FAO European Cooperative
Research Network

RAMIRAN

Recycling of Agricultural, Municipal and Industrial Residues in Agriculture

Network Coordinator: José Martinez, Cemagref, Rennes (France)

RAMIRAN 2002

Proceedings of the 10th International Conference of the RAMIRAN Network

General Theme: Hygiene Safety

Štrbské Pleso, High Tatras, Slovak Republic
May 14 - 18, 2002

Edited by Ján Venglovský and Gertruda Gréserová

ISBN 80-88985-68-4

University of Veterinary Medicine
Research Institute of Veterinary Medicine
Hlinkova 1/A
040 01 Košice
Slovak Republic

SOIL APPLICATION OF ZEOLITE (CLINOPTILOLITE) SATURATED BY AMMONIA FROM WASTE AIR PRODUCED IN THE ANIMAL PRODUCTION

H. KUSÁ[1], P. RUZEK[1], K. CIAHOTNÝ[2]

[1]Research Institute of Crop Production; Drnovská 507, 161 06 Prague 6, Czech Republic; phone: + 420-2-330 22 264; fax: +420-2-333 106 36; e-mail: kusa@vurv.cz
[2]Institute of Chemical Technology; Technická 5, 166 28 Praha 6, Czech Republic; phone: + 420-2-2435-4228; fax: +420-2-24310682; e-mail: karel.ciahotny@vscht.cz

ABSTRACT

Natural zeolite clinoptilolite saturated by ammonia coming from waste air in livestock houses was used for plant fertilization beneficially. Application of 300 mg N/kg of dry soil caused 3 to 3.5 times higher yields of mustard in pot experiment in comparison with control or soil enriched by natural clinoptilolite from deposit without ammonia. The amendment of soil (euthric Cambisol) by natural clinoptilolite did not influence the soil properties as well as plant yield and quality. Two types of clinoptilolite saturated by ammonia were used. The first one was used for ammonia adsorption in natural form the second one was pre-treated with H3PO4.The former contained 10.8 mg NH3/g the latter 26.3 mg NH3/g. The amounts of clinoptilolites in each pot were determined on the base of nitrogen content (the doses of nitrogen in both variants were the same - 300 mg N/kg of dry soil). In case of clinoptilolite pre-treated with acid nitrogen was released into soil solution more slowly and nitrified gradually. There were no statistically significant differences in obtained yields and nutrients (N, P, K, Ca, Mg) content in plants between two forms of clinoptilolite saturated by ammonia.

Key Words: clinoptilolite, ammonia, nitrogen, fertilization

INTRODUCTION

Natural zeolite as clinoptilolite has special physical and chemical properties that could improve the soil properties. Generally, zeolites have been used to improve soil fertility, to develop slow-release fertilizers enriched with ammonium as well as to affect the buffer capacity of soils. Inherent pore size makes zeolites ideal for sorption what is beneficially used e.g. in gas purification. Saturated material can be regenerated or utilized. In case of ammonia sorption one possibility of utilization is application of saturated zeolite into agricultural soil as source of nitrogen for plants fertilization.

MATERIAL AND METHODS

Natural clinoptilolite from deposit Nizny Hrabovec (Tab. 1; Slovakia) was used. In pot experiment the agronomical effects of various forms of clinoptilolite saturated with ammonia from waste air in livestock houses (Ciahotny, in this book) were studied. Tested materials were as follows: natural clinoptilolite saturated with ammonia containing 10.8 mg NH_3/g (var. 3) and clinoptilolite pre-treated with 40% H_3PO_4 before adsorption and containing 26.3 mg NH_3/g (var. 4). These two materials were added into soil in doses of 300 mg N/kg dry soil. Comparative variants of experiment were both non-treated soil (var. 1; euthric Cambisol; pH/KCl = 5.8; pH/H_2O = 6.9) and soil amended by natural non-treated clinoptilolite (var. 2). In each pot (2.4 kg of dry soil) 25 seeds of white mustard were seed. Deionised water was used for irrigation.

Soil solution were sampled during vegetation (using of Rhizon SMS). Samples of cultivated plants were analyzed in two vegetation stages - the 3rd and 7th week after seeding.

The concentrations of nitrogen and other nutrients (P, K, Ca, Mg) in plants (above ground part only) as well as in soil solution during vegetation were determined (ICP-OES Spectrometer Trace Scan).

Tab. 1 Semi-quantitative analyses of natural clinoptilolite (Nizny Hrabovec , Slovakia) (x-ray fluorescence; ARL 9400)

SiO_2	48.2 %	BaO	0.145 %
Al_2O_3	9.09 %	TiO_2	0.139 %
CaO	3.62 %	Na_2O	0.137 %
K_2O	2.78 %	SrO	560 ppm
Fe_2O_3	1.37 %	MnO	280 ppm
MgO	1.01 %	Rb_2O	250 ppm
H_2O	6.67 %	ZrO_2	170 ppm
CO_2	1.34 %	Co_3O_4	56 ppm
LOI	25.4 %		

Fig. 1 Concentration of NH_4-N in soil solution

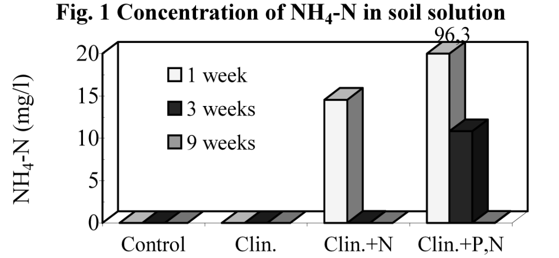


Fig. 2 Concentration of NO_2-N in soil solution

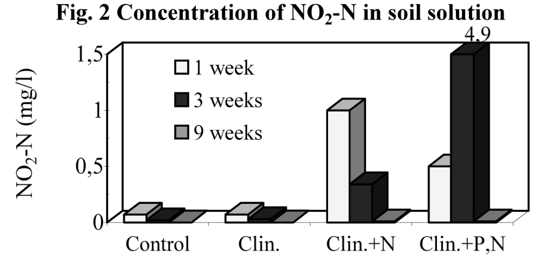
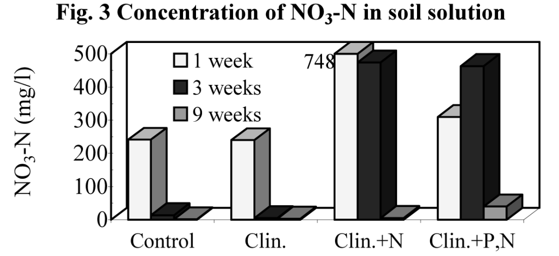


Fig. 3 Concentration of NO_3-N in soil solution



RESULTS AND DISCUSSION

The greatest differences among variants were found in processes of release of mineral forms of nitrogen and phosphorus to soil solution. Fig. 1-3 show found concentrations of inorganic nitrogen in soil solution during vegetation. In control and natural clinoptilolite variants almost every mineral nitrogen was in nitrate form (which is taken by plants) already one week after the experiment establishment. After three weeks the level of plants of all variants was equable. During this time the large amount of nitrogen from soil supply was exhausted in control comparative variants (1 and 2) and nitrogen deficiency showed in the next vegetation phases.

The ammonia release from zeolite and gradual nitrification took place after soil application of clinoptilolites saturated by ammonia. Also in these cases (var. 3, 4) the majority portion of mineral nitrogen in soil solution was the nitrate one but together the significant amounts of nitrogen in lower oxidation states were found. Ammonia release from zeolite utilized for adsorption in natural form took place more quickly and the highest concentrations of all observed nitrogen forms during whole vegetation were found one week after zeolite application in soil. Two weeks later practically no ammoniacal but only oxidized forms of nitrogen were detected. The decrease of their amount was caused by nutrients uptake by plants above all. Ammonia release from pre-treated clinoptilolite (var. 4) took place gradually owing to acid impregnation of zeolite and stronger bonds of ammonia to adsorbent. Fig. 1 shows that in this case higher order concentration of ammoniacal nitrogen in soil solution than in the other variants was found one week after zeolite addition to soil. In this time nitrogen was nitrified only partially. In consequence of slower course of these processes the highest concentrations of nitrites and nitrates in soil solution were determined in the later terms (3 weeks) whereas in the other variants the decrease of their concentration in consequence od plant consumption was observed in this one they were yet amended from fertilizer.

Even after mustard harvest higher concentrations of NH_4-N and NO_3-N were found in soils enriched by clinoptilolites saturated by ammonia. In comparison with control these amounts were three and six times higher in case of natural and pre-treated clinoptilolite respectively.

Fig. 4 Nitrogen concentration in mustard plants

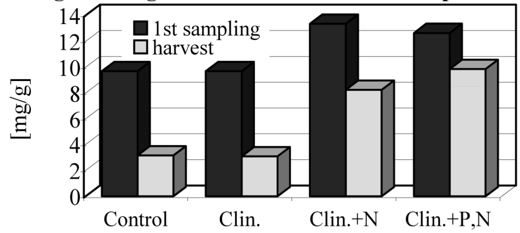


Fig. 5 Phosphorus concentration in soil solution

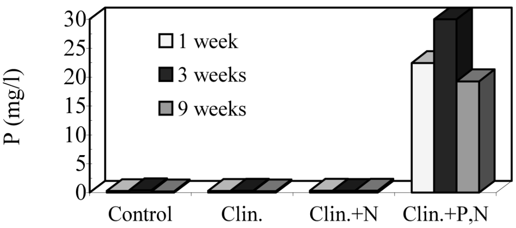
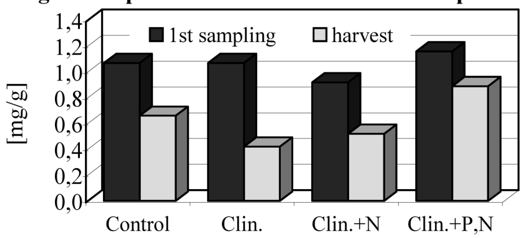
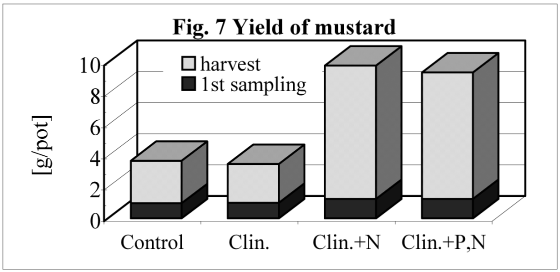


Fig. 6 Phosphorus concentration in mustard plants



Higher concentrations of NO_3-N and NH_4-N in soil solutions of variants enriched by nitrogen containing clinoptilolites also caused elevated contents of nitrogen in plants (Fig. 4). Three weeks after experiments establishment (1st sampling) the highest one was found in case of application of natural clinoptilolite saturated with ammonia. But four weeks later (harvest) the highest nitrogen concentration was determine in plants cultivated on soil fertilized by acid pre-treated clinoptilolite from which where nitrogen was released gradually during vegetation.

Phosphorus concentrations in soil solution (Fig. 5) were low with the exception of variant with clinoptilolite pre-treated with H_3PO_4. In this case higher order concentrations were found during all vegetation the highest one three weeks after zeolite application into soil. Together with soil solution the highest concentration of phosphorus in plants was determined in this variant. The elevation of phosphorus content in plants in this case in comparison with the other variants was statistically significant in both analyses during vegetation (3 and 7 weeks). Higher differences among variants were taken in later growth phases.



Application of various types of clinoptilolite affected neither germination nor plants emergence. No significant differences were observed among tested variants in initial phase of experiment. After four weeks of vegetation the nitrogen deficiency showed in variants without nitrogen fertilization (i. e. control and natural clinoptilolite from the deposit). The obtained yields were therefore 3 to 3.5 times lower than in variants with nitrogen containing clinoptilolites (Fig. 7). The mutually differences between both variants without nitrogen or with nitrogen were lower than 10% and were not statistically significant. Application of natural clinoptilolite from deposit did not affect obtained yield of biomass.

CONCLUSION

Performed experiment showed natural zeolite (as clinoptilolite) after utilization in purification of waste air in animal production can be beneficially used in plant production. Sorbed NH_3 was source of nitrogen for plants and affected obtained yields positively.

Zeolite pre-treated with acid showed higher adsorption capacity than natural non-treated material. Also in consequent soil application it offered one advantage - nutrients were released from zeolite slowly, gradually for longer period. However this material has acid reaction and its applicable dose can be limited by its influence on soil reaction.

ACKNOWLEDGEMENT

The financial supports of the work by the Ministry of Agriculture of the Czech Republic via Research Project No 01-01-01 and the Grant Agency of the Czech Republic via Grant No 104/00/1007 are gratefully acknowledged.