Programme in Higher Education, Research and Development (HERD) in the Western Balkans 2010 – 2014.

Conference under HERD/ Agriculture: Practical use of knowledge and knowledge transfer, institutional development and, sustainability related to agricultural activities.

Tuesday, 1 October 2013, Hotel Radon Plaza, Sarajevo.

Session 2: Agricultural value chains, entrepreneurship and user aspects.

The use of natural zeolite (clinoptilolite) for the treatment of farm slurry and as a fertilizer carrier

University of Belgrade (Faculty of Agriculture and Faculty of Technology and Metallurgy)

University of Sarajevo (Faculty of Agriculture)

Norwegian University of Life Science (Department of Plant and Environmental Sciences)

"The scope, objectives and strategic directions of HERD are outlined in the HERD Programme Document dated 01.03.2010… HERD's Programme 2 is for the Agricultural Sector.

The second call under HERD/Agriculture will prioritise aquaculture and pastureland/grazing, knowledge transfer from academic institutions towards farmers and farmers' organisations, economy and markets (value chains; "from farm to fork"), entrepreneurship and user aspects."

In Balkans, the most diverse grasslands are usually associated with soils of low fertility that have not been agriculturally improved by additions of fertiliser.

Generally, the soils do not possess sufficient (bioavailable) nitrogen which is crucially important yield contributing element for majority of crops, including forages.

Disadvantages of fertilization by mineral N-containing fertilizers:

- production of ammonia (Faber-Bosch process) requires the consumption of remarkable amounts of non-renewable energy sources;

- mineral N-containing fertilizers are expensive for farmers;

- their application diminishes soil fertility;

- their application is related to soils' pollution.

Fertilization by farmyard manure (poultry, pig or cattle) is possible, but, unfavourable aspects are:

- long-range transports and depositions on natural ecosystems;

- the application of manures on weakly buffered, nutrient poor soils can lead to soil acidification and N-enrichment;

- N is lost through ammonia emissions.

Hence, the application of either mineral N-containing fertilizers or manures can result in damages of ecosystems.

Importantly, the shifts from native diverse oligotrophic plant communities to communities dominated by competitive grass species!

Therefore, improved farmyard manure management practices, oriented toward minimization of N-losses are required.

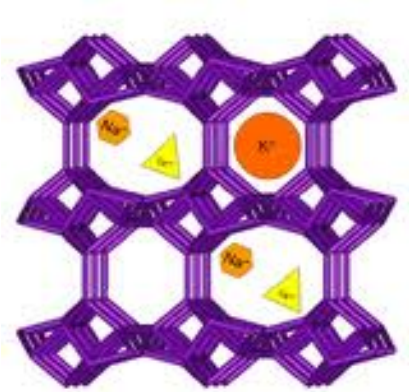
Our idea was to apply natural zeolitic tuff which has an excellent adsorption capacity towards **ammonium** and metal ions.

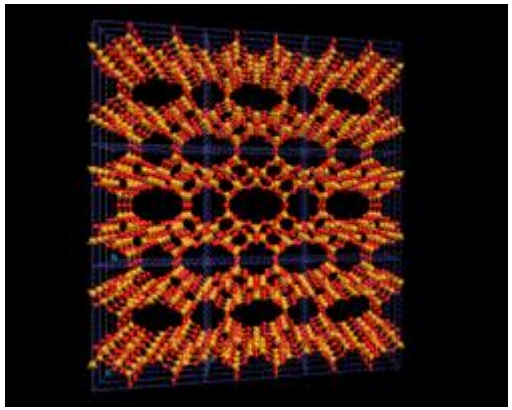
Balkan region is reach in natural zeolites and zeolite like materials.

The most known and the biggest deposits are in south Serbia (Zlatokop, Vranjska Banja) - ~ 670000 tones of zeolitic tuff (~70% clinoptilolite).

Clinoptilolite: the most abundant naturally occurring zeolite;

cheap, available, thermally stable up to 800°C ⇒ environment-friendly!





$Na_{0.122}K_{0.004}Mg_{0.009}(Al_{0.174}Si_{0.833}O_2)$

! Exchangable cations – NH_4^+ can replace them!

NH_4^+ can be released in the environment that contain water and other cations ⇒ it can be released into the soil SLOWLY

Following slides present lists of our:

1. Actions (laboratory and field experiments) we have planned and already completed

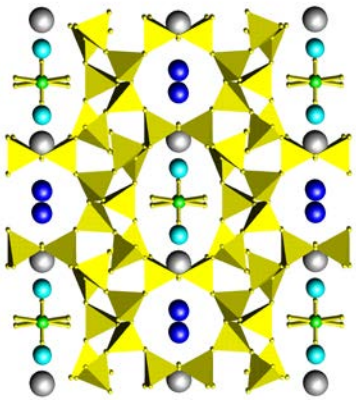
2. Results we obtained up to now

3. Actions we intend to perform

The actions we completed/plan to do were designed in a way to enable the establishment of agricultural value chains and to enable entrepreneurship in the domains linked to forage production.

ACTIONS WE PERFORMED/RESULTS WE OBTAINED …

1. Characterization of zeolitic tuff in terms of:



- structure
- capacity to retain NH_4^+ cations from aqueous solution
- capacity to retain NH_4^+ cations from manure
- extent and rate of NH_4^+ release into aqueous solution aqueous solution of KCl or NaCl

ALL RESULTS HAVE BEEN ALREADY PRESENTED IN FRONT OF HERD BOARD, IN BELGRADE (AUTOMN 2012)

Based on these results; we mixed manure with 10% wt. of zeolite. The fermentation lasted around 4 months.

ACTIONS WE PERFORMED/RESULTS WE OBTAINED …

2. Characterization of soils from experimental fields in Serbia and Bosnia

We have data on so-called "zero state" (before fertilization):

- Both in Serbia and Bosnia: - chemical analysis of soils
  - botanical analysis;
- In Serbia: - microbiological analysis of soil from experimental field in Varna

Soil analysis, the field sites in Kakanj (Bosnia) and Varna (Serbia)

The analysis were performed by Milica Randjelovic, master student from Belgrade under guidance by the chemical engineers at the laboratory at Department of Plant and Environmental Sciences, UMB.

The following analysis were performed on all samples:

* Organic content determination by loss on ignition
* Total carbon and total nitrogen
* pH (in H_2O and in $CaCl_2$)
* Ammonium lactate extraction (AL, pH 3.75) and ICP measurements of the elements: P, K, Mg, Ca, Na, Fe, Mn, Cu, Zn, Al

Kakanj, Bosnia:

	% LOI	Total C (%)	Total N (%)	pH (H2O)	pH CaCl2
Avg.	11,49	5,88	0,47	7,51	7,16
Std.	0,857	0,599	0,057	0,054	0,038
CV (%)	7,46	10,18	12,04	0,72	0,53

Varna, Serbia:

	% LOI	Total C (%)	Total N (%)	pH (H2O)	pH CaCl2
Avg.	4,31	1,37	0,16	5,73	5,07
Std.	0,230	0,130	0,016	0,137	0,201
CV (%)	5,28	9,68	9,86	2,39	3,97

⇒ Soil from Varna has lower N content and it is moderately to strongly acid!

Kakanj: AL extractable elements (mg/kg)

	P	Ca	Cu	K	Mg	Mn	Zn
Avg.	**17,0**	**49750**	**0,58**	**286**	**545**	**141**	**2,44**
Std.	10,10	6835	0,06	110	119	9,28	0,53
CV(%)	**59,55**	**13,74**	**10,34**	**38,62**	**21,86**	**6,58**	**21,74**

Varna: AL extractable elements (mg/kg)

	P	Ca	Cu	K	Mg	Mn	Zn
Avg.	**13,9**	**1**	**0,68**	**115**	**279**	**35**	**0,87**
Std.	5,43	0,1	0,07	45,10	21,90	3,86	0,37
CV(%)	**39,12**	**7,41**	**10,25**	**39,20**	**7,84**	**11,03**	**42,90**

⇒ Soil in Bosnian field is reach in Ca; both experimental fields are poor in P!

ACTIONS WE PERFORMED/RESULTS WE OBTAINED …

3. Field experiments:

-in Serbia village Varna, treatments:

I - control

II - zeolite 3 t/ha

III – manure 30 t/ha

IV - manure+zeolite 10 % wt (30 t/ha)

V – N-spring application of 50 kg/ha N

All treatments were done in 4 replications

Manure and zeolite were mixed, fermentation lasted ~ 4 months

Fertilization was performed beginning of December 2012

Botanical analysis was done after 1st cut in May 2013

After fertilization:

- DM yield;
- botanical analysis
- chemical analysis of obtained forage

DM yield per cut in Varna (t ha^{-1})

Treatments	I cut	II cut	Total
Control	1.99^{c}	1.02^{ab}	3.01^{c}
Zeolite (3 t ha^{-1})	2.38^{c}	0.91^{b}	3.29^{c}
Manure (30 t ha^{-1})	4.53^{a}	1.38^{a}	5.91^{a}
Manure+zeolite (mixed) (30 t ha^{-1})	4.11^{ab}	0.97^{ab}	5.08^{ab}
Nitrogen (50 kg ha^{-1})	3.31^{b}	0.96^{ab}	4.27^{b}

*Values followed by the same letter are not significantly different by Fisher's protected LSD values; LSD0.05 – least significant difference at $P<0.05$

BOTANICAL COMPOSITION

Rank of species in a pasture using an estimate of the percentage contribution

Treatments	Grass	Legumes	Others species
Control	46^{b}	11^{a}	43^{a}
Zeolite	57.25^{ab}	8.5^{a}	34.25^{ab}
Manure	58.5^{ab}	9.25^{a}	32.25^{ab}
Manure+zeolite (mixed)	58.25^{ab}	5.25^{a}	36.5^{ab}
Mineral nitrogen	60.25^{a}	9.25^{a}	30.5^{b}

Estimation of the botanical composition of pasture based on fresh weight (g/m^2) samples

Treatments	Grass	Legumes	Others species
Control	938^{b}	65^{a}	80^{a}
Zeolite	1088^{b}	25^{a}	95^{a}
Manure	1610^{a}	58^{a}	62^{a}
Manure+zeolite (mixed)	1362^{ab}	70^{a}	70^{a}
Mineral nitrogen	1370^{ab}	21^{a}	95^{a}

Chemical analysis of dry matter after 1st and 2nd cut, parameters:

CA - crude ash (% DM – dry matter)
CP - crude proteins (% DM)
CCl - crude cellulose (% DM)
CF – crude fat (% DM)
NFM – N-free extract (% DM)
CHO – total carbohydrates (% DM)
NFC – non-fiber carbohydrates (% DM)
NDF – neutral detergent fibers (% DM)
ADF – acid detergent fibers (% DM)
Hemicellulose (% DM)
Lignin (% DM)
L (%NDF) – percentage of NDF that is lignin
DDM – digestibility dry matter (%)
TP – true proteins (% CP)
NPN - nonprotein nitrogen (% CP)
BSP - true soluble protein – buffersoluble protein (% CP)
IP – insoluble protein (% CP)
NPN (% Sol P) - percentage of soluble protein that is non-protein nitrogen
NDIP – neutral dedergent insoluble protein (% CP)
ADIP - Acid detergent insoluble protein (% CP)
PA –percentage of crude protein in the feedstuff that is non-protein nitrogen (% CP)
PB1 – percentage of crude protein in the feedstuff that is rapidly degraded protein (% CP)
PB2 - percentage of crude protein in the feedstuff that is intermediately degraded protein (% CP)
PB3 - percentage of crude protein in the feedstuff that is slowly degraded protein (% CP)
PC - percentage of crude protein in the feedstuff that is bound protein (% CP)
CB2 – percentage of carbohydrate of the feedstuff that is available fiber (% DM)
CC - percentage of carbohydrate of the feedstuff that is unavailable fiber (% DM)

I cut

Treatments	Lignin	L (%NDF)	TP	NPN	NPN (% Sol P)	PA	PB	PB1	CC
Control	5.70b	9.09b	73.6ab	26.4ab	89.4ab	25.3ab	47.1ab	4.59ab	13.70b
Zeolite (3 t ha^{-1})	5.86b	9.19b	74.2ab	25.8ab	84.6ab	25.4ab	45.4ab	4.37ab	14.06b
Manure (30 t ha^{-1})	6.17ab	9.62b	**64.8b**	**35.2a**	**100a**	**31.8a**	**40.8b**	**0.0b**	14.80ab
Manure+zeolite (mixed) (30 t ha^{-1})	5.88ab	9.28b	**83.5a**	**16.5b**	**65.7b**	**14.7b**	**57.0a**	**9.7a**	14.10ab
Nitrogen (63 kg ha^{-1})	6.81a	10.92a	69.6ab	30.4ab	**96.2a**	23.4ab	47.2ab	0.60ab	16.34a

II cut

Treatments	CA	BEM	NFC	NDF	hemicellulose	lignin	TP	NPN	CB2	CC
Control	9.13ab	51.6ab	12.5b	69.5a	32.4a	6.07b	84.2ab	15.8ab	50.5a	14.6b
Zeolite (3 t ha^{-1})	8.13b	54.2a	16.4ab	66.6ab	25.3ab	6.97a	86.5ab	13.5ab	45.4ab	16.7a
Manure (30 t ha^{-1})	9.35a	51.5ab	14.9ab	66.7ab	27.9ab	6.72ab	**73.9b**	**26.1a**	45.8ab	16.1ab
Manure+zeolite (mixed) (30 t ha^{-1})	9.18a	51.9ab	18.2a	63.1b	25.2b	6.38ab	**91.0a**	**9.0b**	43.4b	15.3ab
Nitrogen (63 kg ha^{-1})	8.62ab	49.5b	14.7ab	66.8ab	25.7ab	6.80ab	80.7ab	19.3ab	45.7ab	16.3ab

Presented results indicate that the usage of zeolite based fertilizer lead to increase of true protein content (decrease of non-protein nitrogen, too!) what has positive influence on forage digestibility!

Microbial status was investigated before fertilization and after the 2nd cut.

Addition of (even 5% wt) zeolite to the manure changed microbial status during maturation of compost during 4 months, and during the later application at the grassland.

Examination of: - total microbial count at 30 °C and 50 °C,

- total number of anaerobic microorganisms at 30°C and 50°C,
- yeasts and molds,
- bacterial spores and enterobacteriaceae

showed that through the addition of zeolite we can influence the microbial picture of manure (by changing the number of different type of microorganisms).

Addition of zeolite to manure influence the increase of total number of mesophylic, anaerobic and enterobacteria which will give better substrate for grassland.

ACTIONS WE PERFORMED/RESULTS WE OBTAINED …

3. Field experiments:
in Bosnia, village near Kakanj, treatments:

I - control

II - zeolite 3 t/ha

III- manure 30 t/ha

IV - manure+zeolite 10 % wt
(30 t/ha)

V - mineral fertilizer
63 kg/ha pure N

All treatments were done in 4 replications
(in February 2013, except V – in March 2013)


KONTROLA


MANURE
ZGORELI STAJNJAK
30t/ha


ZGORELI
STAJNJAK
20 t/ha


MANURE
+ZEOLIT
30 t/ha


AZOT
68 kg/ha

Results (dry matter yields) did not show significant differences for different treatments, particularly after 2nd and 3rd cuts.

In botanical composition:

- Grasses prevailed (70 to 90%); the species were different in different cuts.
- Legumes participated with 10 to 22% the species were different in different cuts.
- Other species, low quality herbs and weeds participated from 9 to 20%.

ACTIONS WE PERFORMED/RESULTS WE OBTAINED …

In order to clear up the role of zeolite in fertilization process, a team in Norway, at Norwegian University of life sciences performed

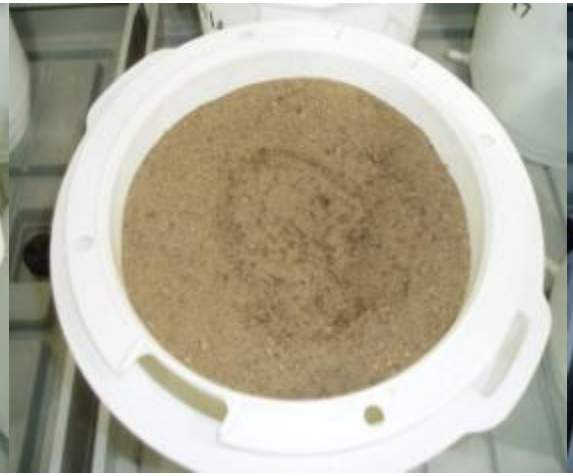
4. Experiments in pots: *Ryegrass*

- Three soil types (loam, sand, silt); soil volume 3 L per pot
- Treatments (initial fertilization)
  - No fertilizer
  - Zeolite loaded with NH_4 only (silt only; other macro- and micronutrients in soil);
  - Manure (liquid; equiv. 120 kg N ha-1)
  - Manure + zeolite (equiv. 120 kg N ha-1)
  - Mineral fertilizer, equiv. 120 kg N ha-1 (+ other macro- and micronutrients)

Soil types

	pH	LOI	Total N	P-AL	K-AL	Sand	Silt	Clay
		%	g kg^{-1}	mg kg^{-1}			%	
Loam	5.2	6.13	2.1	58	195	45	38	17
Sand	5.1	1.29	0.1	16	10	94	3	3
Silt	6.5	3.69	1.0	49	200	2	93	5

Loam

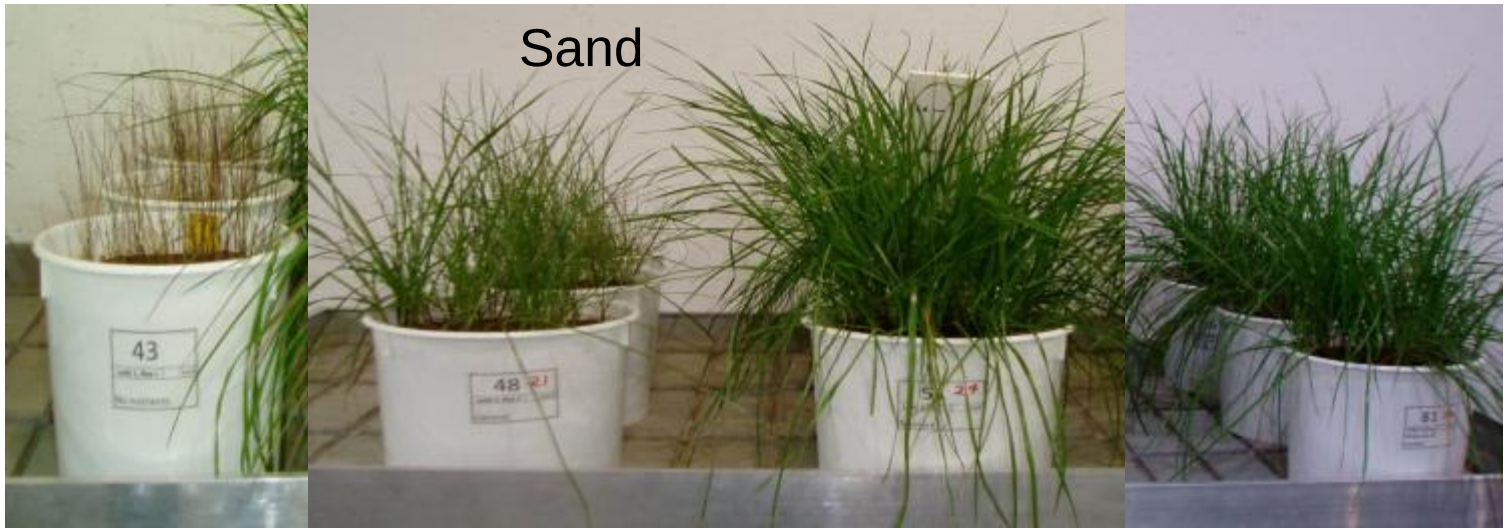


Sand

Silt

Growth experiment before 1st cut

No nutrients | Min. fertilizer | Manure | Manure + zeolite



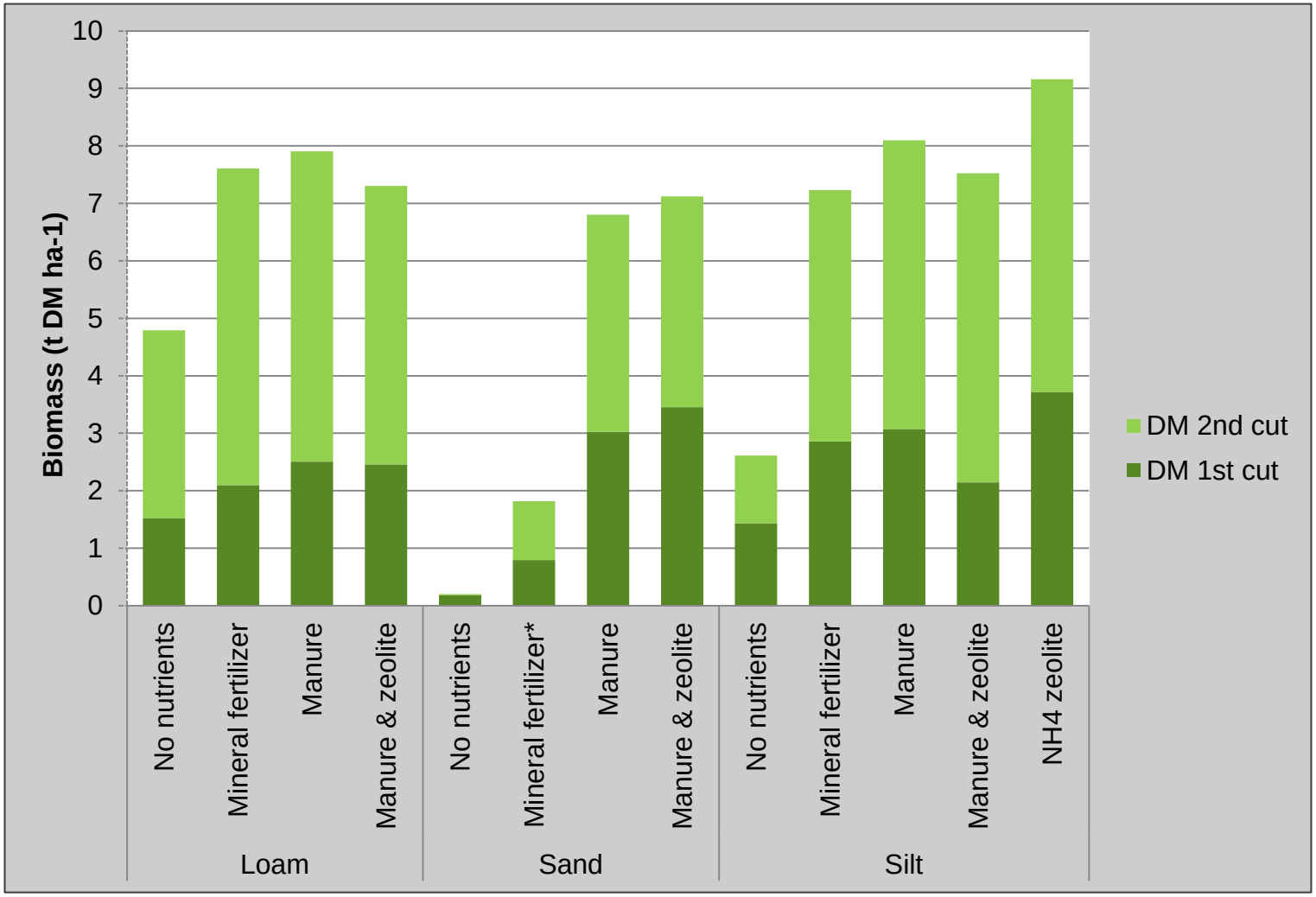
Growth experiment before 1st cut

No nutrients | Min. fertilizer | Manure | Manure + zeolite | NH_4-Zeolite

Silt

HERD-project Zeolite

Biomass



ACTIONS WE PLAN TO DO:

5. We intend to perform parallel experiments in pots in Serbia; using three typical soil types from the country.

ACTIONS WE PERFORMED/RESULTS WE OBTAINED …

We are requested to:
"transfer the knowledge from academic institutions towards farmers and farmers' organisations…"

6. For that reason, we organized meeting with farmers in a known farmer's region in Serbia (Zlatibor mountain), in municipality of Čajetina

ACTIONS WE PERFORMED/RESULTS WE OBTAINED …

7. We investigated the addition of zeolite to chicken manure and making the compost for button mushroom (champignons) production.

⇒The addition of zeolite did not influence the standard process of compost preparation;

⇒We found that there is no difference in yield of mushrooms, but we expect that there will be difference in the contents of micro and macro elements in fruit bodies and that mushrooms with better chemical composition for consumption will be obtained (investigation is in progress).

To conclude:

the obtained results show that:

-The application of zeolite-based fertilizer can improve forage production on poor soils!

-The application of zeolite-based fertilizer can improve the quality of forage (mushrooms, too).

-It provokes the decrease of organic matter losses in the soil and the launch of its state in the direction of the net accumulation of organic matter.

For that reasons, this project can help to achieve following goals:

1.Reduction of input costs in the plant production.

2.Reduction of agricultural production dependence of non-renewable energy.

3. Improvement of organic farming.

$\Rightarrow$

Possible agricultural value chains/ entrepreneurship:

Farmers (<u>improved farmyard manure management</u>) $\rightarrow$ zeolite-based fertilizer $\rightarrow$ improved forage production $\rightarrow$ influence on milk production (yield and quality) $\rightarrow$ industry $\rightarrow$ final users

Farmers (<u>improved farmyard manure management</u>) $\rightarrow$ zeolite-based fertilizer $\rightarrow$ improved mushrooms production $\rightarrow$ improved mushrooms production (incorporation of Se, Mg, etc) $\rightarrow$ improved food functionality $\rightarrow$ final users.

Thank you for your attention!

Dry matter yield, first cut 2013

Dry matter yield in the 1st cut (t/ha); 14.05.

Variants	Repetitions				Total	Average
	1	2	3	4		
Control	3,06	7,07	5,91	5,01	**21,05**	**5,26**
Zeolit 3 t/ha	4,89	5,98	3,77	4,96	**19,6**	**4,9**
Manure 30 t/ha	5,11	3,97	4,83	4,52	**18,43**	**4,6**
Manure+zeolit (mixed) 30 t/ha	4,68	6,31	5,45	3,92	**20,36**	**5,09**
Nitrogen 63 kg/ha	9,33	7,07	7,34	5,15	**28,89**	**7,22**
Manure 20 t/ha	7,36	3,65	5,52	3,66	**20,19**	**5,04**

Botanical composition

In botanical composition:

- Grasses prevailed (70 t0 90%)and the majority of them was Bromus mollis.
- Legumes participated with 10 t0 22% (Trif. pratense. Trif. repens, Lotus corniculatus, Lathyrus sp., Medicago sativa).
- Other (different families) participated from 9 to 20%.

Dry matter yield, second cut 2013

Dry matter yield in the 2nd cut (t/ha); 28.06

Variants	Repetitions				Total	Average
	1	2	3	4		
Control	1,87	3,01	1,61	1,22	**7,71**	**1,92**
Zeolit 3 t/ha	3,37	1,92	0,93	1,44	**7,66**	**1,91**
Manure 30 t/ha	2,65	1,98	1,51	1,40	**7,54**	**1,88**
Manure+zeolit (mixed) 30 t/ha	2,87	2,76	1,66	1,28	**8,57**	**2,14**
Nitrogen 63 kg/ha	2,82	1,58	1,41	1,36	**7,17**	**1,79**
Manure 20 t/ha	2,77	1,34	1,73	1,47	**7,31**	**1,82**

Botanical composition of 2nd cut

- According evaluation on the trial field:
- Grasses prevailed again (55 to 90%)with L. italicum, A. elatior and D. glomerata as most abundant
- Legumes participated with 5 to 10% in which were found: Trif. pratense. Trif. repens, Lotus corniculatus, Lathyrus sp., Medicago sativa).
- Other (different families) participated from 5 to 40% in different plots.
- Hoewer, in kilo green mass, depending of treatment portion of grasses ranged from 62,5 to 77,5%; legumes 10 to 15% and other 10 to 25%.

Dry matter yield, 3rd cut 2013

Dry matter yield in the 3rd cut (t/ha); 06.08.)

Variants	Repetitions				Total	Average
	1	2	3	4		
Control	1,90	2,52	1,58	1,29	**7,29**	**1,82**
Zeolit 3 t/ha	2,28	1,37	0,91	1,76	**6,32**	**1,58**
Manure 30 t/ha	2,41	1,03	1,44	1,03	**5,91**	**1,47**
Manure+zeolit (mixed) 30 t/ha	1,69	1,66	1,52	1,35	**6,22**	**1,55**
Nitrogen 63 kg/ha	1,72	1,11	1,29	1,43	**5,55**	**1,38**
Manure 20 t/ha	1,74	1,31	1,31	1,39	**5,75**	**1,43**

Botanical composition of 3rd cut

- According evaluation on the trial field:
- Grasses prevailed again (45 to 90%)with L. italicum, A. elatior and D. glomerata as most abundant
- Legumes participated with 5 to 15% in which were found: Trif. pratense. Trif. repens, Lotus corniculatus, Lathyrus sp., Medicago sativa).
- Other (different families) participated from 5 to 20% in different plots.
- Hoewer, in kilo green mass, depending of treatment portion of grasses ranged from 57,5 to 80,0%; legumes 10 to 15% and other 7,5 to 22,5%.

Total DM yield in 2013

Total DM yield in the (t/ha) in 2013.

Variants	Cuts			Total
	1	2	3	
Control	5,26	1,92	1,82	**9,00**
Zeolit 3 t/ha	4,90	1,91	1,58	**8,39**
Manure 30 t/ha	4,60	1,88	1,47	**7,95**
Manure+zeolit (mixed) 30 t/ha	5,09	2,14	1,55	**8,78**
Nitrogen 63 kg/ha	7,22	1,79	1,38	10,39
Manure 20 t/ha	5,04	1,82	1,43	**8,29**

Microbial status was investigated before fertilization and after the 2nd cut.

Addition of (even 5% wt) od zeolite to the manure could change microbial status during maturation of compost during 4 months, and during the later application at the grassland.

Examination of: - total microbial count at 30 °C and 50 °C,

- total number of anaerobic microorganisms at 30°C and 50°C,
- yeasts and molds,
- bacterial spores and enterobacteriaceae

Showed that we can influence the microbial picture of manure (by changing the number of different type of microorganisms) by addition of zeolite.

Addition of zeolite to manure influence the increase of total number of mesophylic, anaerobic and enterobacteria which will give better substrate for grassland.