

THE USE OF HEU-TYPE ZEOLITIC TUFF IN SUSTAINABLE AGRICULTURE: EXPERIMENTAL STUDY ON THE DECREASE OF NITRATE LOAD IN VADOSE ZONE LEACHATES

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Abstract

A HEU-type zeolitic tuff of very-high quality (88 wt.% clinoptilolite-heulandite) has been used as an additive to natural soils, aiming to reduce the produced nitrate load in leachates, following a common irrigation scheme. Zeolitic tuff has been added and mixed with agricultural soil in three different proportions (0.2, 0.4 and 0.6%) corresponding to an application of 500, 1000 and 1500 kg per acre. The control soil (without zeolitic tuff) and the three mixtures were exposed in a ten weeks experiment, in which, specific doses of irrigation water enriched in nitrates were added. Results of leachates analyses revealed that the addition of 0.2% zeolitic tuff is not effective and the mixture of soil-zeolitic tuff appears to have similar behaviour with the untreated (reference) soil sample. On the contrary, zeolitic tuff additions by 0.4% and 0.6% showed remarkable results and reduced the nitrate load of leachates by 81 and 86%, respectively. Hence, the impacts from the application of very-high quality HEU-type zeolitic tuff in agricultural soils could be rather positive towards environmental protection and rational farming, an in line with the goals and objectives of the new common agricultural policy imposed by European Union.

Keywords: zeolite, agriculture, nitrates, environmental protection, leachates.

Περίληψη

Στην παρούσα εργασία χρησιμοποιήθηκε ένας πολύ υψηλής ποιότητας ζεολιθικός τόφος τύπου-HEU (88% κ.β. κλινοπιλόλιθος-εουλανδίτης) ως πρόσθετο υλικό σε φυσικά εδάφη, με στόχο την ελάττωση της συγκέντρωσης των παραγόμενων εκπλυμάτων νιτρικών ιόντων, υπό συνήθεις συνθήκες άρδευσης. Ο ζεολιθικός τόφος αναμίχθηκε με το έδαφος σε τρεις αναλογίες (0.2, 0.4 και 0.6%) οι οποίες αντιστοιχούν σε εφαρμογή 500, 1000 και 1500 kg ανά στρέμμα. Στο δείγμα αναφοράς (μάρτυρας – απουσία ζεολιθικού τόφου) και στα τρία μίγματα εδάφους-ζεολιθικού τόφου πραγματοποιήθηκε πείραμα διάρκειας 10 εβδομάδων, στο οποίο, διοχετεύτηκαν σταθερές δόσεις αρδευτικού νερού εμπλουτισμένου με νιτρικά ιόντα. Τα αναλυτικά αποτελέσματα των εκπλυμάτων έδειξαν ότι η προσθήκη ζεολιθικού τόφου κατά 0,2% δεν ήταν αποτελεσματική και το μίγμα συμπεριφέρθηκε ανάλογα του δείγματος

αναφοράς. Αντιθέτως, η προσθήκη ζεολιθικού τόφφου σε περιεκτικότητες 0,4% και 0,6% έδωσε σημαντικά αποτελέσματα, καθώς η συγκέντρωση νιτρικών ιόντων μειώθηκε κατά 81% και 86% αντίστοιχα, σε σχέση με το έκπλυμα του μάρτυρα. Συνεπώς, οι επιπτώσεις από την εφαρμογή πολύ υψηλής ποιότητας ζεολιθικού τόφφου στα αγροτικά εδάφη, μπορεί να έχει σημαντικά θετικές επιπτώσεις στην περιβαλλοντική προστασία και στην αειφόρο γεωργία, γεγονός που είναι συνδεδεμένο άμεσα με τους στόχους της νέας κοινής αγροτικής πολιτικής της Ε.Ε και την σχετική νομοθεσία.
Λέξεις κλειδιά: Ζεόλιθος, καλλιέργεια, νιτρικά, περιβαλλοντική προστασία, εκπλύματα.

1. Introduction

Soil and water quality deterioration has become a significant challenge due to population growth combined with other man-made activities, like e.g. irrational agriculture and industrialization. As a result, a considerable increment of contaminants has been recorded worldwide in the aforementioned compartments, denoting a significant impact to their overall quality and environmental characteristics.

Agricultural areas are by definition vulnerable to environmental pressures related with 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, except flooded soils. 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 can be a challenge for farmers because it requires simultaneous management of two essentials of plant growth; nitrogen (N) and water. Any factor influencing soil moisture (such as rainfall, irrigation, evaporation and transpiration) will impact nitrate movement. In general, more water infiltration results in nitrate moving deeper in the profile. Soil properties also have a major impact on the extent of nitrate movement. However, the extent of nitrate movement to groundwater depends on the underlying soil and bedrock conditions, as well as depth to groundwater.

Nitrate in a field may originate from many sources, including manures, composts, decaying plants, septic tanks, or from fertilizer which is rather common in agricultural soils. Nitrate behaviour does not depend on its sources; the simple fact is that any nitrate available for plant uptake is vulnerable to leaching loss. One 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 use of zeolitic tuffs as a soil conditioner 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 zeolite with the numerous applications is the HEU-type zeolite (clinoptilolite-heulandite) that 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, display unique physical and chemical features and have a great variety of environmental, industrial and agricultural applications (Tsitsishvili *et al.*, 1992; Colella and Mumpton, 2000; Filippidis and Kantiranis, 2007; Filippidis *et al.*, 2008a, 2015a, b; Kantiranis *et al.*, 2011; Tzamos *et al.*, 2011; Vogiatzis *et al.*, 2012; Filippidis, 2013).

Using very-high quality HEU-type zeolitic tuff, the nitrate load reduction were found to be 86-92% in batch treatments of Kilkis city urban wastewaters (Filippidis *et al.*, 2008b, 2012, 2015a; Filippidis, 2008, 2009, 2010; Filippidis and Tsirambides, 2012), 94% in batch treatment of Thessaloniki dyeing industry wastewater (Filippidis *et al.*, 2015b), 54-60% in batch treatments of Sindos industrial area wastewaters (Filippidis *et al.*, 2011a,b, 2013, 2014), 57% in batch treatment of nitrate-solutions (Filippidis, 2007, 2010), 55% in batch treatment of groundwater (Filippidis *et al.*, 2006; Filippidis, 2010), and using surfactant modified clinoptilolitic zeolitic tuff, 96-97% in batch and column treatments of groundwater (Masukume *et al.*, 2011). In leaching experiments, 100% of the nitrate were leached from Kilkis city sewage sludge and Thessaloniki dyeing industry sludge (Filippidis *et al.*, 2008b, 2015a, b; Filippidis, 2009; Filippidis and Tsirambides, 2012). Mixing very-high quality zeolitic tuff with sewage and dyeing industry sludge, the nitrate leaching was reduced 81-91% in the case of Zeolitic tuff + sewage sludge (Filippidis *et al.*, 2008b, 2015a; Filippidis, 2009; Filippidis and Tsirambides, 2012) and 82% in the case of zeolitic tuff + dyeing industry sludge (Filippidis *et al.*, 2015b). The present paper investigates the possibility of reducing the nitrate leaching by the addition-mixing the very-high quality zeolitic tuff in the agricultural soils.

2. Materials and Methods

2.1. Description of experimental processing

The field experiment was performed in the premises of Soil and Water Resources Institute (ISWR) of Hellenic Agricultural Organization “Demeter” in Sindos-Thessaloniki, Greece. The goal of the experiment was to assess nitrate leaching of irrigated agricultural soils after been treated-mixed with zeolitic tuff in different proportions; 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 (see details below). The experiment took place between May and July of 2015 (10 weeks), resembling the dry conditions of a hydrological year.

The experimental procedure included the following intermediate steps:

Four (4) prototype devices were constructed; the devices included a cylinder pipe (column) of 500mm diameter (internal diameter 470mm) and total length of 50cm, which subsequently would be filled with soil and soil-zeolitic tuff mixture in different proportions. To the lower part of the cylinder was attached a fine mesh in order to prevent sediment transport. The cylinder was based on a protected metal pan, which was intended to collect leachates from the column. The columns were roof-protected and not exposed to precipitation or any other external water source.

The next step included the sampling (bulk) of reference agricultural soils with medium soil texture from the wider area of Sindos. Samples belonged to the same soil unit, but were further homogenized with mechanic means and dried naturally (sun exposure). 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 KNO_3 with 100mg/L of NO_3^- was used as irrigation water. Each irrigation dose included 2.5 litres of the prototype solution; in order to increase soil saturation and acquire efficient volume of leachates, 3 extra application doses (4 ½, 5 ½ and 6 ½ weeks) were added between the 4th and the 7th week whilst the amount of irrigation water was doubled (5l) for the applications of 5th, 5 ½th and 6th week. Leachates were scheduled to be collected in a weekly time-span, but eventually a sufficient volume was acquired at the fourth week of the experiment; hence six (6) leachate samples were collected in total, from the 5 ½th to 10th week. The total volume of

irrigation water used was 40L and corresponds to 260mm per year. Samples were analysed immediately in the laboratories of ISWR with the use of a LAMBDA35 PERKIN-ELMER spectrophotometer.

2.2. Analysis and characterization of soil and zeolitic tuff

A bulk soil sample was collected from the same soil unit used in the described experimental process, for further physicochemical and mineralogical analysis. The sample was air-dried and a fraction (<2 mm) was used for laboratory determinations. Particle size distribution was determined by the Bouyoucos hydrometer method (Gee and Bauder, 1986) and pH was measured in a saturation paste (Alexiadis, 1967). Cation exchange capacity (CEC) was determined by CH₃COONa saturation solution of 1N and pH of 8.5 or 7 (Bower *et al.*, 1952). Organic matter was determined by liquid oxidation method. Finally NO₃-N was determined through KCl extraction and N total with Kjeldahl method. The same methodologies were applied in zeolitic tuff physicochemical analyses.

The zeolitic tuff sample (grain-size <0.8 mm) used was supplied by ZEOVET Ouzoundis and GEOVET N. Alexandridis & Co O.E. The mineralogical composition of the zeolitic tuff and soil sample was determined by X-Ray Powder Diffraction (XRPD). The XRPD analysis was performed using a Philips PW1710 diffractometer with Ni-filtered CuK_α radiation on randomly oriented samples. The counting statistics were: start angle 3°, end angle 63° (2θ), step size 0.02° (2θ), time per step 1 sec and scan speed 0.02°/sec. Semi-quantitative estimates of the abundance of the mineral phases were derived from the XRPD data, using the intensity (counts) of certain reflections, the density and the mass absorption coefficient of the identified minerals for CuK_α radiation, the software MAUD-Material Analysis Using Diffraction with the RIETVELD method. Clay mineralogy was identified from air-dried, glycolated and heat-treated oriented samples scanned from 3° to 23° 2θ at a scanning speed of 1.2°/min. The semi-quantitative estimation of the percentage of total amorphous materials was achieved by comparing the area of each broad background hump, which represented the amorphous materials in each sample, with the analogous area of standard mixtures of minerals with different contents of natural amorphous material, scanned under the same conditions (Filippidis and Kantiranis, 2007; Kantiranis *et al.*, 2004, 2005, 2006).

3. Results and Discussion

The physicochemical determinations of soil and zeolitic tuff are presented in Table 1. Based on its texture and organic content (USDA 1987) soil sample is characterized as Sandy-Loam (SaL) with slightly alkaline pH (7.8); organic content is 0.6% and cation exchange capacity (CEC) is 9.5 meq/100g; total nitrogen content (Kjeldahl) is 767 mg/kg and NO₃-N is 48 mg/kg. Regarding zeolitic tuff, total nitrogen is 178 mg/kg and NO₃-N 13 mg/kg, respectively.

Table 1 - Physicochemical characteristics of soil and zeolitic tuff samples.

	Texture			CEC meq/100g	pH	Organic C %	N _{total} (Kjeldahl) mg/kg	NO ₃ -N mg/kg
	Sand (%)	Silt (%)	Clay (%)					
Soil	62	22	16	9.5	7.8	0.6	767	48
zeolitic tuff	-	-	-	-	-	-	178	13

The semi-quantitative mineralogical compositions of the zeolitic tuff and soil sample are presented in Table 2 and Figures 1 and 2. Zeolitic tuff contains 88 wt.% HEU-type zeolite (clinoptilolite-heulandite), 5 wt.% mica + clay minerals, 4 wt.% quartz, 2% amorphous materials and 1% feldspars. Soil sample contains 59 wt.% quartz, 21 wt.% feldspars, 15 wt.% micas+clay minerals and 5 wt.% amphibole.

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 (5.5 week) of nitrates

in R 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 3 and Figure 3).

Table 2 - Semi-quantitative mineralogical composition of Zeolitic tuff and soil samples.

Zeolitic tuff		Soil	
Minerals	Wt.%	Minerals	Wt.%
HEU-type zeolite (clinoptilolite-heulandite)	88	Quartz	59
Micas + Clay-minerals	5	Feldspars	21
Quartz	4	Micas + Clay-minerals	15
Feldspars	1	Amphibole	5
Amorphous	2		
Total	100	Total	100

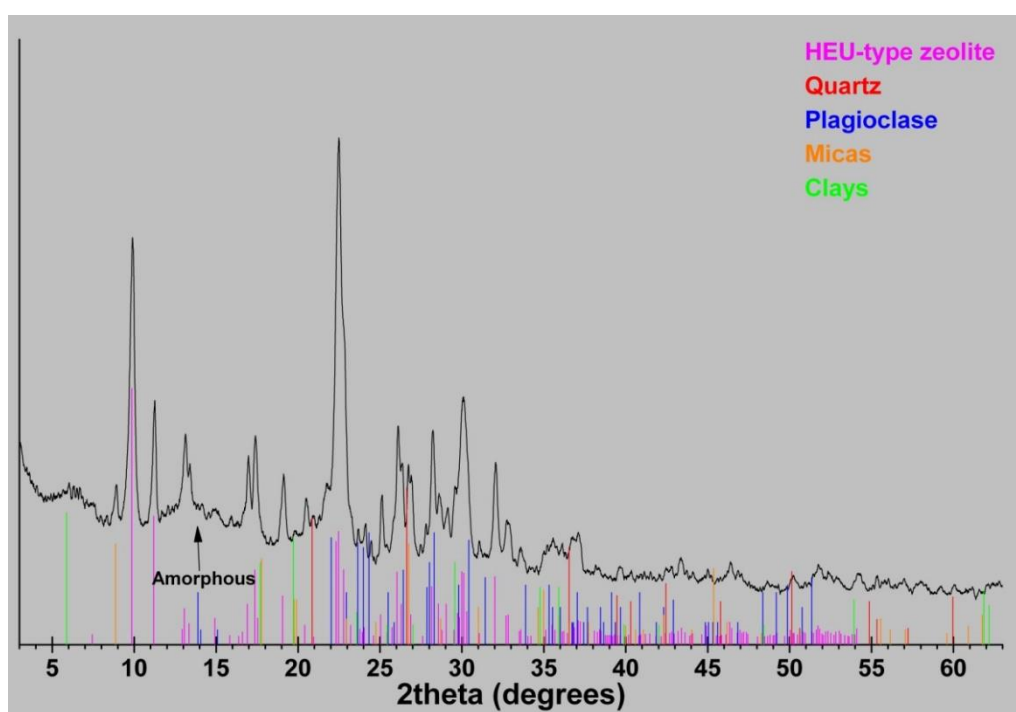


Figure 1 - X-Ray Powder Diffraction pattern of zeolitic tuff sample.

Taken into account that experimental conditions are similar and that soil organic content is in general low (0.6%), it is evident that this significant decrease should be attributed to zeolitic tuff impact. Subsequently, intermediate of the experimental process (8th week), nitrate load concentrations decrease with different rates for A, B and C samples, corresponding to a reduction of 26%, 50% and 55% compared to R leachates. In general, R and A samples follow similar decrease rates for nitrates, denoting an insignificant impact of the 0.2% zeolitic tuff content in soil. This may also be deduced by the concentrations of nitrate load at the end of experiment (10th week), which differ only by 2 mg/L (2%), corresponding to a negligible variation within the standard analytical error. On the contrary, it is rather promising that the final concentrations of nitrate load in samples B and C, has been decreased significantly compared to R sample by 81% and 86%, respectively.

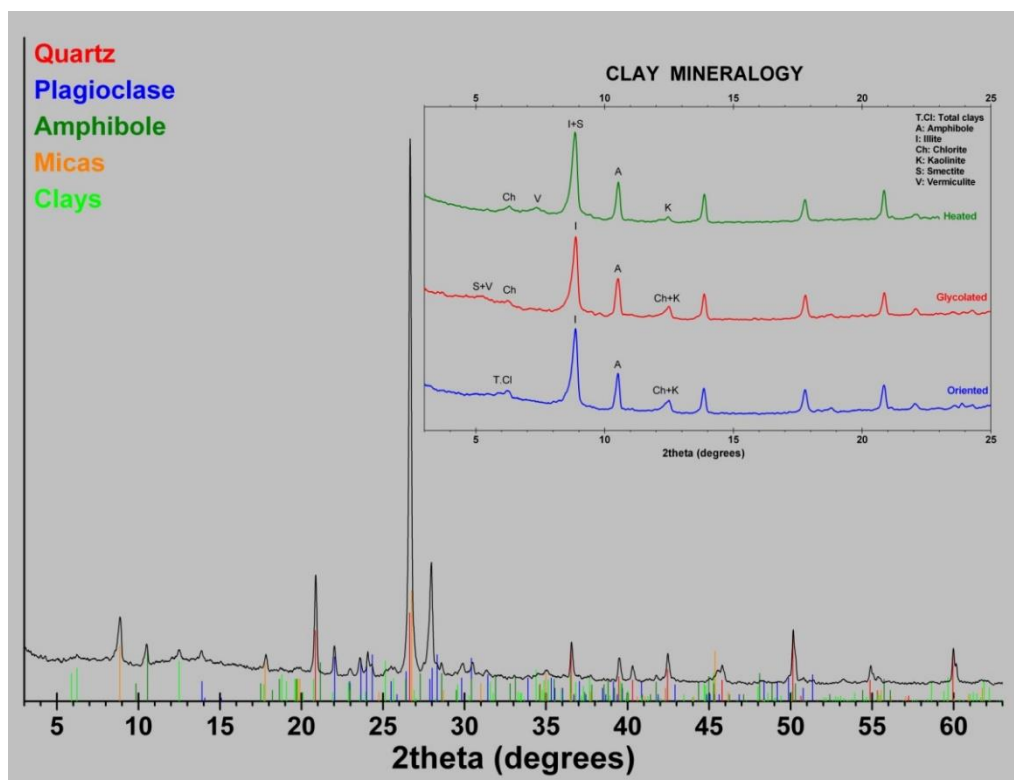


Figure 2 - X-Ray Powder Diffraction pattern of soil sample. Clay mineralogy: Illite, smectite, kaolinite, vermiculite and chlorite.

Table 3 - Percentages of nitrate load reduction in leachates compared to reference sample.

	Start (5.5 th week)	Intermediate (8 th week)	End (10 th 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) are rather successful; nitrate load was decreased in 0.4% ZT sample by 81%, whilst in 0.6% ZT sample by 86%. So far, similar decrease percentages have been recorded using very-high quality HEU-type zeolitic tuff and surfactant modified clinoptilolitic zeolitic tuff, (86-92%) in batch treatments of urban wastewaters (Filippidis *et al.*, 2008b, 2012, 2015a; Filippidis, 2008, 2009, 2010; Filippidis and Tsirambides, 2012), (94%) in batch treatment of dyeing industry wastewater (Filippidis *et al.*, 2015b), (54-60%) in batch treatments of industrial area wastewaters (Filippidis *et al.*, 2011a,b, 2013, 2014), (57%) in batch treatment of nitrate-solutions (Filippidis, 2007, 2010), (55%) in batch treatment of groundwater (Filippidis *et al.*, 2006; Filippidis, 2010), and (96-97%) in batch and column treatments of groundwater (Masukume *et al.*, 2011). In leaching experiments, 100% of the nitrate were leached from Kilkis city sewage sludge and Thessaloniki dyeing industry sludge (Filippidis *et al.*, 2008b, 2015a, b; Filippidis, 2009; Filippidis and Tsirambides, 2012). Mixing very-high quality zeolitic tuff with sewage and dyeing industry sludge, the nitrate leaching was reduced 81-91% in the case of Zeolitic tuff + sewage sludge (Filippidis *et al.*, 2008b, 2015a; Filippidis, 2009; Filippidis and Tsirambides, 2012) and 82% in the case of zeolitic tuff + dyeing

industry sludge (Filippidis *et al.*, 2015b); nevertheless zeolite modification is a non viable process in financial terms for common agricultural practices. In comparison with this study, nitrate removal with a zeolitic rock (70-75 wt.% clinoptilolite) achieved percentages of less of than 10% (Mazeikiene *et al.*, 2008), and proved to be an insufficient for nitrate retention.

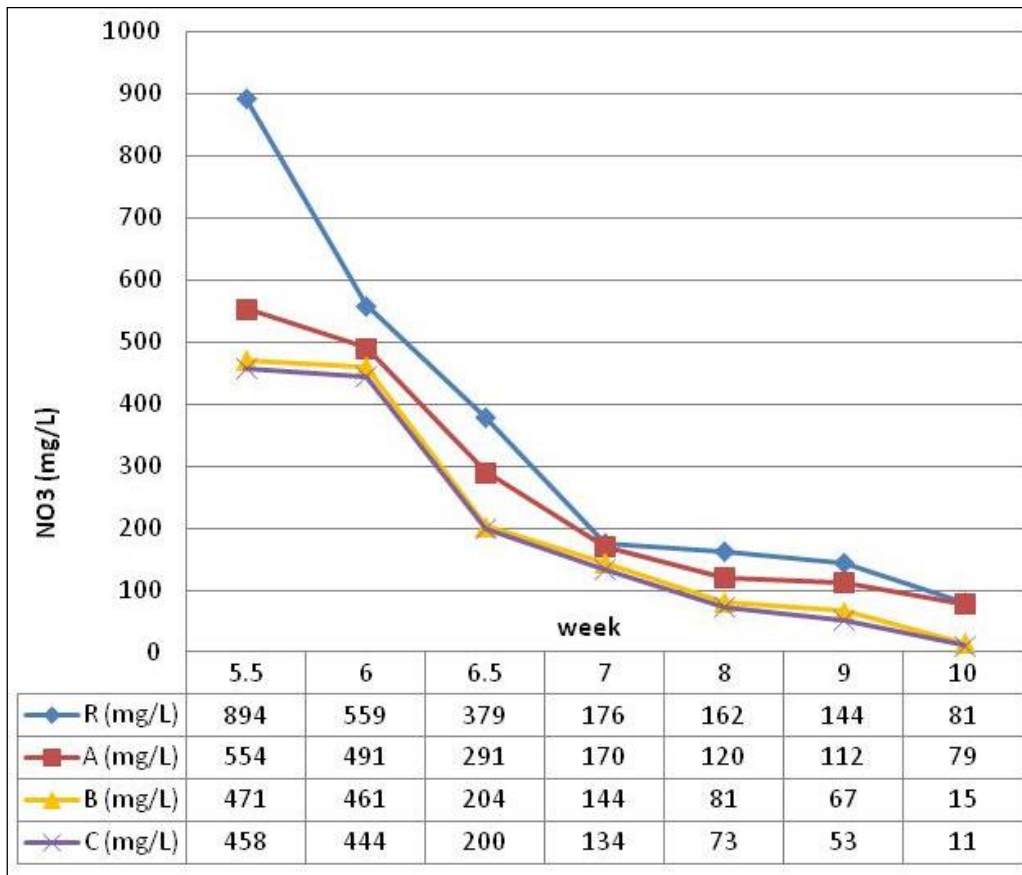


Figure 3 - Nitrate load concentrations in leachates.

On the contrary, the used very-high quality HEU-type zeolitic tuff has proven to be a unique sorbent of bacteria, gases, inorganic, organic and organometallic compounds, and achieves to buffer pH of soils and waters to neutral (e.g., Filippidis and Kantiranis, 2007; Filippidis *et al.*, 2008a, b, 2015a, b; Filippidis, 2010, 2013). The sorption and fixation of the different components from their solutions by the micro/nano-pores of HEU-type zeolite, as well as from meso- and macro-pores of the zeolitic tuff, is attributed to absorption (ion exchange), adsorption and surface precipitation processes (Godelitsas *et al.*, 1999, 2001, 2003; Fu and Wang, 2011; Kantiranis *et al.*, 2011; Malamis and Katsou, 2013). The HEU-type zeolite is characterized by Brønsted acidic and the Lewis basic active sites, that react with the negatively or/and positively charged chemical components, even with molecules in gas condition. These chemical processes are related to sorption and fixation physicochemical phenomena of ions and molecules, and are related both to the structural void spaces (micro/nano-pores) and the surface of the HEU-type zeolite crystals, consequently the meso- and macro-pores of the zeolitic tuff. Finally, HEU-type zeolite shows an ability to neutralize the pH of acidic and basic waters, acting either as a proton acceptor or donor, exhibiting thus an amphoteric character (Misaelides *et al.*, 1995; Godelitsas *et al.*, 1999, 2001, 2003; Kantiranis *et al.*, 2011).

4. Conclusions

A very-high quality HEU-type zeolitic tuff containing 88 wt.% clinoptilolite-heulandite, has been used as a mixing material with soil samples from Sindos area, Thessaloniki. Zeolitic tuff-soil mixture was added on the top 20cm of a totally 50cm column (the remaining covered with untreated soil) in different proportions (0.2, 0.4 and 0.6%) corresponding to an application of 500, 1000 and 1500 kg per acre. Samples were subjected to common irrigation scheme with stable doses, simulating a total volume of 40 L or 260 mm per year. 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 still under conditions within the margins of financial viability form common farmers. However, results should be further exploited and verified in field conditions, with real irrigation and cultivations schemes, and external effects. Nevertheless, 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. The latter is 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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