29 November 2022

WPI3.3.3 Site specific report of the on-site demonstration for vegetal production and ecocatalyst synthesis

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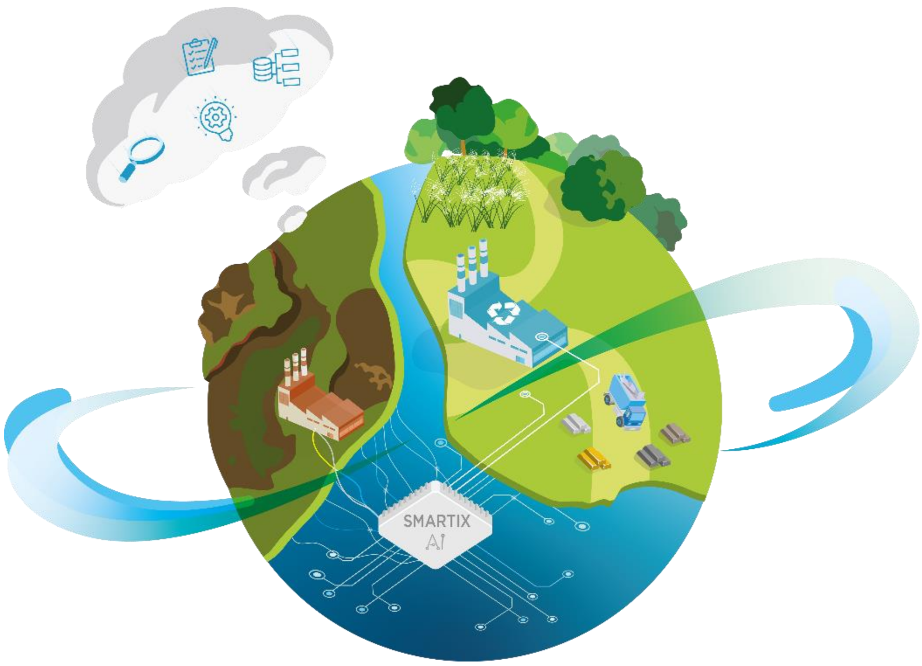

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EXECUTIVE SUMMARY

Based on ex-situ experiment realized with soils sampled from DUFERCO, we selected an area considered as interesting to realise *in situ* experiment and ryegrass cultivation.

This deliverable explains the methodology employed to allow vegetal production on the DUFERCO site. It described the construction condition of the experimental plots with soil preparation, amendments, ryegrass sowing and harvest but also the difficulties encountered during the experiment.

1 SYNTHESIS OF EX-SITU EXPERIMENT (DELIVERABLE T2.3.2)

Greenhouse experiment have been realized with two soil samples collected from DUFERCO (DFC4 and DFC5). Four soil mixes have been used in this experiment. Moreover, we also evaluated the effects of two amendments: bone ash and hydroxyapatites.

The experiment revealed a good ryegrass development but no effect of the amendments on soil properties. Moreover, metal concentrations (Cd, Pb, Zn and Cu) were very low for all the conditions. Due to the low concentration of Zn in ryegrass, we decided to determine the concentrations of Fe, Ca, Mg, Na and K in ryegrass. Indeed, these elements can also be considered as interesting for ecocatalyst production despite few available data in the literature about this potential. Analyses revealed a high Fe concentration in ryegrass cultivated on DFC4 and high Ca concentrations in ryegrass cultivated on DFC5. Thus, the efficiency of ryegrass to produce ecocatalysts rich in Fe and Ca has been tested. The potential use of Fe-enriched and Ca-enriched ecocatalysts in the synthesis of compounds derived from pyroglutamic acid (PGA) has been evaluated. The Fe-ecocatalyst gave the best results for the reaction progression. This is an improvement on making this synthesis greener.

2 AMENDMENT

2.1 AMENDMENT SELECTION

The amendments tested in the greenhouse experiment were bone ash and hydroxyapatites. They were chosen because they have the ability to fix metals considered as undesirable for ecocatalyst production in the soil (e.g. Cd, Pb) while allowing the transfer of desirable elements from the soil (Zn) to the aerial biomass of the plant. However, results obtained from the greenhouse experiment revealed no clear effect of bone ash and hydroxyapatites. Analyses of ryegrass biomass revealed low metal transfer from soil to plants, except for Fe, explaining the absence of amendment effects.

Thus, it has been decided to evaluate the efficiency of another amendment for *in situ* experiment which is Diammonium Phosphate (DAP 18-46-0: 18 % N, 46 % P_2O_5, 0 % K_2O)). DAP is currently used in agriculture as a fertilizer and can slightly decrease soil pH. Our hypothesis is that DAP can increase metal phytoavailability by decreasing soil pH.

2.2 Amendment rate

Thus, to determine the amendment rate, we evaluated the need of N and P for ryegrass development and, according to the content of N and P in DAP, we used the following equation:

$$Amount\ of\ DAP\ to\ be\ applied\ (kg\ ha^{-1}) = \frac{concentration\ needed\ for\ ryegrass\ (U) x\ 100}{concentration\ in\ DAP\ (\%)}$$

- Amount to be supplied to meet N requirements:

$$\frac{40\ x\ 100}{18} = 222{,}2\ kg\ ha^{-1} = 22{,}2\ g\ m^{-2}$$

- Amount to be supplied to meet P requirements:

$$\frac{150\ x\ 100}{46} = 326{,}1\ kg\ ha^{-1} = 32{,}6\ g\ m^{-2}$$

Based on these equations, we selected the highest amendment rates, which corresponds to 32,6 g of DAP / m² of soil.

3 1ST Site preparation

3.1 Experimental design

For *in situ* experiment, we tested two conditions: unamended soil and soil amended with DAP. These treatments have been realized in triplicates (**Figure 1**). Ryegrass was sown at a rate equal to 60 kg ha^{-1}, according to the supplier reference, and each plot measured 6 m².

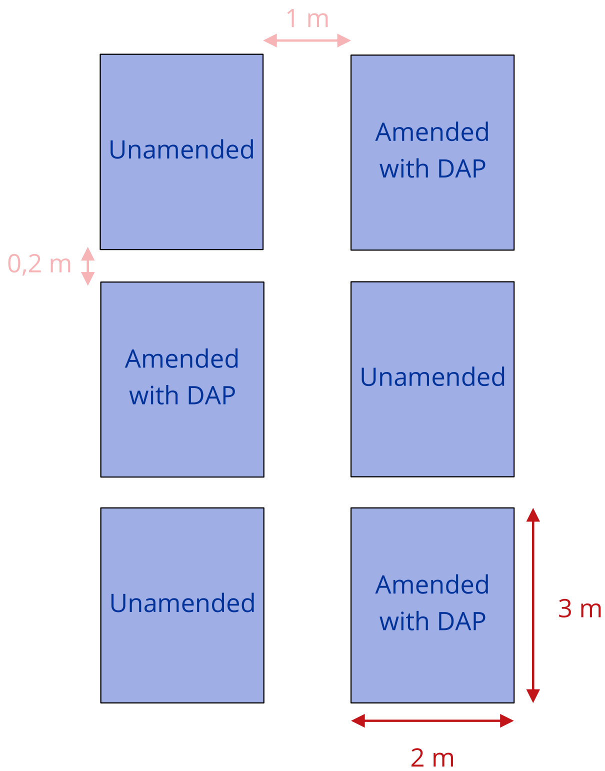

Figure 1: 1st experimental design on DUFERCO site for ryegrass cultivation

3.2 SITE PREPARATION

Based on the greenhouse results, the *in situ* experiment has been realized on the DFC4 area (**Figure 2**).

Figure 2: Location on DUFERCO site for in situ experiment

Ryegrass cultivation has been launched the 29th of April 2021, following a soil preparation (land clearing and digging). **Figure 3** presents some pictures of the area preparation.

Figure 3: 1st soil preparation for ryegrass cultivation (29/04/2021)

3.3 DIFFICULTIES ENCOUNTERED

Despite a good soil preparation and ryegrass sowing, the plant did not germinate. Indeed, a site visit realised the 25th of June 2021 revealed that other plants initially present on the site took advantage of the ryegrass and prevented its germination and a high heterogeneity between the plots was also observed (**Figure 4**).

Figure 4: Weeds development limiting ryegrass development and heterogeneity between the plots (25/06/2022)

In order to better explain the absence of ryegrass and the heterogeneity between the plots, soil samples have been made and characterized. The results obtained are presented in **Table 1**.

Results revealed similar chemical parameters than those observed with the greenhouse experiment with a quite low heterogeneity between the plots. Thus, chemical parameter cannot explain the absence of ryegrass development. However, physical parameters revealed a high content of coarse elements, especially in the plot "Un – 3", with a high heterogeneity between the plots.

To remedy this problem, a new soil preparation has been planned.

Table 1: Agronomic parameters of the 6 plots from the in situ experiment

Sample	Texture	Fraction > 2 mm	pH	$CaCO_3$	OM	total N	C_{org}/N_{total}	CEC	Available P
		$g\ kg^{-1}$	-	$g\ kg^{-1}$	$g\ kg^{-1}$	$g\ kg^{-1}$	-	$cmol^+\ kg^{-1}$	$g\ kg^{-1}$
Un – 1	Sand	12,1	7,9	121	74,1	1,15	37,4	10,7	0,713
Un – 2	Sand	34,2	8,4	128	127,6	1,29	57,4	8,8	0,982
Un – 3	Loamy sand	492	8,6	119	79,3	1,01	45,5	12,7	1,068
DAP – 1	Sand	33,3	8,0	132	75,9	0,83	53,0	9,9	1,506
DAP – 2	Loamy sand	83,1	8,0	120	72,4	0,75	56,0	8,4	1,409
DAP – 3	Sand	13,3	8,1	133	67,2	0,58	67,2	2,9	1,065

fertility = 0/3 ; fertility = 1/3 ; fertility = 2/3 ; fertility = 3/3

4 2ND SITE PREPARATION

4.1 EXPERIMENTAL DESIGN

The same experimental design has been applied for the 2nd site preparation. However, plot layout was slightly modified according to the soil results (**Figure 5**).

The equipment used to prepare the soil was more substantial than during the first soil preparation. Indeed, a tiller was employed to turn the soil and the soil was sieved with a wheelbarrow sieve (mesh size: 17 x 40 mm). Moreover, ryegrass was sown at a rate equal to 120 kg ha^{-1}, to densify plant cover, and each plot measured 4 m².

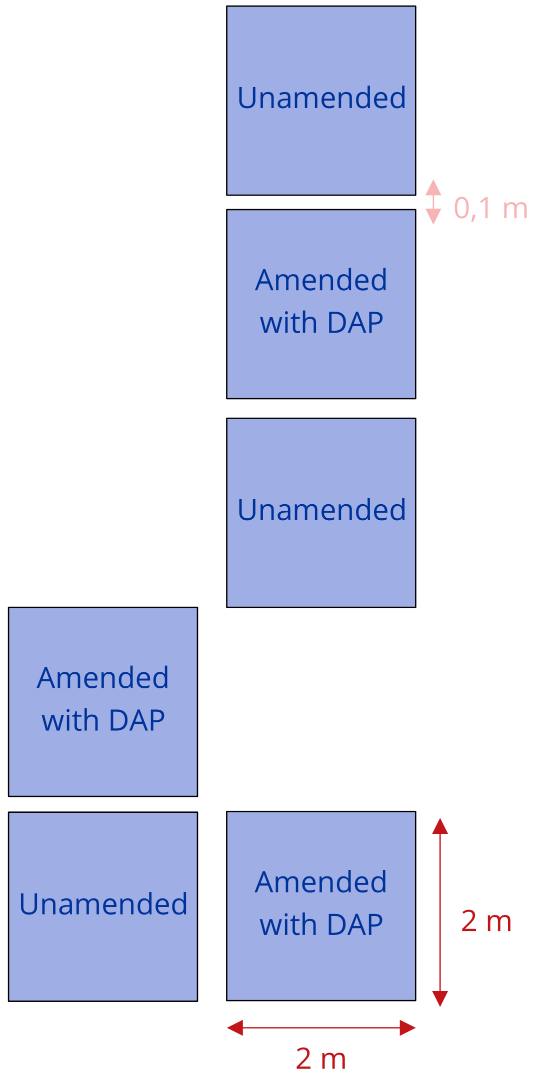

Figure 5: 2nd experimental design on DUFERCO site for ryegrass cultivation

4.2 Site preparation

Ryegrass cultivation has been launched the 9th of September 2021, following soil preparation. **Figure 6** presents some pictures of the area preparation.

Due to bad weather conditions in autumn 2021, ryegrass development was slow, but it took the advantage of weeds contrary to the 1st ryegrass sowing. Thus, no harvesting was realized in 2021 because the yield was low. A new ryegrass sowing was realized in spring 2022 (23/03/2022) to densify the plant cover and allow a great harvest.

Figure 6: 2nd soil preparation for ryegrass cultivation (09/09/2021)

5 RYEGRASS CULTIVATION AND HARVEST

5.1 RYEGRASS DEVELOPMENT

Regularly, DUFERCO's partners checked the ryegrass development and took pictures. **Figure 7** presents ryegrass development during spring 2022.

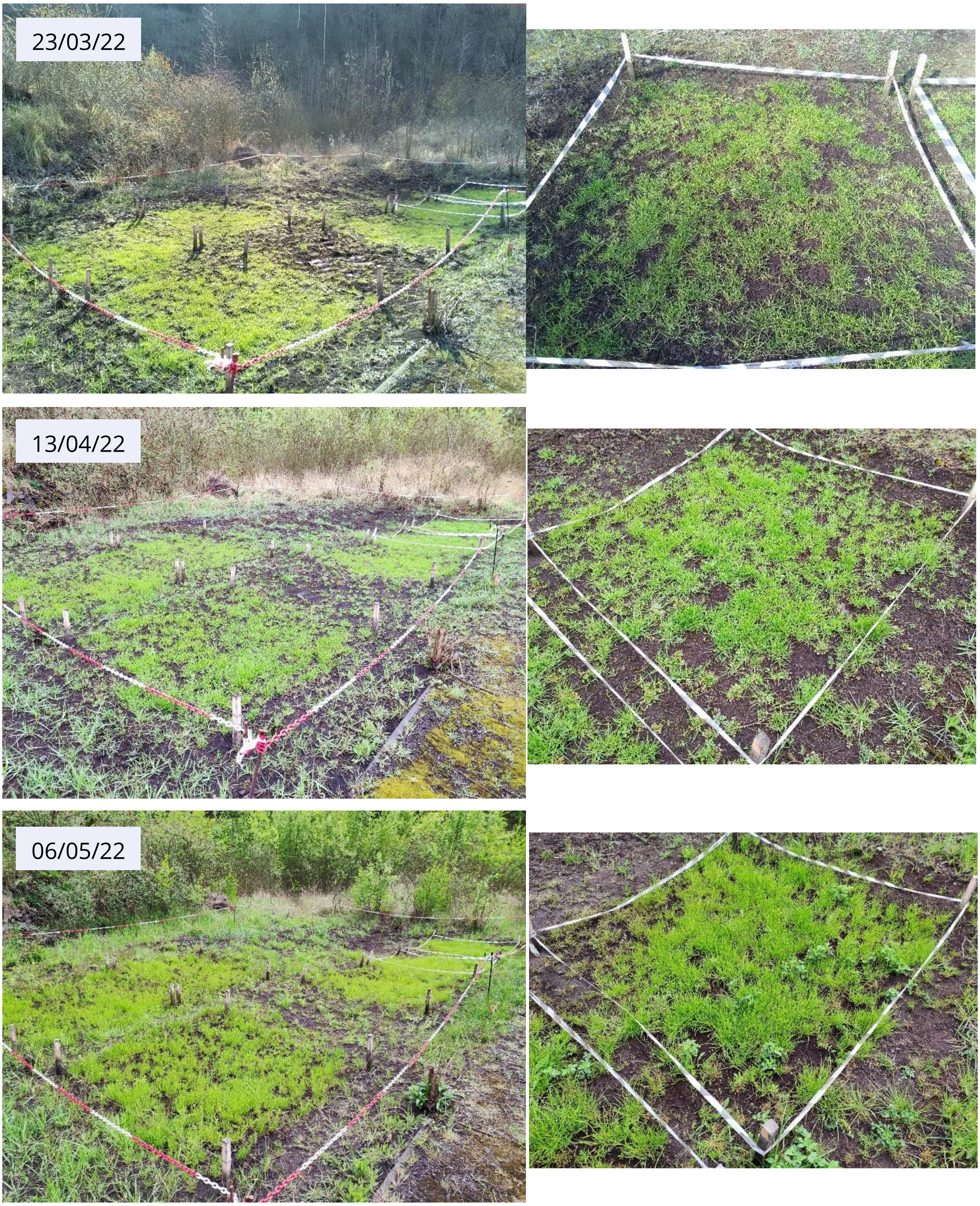

Figure 7: Ryegrass development during the spring 2022

5.2 Ryegrass harvest

Ryegrass harvest was realized the 20th of May 2022 with Junia's partner. **Figure 8** presents the harvesting steps.

Figure 8: Ryegrass harvest (20/05/2022)

After harvesting, ryegrass was washed three times (twice with tap water and once with osmosed water) and dried at 40°C (**Figure 9**). The following dry mass of ryegrass were obtained: 615 g for ryegrass cultivated on the unamended plots and 675 g for ryegrass cultivated on the plots amended with DAP. Then, ryegrass will be calcined to obtain ashes that will be used to produce ecocatalyst.

Figure 9: Ryegrass obtained after harvest

6 Conclusion

Greenhouse experiment conducted with two soils from DUFERCO allowed us to select one area (DFC4) potentially interesting to cultivate ryegrass and extract Fe from soil to produce ecocatalyst.

Two conditions were tested on site: unamended soil and soil amended with diammonium phosphate (DAP). The interest of DAP is to slightly decrease the soil pH in order to increase metal phytoavailability in soil.

A first soil preparation and ryegrass sowing were realized in April 2021. However, due to a high content of coarse elements in soil, ryegrass didn't germinate and weeds covered all the plots. Thus, a second soil preparation with more materials (to eliminate coarse materials) was realized in September 2022. Ryegrass was sowing in September 2021 and Mars 2022 and a harvest was realized in May 2022. It allowed to obtain a very high quantity of ryegrass that will be analysed in order to produce ecocatalyst rich in iron.