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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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Introduction

Nitrates (NO_3^-): A significant environmental contaminant for water resources

- Nitrate levels in water bodies is a focal point for European environmental policy (Council Directive 1991/676)
- Diffuse contamination from intensive agriculture (N-fertilizers and manure) is the main source of nitrates in groundwater
- The severity of nitrate contamination problem is illustrated by European Environment Agency (EEA, 2007).

→ The proportion of groundwater bodies with mean nitrate concentration>25 mg/L was reported as being ca. 80% in Spain, 50% in the UK, 36% in Germany, 34% in France and 32% in Italy.

In the UK, the **cost of treatment** to ensure potable water supplies below 50 mg/L of NO_3^- amounted to:
→ **£16 million** per annum during 1992–1997 (Dalton and Brand-Hardy, 2003), and
→ is predicted to rise to **£58 million per annum** by the next 30-40 years (Defra, 2006)

Introduction

Nitrates (NO_3^-) : A significant environmental contaminant for water resources

→ Decrease of nitrate loads in soils and vadose zone leachates would have significant environmental and financial benefits , due to the decrease of aquifer contamination:

a) minimization of health risk effects to humans (methaemoglobianamia and/or cancer) and environmental stresses,

b) increase of available water resources for variable uses.

Research goals

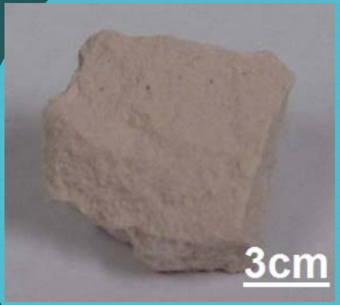
- **investigate the overall efficacy of low cost natural materials to reduce nitrate concentrations in soils and vadose zone leachates**
- **investigate financial viability of their application for farmers.**

Introduction

Zeolites: A geogenic versatile material for environmental applications

- **Zeolites** exist in nature in many forms; a common form is the zeolitic tuff which contains high amounts (>65%) of one or more different zeolitic (mineralogical) phases.

Fig.1: Zeolitic tuffs of variable colors (color is invariable of their quality) (Filippidis, 2015)



- The zeolite with the most applications is the **HEU-type zeolite** (clinoptilolite–heulandite) that shows tabular crystals and contains micro/nanopores in a framework of channels

- Very-high quality HEU-type zeolitic tuffs, display unique physical and chemical features and have a great variety of environmental, industrial and agricultural applications like:

  → industrial catalysis,
  → gas separation,
  → purification of water solutes
  → remediation of soils and improvement of physicochemical properties

Methodology

Description of experiment

Step 1:

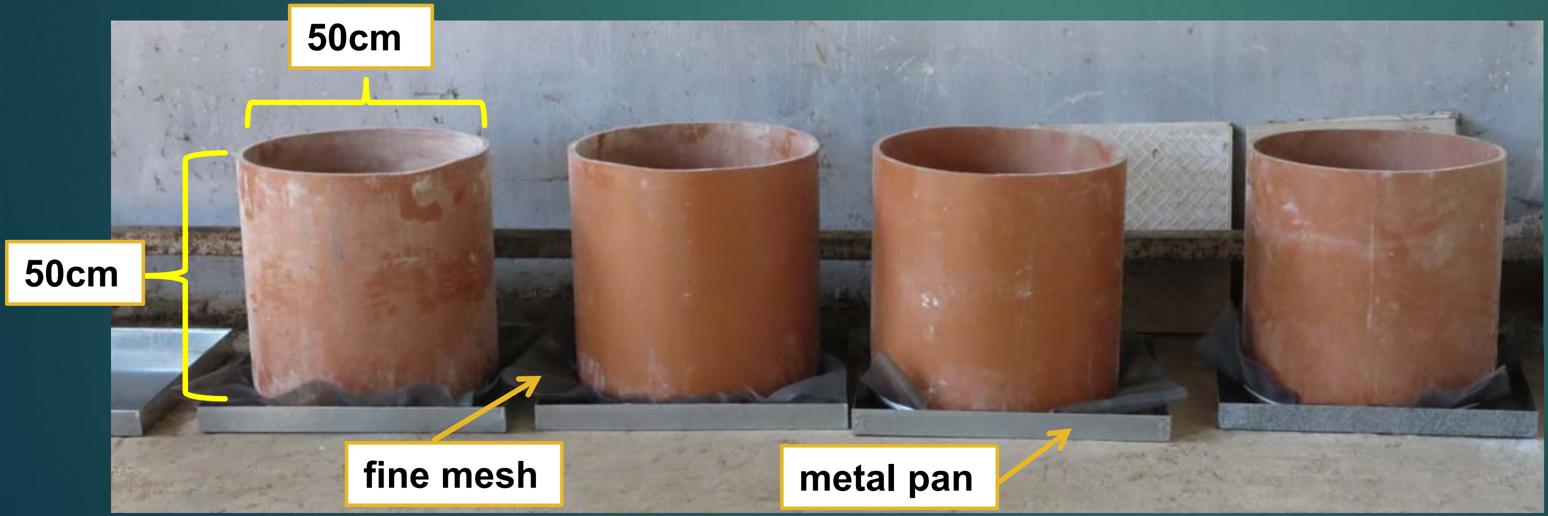
- **Construction of four (4) prototype devices**:

→ a cylinder pipe (column) of 47cm (internal) diameter and 50cm total length,

→ attachment of a fine mesh to its lower part in order to prevent sediment transport.

→ cylinder was based on a protected metal pan, which was intended to collect leachates from the column.

→ columns were roof-protected and not exposed to precipitation or any other external water source.



Methodology

Description of experiment

Step 2:

• sampling (bulk) of agricultural soils with medium soil texture from Sindos area.

• samples belonged to the same soil unit, but were further homogenized with mechanic means and dried naturally.

Methodology

Description of experiment

Step 2:

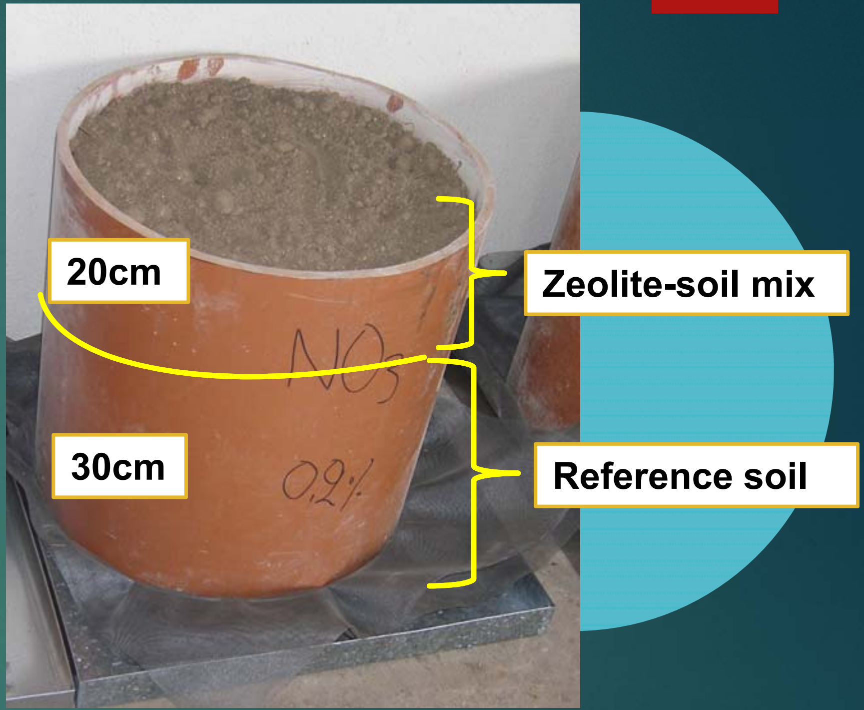
- **Lower 30 cm** were filled with soil,
- **Upper 20 cm** were filled with the zeolite-soil mixture in 3 proportions :

→ **0%** (reference) (R),

→ **0.2%** (A),

→ **0.4%** (B) and

→ **0.6%** (C)



Proportions correspond to application of **500 (0.2%)**, **1000 (0.4%)** and **1500 (0.6%) kg** of zeolitic tuff per acre.

⇩

! **Zeolite quantities are realistic in terms of financial viability for the farmers** (depending on the case).

Methodology

Description of experiment

Step 3:

- 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.

Methodology

Description of experiment

Step 3:

- **Application of one irrigation dose per week, for a total timespan of 10 weeks** (19/5-21/7/2015)

  → in order to increase **soil saturation** and acquire efficient volume of leachates, **3 extra application doses** were added between the **4th** and the **7th week**, whilst the **amount of irrigation water was doubled (5lt)** for the applications between the **5th** and the **6th week**.

  → Sufficient leachates volumes were acquired at the **5 ½ th week** till the end of the experiment **10th week**.

  → The **total volume** of irrigation water used was **40L** and corresponds to **260mm per year**.

Week	1	2	3	4	4,5	5	5,5	6	6,5	7	8	9	10	Total
0 % ZT	X*	X	X	X	X	XX	XX	XX	X	X	X	X	X	16X=40 L
0.2 % ZT	X	X	X	X	X	XX	XX	XX	X	X	X	X	X	
0.4 % ZT	X	X	X	X	X	XX	XX	XX	X	X	X	X	X	
0.6 % ZT	X	X	X	X	X	XX	XX	XX	X	X	X	X	X	
X*= 2,5 L solution of100 mg/L NO_3														

- Samples were **analysed** with the use of a LAMBDA35 PERKIN-ELMER **spectrophotometer**

Results – Analyses

Physicochemical analyses

	Texture			CEC	pH	organic C	Ntotal (Kjeldahl)
	Sand (%)	Silt (%)	Clay (%)	meq/100g		%	mg/kg
Soil	62	22	16	9.5	7.8	0.6	767
ZT	-	-	-	-	-	-	178

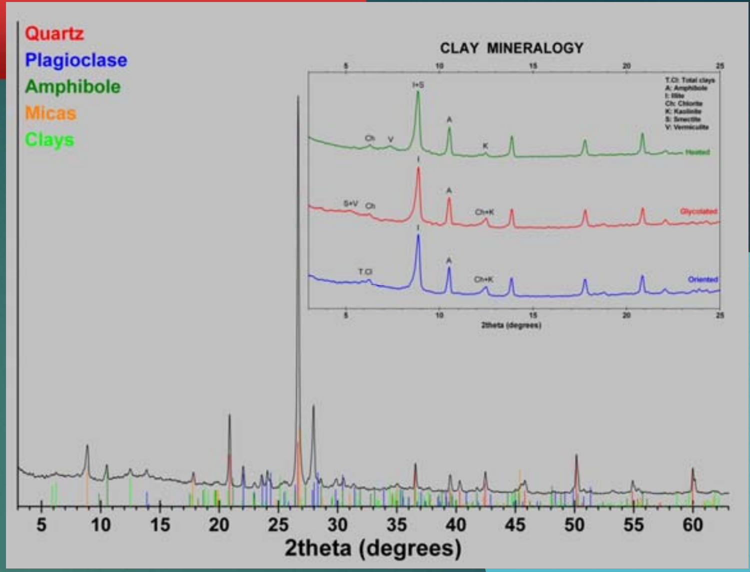


Figure 3: X-Ray Powder Diffraction pattern of soil sample. Clay mineralogy: Illite, smectite, kaolinite, vermiculite and chlorite.

Semi-quantitative mineralogical analyses

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

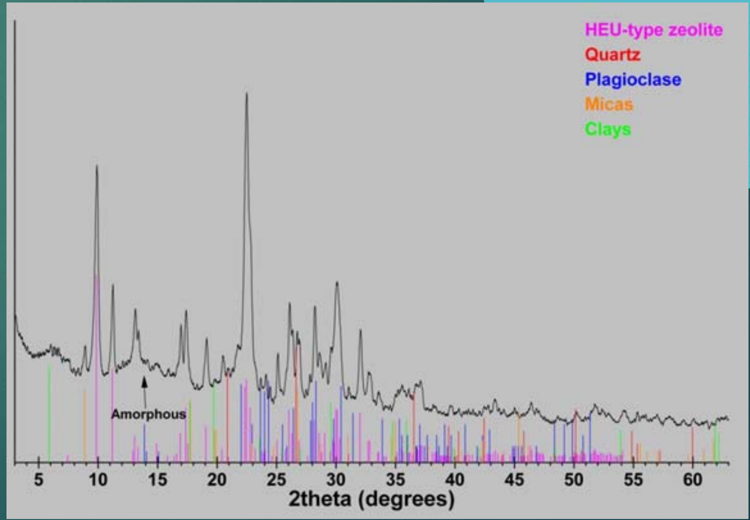
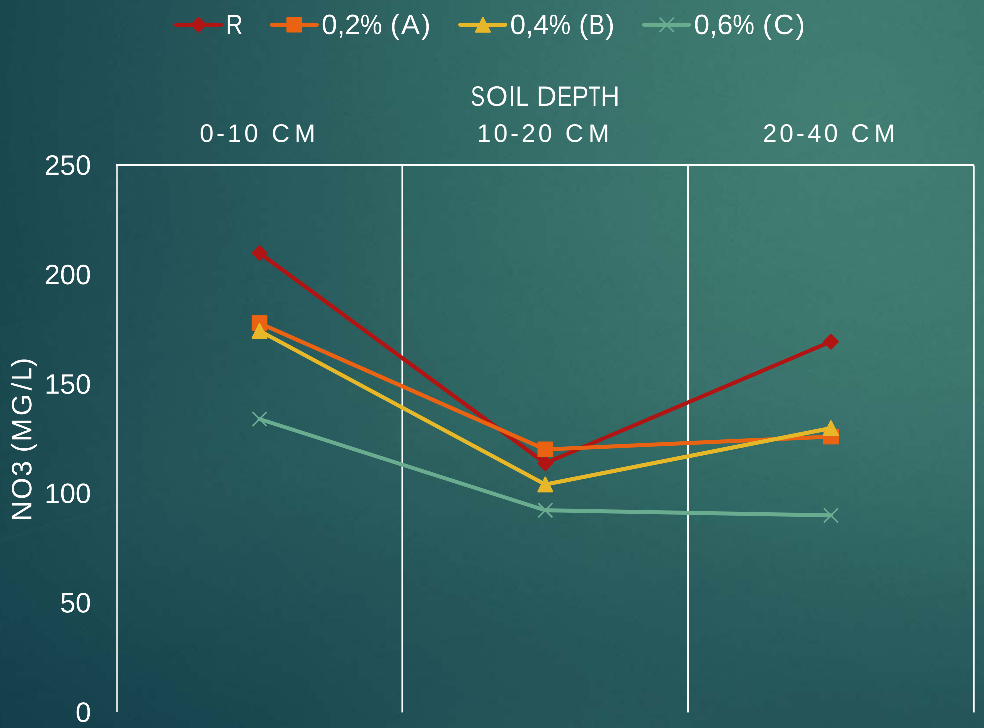


Figure 2: X-Ray Powder Diffraction pattern of zeolitic tuff

Results - Soil

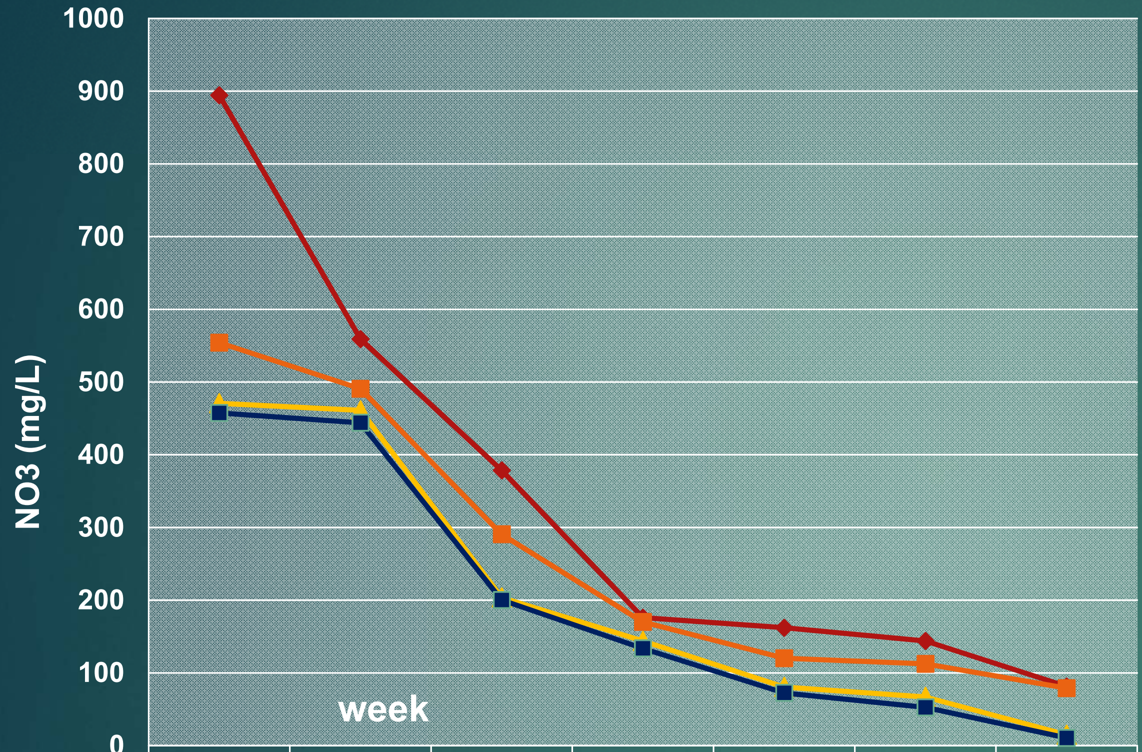
0-10cm: all mixtures (A, B, C) zeolite appeared to be effective → NO3 decrease
10-20 cm: the decrease of NO3 is still effective → further NO3 decrease
20-40cm: NO3 are increasing for the R sample and A, B mixtures, whilst, for the C mixture nitrates are still decreasing.

→ the retention capacity of A and B mixtures is exhausted
→ the retention capacity of C mixture which is still effective and leads to a minor, yet steady further decrease rate of nitrates



depth (cm)	R	0,2% (A)	0,4% (B)	0,6% (C)
0-10 cm	210 (mg/L)	178	174	134
10-20 cm	114 (mg/L)	120	104	92
20-40 cm	170 (mg/L)	126	130	90

Results – vadose zone leachates



	5,5	6	6,5	7	8	9	10
R (mg/L)	894	559	379	176	162	144	81
A (mg/L)	554	491	291	170	120	112	79
B (mg/L)	471	461	204	144	81	67	15
C (mg/L)	458	444	200	134	73	53	11

Figure 3: Nitrate load concentrations in leachates

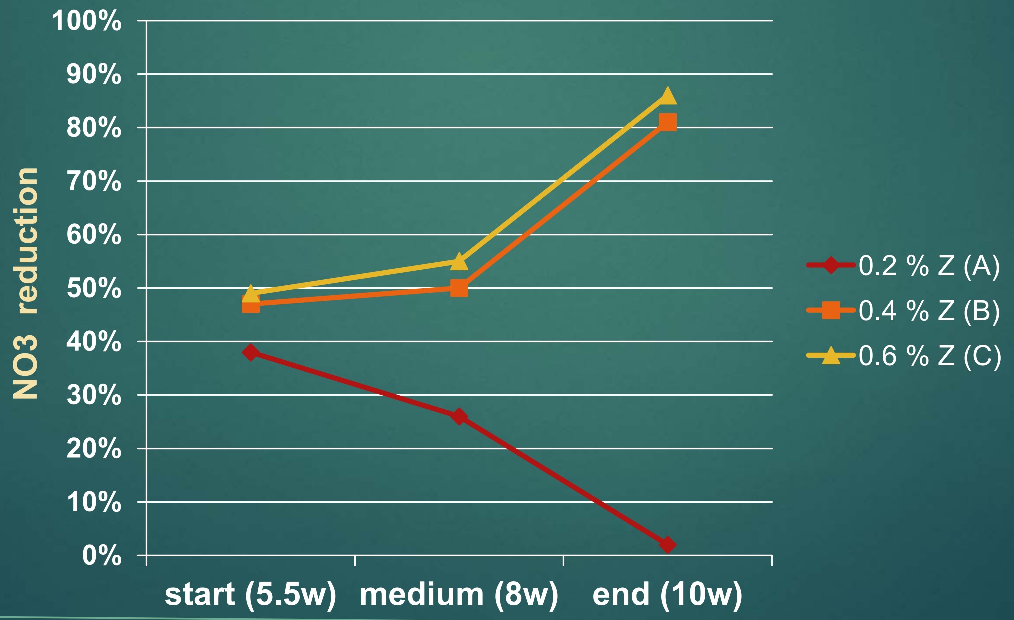
Percentages of nitrate load reduction in leachates compared to reference sample

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

Discussion

- **Nitrate load decrease** should be attributed to **zeolitic tuff** (soil organic content is in general low - 0.6%)
- Reference (R) and A (0.2 Z) samples follow similar decrease rates for nitrate reduction → **insignificant impact**
- Samples B (0.4 Z) and C (0.6 Z) follow similar increasing trends for nitrate reduction → **Significant impact**

! trends are low at the start of the experiment and high the end → critical threshold



Discussion

The results of nitrate load reduction from soil mixing with natural HEU-type ZT are **very promising**

- Similar decrease percentages (96-97%) on nitrate load in groundwater leachates have been recorded **only** using surfactant modified zeolitic tuff (Masukume et al. 2011).

→ **Zeolite modification** is a non viable process in **financial terms** for **common agricultural practices**.

→ Other attempts (Mazeikiene et al. 2008) of nitrate removal with a natural zeolitic rock (70-75 wt.% clinoptilolite) achieved percentages of less than **10%** for nitrate removal and proved to be an **insufficient for nitrate retention**.

Discussion

Processes affecting nitrate load reduction

- Nitrate load reduction is attributed to **absorption** (ion exchange), **adsorption** and **surface precipitation** processes (e.g. 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 and/or positively charged chemical components.

- 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**

Conclusions

- Results revealed that **HEU-type zeolitic tuff - soil mixture** may act as an efficient **natural sorbent** with a **remarkable ability to retain nitrate leachates from soils**
- The **maximum retention percentage (86%) for leachates** was achieved with a **0.6% addition of zeolitic tuff**,
- The **maximum retention percentage for soils** was achieved with a **0.6% addition of zeolitic tuff**,
- → 0.6% ZT (1500 kg per acre) is **financial viable** for common farmers (depending on case)

→ **Results should be further verified in field conditions, with real irrigation and cultivations schemes, and impacts from external factors.**

Very High Quality HEU-type Zeolitic Tuff

! **Supplementary tool for integrated fertilization, water resources management, and environmental protection**

! **Nitrate load reduction may have beneficial impact on rational agricultural practices towards the achievement of the objectives set by the new common EU agricultural policy (CAP).**

Thank you for your attention!