resting time variable between 8 and 12 hours. These conditions have been successfully applied in a prototype tank for large scale production of  $\text{NH}_4\text{CZ}$  to be added in an experimental agricultural field. Prototype  $\text{NH}_4\text{CZ}$  contains an average of 0.41 mmol/g of ammonium, and the treatment favours the precipitation of phosphorus in the residual solid, making it a corrective capable to allow a reduction in the amount of NPK fertilizers.

## Acknowledgements

Authors thanks Paolo Chiarelli for his technical support in the preparation and during the laboratory batch experiments, and Dino Lanzarri and Bruno Saraceno for prototype assistance. This work has been sustained by the EU-funded ZeoLIFE project (LIFE+10/ENV/IT/000321).

## References

- Antoniadis V., Damalidis K. and Koutroubas S.D. (2012) - Nitrogen and phosphorus availability to ryegrass in an acidic and limed zeolite-amended soil. *Agrochimica*, 56, 309-318.
- Arbat G., Roselló A., Domingo Olivé F., Puig-Bargués J., González Llinàs E., Duran-Ros M., Pujol J. and Ramírez de Cartagena F. (2012) - Soil water and nitrate distribution under drip irrigated corn receiving pig slurry. *Agricultural Water Management*, 120, 11-22.
- Aschonitis V.G., Mastrocicco M., Colombani N., Salemi E., Kazakis N., Voudouris K. and Castaldelli G. (2012) - Assessment of the intrinsic vulnerability of agricultural land to water and nitrogen losses via deterministic approach and regression analysis. *Water, Air, & Soil Pollution*, 223, 1605-1614.
- Benbi D.K. (2013) - Greenhouse gas emissions from agricultural soils: sources and mitigation potential.

- Journal of Crop Improvement*, 27, 752-772.
- Bish D.L. and Ming D.W. (2001) - Natural zeolites: occurrence, properties, applications. Reviews in Mineralogy & Geochemistry, The Mineralogical Society of America, Washington, DC, 654 pp.
- Bortone G., Gemelli S., Rambaldi A. and Tilche A. (1992) - Nitrification, Denitrification and Biological Phosphate Removal in Sequencing Batch Reactors Treating Piggery Wastewater. *Water Science and Technology*, 26, 977-985.
- Colombani N., Mastrocicco M., Di Giuseppe D., Faccini B. and Coltorti M. (2014) - Variation of the hydraulic properties and solute transport mechanisms in a silty-clay soil amended with natural zeolites. *Catena*, 123, 195-204.
- Del Amo Y., Le Pape O., Tréguer P., Quéguiner B., Ménesguen A. and Aminot A. (1997) - Impact of high-nitrate freshwater inputs on macrotidal ecosystems. I. Seasonal evolution of nutrient limitation for the diatom-dominated phytoplankton of the Bay of Brest (France). *Marine Ecology Progress Series*, 161, 213-224.
- De Wit R., Leibreich J., Vernier F., Delmas F., Beuffe H., Maison Ph., Chossat J.-C., Laplace-Treytore C., Laplana R., Clavé V., Torre M., Aubyc I., Trut G., Maurer D. and Capdeville P. (2005) - Relationship between land-use in the agro-forestry system of les Landes, nitrogen loading to and risk of macro-algal blooming in the Bassin d'Arcachon coastal lagoon (SW France). *Estuarine, Coastal and Shelf Science*, 62, 453-465.
- Di Giuseppe D., Faccini B., Mastrocicco M., Colombani N. and Coltorti M. (2014) - Reclamation influence and background geochemistry of neutral saline soils in the Po River Delta Plain (Northern Italy). *Environmental Earth Sciences*, 72, 2457-2473.
- Galli E. and Passaglia E. (2011) - Natural zeolites in environmental engineering. In: Zeolites in chemical engineering. (eds): H. Holzapfel, Process Eng Engineering GmbH, Vienna, 392-416.
- Goldberg V.M. (1989) - Groundwater pollution by nitrates from livestock wastes. *Environmental Health Perspectives*, 83, 25-29.
- Karapinar N., (2009) - Application of natural zeolite for phosphorus and ammonium removal from aqueous solutions. *Journal of Hazardous Materials*, 170, 1186-1191.
- Faccini B., Di Giuseppe D., Mastrocicco M., Coltorti M., Colombani N. and Ferretti G. (2014) - Sustainable agriculture and nitrogen reduction: an open-field experiment using natural zeolites in silty-clay reclaimed soil at Codigoro (Po River Delta, Ferrara, Italy). EGU General Assembly 2014, Vienna, 14564.
- FAO (2006) - Livestock long shadow. FAO Eds., Rome, Italy, 390 pp.
- Franzini M., Leoni L. and Saitta M. (1975) - Revisione di una metodologia analitica per fluorescenza-X, basata sulla correzione completa degli effetti di matrice. *Rendiconti della Società Italiana di Mineralogia e Petrologia*, 31, 365-378.
- Hedström A. (2001) - Ion exchange of ammonium in zeolites: a literature review. *Journal of Environmental Engineering*, 127, 673-681.
- Lai T-M. and Eberl D.D. (1986) - Controlled and renewable release of phosphorous in soils from mixtures of phosphate rock and NH<sub>4</sub>-exchanged clinoptilolite. *Zeolites*, 6, 129-132.
- Leoni L. and Saitta M. (1976) - X-ray fluorescence analysis of 29 trace elements in rock and mineral standards. *Rendiconti della Società Italiana di Mineralogia e Petrologia*, 32, 497-519.
- Malferrari D., Laurora A., Brigatti M.F., Coltorti M., Di Giuseppe D., Faccini B., Passaglia E. and Vezzalini M.G. (2013) - Open-field experimentation of an innovative and integrated zeolite cycle: project definition and material characterization. *Rend. Fis. Acc. Lincei*, 24, 141-150.
- Mastrocicco M., Colombani N., Di Giuseppe D., Faccini B. and Coltorti M. (2013) - Contribution of the subsurface drainage system in changing the nitrogen speciation of an agricultural soil located in a complex marsh environment (Ferrara, Italy). *Agricultural Water Management*, 119, 144-153.
- Ming D.W. and Allen E.R. (2001) - The use of natural zeolites in agronomy, horticulture, and environmental soil remediation, in: Natural zeolites: occurrence, properties, applications. (eds): D.L. Bish and D.W. Ming, Reviews in Mineralogy & Geochemistry 45, The Mineralogical Society of America, Washington (USA), 619-654.
- MO2013A000354 Patent (2013) - "Impianto per trattare sostanze organiche e produrre un materiale fertilizzante".
- Obaja D., Macé S., Costa J., Sans C. and Mata-Alvarez J. (2003) - Nitrification, denitrification and biological phosphorus removal in piggery wastewater using a sequencing batch reactor. *Bioresource Technol*, 87, 103-111.
- Passaglia E. (2008) - Zeoliti naturali, zeoliti e loro applicazioni. Arvan, Padova, 99 pp.
- Passaglia E. and Laurora A. (2013) - NH<sub>4</sub> exchange in chabazite, heulandite-clinoptilolite and phillipsite. *Rend. Fis. Acc. Lincei*, 24, 369-376.
- Rivett M.O., Buss S.R., Morgan P., Smith J.W.N.

- and Bemment C.D. (2008) - Nitrate attenuation in groundwater: A review of biogeochemical controlling processes. *Water Research*, 42, 4215-4232.
- Sebilo M., Mayer B., Nicolardot B., Pinay G. and Mariotti A. (2013) - Long-term fate of nitrate fertilizer in agricultural soils. *PNAS*, 110, 18185-18189.
- Skinner C., Gattinger A., Muller A., Mäder P., Fließbach A., Stolze M., Ruser R. and Niggli U. (2014) - Greenhouse gas fluxes from agricultural soils under organic and non-organic management - A global meta-analysis. *Science of The Total Environment*, 468-469, 553-563.
- Statham P.J. (2012) Nutrients in estuaries - An overview and the potential impacts of climate change. *Science of The Total Environment*, 434, 213-227.
- Vassileva P. and Voikova D. (2009) - Investigation on natural and pretreated Bulgarian clinoptilolite for ammonium ions removal from aqueous solutions. *Journal of Hazardous Materials*, 170, 948-953.
- Velthof G.L., Lesschen J.P., Webb J., Pietrzak S., Miatkowski Z., Pinto M., Kros J. and Oenema O. (2014) - The impact of the Nitrates Directive on nitrogen emissions from agriculture in the EU-27 during 2000-2008. *Science of The Total Environment*, 468-469, 1225-1233.
- Wang L., Butcher A.S., Stuart M.E., Gooddy D.C. and Bloomfield J.P. (2013a) - The nitrate time bomb: a numerical way to investigate nitrate storage and lag time in the unsaturated zone. *Environmental Geochemistry and Health*, 35, 667-681.
- Wang X-S, Jimmy Jiu Jiao J.J., Wang Y., Cherry J.A., Kuang X., Liu K., Lee C. and Gong Z. (2013b) - Accumulation and transport of ammonium in aquitards in the Pearl River Delta (China) in the last 10,000 years: conceptual and numerical models. *Hydrogeology Journal*, 21, 961-976.
- Wick K., Heumesser C. and Schmid E. (2012) - Groundwater nitrate contamination: factors and indicators. *Journal of Environmental Engineering*, 111, 178-186.
- Widory D., Kloppmann W., Chery L., Bonnin J., Rochdi H. and Guinamant J-L. (2004) - Nitrate in groundwater: an isotopic multi-tracer approach. *Journal of Contaminant Hydrology*, 72, 165-188.
- Williams P.E.V. (1995) - Animal production and European pollution problems. *Animal Feed Science and Technology*, 53, 135-144.