The use of HEU-type zeolitic tuff in the management of agricultural nitrate load: Experimental study on soil and vadose zone leachates

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Keywords: zeolite, nitrates, soil, leachates, sustainable agriculture
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Abstract

Agricultural areas are by definition vulnerable to environmental pressures related to excessive use of fertilizers and agrochemicals. Nitrogen leaching from cropland contributes to increased nitrate levels in ground and surface water (Lichtenberg and Shapiro 1997) and constitutes a focal point for European legislation (Council Directive 1991) in terms of environmental protection and mitigation of potential threats. Depending on the concentration, elevated N levels may cause adverse effects to aquatic ecosystems and humans, particularly to infants and also result in collateral financial impacts for farmers due to the expense of fertilizers (Perrin et al. 1998).

Nitrates (NO3-) are present to some degree in almost all cropland. Depending on soil's leaching potential, when water is added in excess of the soil's field capacity (e.g. through precipitation and/or irrigation) it will carry nitrate and other salts downward. Controlling nitrate leaching is challenging because it requires simultaneous management of two essentials of plant growth; nitrogen (N) and irrigation water. Any factor influencing soil moisture (such as rainfall, irrigation, evaporation and transpiration) will impact nitrate movement. A key practice for reducing leaching losses is to minimize the amount of nitrate present in the soil at any given time. This goal can be difficult to achieve because rapidly growing crops require adequate N. Hence, integrated agriculture is seeking for alternatives in order to achieve optimal conditions for both plants and their environment. Such an alternative may be considered the zeolitic tuffs; they may be applied as soil amendments, aiming to reduce nitrate leaching, and in parallel, to improve critical parameters for crops like soil humidity.

Zeolites exist in nature in many forms; a common form is the zeolitic tuff which corresponds to a rock that contains high amounts of one or more from the different (>65) phases of zeolites. The HEU-type (clinoptilolite–heulandite) is zeolite with variable applications; it shows tabular crystals and contains micro/nanopores in a framework of channels with 10- and 8-member rings, in dimensions of 7.5×3.1 Å, 4.6×3.6 Å and 4.7×2.8 Å (Baerlocher et al. 2007; Mitchell et al. 2012). Very-high quality HEU-type zeolitic tuffs, displays unique physical and chemical features and has a wide range of environmental, industrial and agricultural applications (Tsitsishvili et al. 1992; Colella and Mumpton 2000; Filippidis and Kantiranis 2007; Filippidis et al. 2008; Filippidis et al. 2015a,b; Kantiranis et al. 2011; Tzamos et al. 2011). In this context, the present research aims to investigate the overall efficacy of HEU-type zeolite to reduce nitrate concentrations in soils and subsequently in nitrate leaching; all experiments took into account, apart from the environmental performance of the material, the financial viability of the applications, in order to provide farmers a with a realistic, yet robust, soil amendment.

The field experiment was performed in the premises of Soil and Water Resources Institute (SWRI) of Hellenic Agricultural Organization "Demeter" in Sindos-Thessaloniki, Greece. Irrigation water was enriched in nitrates (totally 80L with 100 mg/L concentration) and was applied in doses following a common irrigation scheme for cultivations. The experiment took place between May and July of 2015 (10 weeks), resembling the dry conditions of a hydrological year. The experiment included the construction of four (4) prototype devices composed of a cylinder pipe (column) of 500mm diameter, which were subsequently filled with soil and soil-zeolitic tuff mixture in different proportions. The lower 30cm of the columns were filled with the homogenized reference soil, whilst the upper 20 cm were filled with the zeolitic tuff-soil mixture in three (3) different proportions, namely 0% (reference) (R), 0.2% (A), 0.4% (B) and 0.6% (C) zeolitic tuff in the mix, respectively. The above quantities were selected intentionally as they correspond to application of 500, 1000 and 1500 kg of zeolitic tuff per acre. These quantities are higher than the common applications used annually in agriculture, but may be achieved through the cumulative additions of zeolitic tuff quantities, hence remain on the verge of financial viability for the farmers (depending on the case). A prototype solution of KNO3 with 100mg/L of NO3- was used as irrigation water. Each irrigation dose included 2.5 litres of the prototype solution. The total volume of irrigation water used was 40L and corresponds to 260mm per year.

Based on the analytical results of leachates, nitrate load is decreased significantly in zeolite treated soils compared with the reference (untreated) sample. The initial concentration of nitrates in reference ® sample is 894 mg/L, whilst the initial concentrations in leachates of A, B and C samples are 554, 471 and 458 mg/L respectively, corresponding to a decreased concentration of 38, 47% and 49% of initial R leachates (Table 1).

Table 1 – Percentages of nitrate load reduction in leachates compared to reference sample

	Start (5.5th week)	Intermediate (8th week)	End (10th week)
Reference (R)	894 mg/L	162 mg/L	81 mg/L
0.2 % Z (A)	38%	26%	2%
0.4 % Z (B)	47%	50%	81%
0.6 % Z (C)	49%	55%	86%

The results of nitrate load reduction obtained from soil mixing with natural HEU-type zeolitic tuff (ZT) were promising; nitrate load was decreased in 0.4% ZT sample by 81%, whilst in 0.6% ZT sample by 86%. Results revealed that zeolitic tuff mixture may act as an efficient natural sorbent with a remarkable ability to retain nitrate leachates from soils, up 86% of the initial leachates of the reference (untreated) sample. The maximum retention percentage was achieved with a 0.6% addition of zeolitic tuff, which is within the margins of financial viability for common farmers

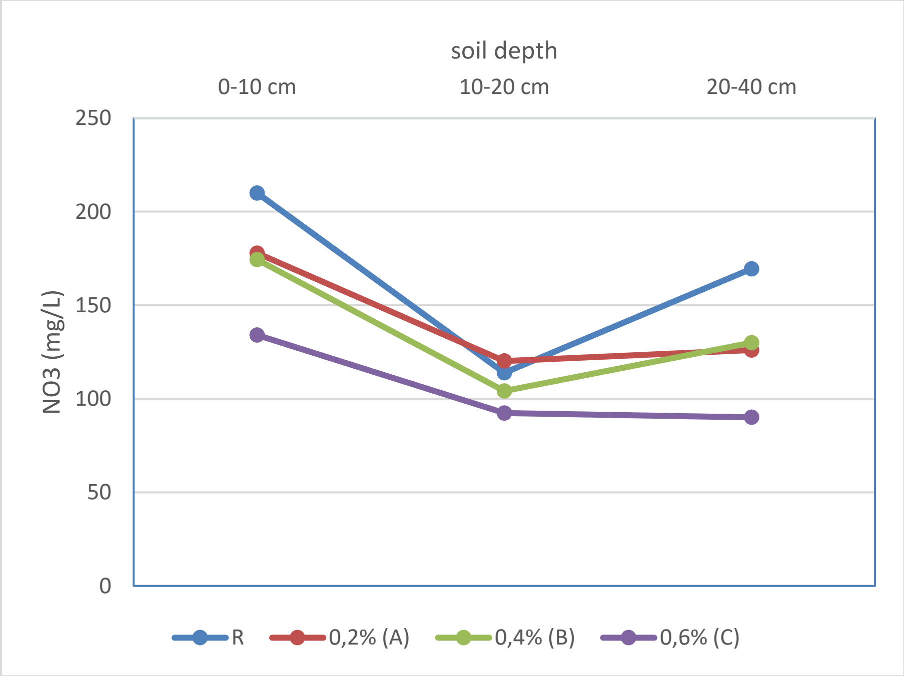

Figure 1 – Residual concentrations (mg/L) of nitrates in soil for different proportions of zeolite mix

Based on the analytical results of soil samples, all mixtures (A, B, C) appeared to be effective for the 0-10cm, as may be documented by their concentrations in nitrates (178, 174 and 134 mg/L, for A, B and C mixtures, respectively) which are significantly lower compared to the reference sample (210 mg/L). From 10-20 cm, the decrease of nitrates is still effective, and further lowers the concentrations of nitrates. However, from 20-40cm, the nitrates are increasing for the reference sample and A, B mixtures, whilst, for the C mixture nitrates are still decreasing. The latter outlines that the retention capacity of A and B mixtures is exhausted, on the contrary to C mixture which is still effective and leads to a minor, yet steady further decrease rate of nitrates, even below 20 cm soil depth.

Conclusively, the results obtained in laboratory scale from this study are quite promising for the efficacy of zeolitic tuff as natural sorbent and its contribution to rational agricultural practices against nitrate contamination, both for soil and vadose zone leachates that may impact surface and groundwater resources. The promising outcomes are in line with the objectives of the new common EU agricultural policy, and may act as a supplementary tool for integrated fertilization, water resources management and environmental protection.

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