



### Project<sup>1</sup> Number: 101006873

### Project Acronym: GOLD

**Project title:** "Bridging the gap between phytoremediation solutions on Growing energy crOps on contaminated LanDs and clean biofuel production"

### **Periodic Technical Report**

### Part B

Period covered by the report: from1/11/22 to 30/4/24

Periodic report: [2nd]

<sup>&</sup>lt;sup>1</sup> This project has received funding from the European Union's Horizon 2020 research and innovation programme under the grant agreement No. 101006873.

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# 1 Explanation of the work carried out by the beneficiaries and Overview of the progress

The context of the project: Soil pollution is a global problem occurring where intensive industrial activities, inadequate waste disposal, mining, extensive use of agrochemicals (pesticides and fertilizers), combustion of fossil fuels, etc. introduced excessive amounts of organic and/or inorganic pollutants into the soil. It has been estimated that in Europe there are 2.5 million of potentially contaminated sites, of which about 14% (340,000 sites) are expected to be contaminated and will require remediation. A total area covering roughly 650,000 ha could be defined as contaminated with organic and/or inorganic pollutants, almost 60% relates to mineral oil and/or metal(loid)s . So far, remediation methods for heavily polluted soils traditionally rely on excavation and landfilling ('dig-and-dump'). Additional methods like pump and treat, soil washing, soil flushing, stabilization using physical and chemical methods and electro-kinetic techniques have been applied on a far smaller scale. Some of these methods are fast and effective, but they also have disadvantages like their high costs, intensive labor requirement and, in some cases, they cause irreversible changes in the geomorphology and in soil properties, severe disturbance of native soil microflora, and loss of land cropping function.

Phytoremediation is a relatively cheap, non-invasive and publicly acceptable mainly solar energy driven technology. This method is effective and economically viable when: (i) applied in sites with low to medium concentrations of pollutants so that phytotoxicity remains low and plants can grow, (ii) the used crops produce high added-value biomass providing a revenue, (iii) the site is unused/abandoned arable land and agricultural practices and mechanization can be applied. A disadvantage of phytoremediation is that, it is slow and depends on the number of growing cycles to remediate a soil. Currently, it is considered as a practical and commercially-viable technology for environmental clean-up for both organic and some inorganic contaminants and its success strongly depend on the selection of the appropriate crops. Lignocellulosic energy crops have been proven to be tolerant to the majority of metal(loid)s and xenobiotics in excess, and therefore they can grow on contaminated lands for biofuels, avoiding the food vs fuel competition, and turning a problem into an opportunity: biofuel production and land decontamination.

In this context, GOLD aims, in short term, to produce clean low-ILUC biofuels by growing selected high-yielding lignocellulosic crops on contaminated lands, and, in long-term, to return these lands back to the agricultural production (Figure 1).



Figure 1: Main driving forces for GOLD project.

### 1.1 Objectives

The *specific objectives* of the project are:

# 1. To optimize selected high-yielding lignocellulosic energy crops for phytoremediation purposes and biofuel production targeting different classes of soil-pollutants → WP1

In WP1 the optimization of selected energy crops (miscanthus, switchgrass, biomass sorghum and industrial hemp) for phytoremediation purposes are being addressed in two continents (Europe and Asia) in soils contaminated with inorganic and/or organic pollutants. The energy crops optimization targets to increase (1) the plants metal(loid)s uptake, (2) the degradation of soil organic contaminants, (3) the growth of the plants' root systems and (4) the biomass productivity. Optimized phytoremediation solutions will be consolidated and presented in the form of lessons learnt, and will be further exploited (WP3) to develop replicability options for remediating contaminated sites in the whole of Europe and an integrated sustainability assessment. Plant materials from best performing practices in terms of phytoremediation and feedstock production will be converted to clean liquid biofuels assuring at the same time that soil pollutants are collected in concentrated forms (WP2).

#### To convert the produced biomass feedstock to biofuels with low ILUC risks and to ensure the extraction of the soil pollutants in concentrated form ➡ WP2

The aim of WP2 is to convert actually produced plant materials from WP1 to clean liquid biofuels, while at the same time assuring that soil pollutants are collected in concentrated forms. To do so, two thermochemical conversion routes will be elaborated. In the first route, followed by the European partners, the produced biomass is being pre-treated (by Torwash, torrefaction and slow pyrolysis) and gasified at high temperature and the produced syngas will be subsequently fermented into liquid biofuels. The second route conducted by the Canadian partner, consists of a pyrolysis-based solution with the subsequent upgrade of the pyrolysis products to refinery-compatible intermediates and Fischer–Tropsch Fuels (FT-fuels), respectively. Synergies between routes have been also scheduled.

# 3. To bridge the gap between the clean biofuel production and the optimized phytoremediation solutions on contaminated land ➡ WP3

The aim of WP3 will be accomplished through an integrated assessment and modelling of selected value chains, which will be analysed in environmental, economic, and social terms. In addition, the replication potentials of the proposed strategies in Europe will be assessed, using mapping and explicit models, along with a comparative assessment on how the exploitation of contaminated lands can help achieving progress in Sustainable Developments Goals (SDGs).

# 4. To disseminate and communicate the project results as well as to boost the international collaboration ➡ WP4

A robust communication and dissemination plan is scheduled for maximizing the visibility of the project findings. Particular emphasis is laid on the international collaboration as partners from India, China and Canada are participating on both optimization of selected energy crops for phytoremediation (China and India) and clean biofuel production (Canada). During the 1<sup>st</sup> reporting period one common workshop had been organished with the two sister projects of GOLD namely CERESiS and Phy2Climate as well as several presentations in workshops (final workshop of MAGIC project, etc.), conferences (like EUBCE2022, AAIC 2021) and exhibitions (like EXPO2020).

# 5. To carry out the management and coordination of the project and to ensure its successful implementation between EU and the project partners ⇒ WP5

A coordination and management plan has been set among the members of the consortium, as well as, between GOLD and INEA, DG Energy, DG Agriculture and DG Environment. An advisory board has been set up to advise on international developments of phytoremediation, biofuels production, sustainability issues and SDGs. An editorial board has been also set up to coordinate the projects publications.

### **1.2 Explanation of the work carried per WP**

Work Package 1: Optimization of lignocellulosic energy crops for phytoremediation purposes

Leader: AUA, partners: CRES, UMCS, UNIBO, INRAE, JUNIA, FCT, ICL, WR, METE, HUNAN, IBFC

Tasks	Title	Months	Leader	Participants	Status
1.1	Site characterization and description	1-10	AUA	All partners of WP1	Completed
1.2	Pot trials	1-46	UNIBO	All partners of WP1	On-going
1.3	Pilot scale-small field trials	3-48	JUNIA	All partners of WP1	On-going
1.4	Optimised phytoremediation solutions	6-48	AUA / INRAE	All partners of WP1	On-going

**Objective**: The main objective of WP1 is to optimize selected high-yielding lignocellulosic energy crops for phytoremediation, targeting different classes of soil pollutants.

The *specific objectives* are:

- to compare different phytoremediation practices on contaminated soils polluted with organic and inorganic pollutants when growing selected high-yielding lignocellulosic energy crops,
- → to apply the best performing phytoremediation practices on pilot small scale field trials and
- to develop optimised phytoremediation solutions for the selected crops in the form of lessons learnt.

**Progress toward the objectives**: GOLD has been designed to successfully phytoremediate soils bearing organic and inorganic pollutants using energy crops. Four high-yielding lignocellulosic energy crops have been selected: i) **two perennial grasses** with economic lifespan of 10-20 years, namely miscanthus and switchgrass, and ii) **two annual spring crops**, namely biomass sorghum and industrial hemp. Each partner carries out pot and field trials for three (or two in China) of the selected energy crops (depending on the climatic zone).

The optimization process for the selected energy crops have been organised at two TRL levels; a) <u>pot trials</u>, TRL: 3-4 (M1-42; Task 1.2) and b) <u>pilot small scale field trials</u>, TRL: 4-5 (M3-48; Task 1.3). Two phytoremediation practices are being evaluated: plant associated microorganisms and biostimulants. The trials are being implemented for identifying the best combination of phytoremediation practice X best performed crop (in terms of biomass yields and quality as well as uptake of inorganic/degrade of organic pollutants) under a broad range of soil pollutants. In Europe, five sites representing different climatic zones and different types of soil pollutants are being used. In Asia three sites are being used, one in India and two in China. Optimised phytoremediation solutions (task 1.4) will be developed in the form of lessons learnt based on the results of tasks 1.2 & 1.3 as well as on previous and/or ongoing phytoremediation activities and applications from WP1 partners. Partners, countries and climatic zones, pollutants, phytoremediation strategies and targets are summarized in the table below.

#### Table 1: Partners, pollutants and phytoremediation strategies.

Partners, countries and climatic zones	Pollutants / Phytoremediation strategies and targets
AUA-GR (MED-S)	Inorganic pollutants (metal(loid)s, e.g., Cd, Pb, Zn, Ni, As)
UNIBO-IT (MED-N)	Phytoextraction: a) to increase the crop bioaccumulation potential of
YRCREA-FR (ATL-N)	the inorganic pollutants and/or b) to increase the aerial biomass
<b>UMCS-PL</b> (CON)	produced and thus the final metal(loid)s removal
CRES-GR / METE-GR	Organic pollutants (e.g., POPs, DDT, DDE, DDD, α-ε-HCH)
(MED-C)	Bioaugmentation: a) to increase the dissipation (i.e., biodegradation
HUNAU-China (Cfa)	and other processes) of the organic pollutants and/or b) to increase
IBFC-China (Cfa)	the root system and aerial biomass production
CTD- India	-

# **Task 1.1: Site characterization and description** (*M1-10, this activity was reported in* 1<sup>st</sup> periodic report)

During the  $1^{st}$  reporting period the characterisation and description of the contaminated sites have been completed and reported in **D1.1**. In Figure 2 presented the sites of the field trials.



#### Figure 2: Contaminated sites in GOLD

#### ► Task 1.2: Pot trials (M1-46)

**Objective:** To set up pot trials to evaluate different phytoremediation practices and to select the most promising in terms of soil remediation (phytoextraction, bioaugmentation), plant growth and biomass productivity and quality. Two biostimulants [protein hydrolysates (B1) and fulvic/humic acids (B2)] and a mycorrhiza (M) are applied singularly or combined (B1xM and B2xM).

**Progress toward the objectives:** For the pot experiment approximately 1 ton of soil was collected from the contaminated experimental field of each partner and was transferred to the area of the greenhouses. It was homogenized, sieved through a 10 mm mesh, mixed thoroughly with the fertilizer (in the proportion of 20 g of 20-5-10 N-P-K per pot), and placed into pots (12 kg of soil per pot).

Plant material was allocated to each partner (Table 2), namely:

- miscanthus: micro-propagated plants of Miscanthus x giganteus purchased from Rhizosfer© (France)
- switchgrass (Panicum virgatum L.) variety KANLOW, obtained from CRES, Greece.
- sorghum (Sorghum sudanense x bicolor) variety BULLDOZER, obtained from UNIBO, Italy

→ fibre hemp (Cannabis sativa L.) variety FUTURA 75, obtained from CRES, Greece.

The **biostimulants** were purchased and were applied singularly or in combination:

- **B1**: protein hydrolysates (SIAPTON, Company: Agrology, Greece)
- B2: fulvic/humic acids (LONITE 80 SP, Company: Alba Milagro, Italy)
- → M: mycorrhiza (SYMBIVIT, Company: Symbiom, Czech Republic).
- B1 (protein hydrolysates) X M (mycorrhiza)
- **B2** (fulvic/humic acids) X **M** (mycorrhiza).

During the trial, the plants were monitored for phytotoxicity symptoms (chlorosis, necrosis, changed pigment contents, etc.) and for their growth (by measuring their height, number of leaves and tillers). The following parameters were determined for each crop at plant harvest:

- fresh and dry weight of aerial plant parts (during the 1<sup>st</sup> technical meeting of WP1 partners it was decided that the root biomass will not be determined as not relevant in a pot experiment),
- plant total height, number of leaves, number of tillers, number of inflorescences,
- clear phytotoxicity symptoms,
- metal(loid) concentration of aboveground plant parts,
- the biomass quality characteristics (ash content, calorific value, etc.),
- extractable metal(loid) concentrations in the soil (following 0.01 M Ca(NO3)2 extraction), soil pH, organic pollutant concentrations.

Based on the results obtained (mainly the highest shoot biomass and height combined with the highest metal(loid) concentration), the best two treatments should be selected by each partner for the pilot scale-small field trials.

 Table 2: Plant allocation per partner

	AUA	CRES	UMCS	UNIBO	JUNIA	HUNAU	IBFC
Miscanthus	+	+	+	+	+	+	
Switchgrass						+	
Hemp	+		+	+	+		
Sorghum		+		+			+
Kenaf							+

**Results and achievements**: The best effect on biomass production and metal accumulation for all crops was achieved with the application of B2xM. Therefore, this treatment was chosen as a common one for the field experiments of all partners. Application of other treatments in different plant species did not provide such evident results. Based on own results and experience, and supported by the PCA analysis, each partner had to choose the second treatment for their own field experiments. The treatments used by each partner for each plant crop tested in pilot scale-small field trials are summarized/presented in Table 3.

Partner	Plant species	Treatments selected for field trials							
i ditilei		B1	B2	М	B1xM	B2xM	Control		
UMCS, Poland	miscanthus		Х			X	Х		
	industrial hemp		Х			X	Х		
	sorghum		Х			X	Х		
AUA, Greece	miscanthus			X		X	Х		
	industrial hemp			X		X	Х		
	sorghum			X		X	Х		
CRES, Greece	miscanthus				Х	X	Х		
	sorghum				Х	X	Х		
	switchgrass				Х	X	Х		
UNIBO, Italy	miscanthus		Х			X	Х		
	industrial hemp	X				X	Х		
	sorghum				X	X	Х		
JUNIA, France	miscanthus		X			X	Х		

Table 3: Treatments selected by each partner for field experiments for task 1.3.

	industrial hemp		X			X	Х
	sorghum		Х			Х	Х
IBFC, China	industrial hemp → kenaf	Х				Х	Х
	sorghum			Х		Х	Х
HUNAU, China	miscanthus				Х	Х	Х
	switchgrass				X	X	X

During the 1<sup>st</sup> reporting period the 1<sup>st</sup> part of Task 1.2 was completed and reported in 1<sup>st</sup> periodic report. Pot trials will be carried out in the 3<sup>rd</sup> reporting period the humic acids that have been isolated in Towash technology will be applied on pot trials as biostimulants and the results from this activity will be reported in **D1.3**.

No milestones have been foreseen for this reporting period in Task 1.2.

#### Task 1.3: Pilot scale-small field trials

**Objective**: To establish small scale field trials to test the two best treatments selected for each crop and compare them with un-treated crops to evaluate the biomass production and phytoremediation potential.

Results and achievements: Field trials had to be established in five contaminated sites in Europe (two in Greece-at AUA and CRES fields, one in Poland-UMCS field, one in Italy-UNIBO field, and one in France-JUNIA field) and two in China-HUNAU and IBFC fields. All appropriate agronomic technics for a successful crop establishment were applied, i.e., soil analyses, ploughing, chemical weeding, basic fertilization, harrowing, irrigation facilities, and seeding/transplanting in plots following the completely randomized experimental design with three replications. The best two phytoremediation practices (as shown in Table 2) were applied following the same protocols as defined during internal meetings of WP1 partners. Each European partner carried out pilot trials for three energy crops, apart from the Chinese partners (HUNAU and IBFC) that are working with two crops each (Table 2). During the growing cycle, any symptoms of phytotoxicity from the contaminants were monitored. At the end of growing period, the central part of each plot was harvested for biomass yield estimations; morphological traits and fresh and dry biomass were determined. Plant samples per treatment were used to determine the moisture content, the concentrations of metal(loid)s, and the biomass characterization. Hemp and sorghum were harvested in all fields; the shoots of miscanthus were left intact to allow nutrients allocation into rhizomes and to protect the rhizomes from the frost during winter.

The growth and development of crops differed among the experimental fields mainly due to the differences in the type and level of contamination. For this reason, the results will be presented per partner.

#### AUA



Figure 3: Type and level of contamination at the AUA experimental field

This experimental field is the most contaminated of all, with Pb, Zn, Cd, Ni, As and Sb at concentrations much higher than the common values found in healthy soils (Figure 3).

Miscanthus, hemp and sorghum were affected by the contaminants and the plants were smaller than could be expected, and consequently also the produced biomass. Phytotoxicity symptoms were observed in the plantations, as reporting in the 1<sup>st</sup> reporting period.



Figure 4: View of the field trials in the 2<sup>nd</sup> growing period (2023) for AUA.

Plant samples have been taken from all the plots for biomass characterization and the determination of heavy metals and metalloids. Miscanthus was harvested at the end of the 2<sup>nd</sup> growing period. The dry matter yields for all crops are presented in Figure 5.



Figure 5: Dry matter yields (t/ha) for the three under study crops (2 years data for the two annual crops; hemp and sorghum and one year for the perennial; miscanthus).

In terms of *industrial hemp*, the control plants in both years gave the highest biomass than the treated ones (Figure 5). However, the statistical analyses detected significant differences only for 2023, between control and M treatments. The mycorrhiza treatment had a moderate biomass, and it slightly increased from 2022 to 2023. The B2xM treatment, while having the

lowest biomass in 2022, experienced a significant increase in biomass in 2023. Average biomass for control plots for 2022 and 2023 were 1.63 t ha-1- and 2.78 t ha-1, respectively.

Regarding **sorghum** the highest dry matter yields for both years have been recorded under the B2xM when compared with control and mycorrhiza treated plots; however, no significant differences were observed (Figure 5, B). The dry matter yields for B2xM treatment were 12.5 t ha-1 for 2022 and 30.8 t ha-1 for 2023 (an increase of 246%).

Finally, for *miscanthus* no significant differences were observed among treatments (Figure 5, C). The highest yields had been recorded in B2xM treated plots, reaching 5.1 t ha-1.



## Figure 6: Heavy metals and Sb concertation (mg/kg) for the two annual crops (hemp and sorghum).

In terms heavy metal concertation, it was found that both annual crops (hemp and sorghum) could concentrate metal(loid)s in their aerial biomass (Figure 6). Hemp could accumulate more Ni, Cu, Pb, Sb and sorghum concentrated more Cd and Zn.

#### CRES

This experimental field is mainly contaminated with Ni (729 mg/kg), and in a much lower degree with As (4.5 mg/kg) (Figure 7).



Figure 7: Contamination with heavy metals in the field of CRES in Kozani, Greece.

The three studied crops had a good establishment and development in Kozani (Mete premises). In 2022 the establishment was done by seeds for sorghum and switchgrass and by rhizomes for miscanthus. At the establishment year the sowing of sorghum was done in the 1st half of May (variety: Bulldozer) and for switchgrass in the 1st half of June (due to late seeds arrival, variety: Blackwell). The establishment of miscanthus was done at the end of May 2022.



Figure 8: View of the field trials in Kozani at the end of the growing period.

For all crops and years, the highest dry matter yields had been measured for the plots that M X B2 was applied (Figure 9). The yields of switchgrass were double in the 2<sup>nd</sup> growing period, while for miscanthus the increase more quadruple. Higher yields were also recorded in the 2<sup>nd</sup> year even for the annual crop (sorghum).



Figure 9: Dry matter yields (t/ha) for the three under study crops (switchgrass, miscanthus, sorghum) at the end of both growing seasons.

The Ni concertation for the under-study crops is presented in Figure 10. Although switchgrass had the highest Ni concertation among the three crops, the highest Ni uptake was recorded by sorghum due to its higher biomass yields (Figure 11).





Figure 10: Ni concentration for the studied crops (sorghum, miscanthus, and switchgrass) and both plant fractions (stems, leaves) in both years (2022, 2023).



Figure 11: Ni uptake (mg ha-1) for the studied crops (sorghum, miscanthus and switchgrass) in both years (2022, 2023) for both treatments (MXB1 and MXB2 vs. control).

#### UMCS

The experimental field in Poland is contaminated mainly with As (94.1 mg kg<sup>-1</sup>), Cd (51.6 mg kg<sup>-1</sup>), Pb (2939.7 mg kg<sup>-1</sup>), and Zn (8057.1 mg kg<sup>-1</sup>) (Figure 12).

All crops were growing very well without showing significant toxicity symptoms reaching up to 3.3 m (sorghum) and 3.5 m (hemp) height (Figure 13). The highest biomass production, both in case of sorghum and hemp was noted for B2 (fulvic/humic acids) treatment (Figure 13). It can be noted that the biomass productivity was more than double for sorghum compared to hemp.

Of all three plant species tested, sorghum was characterised by the highest shoot production ranging from 15 to 21 ton of dry weight (DW) per ha (Figure 14). Application of humic substances (B2) and humic substances combined with mycorrhiza (B2xM) resulted in higher biomass of the above-ground parts of sorghum (Figure 14 A). The mean dry biomass of hemp ranged from 6.5 to 7.5 t ha-1 and increased after application of B2 in comparison to non-treated control plants (Figure 14 B). The growth (shoot biomass and height) of miscanthus was only determined in the second growth season (2023) since the first one was to establish its

plantation. Its biomass ranged from 5.4 to 6.1 ha-1 and was not affected by any treatment (Figure 14 C). Figure



12:



Experimental field in Poland (marked with yellow) contaminated with heavy metals (Zn, Pb, Cd) and metalloid As.



Figure 13: Photographs from the experimental field of UMCS (2023).



Figure 14: Dry matter yields (t ha-1) of sorghum (A), hemp (B), and miscanthus (C) per treatment. Values are mean from 2022 and 2023, in case of miscanthus the data of the second growth season are presented only.

The three under study crops could accumulate heavy metals (Figure 15). In the 2<sup>nd</sup> year lower concentrations in the aerial biomass have been measured.

	(	:	B	2	B2	×М				С		E	2	B2:	×M
	2022	2023	2022	2023	2022	2023			20	22	2023	2022	2023	2022	2023
Zn	276.2 a	162.2 A	295.4 a	125.7 A	274.7 a	161.1 A		Zn	200.	.1 a	32.4 A	183.6 a	30.4 A	206.1 a	38.5 A
Pb	3.99 a	4.4 A	4.77 a	5.4 A	4.18 a	5.6 A		Pb	20.4	4 a	9.6 A	18.4 a	8.1 A	17.8 a	8.4 A
Cd	18.0 a	4.6 A	21.5 a	5.4 A	18.2 a	6.5 A		Cd	1.1	а	0.76 A	1.2 a	0.6 A	1.5 a	0.8 A
					С		E	32			B2xM				
				2022	202	3 20	22	20	23	2022	2 202	3			
			z	<b>n</b> 166.3	a 125.5	5 A 180	.3 a	65.0	D A	159	a 70.3	3 A			
			Р	<b>b</b> 3.2 a	a 4.9	A 3.5	Ба	4.7	A	3.23	a <u>3.5</u>	A			
			С	<b>d</b> 2.1 a	a 1.1	A 2.3	3 a	0.7	A	1.97	a 0.9	A			

Figure 15: Metal concentrations (mg Kg-1) for sorghum, hemp and miscanthus.

Based on UMCS results (yields data and heavy metals concentrations), it was found that harvesting the biomass of sorghum one could remove from the soil up to 4440 g of Zn, 280 g of Cd, and 107 g of Pb per ha. Comparable level of Pb removal was also recorded for hemp; however, Zn and Cd removal from the soil was much less efficient – 5-fold less in case of Zn and 35-fold less in case of Cd. Miscanthus was the least efficient crop in metal removal for all metals.

#### UNIBO

The contaminated site in Italy is located in the surroundings of Bologna (44° 50' N, 11° 28' E). It is part of a former illegal landfill, subject since the end of World War II to dumping and deposits of waste of various origins (war residues, stockpiles, artisanal waste, raw materials, industrial waste). The main inorganic contamination of the field is due to Pb (159 mg kg<sup>-1</sup>), Cu (137 mg kg<sup>-1</sup>), Ni (209 mg kg<sup>-1</sup>), Zn (455 mg kg<sup>-1</sup>), and Sn (8.8 mg kg<sup>-1</sup>) (Figure 16). The field is also contaminated with organics and the analyses are in process.



Figure 16: Soil contamination in the experimental field in Italy-UNIBO.

The under-study crops showed some phytotoxicity symptoms are presented in Figure 17.



Figure 17: Sorghum and hemp plantations at UNIBO experimental field (A, B). Phytotoxicity symptoms in hemp (C, D).

After the harvesting of two subsequent growing seasons, it was found that the highest biomass yields for hemp was recorded in the control plots (Figure 18). In terms of miscanthus the highest yields were recorded in the treated plots and for miscanthus was in the B2 treatment followed by B2 treatment. Regarding sorghum, the highest biomass yields had been recorded in B2 plots in 2022 and in MB2 in 2023.



Figure 18: Dry matter yields for the three under study crops and both years (2022, 2023).



#### Figure 19: Plants at harvest, top left hemp, top right miscanthus, bottom sorghum.

In Figure 20 the metal concentration (mg kg-1) for copper and zinc per crop and year is presented. It was found that the concentrations in the second year were higher than in the first for both metals and for all crops. It was also found that for hemp the Hemp higher metals concentrations were measured for control plots compared to the treated ones, with the exception of Zn in 2022.



Figure 20: Metals concentrations (mg Kg-1) per year and per under study crop.

#### JUNIA



The soil of this experimental field is contaminated with Cd (11.0 mg kg<sup>-1</sup>), Pb (536 mg kg<sup>-1</sup>), and Zn (935 mg kg<sup>-1</sup>) (Figure 21). No significant organic contamination was determined in the site. During the growing season, slight phytotoxicity symptoms were observed in both cultivations (Figure 22).

Due to failure of miscanthus fields the trials had been carried out with the two annual crops (hemp and sorghum). The failure of a successful establishment of miscanthus plantation due to: i) a long delivery period of rhizomes and, thus, many of them were too dried when received, ii) an extremely dry period followed the transplantation harming the young miscanthus plants.





Figure 22: Phytotoxicity symptoms in hemp and in sorghum - A. Photos of the field in late July - B and in October before harvesting - C.

As it is presented in Figure 23 no significant differences were recorded between the treatments. Higher yields were observed in the second year, but not statistically significant.

As it is presented in Figure 24 no significant differences between treatments were observed in

terms of metal concertation. Cd and Zn concentrations in sorghum were significantly higher than in hemp.



Figure 23: Dry matter yields (t/ha) for the two under study crops per treatment and year.





#### HUNAU

The trials in China (HUNAU) started in 2022 but due to the poor establishment rate for both perennial crops (miscanthus and switchgrass) both trials had to reestablished in 2023. The failure of the 1<sup>st</sup> year was due to unexpectedly heavy rains and water flooding early in spring 2022, right after the transplantation of the rhizomes. The field was submerged in water for long time, which led to poor establishment rate. The new established trials are presented in Figure 25.



Figure 25: Visual impressions of the field trials with miscanthus and switchgrass at HUNAU, China

The mean dry biomass yield of switchgrass was higher than miscanthus across all treatments. It is mainly because during first year of field trials, crops were destroyed due to persistent rains and flooding right after the setting-up of the field trials and extensive replantation was carried out in the following year. Thus, in reality it is first year of dry biomass yield for both crops. Miscanthus needs relatively longer time to establish than switchgrass, which is why this dry biomass yield difference was observed. Overall, for both crops no significance difference was recorded between treatments on dry biomass yield. For miscanthus, the best performing treatment was B2 with dry biomass yield well below 1 t ha-1, whereas in switchgrass B2M treatment outperformed others with mean dry biomass yield of 4 t ha-1 (Figure 26).



Figure 26: Dry matter yields (t/ha) for the two under study crops per treatment at the end of 2023 (establishment year of both perennial crops).



fractions Both plants (stems and leaves) had been analysed in terms of metal concertation and the results are presented in Figure 27. Statistically, no significant difference was recorded among treatments for both crops. For miscanthus, the Cd content in leaf samples varied from 0.11 to 0.15 mg kg-1, whereas the stem content ranged from 0.13 to 0.25 mg kg-1. The Cd content in switchgrass leaf and stem varied from 0.14 to 0.17 mg kg-1 DW and from 0.08 to 0.09 mg kg-1DW, respectively. The trend clearly indicates that switchgrass tend to accumulate more Cd in leaves than stems.

Figure 27: Metal concertation (Cd, mg kg-1) for the two under study crops and plant fractions (leaves,

stems). Same superscripts refer to no significant differences. Error bars are calculated for replications.



# Figure 28: Metal concertation (Cr, mg kg-1) for the two under study crops and plant fractions (leaves, stems). Same superscripts refer to no significant differences. Error bars are calculated for replications.

Based on the metal content and total dry biomass, the metal uptake per hectare was calculated for each crop under the tested treatments. For both crops, dry biomass yield was the main determinant of total metal uptake. As switchgrass outperformed miscanthus in dry biomass yield, the total metal uptake was also higher in switchgrass than miscanthus. The total Cd uptake per hectare for miscanthus varied from 43 to 108 mg ha-1 for leaf biomass, whereas for stem it was 34 to 49 mg ha-1. For switchgrass, total Cd uptake in leaf and stem varied from 229 to 365 mg ha-1 and from 440 to 659 mg ha-1, respectively. The total Cr uptake in leaf and stem of miscanthus ranged from 1212 to 2490 mg ha-1 and from 1172 to 2088 mg ha-1, respectively. In switchgrass, the total Cr uptake for leaf varied from 9409 to 24392 mg ha-1, whereas for stem it ranged between 13394 to 34975 mg ha-1.

#### **IBFC**

The field trials in 2022 with the two annual crops (sorghum and kenaf) were failed. The main reason was the extremely precipitation occurred in spring 2022 that affected the seeds germination. A second seeding was accomplished later, but unfortunately the extreme drought weather significantly affected the survival of both crops leading to the failure of the field trial. Thus, the first successful field trials were the ones of 2023.



Figure 29: View of both crops (sorghum on the left and kenaf on the right) at the end of the growing period.

Different additives showed different effects on the plant height of sorghum. Compared with the control, the protein hydrolysate (SI) significantly decreased the plant height, however, the other treatments showed no significant impacts on the plant height. SY and SY+LO have the potential for increasing sorghum plant height (Figure 30). Different additives did not significantly affect the stem diameter of sorghum (Figure 30). Compared with the control, the protein hydrolysate (SI) has the potential to decrease the stem diameter, however, the other treatments have the potential to increase sorghum stem diameter.



Figure 30: Plant height and stem diameter of sorghum under different treatments. Note: CK, no treatment applied; SY, symbivit (mycorrhiza inoculum); LO, Lonite (humic/fulvic acids); SI, siapton (protein hydrolysate); SY+LO, symbivit (mycorrhiza) + Lonite (humic/fulvic acid); SY+SI, symbivit (mycorrhiza) + siapton (protein hydrolysate).

Compared with CK, all of the test additives can increase the plant height of kenaf to different extent, however, no significant differences were found between the treatments (Figure 31). Compared with CK, SI significantly increase the stem diameter of kenaf. However, no significant differences were found between CK and the rest treatments. Furthermore, the stem diameter of SI was also significantly higher than those of SY, SY+LO and LO.



Figure 31: Plant height and stem diameter of kenaf under different treatments. Note: CK, no treatment applied; SY, symbivit (mycorrhiza inoculum); LO, Lonite (humic/fulvic acids); SI, siapton (protein hydrolysate); SY+LO, symbivit (mycorrhiza) + Lonite (humic/fulvic acid); SY+SI, symbivit (mycorrhiza) +siapton (protein hydrolysate).



Different treatments affected the Cd concentrations in the aboveground part of sorghum and kenaf (Figure 32). All of the additives can increase the shoot Cd concentration of sorghum compared with CK and SY+LO performed best. Figure 32: Cd concentrations in the aboveground part of sorghum and kenaf

*Problem, delay or deviation*: No problems, delays or deviations have been detected.

Corrective actions undertaken: None.

D. no	Title	Leader	Delivery date (planned)	Delivery date (actual)
D1.4	Report on "Application of best performing phytoremediation practices on pilot small-scale field trials"	Junia	M36	M37

No milestones have been foreseen for this reporting period in Task 1.3.

#### Task 1.4: Optimised phytoremediation solutions

**Objective**: To develop optimised phytoremediation solutions for the selected crops in the form of lessons learnt.

**Progress toward the objectives:** The results of the previous tasks will be critically reviewed, along with the results from several ongoing and/or completed projects on soil phytoremediation using energy crops (like FORTE, INTENSE, New-C-Land, MAGIC, OPTIMA). The long-term experience of several WP1 partners will be exploited as cross-fertilization throughout the project lifetime. The aim of this task is twofold: a) to provide information regarding optimised phytoremediation solutions for the selected energy crops on specific contaminated soils, which will be further analysed in WP3 and b) to outline lessons learnt for optimised phytoremediation solutions in the form of factsheets per case study.

Each lesson learnt will present how the combination "**contamination site X energy crops X management practices**" affect the growth, yield and quality of biomass and yields of the cultivated crops and finally how this combination affected the land decontamination either via pollutants uptake for the inorganics or via degradation for the organics.

In the table below the previous and ongoing activities on phytoremediation of WP1 partners are summarized (Table 4).

Partner	Previous and ongoing phytoremediation activities on the selected energy crops
AUA	MAGIC: Pot trials for <u>switchgrass</u> and <u>biomass sorghum</u> in soils that have been
	artificially contaminated with metals (Zn, Cr, Pb, Cd, Ni, Cu) (on-going).
	FORTE: Industrial hemp, among other crops, is being grown in contaminated
	lands with heavy metals in Lavreotiki area (close to Athens)
	Previous research activities in the projects: JatroMed, BECY, RICINUS
JUNIA	Previous research activities in the projects: MISCHAR, PHYTENER, PHYTEXPPO,
(formers	POTAGER and in on-going in New-C-land.
YNCREA)	<ul> <li>Miscanthus fields on contaminated lands around the former MetalEurop Nord</li> </ul>
	Pb/Zn smelter have been established in 2010 and are still on-going.
INRAE	Previous research activities in the projects: PHYTOSUDOE, INTENSE,
	GREENLAND and PHYTOCHEM
	On-going trials on <u>miscanthus</u> on real Cu/PAHs-contaminated lands. Miscanthus
	shoots and rhizomes have been kept for analysis.
UMCS	Previous research activities in the projects: INTENSE, GREENLAND,
	ENTEGRADE, PHYTAC, COST action FA1103.
	<ul> <li>Mechanisms of adaptations in plants inhabiting Zn-Pb waste deposits – ecological,</li> </ul>
	floristic, and physiological studies.
FCT UNL	<ul> <li>OPTIMA: Pot trials for <u>miscanthus</u> in soils contaminated with Zn (2012-15)</li> </ul>
	MAGIC: Pot trials for <u>switchgrass</u> and <u>miscanthus</u> in soils artificially
	contaminated with heavy metals (Zn, Cr, Pb, Cd, Ni, Cu) (started in 2018, on-
	going).
CTD (the	<ul> <li>OPTIMA: <u>Switchgrass</u>, among other perennial grasses, have been tested under</li> </ul>
new	different phytoremediation practices (mycorrhiza, bio stimulants).
Indian	
partner)	

Table 4: Previous and on-going activities of GOLD partners in terms phytoremediation

During the 2<sup>nd</sup> reporting period D1.6 was consolidated entitled "Optimised phytoremediation solutions". In this deliverable it was studied the optimised phytoremediation solutions for the two annual crops in GOLD (sorghum and hemp), while the other two will be included in D1.8 that will report the final findings of Task 1.4.

From the surveys accomplished in this D1.6, it has been highlighted how phytoremediation has attract the interest worldwide in the last decades. This set of phytotechnologies can contribute to the exploitation and remediation of polluted sites, releasing at the same time valuable agricultural land for food and feed production, and supporting the targets of the Renewable Energy Directive for 2023 (consumption of at least 27% of renewable energy).

The implementation of WP1 so far showed that the four energy crops of GOLD were successfully selected since they were well established in all the field trials, despite the type and level of contamination and the pedo-climatic conditions of each site. In addition, the biostimulant used in most cases improved the phytoremediation capacity of the crops. Details on these results are given in Deliverable 1.4.

The further steps in this task are to:

- present the data and information gathered from the literature and other projects for the perennials miscanthus and switchgrass
- finalize the activities of Task 1.3 (field trials) and to gather the final results for the optimised phytoremediation solutions concerning the selected energy crops
- outline lessons learnt for optimized phytoremediation solutions in the form of factsheets per case study

 evaluate and present the conclusions on how the contamination site X energy crops X management practices affects: (i) the growth, yield and quality of biomass and yields of the cultivated crops, and (ii) the land decontamination either via pollutants uptake for the inorganics or via degradation for the organics.

Problem, delay or deviation: No problems, delays or deviations have been detected.

Corrective actions undertaken: None.

D. no	Title	Leader	Delivery date	Delivery date
			(planned)	(actual)
D1.6	Report on "Optimised	INRAE	M36	M37
	phytoremediation solutions"			

No milestones have been foreseen for this reporting period in Task 1.4.

All WP1 milestones have been accomplished in 1<sup>st</sup> reporting period.

#### Key findings/achievements of the 2<sup>nd</sup> reporting period are presented in the Box 1:

- Small pilot fields in 7 sites (5 in Europe and 2 in China). In five EU countries field trials had been carried out for two subsequent years (2022 & 2023). The field trials in China have results only from 2023 since the ones established in 2022 were failed due to extreme climatic conditions (excess precipitations and/or drought). The trials in India started during the 2<sup>nd</sup> reporting period and in order to speed up are being carried out indoors. The results from the Indian site will be reported in the 3<sup>rd</sup> reporting period.
- Results from field trials in terms of under study crops. The results obtained so far indicate that hemp is a crop capable of growing well in soils contaminated with several metal(loid)s, as it is also the case for Miscanthus. Sorghum performed very well in all sites although they differ a lot in terms of average temperatures and lower precipitation rates.
- Overall, there was no significant effect of the applied treatments on the crops. In the case of sorghum in France it was found it that sorghum roots demonstrated a good mycorrhization rate. The combination of humic/fulvic acids with mycorrhiza had a tendency to increase the biomass yield of sorghum and miscanthus plants in some of the understudy sites. For hemp, the treatment showing the most beneficial effect was the application of humic/fulvic acids. In the majority of the sites higher biomass yields had been recorded in the 2<sup>nd</sup> growing period.
- Collective results on metal(loid) concentrations in the shoots generally showed no significant effect of the treatments on the studied crops. However, the combination of humic/fulvic acids with mycorrhiza slightly increased the shoot concentration of Cu and Zn for sorghum in year 2 at the site of AUA, Greece. Clearly, highest shoot Cd concentrations were evidenced at the Polish and French sites, both being large areas contaminated by fallout from smelters. In contrast, hemp and miscanthus displayed a similar pattern (metal-excluder) for shoot Cd and Zn concentrations at all sites.
- The highest metal(loid) bioaccumulation/uptake values obtained for sorghum were significantly higher than those for hemp and miscanthus. These results obtained in the different sites demonstrate the potential of this crop for Cd and Zn phytoextraction under a wide range of edaphoclimatic conditions and with different types of contamination. The highest amounts of Cd and Zn were phytoextracted at the Polish and French sites, and also for Zn in year 2 at the AUA site.
- Higher metal(loid) bioaccumulation/uptake was recorded in the majority of the sites in year 2 mainly due the higher biomass productivity in year 2 compared to year 1.
- The yields varied a lot among the partners and strongly connected with the levels of the soil contamination. In terms of hemp the yields varied from 4 t/ha (Lavrion) to 12 t/ha (MetalEurop). The corresponding values for sorghum varied from 15 t/ha (MetalEurop) to 30 t/ha (Kozani). Regarding the perennial crop miscanthus the yields at the 2<sup>nd</sup> year varied from t t/ha (Lavrion) to 28 t/ha (Kozani). Switchgrass was only tested in Kozani where the yields at the 2<sup>nd</sup> year were 15 t/ha.

#### Work package 2: Conversion process for clean liquid biofuel production Leader: TUM; partners: TNO, CERTH, RECORD, UDES

Tasks	Title	Months	Leader	Participants	Status
2.1	Characterization of biomass materials and by-products, conversion process considerations, balance and recovery options of elements	1-48	CERTH	All WP2 partners	On-going
2.2	Biomass pre-treatment for entrained flow gasification (EFG)	3-36	TNO	RECORD	On-going
2.3	Entrained flow gasification and gas cleaning	6-48	TUM- CES		On-going
2.4	Syngas fermentation	25-48	TUM- CBE		On-going
2.5	High temperature autothermal pyrolysis and upgrading	3-48	UDES		On-going

The main objective of WP2 is to consolidate the appropriate conversion steps towards the production of clean low-ILUC biofuels using biomass produced in contaminated lands. Two conversion routes identified are: 1) pretreatment, high temperature entrained flow gasification (EFG) producing a non-leachable vitrified ash melt, gas cleaning and syngas fermentation towards ethanol and 2) bubbling fluid-bed autothermal pyrolysis (BFB-ATP) and product upgrading.

In WP2 clean biofuels will be produced using the contaminated feedstock produced in pilot trials of WP1. Two conversion routes will be studied and evaluated: The **1**<sup>st</sup> **conversion route** (tasks 2.1 to 2.4) starts with biomass pre-treatment, where three options will be tested: Torwash (TNO), torrefaction (TNO) and slow pyrolysis (RE-CORD). The pre-treated solids will be sent to TUM to feed the entrained flow gasifier (at temperatures of 1300-1500°C), where the metal(loid)s will be collected in a concentrated form as slag or ash and the produced syngas after its cleaning will be used for a fermentation step to produce clean liquid biofuels (alcohols). The humic acids derived from the Torwash will be sent to WP1 partners to be tested as biostimulants in the 2<sup>nd</sup> half of the project. The **2nd conversion route** (task 2.5) will be based on an autothermal pyrolysis and FT synthesis to fuels, led by the Canadian partners (UdeS). Here, the pollutant recovery will take place via the pyrolysis char. Synergies between the two routes have been scheduled (WP2 leader: TUM).

The specific objectives of the 1<sup>st</sup> route (European proprietary) are:

- To optimize pretreatment methods for transforming diverse feedstock into a material suitable for EFG, determine the fate of the contaminants, through extensive analyses of the raw and pre-treated feedstocks, and optimize the separation methods.
- To convert the solid fuel by EFG into a high-quality syngas with a desirable chemical composition for the liquid fuel production. Suitable gas cleaning and ash separation methods are included. To evaluate the level of capture and reduced leachability of the heavy metals (pollutants) collected in vitrified form.
- To prove the syngas use in the newly developed fermentation, with specialized bacterial strains towards C2-C6 alcohols, that does not necessitate high pressures, thus lowering the EFG size requirements.

The specific objectives of the 2<sup>nd</sup> route (Canada proprietary) are:

- To optimize BFB-ATP operating conditions for producing non-contaminated biooil intermediate and maintain undesired constituents into the solid phase product of the process.
- To propose a protocol allowing the conversion of the pyro-liquids into a conventional refinery fluid catalytic cracking (FCC) compatible feedstock for its upgrading avoiding contamination/poisoning.
- To optimize the exploration of pyro-gases through catalytic reforming into a Fischer-Tropsch Synthesis (FTS) compatible syngas (SG) avoiding contamination/poisoning and targeting mainly the maximization (FTS) production of jet biofuel.

1<sup>st</sup> convention route: High temperature gasification with syngas fermentation (Leader: TUM, partners: TNO, RE-CORD, CERTH, UdeS)

AUA's Lavrion site was selected as primary source of biomass samples for WP2 trials due to its high contamination levels and simultaneously high yields. CRES's Kozani site was selected as a fall-back option if biomass samples from AUA were not sufficient in quantity. Homogenization and shipment of all large samples were conducted at CRES in Greece.

Agricultural University of Athens (AUA) provided 164 kg dry of Sorghum from their pilot field trials in Lavrion, Greece, using MB2. The biomass was delivered to the WP2 partners following the homogenization protocol (maximum particle size: 5 mm, Moisture content: <10%) according to plan in Nov 2022. CERTH received 3 kg dry, TUM 1 kg dry, RE-CORD about 50 kg dry and TNO about 110 kg dry.

During preparation of the experiments for processing hemp, TNO found out that according to the Dutch opium law, operation such as importing, transporting, storing and processing hemp (and all parts of hemp plants) without a permit is a criminal act. To be able to apply for a permit to store and process hemp, a number of security facilities and procedures have to be realized. The preparation for, the application for and approval of a permit will take at least 6 months. There is no assurance that after the application is filed that the permit will be obtained. As a consequence, TNO will not be able to conduct experiments using hemp in the GOLD project. Instead, hemp will be analysed by the other GOLD WP2 partners and at the Institut Polytechnique UniLaSalle in TNO's stead. Alternatively, TNO will be using Miscanthus from CRES's Kozani site to conduct TORWASH experiments. Hemp was provided in late January 2024 from AUA, Lavrion, Greece. 2 kg dry were shipped to CERTH, 1 kg dry to TUM, 1 kg dry to RE-CORD and 2 kg dry to UniLaSalle (Originally planned: 110 kg dry to TNO).

Switchgrass and Miscanthus were provided by CRES from Kozani, Greece, using MB2. In September 2023 each partner received 1kgdry for analysis. In February 2024, TNO received another 25 kg dry each for TORWASH.

Miscanthus from 2023's AUA/Lavrion site was provided in early February 2024 with 1 kg dry to each partner for analysis. In late February 2024 another 60-70 kg dry were received at TNO for torrefaction and TORWASH, and another 60-70 kg dry at RE-CORD for pyrolysis.

# Task 2.1: Characterization of biomass materials and by-products, conversion process considerations, balance and recovery options of elements

**Objective:** To characterize the biomass materials and by-products, conversion process considerations, balance and recovery options of elements.

**Progress toward the objectives**: Characterization of biomass materials and by-products, conversion process considerations, balance and recovery options of elements. The work in task 2.1 has been organished in the following subtasks.

Sub- task	Description	Leader	Partners	Duration	Status
Task 2.1.1	Physical and chemical characterization of feedstock and by-products	CERTH	TUM, TNO, UdeS, RE- CORD	M1-M48	Ongoing

Task 2.1.2	Generalized element's mass balance closure for major trace pollutants	CERTH	TUM, TNO	M1-M48	Ongoing		
Task 2.1.3	Process and gas phase modelling	CERTH	TUM	M1-M48	Ongoing		
Task 2.1.4	Potential leachability and release pattern of trace pollutants	CERTH	-	M1-M48	Ongoing		
Table 5	Activities and achievements in Task 2	2.1					
	Activity		Achi	evement			
Samp conta	le preparation and pre-treatment of minated biomass samples	f Fiv (so an	Five homogenized biomass samples (sorghum, switchgrass, miscanthus (2) and hemp)				
		Se an	cure sufficient s alyses	ample size fo	or		
Samp pre-tr	le preparation and pre-treatment of eated biomass samples	f Fo (T <sup>r</sup> ox	Four pretreated sorghum samples (TORWASH, torrefaction, inert pyrolysis, oxidative pyrolysis)				
Analysis of pretreated biomass samples			Four pretreated sorghum samples (TORWASH, torrefaction, inert pyrolysis, oxidative pyrolysis)				
Mass pollut	balance closure for major trace ants	Up so	otake in TORWA	SHed and to hum)	rrefied		
		Up (so py	otake in char, aqu orghum) of oxida rolysis	ueous and of tive and iner	il phase t		
Proce	ess and gas phase modelling	fire	st draft of a thern	nodynamic p	rocess		

During the 2<sup>nd</sup> reporting period, special effort was put into the chemical characterization and contamination level of biomass samples from WP1 partners presented in Table 6.

 Table 6: Overview of contaminated biomass samples

Sample	Codename	Location	Partner
Sorghum	2023 Sorghum	Lavrion	AUA
Switchgrass	2023 Switchgrass	Kozani	CRES
Miscanthus	2023 Miscanthus	Kozani	CRES
Miscanthus	2024 Miscanthus	Lavrion	AUA
Industrial hemp	2024 Hemp	Lavrion	AUA

During the 2<sup>nd</sup> reporting period **D2.1** entitled "Characterization of biomass materials and byproducts, process considerations, balance of elements and recovery options – 1st version" was submitted. This deliverable provided an initial report on physical and chemical characterization of the contaminated biomass (sorghum) produced from WP1 (moisture content, elemental analysis, ash content, calorific value and concentrations of metal(loid)s), the evaluation of contamination level (inorganic contaminants) and the comparison of analyses performed by the partners of WP2.

D. no	Title	Leader	Delivery date (planned)	Delivery date (actual)
D3.1	Report on "Characterization of biomass materials and by-products, process considerations, balance of elements and recovery options"	CERTH	M18	M24

 Table 7: Analyses per partner

Partner	Description of the analysis
TUM, CERTH, UdeS	Proximate analyses (fuels) and loss of ignition of solid samples
TUM, CERTH, UdeS	Specific surface area-BET and pore size distribution studies
TUM, CERTH, UdeS	Density, porosity, mineralogical and elemental analysis
TUM, CERTH	Grain size analysis
CERTH, UdeS	Chemical analysis of major/trace elements by ICP-AES, ICP-MS, GHAAS, GFAAS
CERTH	Hg content using Au-amalgam-AAS for speciation of solid and gas samples
CERTH, UdeS	Morphological and microchemical analysis by SEM-EDX, TEM
CERTH, RE-CORD, UdeS	Thermogravimetric Analysis, TGA
TUM, CERTH	CI and F analysis by oxygen bomb combustion/ion selective electrode methods
TUM	Direct analysis of flue gas composition
UdeS	Direct analysis of pyrolysis liquid and gas composition by GC, HPLC
ΤΝΟ	Humic acid concentration and total organic carbon (TOC) in the Torwash effluent
ΤΝΟ	SEM work on the dried solid from Torwash to establish the heavy metal distribution

Specifically, in this stage of the project, CERTH focused on the chemical characterization and contamination level evaluation of biomass feedstocks (sorghum, switchgrass, miscanthus, and industrial hemp) provided by WP1 partners. These analyses provided crucial insights into the physical and chemical properties of the selected energy crops for phytoremediation. This information is essential for accurately predicting the behavior of trace elements in the gas phase during entrained flow gasification. Additionally, the results facilitate the selection of optimal process parameters for the three pretreatment options (TORWASH, torrefaction, and slow pyrolysis). Additionally, CERTH investigated the chemical composition and contamination levels of the solid by-products, obtained after TORWASH, torrefaction, and slow pyrolysis under inert and oxidative atmospheres, generated from the pretreatment of sorghum feedstock (WP2). Finally, CERTH assessed the uptake of major trace pollutants by (a) the solid residues from TORWASH and torrefaction (TNO), and (b) the char, aqueous phase, and oil phase fractions produced during slow pyrolysis (inert and oxidative – RE-CORD). Table 8 provides an overview of the pretreated biomass samples that were analyzed during the 2<sup>nd</sup> reporting period.

#### Table 8: Overview of pretreated biomass samples

Feedstock	Pretrea	tment Sample	Partner
Sorghum	TORV	VASH Solid fraction	on TNO
Sorghum	Torrefa	action Solid fraction	on TNO
Sorghum	Inert py	rolysis Char	RE-CORD
Sorghum	Oxidative	pyrolysis Char	RE-CORD

Table 9 summarizes the standards and methods that were employed for the chemical characterization and contamination level evaluation of the samples.

characterization and contamination level evaluation of the samples.	
Table 9: Standards/Methods for samples analyses	
Торіс	Standard/Method
Solid biofuels – Sample Preparation	ISO 14780
Solid biofuels – Determination of moisture content – Oven dry method – Part 1: Total moisture – Reference method	ISO 18134-1
Solid biofuels – Determination of moisture content – Oven dry method – Part 3: Moisture in general analysis sample	ISO 18134-3
Solid biofuels – Determination of ash content at 550 °C	ISO 18122
Solid biofuels – Determination of the content of volatile matter	ISO 18123
Solid biofuels – Determination of total content of carbon, hydrogen and nitrogen	ISO 16948

Solid biofuels – Determination of elemental composition by X-ray fluorescence	ISO/TS 16996
Solid biofuels – Determination of calorific value	ISO/DIS 18125
Solid biofuels – Determination of major elements – Al, Ca, Fe, Mg, P, K, Si, Na and Ti	ISO 16967
Solid biofuels – Determination of minor elements	ISO 16968
Mercury in solids and solutions be thermal decomposition, amalgamation and atomic spectrophotometry	EPA Method 7473

#### Main results and achievements

The results of characterization are presented in Tables 10-24.

#### Table 10: Characterization results of 2023 Sorghum samples

Proximate	Proximate analysis								
		тим	CERTH	CERTH (from RE-CORD)	RE- CORD	TNO (1 kg)	TNO (50 kg)	Deviation	
Moisture	wt% (ar)	5.12	5.19	6.50	5.65	13.24	8.11	3.11	
Volatiles	wt% (db)	73.31	-	75.50	73.03	74.24	73.66	0.98	
Ash	wt% (db)	7.10	7.58	8.20	9.04	6.95	8.50	0.82	
Fixed-C	wt% (db)	19.59	-	16.30	17.93	18.81	17.84	1.23	
Ultimate ar	nalysis								
С	wt% (db)	40.23	39.10	44.63	43.69	43.93	43.00	2.23	
Н	wt% (db)	6.08	5.43	5.82	5.55	6.01	5.83	0.25	
N	wt% (db)	1.21	1.00	0.90	0.85	1.02	1.02	0.13	
S	wt% (db)	0.20	0.12	0.14	0.21	0.14	0.18	0.04	
0	wt% (db)	43.66	46.77	46.93	40.66	43.15	42.49	2.47	
CI	wt% (db)	1.52	-	1.58	-	1.52	1.58	0.03	
HHV	kJ/kg (db)	17711.97	14926.07	17230.13		17584.61	17362.58	1154.06	

## Table 11: Characterization results of 2023 Switchgrass samples

Proximate analysis						
		тим	CERTH	RE- CORD	TNO (1 kg)	Deviation
Moisture	wt% (ar)	7.82	4.47	7.10	7.98	1.63
Volatiles	wt% (db)	74.48	-	75.30	75.49	0.54
Ash	wt% (db)	10.44	8.55	8.50	9.61	0.93
Fixed-C	wt% (db)	15.08	-	16.20	14.90	0.70
Ultimate analysis						
С	wt% (db)	41.64	41.93	41.70	43.49	0.88
Н	wt% (db)	4.12	5.28	5.90	5.78	0.81
Ν	wt% (db)	0.56	0.26	0.30	0.36	0.13
S	wt% (db)	0.14	0.06	0.10	0.08	0.03
0	wt% (db)	43.04	43.92	43.40	41.19	1.19
CI	wt% (db)	0.06	-	-	0.09	0.02
HHV	kJ/kg (db)	16880.89	16001.10	-	17733.95	866.46
O CI HHV	wt% (db) wt% (db) wt% (db) kJ/kg (db)	43.04 0.06 16880.89	43.92 - 16001.10	43.40 - -	41.19 0.09 17733.95	1.19 0.02 866.46

# Table 12: Characterization results of 2023 Miscanthus samples Proximate analysis

		TUM	CERTH	RE- CORD	TNO (1 kg)	TNO (50 kg)	Deviation	
Moisture	wt% (ar)	7.40	2.78	5.90	6.30	7.98	2.02	
Volatiles	wt% (db)	76.67	-	75.50	76.51	75.49	0.64	
Ash	wt% (db)	7.72	8.06	7.90	8.43	9.61	0.76	
Fixed-C	wt% (db)	15.62	-	16.50	15.06	14.90	0.72	
Ultimate analysis								
С	wt% (db)	44.43	43.56	42.70	44.12	43.49	0.66	
Н	wt% (db)	4.34	4.72	6.00	5.87	5.78	0.76	
N	wt% (db)	0.51	0.50	0.30	0.37	0.36	0.09	

S	wt% (db)	0.09	0.04	0.20	0.06	0.08	0.06
0	wt% (db)	42.74	43.12	42.90	41.19	41.19	0.96
CI	wt% (db)	0.17	-	-	0.15	0.09	0.04
HHV	kJ/kg (db)	17055.02	16018.74		18098.06	17733.95	913.82

### Table 13: Characterization results of 2024 Miscanthus samples Proximate analysis

r roximate analysis				
		CERTH	RE-CORD	Deviation
Moisture	wt% (ar)	7.00	8.79	1.27
Volatiles	wt% (db)	76.10	74.54	1.10
Ash	wt% (db)	6.30	5.88	0.30
Fixed-C	wt% (db)	17.60	19.58	1.40
Ultimate analysis				
С	wt% (db)	46.59	42.86	2.64
Н	wt% (db)	5.94	6.09	0.11
Ν	wt% (db)	0.50	0.44	0.04
S	wt% (db)	0.10	0.14	0.03
0	wt% (db)	46.03	44.60	1.01
CI	wt% (db)	0.84	-	-
HHV	kJ/kg (db)	18.3 <mark>49.76</mark>	-	-

 Table 14: Characterization results of 2024 Industrial hemp

 Proximate analysis

, , , , , , , , , , , , , , , , , , , ,				
		CERTH	RE-CORD	Deviation
Moisture	wt% (ar)	6.60	6.00	0.42
Volatiles	wt% (db)	76.50	73.90	1.84
Ash	wt% (db)	8.90	8.10	0.57
Fixed-C	wt% (db)	14.60	17.90	2.33
Ultimate analysis				
С	wt% (db)	44.09	41.40	1.90
Н	wt% (db)	5.77	5.90	0.09
Ν	wt% (db)	1.21	0.90	0.22
S	wt% (db)	0.19	0.20	0.01
0	wt% (db)	47.05	43.70	2.37
CI	wt% (db)	1.69	-	-
HHV	kJ/kg (db)	17341.00	-	-

#### Table 15: Overview of characterization results (raw feedstock comparison)

Proximat	e analysis					
		2023	2023	2023	2024	2024
		Sorghum	Switchgrass	Miscanthus	Miscanthus	Hemp
Moisture	wt% (ar)	7.30	6.84	6.07	7.90	6.30
Volatiles	wt% (db)	73.95	75.09	76.04	75.32	75.20
Ash	wt% (db)	7.90	9.27	8.34	6.09	8.50
Fixed-C	wt% (db)	18.09	15.40	15.52	18.59	16.25
Ultimate a	analysis					
С	wt% (db)	42.43	42.19	43.66	44.73	42.75
Н	wt% (db)	5.79	5.27	5.34	6.02	5.84
Ν	wt% (db)	1.00	0.37	0.41	0.47	1.06
S	wt% (db)	0.16	0.09	0.09	0.12	0.20
0	wt% (db)	43.94	42.89	42.23	45.32	45.38
CI	wt% (db)	1.55	0.08	0.14	0.84	1.69
HHV	kJ/kg (db)	16963.07	16871.98	17226.44	18349.76	17341.00

#### Table 16: Characterization results of TORWASHed 2023 Sorghum

Proximate analysi	S					
		TUM (ar)	TUM (milled)	CERTH	TNO	Deviation
Moisture	wt% (ar)	5.14	4.15	2.90	4.27	0.92
Volatiles	wt% (db)	61.03	61.55	-	63.54	10.80
Ash	wt% (db)	3.94	4.18	3.99	4.28	0.16
Fixed-C	wt% (db)	35.03	34.27	-	32.18	10.74
Ultimate analysis						
С	wt% (db)	56.36	55.65	58.56	55.65	1.38
Н	wt% (db)	4.76	4.75	4.78	5.35	0.30
Ν	wt% (db)	1.00	1.20	1.43	1.07	0.19
S	wt% (db)	0.07	0.06	0.12	0.12	0.03
0	wt% (db)	33.38	33.65	31.12	32.79	1.14
CI	wt% (db)	0.49	0.51	-	0.42	0.05
HHV	kJ/kg (dB)	23501.05	23809.14	22672.99	22437.22	654.53

## Table 17: Characterization results of torrefied 2023 SorghumProximate analysis

,					
		TUM (ar)	TUM (milled)	TNO	Deviation
Moisture	wt% (ar)	3.27	3.72	3.70	0.25
Volatiles	wt% (db)	48.37	47.07	48.90	0.94
Ash	wt% (db)	15.71	17.17	18.41	1.35
Fixed-C	wt% (db)	35.91	35.76	32.69	1.82
Ultimate analysis					
С	wt% (db)	53.49	52.69	52.91	0.41
Н	wt% (db)	4.10	3.57	4.67	0.55
Ν	wt% (db)	1.61	1.67	1.42	0.13
S	wt% (db)	0.22	0.14	0.24	0.05
0	wt% (db)	21.85	21.84	25.02	1.83
CI	wt% (db)	3.01	2.92	2.33	0.37
HHV	kJ/kg (dB)	22559.70	22790.30	21627.58	615.62

#### Table 18: Characterization results of pyrolyzed (inert) 2023 Sorghum

Proximate analysis								
		TUM (ar)	TUM (milled)	CERTH (from RE- CORD)	RE- CORD	Deviation		
Moisture	wt% (ar)	3.68	3.64	1.30	2.21	1.16		
Volatiles	wt% (db)	8.60	7.49	14.20	9.93	2.94		
Ash	wt% (db)	25.92	27.23	25.20	25.92	0.85		
Fixed-C	wt% (db)	65.47	65.28	60.60	64.15	2.26		
Ultimate a	nalysis							
С	wt% (db)	64.27	62.32	68.86	68.37	3.18		
Н	wt% (db)	0.51	0.01	1.78	1.70	0.88		
Ν	wt% (db)	1.41	1.59	1.26	1.36	0.14		
S	wt% (db)	0.16	0.11	0.23	0.40	0.13		
0	wt% (db)	2.38	2.68	-	2.25	10.78		
CI	wt% (db)	5.35	6.05	3.88	-	1.11		
HHV	kJ/kg (db)	24924.99	25078.09	25127.85	-	105.72		

### Table 19: Characterization results of pyrolyzed (oxidative) 2023 Sorghum

Proximate	e analysis					
		TUM (ar)	TUM (milled)	CERTH (from RE- CORD)	RE- CORD	Deviation
Moisture	wt% (ar)	3.34	3.00	1.60	2.33	0.77

Volatiles	wt% (db)	8.64	7.72	14.10	9.85	2.82
Ash	wt% (db)	26.26	28.04	25.50	25.74	1.15
Fixed-C	wt% (db)	65.09	64.24	60.40	64.41	2.12
Ultimate a	nalysis					
С	wt% (db)	63.82	61.32	68.52	67.95	3.44
Н	wt% (db)	0.30	0.60	1.65	1.65	0.70
Ν	wt% (db)	1.64	1.41	1.38	1.53	0.12
S	wt% (db)	0.15	0.13	0.26	0.45	0.15
0	wt% (db)	1.19	3.43	-	2.68	1.14
CI	wt% (db)	6.63	5.08	4.58	-	1.07
HHV	kJ/kg (db)	25042.93	24985.57	24865.51	-	90.54

 Table 20: Overview of characterization results (pretreated feedstock comparison)

 Proximate analysis

		TORWASH	Torrefaction	Inert pyrolysis	Oxidative pyrolysis
Moisture	wt% (ar)	4.11	3.56	2.71	2.57
Volatiles	wt% (db)	67.41	48.12	10.05	10.08
Ash	wt% (db)	4.10	17.10	26.07	26.39
Fixed-C	wt% (db)	28.49	34.79	63.88	63.54
Ultimate an	alysis				
С	wt% (db)	56.56	53.03	65.96	65.40
Н	wt% (db)	4.91	4.11	1.00	1.05
Ν	wt% (db)	1.17	1.57	1.41	1.49
S	wt% (db)	0.09	0.20	0.23	0.25
0	wt% (db)	32.74	22.91	7.82	2.43
CI	wt% (db)	0.47	2.75	5.10	5.43
HHV	kJ/kg (db)	23105.10	22325.86	25043.64	24964.67

Table 21: Elements and trace elements in biomass samples (raw feedstock comparison)

		2023	2023	2023	2024	2024
		Sorghum	Switchgrass	Miscanthus	Miscanthus	Hemp
AI	mg/kg <sub>db</sub>	420.16	483.89	320.25	203.95	769.61
As	mg/kg <sub>db</sub>	6.86	2.53	2.81	1.76	6.71
В	mg/kg <sub>db</sub>	9.55	3.77	4.08	8.00	11.00
Ва	mg/kg <sub>db</sub>	11.16	14.21	12.76	12.42	19.39
Ca	mg/kg <sub>db</sub>	7219.95	5486.01	3736.63	5732.50	14339.04
Cd	mg/kg <sub>db</sub>	12.80	0.12	0.17	3.40	2.36
Со	mg/kg <sub>db</sub>	2.66	0.98	0.66	0.16	0.37
Cr	mg/kg <sub>db</sub>	3.27	25.62	16.65	1.34	3.42
Cu	mg/kg <sub>db</sub>	6.39	3.83	3.25	2.44	6.82
Fe	mg/kg <sub>db</sub>	367.92	770.59	345.21	165.76	614.96
Κ	mg/kg <sub>db</sub>	21127.67	3134.13	3110.14	6463.51	10773.51
Li	mg/kg <sub>db</sub>	-	-	-	-	1.00
Mg	mg/kg <sub>db</sub>	2479.56	2552.07	2532.12	1077.06	2947.03
Mn	mg/kg <sub>db</sub>	77.36	65.83	89.32	110.28	126.97
Мо	mg/kg <sub>db</sub>	0.95	0.00	2.21	0.00	-
Na	mg/kg <sub>db</sub>	1370.84	56.76	138.16	1709.33	8410.10
Ni	mg/kg <sub>db</sub>	2.74	17.51	9.89	1.23	3.79
Ρ	mg/kg <sub>db</sub>	785.23	260.93	178.84	189.00	643.00
Pb	mg/kg <sub>db</sub>	82.09	1.21	1.20	22.10	82.00
S	mg/kg <sub>db</sub>	1189.12	456.63	490.47	-	-
Sb	mg/kg <sub>db</sub>	1.12	0.01	0.03	0.32	2.10
Se	mg/kg <sub>db</sub>	0.06	-	0.06	0.01	0.06
Si	mg/kg <sub>db</sub>	7464.57	20094.79	21655.95	319.00	394.00
Sn	mg/kg <sub>db</sub>	0.15	-	0.25	-	-
Sr	mg/kg <sub>db</sub>	18.03	13.94	10.19	-	-

Ti	mg/kg <sub>db</sub>	15.31	40.75	19.78	8.00	34.35
V	mg/kg <sub>db</sub>	1.73	0.77	0.77	0.44	1.37
W	mg/kg <sub>db</sub>	45.10	-	-	-	-
Zn	mg/kg <sub>db</sub>	320.77	13.67	12.10	120.35	91.70
Hg	mg/kg <sub>db</sub>	4.48	0.02	0.01	0.01	0.01

#### Table 22: Uptake by TORWASHed and torrefied 2023 Sorghum (solid fraction)

		TORWASHed	Torrefied
Pb	mg/kg <sub>db</sub>	30.80%	142.43%
Zn	mg/kg <sub>db</sub>	20.99%	88.69%
Ni	mg/kg <sub>db</sub>	1716.31%	1232.64%
Cd	mg/kg <sub>db</sub>	16.76%	89.61%
As	mg/kg <sub>db</sub>	79.71%	150.38%
Sb	mg/kg <sub>db</sub>	178.27%	194.78%
Cu	mg/kg <sub>db</sub>	130.59%	84.81%

Table 23:Uptake by the char, aqueous phase, and oil phase fractions of pyrolyzed (inert) 2023 Sorghum

		Char	Aqueous phase	Oil phase
Pb	mg/kg <sub>db</sub>	134.06%	-	1.47%
Zn	mg/kg <sub>db</sub>	91.39%	-	1.34%
Ni	mg/kg <sub>db</sub>	94.35%	-	-
Cd	mg/kg <sub>db</sub>	11.02%	-	22.19%
As	mg/kg <sub>db</sub>	93.69%	-	-
Sb	mg/kg <sub>db</sub>	102.65%	-	-
Cu	mg/kg <sub>db</sub>	175.35%	-	-

 Table 24: Uptake by the char. aqueous phase. and oil phase fractions of pyrolyzed (oxidative)

 2023 Sorghum

		Char	Aqueous phase	Oil phase
Pb	mg/kg <sub>db</sub>	94.24%	-	1.13%
Zn	mg/kg <sub>db</sub>	75.46%	-	-
Ni	mg/kgdb	243.64%	-	-
Cd	mg/kgdb	12.25%	-	11.97%
As	mg/kgdb	68.42%	-	-
Sb	mg/kgdb	47.17%	-	-
Cu	mg/kg <sub>db</sub>	135.79	-	-
As Sb Cu	mg/kg <sub>db</sub> mg/kg <sub>db</sub> mg/kg <sub>db</sub>	68.42% 47.17% 135.79	- - -	

Problem, delay or deviation: TNO couldn't receive hemp to work due to Dutch laws.

*Corrective actions undertaken*: Hemp was sent to UniLaSalle in France, TNO is collaborated with UniLaSalle.

Subtask 2.1.3: The activities for subtask 2.1.3 are presented in the table below.

Table 25: TUM-CES activities and achievements in Task 2.1.3			
Activity	Achievement		
Gas phase modelling using FactSage	Thermodynamic equilibrium model to determine heavy metal fate under entrained flow conditions developed		
Process modelling using Aspen Plus	Thermodynamic process model and different process options developed and compared		

During the 2<sup>nd</sup> reporting period, special effort was put into the development of simulation models predicting the fate of heavy metals and metalloids during gasification, and determining key performance indicators of the overall process. A thermodynamic model is used to estimate industrial-scale syngas compositions. The process model by TUM-CES optimizes equipment interaction and overall design, increasing carbon efficiency to 40%.

Process and gas phase modelling of the GOLD project investigate the WP2 process route 1 via entrained-flow gasification at high temperatures and moderate pressure and, after gas cleaning, the fermentation of the created synthesis gas in a bioreactor. CERTH and TUM-CES intend to derive theoretical predictions based on literature data for the evolution of trace

element species in gas phase, in different atmospheres and temperatures, using thermodynamic equilibrium data. Possible reactions of these species with fly ash particles of different composition and with sorbents are to be evaluated. For that purpose, first Fact-Sage modelling investigation activity has started. For this purpose, TUM-CES investigates the fate of heavy metals from a process-level perspective employing simulative methods. Thermodynamic equilibrium modelling is employed to investigate the phase transition behaviour from solid to gas phase during entrained flow gasification. Aspen Plus is used to model the overall GOLD process from biomass to liquid biofuels.

In Task 2.1.3, a simulation model has been developed and validated based on global equilibrium analysis using FactSage [Ritz et al. 2024]. The modelling framework developed at TUM-CES and described in detail in D2.4 is used to predict the phase transition behavior of heavy metals and metalloids from solid phase to gas phase in EFG and from gas phase to solid phase during full water quench. The modelling software. The output is the concentration of the chemical species present at thermodynamic equilibrium at the given temperature and pressure. To simulate the release behaviour of the heavy metal metalloid contaminants in EFG, the elemental composition of the biomass, which is obtained from fuel analysis, is directly used as input. The fuel analysis of the contaminated biomass as carried out by the TUM-CES includes the proximate analysis, the ultimate analysis, and the determination of LHV and HHV according to DIN 51900-1. The mass fraction of all metals, including heavy metals and metalloids, was measured by ICP-OES. The remaining model input parameters are linked to the operating conditions. The temperature is varied from 900 °C to 2200 °C in steps of 100 °C. The equivalence ratio is chosen to be 0.34, which is typical for EFG. Thus, the corresponding temperature, 1800 °C, is the actual gasification temperature. [Ritz et al. 2024]

To model the temperature dependent phase transition behaviour of heavy metals and metalloids during EFG and the water quench, both, oxidative and inert gasification conditions are investigated. The input for the respective modelling consists of the fuel data and the operating conditions, the gasification temperature, i.e. equivalence ratio, is varied between 400 °C and 2400 °C. The gasification agent used in this work is pure O<sub>2</sub>. An Aspen Plus model is used to determine the respective equivalence ratio that is necessary to achieve a desired gasification temperature, taking into account the CO<sub>2</sub> employed as carrier gas at a loading of fuel per carrier gas rate of 300kg/m<sup>3</sup>. Simulating the EFG reaction chamber, all gas phase reactions are assumed to have reached equilibrium due to the high temperatures. When modelling the water guench, the assumption that all reactions have reached equilibrium cannot be made as the system is merely cooled down and species are not participating in further reactions. Therefore, the gas phase that is received from the modelling of the reaction chamber at gasification temperature (1800 °C) is used as input and the temperature is varied down from 1800 °C to 200 °C. Only the heavy metals and metalloids are included in an inert environment consisting of nitrogen (N) and an excess of quench water ( $H_2O$ ), to prevent reactions. The concentration is taken from the mass of the heavy metals compared to the total mass of the gas phase and the phase transition behaviour in elemental form at the respective partial pressure is received. The validation of modelling under oxygen-blown conditions is presented in Task 2.3. [Ritz et al. 2024]

The used databases in this work are FactPS, a database containing vast amounts of pure substance data. Further, the gas phase is treated as real or ideal. The suitability of any combination of databases and settings was validated by reproducing literature data as stated in D2.4. A combination of FactPS and GTOx, an oxide database consisting of data for slag, liquid metal, and liquid sulfite as well as many solid solution and stoichiometric phases, is used for the modelling of slag formation, fouling, and condensation during biomass gasification by GTT-Technologies. [Ritz et al. 2024]

A final process model based on measurements and gas phase modelling with the aim to evaluate overall energetic efficiencies, potential heat integration options between process steps and waste stream management is to be developed. During the second report period, a respective thermodynamic has been finalized to the extent possible based on literature data. In addition to the removal of trace substances, especially heavy metals, the main gas composition after gasification is of decisive interest for the subsequent syngas fermentation. The interaction of these two main conversion processes also determines the performance of the overall process. The crucial link here is gas cleaning and purification. For a GOLD BtL (Biomass-to-Liquid) route to become economically viable in the long term, the overall process must be considered as such. A process simulation offers the possibility to consider not only the interaction of the unit operations connected in series, but also various process-side optimization options that cannot be represented experimentally, such as industrial scale entrained flow gasification.

#### Main results and achievements

The results for the simulation of the phase transition of the heavy metals and metalloids from the solid phase to the gas phase during gasification at atmospheric pressure are shown in in Figure 33 under entrained flow gasification conditions and Figure 3434 under inert conditions.

The results for the simulation of the phase transition of the heavy metals and metalloids from the solid phase to the gas phase during EFG indicate that the release behaviour of the heavy metals is similar in all investigated pretreatment methods. Further, it shows that cadmium (Cd), lead (Pb), and zinc (Zn), are the volatile elements and are entirely volatilized at a temperature of 1800 °C, which is a typical temperature in the hot zone during EFG. Cd is volatilized at temperatures between 500 °C and 600 °C, while the volatilization of Pb occurs over a wider temperature range between 500 °C and 900 °C. Most of the Zn is volatilized between 800 °C and 100 °C. Then, the volatilization of Zn is delayed between roughly 1000 °C and 1500 °C due to the formation of a slag phase in this temperature range. Cu, which is only contained in raw sorghum, is volatilized between 900 °C and 1200 °C. during gasification. The other elements, namely nickel (Ni), iron (Fe), manganese (Mn), chromium (Cr), titanium (Ti), and vanadium (V), which is only contained in the raw sorghum, are non-volatile. Their volatilization doesn't considerably start at temperatures below 2000 °C and less than 10% of these elements is in the gas phase at the gasification temperature of 1800 °C. Mn is an exception to this, as it shows partial volatilization at lower temperatures in case of the two types of pyrolyzed sorghum, and Cr is also starting to volatilize at 1700 °C in the case of TORWASHed sorghum. Ti is the least volatile element and not substantially released in the investigated temperature range. [Ritz et al. 2024]

Figure 34 shows that the same general trends are observed for the gasification under inert conditions as described for the gasification conditions. However, the release of the heavy metals and metalloids is shifted to lower temperatures in all cases. Cd, the most volatile of the investigated elements, is already entirely volatilized at a temperature of 500 °C and Pb is released between 500 °C and 700 °C. Zn is volatilized between 600 °C or 700 °C and 800 °C and a delay of the volatilization due to the formation of a slag phase is not observed. Cu, which is only contained in raw sorghum, is also volatilized below 1000 °C. Out of the remaining elements, Mn is the most volatile and is released at temperatures between 1300 °C and 1800 °C. Again, inertly pyrolyzed sorghum, where Mn is partially volatilized at lower temperatures, is an exception. Cr, Fe, and Ni are mostly released between 1700 °C and 1900 °C. Ti is the least volatile element and its release only starts at temperatures above 2000 °C. [Ritz et al. 2024]



Figure 33: FactSage modelled phase transition of the heavy metals from solid phase to gas phase during entrained-flow gasification of (a) torrefied (TNO), (b) inertly and, (c) oxidative pyrolyzed (both RE-CORD), (d) TORWASHed (TNO), and (e) raw sorghum from AUA [Ritz et al. 2024].



Figure 34: FactSage modelled phase transition of the heavy metals from solid phase to gas phase during gasification in inert atmosphere of (a) torrefied (TNO), (b) inertly and, (c) oxidative pyrolyzed (both RE-CORD), (d) TORWASHed (TNO), and (e) raw sorghum from AUA [Ritz et al. 2024].

The phase transition of the heavy metals and metalloids contained in the gas phase after the reaction zone to the solid phase during the water quench is simulated using the Scheil-Gulliver cooling approach. The results shown in Figure 355 indicate that all mass fractions are given in relation to their total mass entering the water quench in the gas phase at 1800 °C. All semi-and non-volatile elements start to recondense immediately after leaving the hot zone. Only small amounts of Ni and Ti are in the gas phase entering the water quench and, in most cases, they immediately solidify. The solidification of the other elements takes place over a wider temperature range, but all non-volatile elements, except for Mn and Fe, are entirely solidified at a temperature of 1000 °C. However, the formation of metal complexes and slag phases
delays the solidification in many cases, leading to plateaus in the plot. This effect is especially pronounced for Mn and Fe, which is why a fraction of those two elements remains in the gas phase even at temperatures below 1000 °C in many cases. The volatile elements, on the other hand, start to solidify at temperatures below 90 °C. Zn starts to solidify first and is entirely solidified in the temperature range between 900 ° and 500 °C, apart from inertly pyrolyzed sorghum, where the solidification is delayed due to the formation of complexes. Cd is rapidly solidified between 600 °C and 400 °C. Pb solidifies between 800 °C and 400 °C, while the solidification is delayed in the case of the two types of pyrolyzed sorghum. [Ritz et al. 2024]



Figure 35: Phase transition of the heavy metals from gas phase to solid phase during the water quench of (a) torrefied (TNO), (b) inertly and, (c) oxidative pyrolyzed (both RE-CORD), (d) TORWASHed (TNO), and (e) raw sorghum from AUA [Ritz et al. 2024].

Within subtask 2.1.3 a process model was developed by TUM-CES using Aspen Plus based on the process design of GOLD thermochemical Route 1. The base case model shown in Figure 36 uses drying, torrefaction and milling as pretreatment option, followed by oxygenblown entrained flow gasification and a full water quench. Slag separation, and gas cleaning via water scrubber, cyclone and hot gas filter is included. Adsorptive gas cleaning is employed and  $H_2$  and  $CO_2$  are removed from the main syngas stream using PSA. The final synthesis to produce higher alcohols via syngas fermentation is modelled in a continuous stirred tank reactor (CSTR) using TUM-CBE derived gas fermentation kinetics.



Figure 36: Simplified flowsheet of Aspen Plus base case reference model of GOLD Route 1 including torrefaction, entrained flow gasification and full water quench, adsorptive gas cleaning,  $H_2$  and  $CO_2$  separation via pressure-swing adsorption (PSA) and syngas fermentation in a continuous stirred tank reactor (CSTR) with gas and liquid recycle applying TUM-CBEderived gas fermentation kinetics [Dossow et al., 2023].

Since the developed process model contains more than eight hierarchy units with multiple unit operations nested within, a detailed description of all process steps is not provided here. The process model is based on the biomass-to-syngas train including gas cleaning developed in [Dossow et al., 2021]. The oxygen-blown EFG (T<sub>EFG</sub>=1400 °C) biomass input is specified as 10 MW<sub>th</sub> representing a feasible scale for the process based on a preliminary analysis (see D2.4). Based on the findings from experimental gasification trials (Task 2.3) and thermodynamic modelling (see above), it is assumed that all relevant contaminants are fully gasified in EFG and later completely collected during solid removal. The final syngas fermentation is modelled using kinetics based on TUM-CBE experimental data applied to a CSTR with internal and external recycle design. For more details of the process technologies involved, see Deliverable D2.4. As the torrefaction, syngas cleaning and fermentation models are characterized by their specific design for the GOLD process, they are explained in more detail in D2.4. After the base case model is completed, optimization efforts were made to improve the overall process performance. This mainly includes overall energy yield, product yield, carbon efficiency and selectivity towards higher alcohols. The Aspen Plus GOLD route 1 model and its optimization was presented at EUBCE 2023 [Dossow et al. 2023].

The process model aims to evaluate the interaction of the major equipment, considering the experimental results, while optimizing overall process design. A base case model, the so-called "once-Through" model design, which is characterized by an internal syngas recycle for syngas fermentation separating  $H_2$  and  $CO_2$  from the syngas stream before synthesis, is investigated. Applying the learnings from experimental work and process development, the model is further optimized in terms of overall key performance indicators such as product and energy yield, carbon efficiency and energy efficiency.

The "once-through" design results in a syngas fermentation bioreactor size of about 4800 m<sup>3</sup> to ensure 95% CO conversion. With a maximum CSTR scale of 300 m<sup>3</sup>, that results in a train of 16 gas fermenters. Since each reactor has a specific power requirement of 2 kWel/m<sup>3</sup> for stirring purposes, an overall installed stirrer power of about 10 MW<sub>el</sub> is required. Despite the almost complete CO conversion in syngas fermentation, carbon efficiency is limited to 29%. The overall achieved product yield is 0.28 t<sub>product</sub>/t<sub>Biom,dry</sub> (0.25 t<sub>alc</sub>/t<sub>Biom,dry</sub> + 0.03 t<sub>H2</sub>/t<sub>Biom,dry</sub>), if H<sub>2</sub> is considered a by-product. From an energetic point of view, that corresponds to an overall energy yield of 58.8%. If H<sub>2</sub> which in the employed model cannot be converted to biofuels in fermentation, wasn't part of the product mix, liquid energy yield would be reduced to 0.39 MJ<sub>alc</sub>/MJ<sub>Biom,dry</sub> (0.19 MJ<sub>H2</sub>/MJ<sub>Biom,dry</sub>). In any case, 42% of the initial energy in the biomass is lost to the environment, mostly in the form of unconverted syngas and heat losses in

gasification. If CSTR power requirements were included in the analysis, energy efficiency based on all products would be about 30% or 20% for only liquid products.

To increase product and energy yield, especially of the liquid product fraction, the process was optimized with respect to liquid fuel production capacity while maintaining biomass input at 10 MW<sub>th</sub>. In that case, the general Biomass-to-Syngas train remains unchanged and 15% of the unconverted syngas recycled from the fermentation reactor is supplied to an earlier stage of the process. Here, after gas cleaning, a reverse WGS reactor is used to convert H<sub>2</sub> and CO<sub>2</sub>, that otherwise would not be used in syngas fermentation, into CO that now can serve as a substrate for the bio-reaction. As the rWGS follows an equilibrium approach at 800 °C heated by exhaust heat from gasification, the remaining H<sub>2</sub> and CO<sub>2</sub> is removed from the syngas before fermentation. The bioreactor is kept at a constant 4800 m<sup>3</sup> reactor volume based on the "once-through" model.

The process model results in terms of KPIs. Despite the slightly decreased overall CO conversion (now at 92% as opposed to 95% in "once-through" design), carbon efficiency is increased to 40%. The overall achieved product yield is 0.35  $t_{product}/t_{Biom,dry}$  with almost no H<sub>2</sub> present in the off-gases. In absolute numbers, a product yield of ethanol, acetic acid, butyric acid, butanol and hexanol of 728 kg/h is achieved. The high selectivity towards ethanol remains unchanged. Overall energy yield is slightly decreased from 58.8% to 55%. However, high-value biofuel energy yield is massively increased from 0.39 MJ<sub>alc</sub>/MJ<sub>Biom,dry</sub> to 0.55 MJ<sub>alc</sub>/MJ<sub>Biom,dry</sub>. Still, 44% of the initial energy in the biomass is lost and energy efficiency is about 28% as CSTR power requirements are included in the analysis.

Both process models show, that for industrial scale application, the power input by the stirrer to a stirred-tank bioreactor is typically the main operating expense. Thus, syngas fermentation on an industrial scale typically uses bubble column or gas-lift reactor due to the lower power input and more efficient syngas conversion high hydrostatic pressure of the water column allowing for higher solubilities of the syngas components at the bottom. Acetogen conversion of CO reduces the CO content in the rising gas bubbles over the height of the reactor, allowing a well-designed bubble column reactor to achieve high conversion of CO in the lower part of the reactor and subsequent conversion of CO<sub>2</sub> and H<sub>2</sub> in the upper part of the bubble column. [Rückel et al., 2022] Such an improved model, would not only require more data on CO<sub>2</sub> and H<sub>2</sub> as substrate in a continuous reactor setup, but also a BCR model that incorporates hydrostatic pressure for each height tray. One approach would be the use of Aspen Plus's RadFrac model allowing reactions to take place on every theoretical tray. Another way to further increase process performance is a cascade reactor network. This could be designed either as a cascade of bioreactors, each tailored for the respective gas feed composition, or as a cascade of bio- and chemical-catalytic reactors, that would make use of the  $H_2$  and  $CO_2$ rich off-gas of the reactor. However, such extensive modelling of the syngas fermentation process is out of scope for the GOLD project und subject to future work. Furthermore, the GOLD process based on the developed process model, could be investigated from a technoeconomic and lifecycle perspective. As this is part of the WP3 work in GOLD, relevant process data is supplied to the respective partners.

# Problem, delay or deviation: None

## Corrective actions undertaken: None

Milestone M4 entitled "**Process model of conversion routes**" that had due day 30.4.23 was completed in April 2023. The respective Model was presented at the EUBCE 2023 in Bologna [Dossow et al. 2023].

# References

[Dossow et al., 2021] Dossow, M.; Dieterich, V.; Hanel, A.; Fendt, S.; Spliethoff, H.: Improving carbon efficiency for an advanced Biomass-to-Liquid process using hydrogen and oxygen from electrolysis. Renewable and Sustainable Energy Reviews 152, 2021, 111670

[Dossow etl al. 2023] Dossow, M.; Leuter, P.; Spliethoff, H. Fendt, S.: Process Modelling of Biofuel Production from Contaminated Biomass Through Entrained Flow Gasification and Syngas Fermentation. At 31<sup>st</sup> European Biomass Conference & Exhibition, in Bologna, Italy, 5<sup>th</sup> June 2023.

[Ritz et al. 2024] Ritz, M.; Dossow, M.; Mörtenkötter H., Spliethoff H., Fendt, S.: Experimental investigation of heavy metal release in entrained-flow gasification [submitted to Fuel]

# Task 2.2: Biomass pre-treatment for entrained flow gasification (EFG)

Work for Task 2.2 was divided into 2 subtasks, listed in Table 26.

Sub- task	Description	Leader	Partners	Duration	Status
Task	TORWASH on contaminated	TNO		M3-M36	Ongoing
2.2.1	feedstock				
Task	Alternative contaminated	RECORD	TNO,	M3-M36	Ongoing
2.2.2	feedstock pretreatment methods:		CERTH		
	torrefaction and slow pyrolysis				

Table 26: Task 2.2 breakdown

**Objective:** To optimize pretreatment methods for transforming diverse feedstock into a material suitable for EFG, determine the fate of the contaminants, through extensive analyses of the raw and pre-treated feedstocks, and optimize the separation methods.

**Progress toward the objectives:** During the 2<sup>nd</sup> reporting period, special effort was put into finishing optimization tests for all of the contaminated biomass feedstocks, in preparation for larger-scale tests. In addition, large scale tests of Sorghum feedstock were conducted and processing of the liquid effluent from Sorghum treatment to isolate humic substances was investigated via precipitation and membrane filtration.

The pre-treatment of contaminated biomass samples was optimized for all contaminated feedstocks, with the exception of TORWASH pre-treatment of hemp (**Error! Reference s ource not found.**). Large-scale pre-treatment to produce solids for entrained flow gasification has been completed for slow pyrolysis and torrefaction, for all samples planned. For TORWASH pre-treatment, large-scale tests with Sorghum feedstock have been completed.

Crop type	Site	Main heavy metal contaminants	Type of pre- treatment	Lab tests (0ptimization)	Large scale tests
Sorghum	Lavrion	Al, Cr, Cu, Fe, Pb, Zn	Torrefaction, TORWASH, Slow Pyrolysis	Complete	Complete
Miscanthus	Kozani	Ni, Zn	TORWASH, Slow Pyrolysis	Complete	Slow Pyrolysis complete
Miscanthus	Lavrion	Cd, Ni, Pb, Zn	Torrefaction, TORWASH, Slow Pyrolysis	Complete	Torrefaction and slow pyrolysis complete
Switchgrass	Kozani	Pb, Zn, Ni, Cd	TORWASH, Slow Pyrolysis	Complete	Slow pyrolysis complete
Hemp	Lavrion	Pb, Zn, Ni, Cd	Slow Pyrolysis TORWASH	Slow pyrolysis complete	N/A

Table 27: Summary of pre-treatment tests for various feedstock samples and completion as of end of RP2.

Deliverable **D2.3** Pre-treatment options and contaminant separation as well as concentrated recovery: This deliverable provides a summary of pre-treatment options for contaminated biomass, namely TORWASH, Torrefaction and Slow Pyrolysis. The results include optimized conditions for each pre-treatment process upstream of gasification as well as information about the fate of heavy metal contaminants in the biomass during the processes.

**D2.3** (TNO) was submitted according to plan. Note the deliverable will be updated once all large-scale lab tests are completed.

Milestone M5 (Low contaminant Feedstock (obtained by TORWASH) due by M12 accumulated a 10-month delay and was reached by M22 during RP2. M5 had to be postponed due the late harvesting of the biomass produced in GOLD fields. The field trials were established on fields from M11 (04/2022) to M13 (06/2022) and the harvesting started from mid of M17 (09/2022) and was completed by M20 (12/2022). The harvested biomass was sent to CRES for chipping and drying and the first packages started to be sent by M20 (12/2022) of the project. The milestone was achieved by M22, 02/2023.

**Subtask 2.2.1:** Activities and achievements of the 2<sup>nd</sup> reporting period are presented in Table 28.

 Table 28: Activities and achievements in Task 2.2

Activity	Achievement
Investigation of metals release from biomass at	Acidic pH (2 or less) for release of many
different pH conditions	heavy metals from biomass
Optimization tests of contaminated hay	Indication of optimized TORWASH
samples	conditions (temperature, pH) for metal
	release from contaminated biomass
Investigation of techniques for metals removal	Indication of best approaches for humic
from liquid phase	acids recovery and metals removal from
	liquid fraction post-TORWASH
Large scale TORWASH of Sorghum	TORWASHed Sorghum delivered to
	TUM-CES (Task 2.3)

TORWASH pre-treatment was applied/optimized to all contaminated biomass samples in RP2, with the exception of hemp. In general, the optimization tests demonstrated that similar conditions should be applied to all types of biomass tested, to optimize metals removal from the biomass. In general, the higher the temperature and the lower the pH, the more metals partition to the liquid phase and out of the solids. In addition, the type of acid used to adjust the pH also has an effect, with organic acids performing better than inorganic acids. In typical TORWASH practice, temperatures of 200 °C and a pH of 2 (with citric acid) are readily achievable, thus these were determined to be the optimized conditions.

At these conditions, for Sorghum, large-scale testing produced 6.3 kg of dried solids for gasification trials. In these solids, most (>50%) of the metals' cadmium, lead, and zinc partitioned out of the solids into the liquid fraction. Approximately half of the ash content (550 C) and 12% of the volatile matter was also removed from the Sorghum biomass during TORWASH treatment at large scale, and the heating value of the solids also increased from 17.4 to 22.3 MJ/kg (dry basis).

The liquid fraction from TORWASH tests of Sorghum (large-scale tests) was further treated in RP2. Both membrane filtration and acidification/precipitation were explored as treatment options. Membrane filtration with a nanofiltration membrane resulted in severe fouling of the membrane and very slow filtration. Therefore, acidification tests were performed. TORWASH liquid effluent was acidified to a pH of 1 with nitric acid and precipitation of the organic matter was allowed to occur overnight, after which the precipitate was removed. The precipitate was measured to be rich in organic matter (i.e., humic substances) but low in metals concentration. Therefore, heavy metals in the TORWASH effluent remain in the liquid phase and do not precipitate with the organic matter (Figure 37). This is a promising result, as the organic matter fraction will be tested as a soil amendment in subsequent months as part of the GOLD project.



Figure 37: Partitioning of heavy metals in TORWASH effluent of treated Sorghum biomass. Precipitate represents the humic acids fraction after acidification and filtrate represents the remaining liquid effluent after precipitation.

# **Deviations/obstacles and respective mitigation plans**

There were delays in harvesting of the GOLD project contaminated biomass, in particular Miscanthus, Switchgrass and Hemp. To mitigate this, small samples (1 kg) of each of Switchgrass and two Miscanthus samples (from two sites) was sent to TNO in advance of larger samples being shipped. This allowed us to do optimization testing to prepare for large-scale testing when the biomass was received.

Hemp samples were not allowed to be received at TNO due to Dutch legislative bans on importing any plants of the genus *Cannabis* without first meeting strict requirements, including related to storage (see "Biomass provision from WP1"). As a mitigation measure, 1 kg of hemp was sent to University LaSalle in France, where a PhD student is doing some tests with TNO related to adsorption of metals onto pyrolysis char. Lab-scale optimization tests with hemp will be done with the sample shipped to France and included in an updated version of D2.3. Instead, TNO will use Miscanthus from CRES's Kozani site to conduct TORWASH experiments.

In addition to delays in feedstock harvest and shipping, TNO experienced further delays in conducting the large-scale tests on Miscanthus and Switchgrass due to equipment in the lab breaking down. This resulted in an approximate 1-month delay while the equipment was repaired.

Alternative contaminated feedstock pretreatment methods: Torrefaction and slow pyrolysis.

Task 2.2.2: Activities and achievements of the 2<sup>nd</sup> reporting period are presented in Table 5.

Activity	Achievement
Torrefaction (TNO)	Conversion of two contaminated biomass samples. Torrefied Sorghum delivered to TUM-CES (Task 2.3).
Lab-scale pyrolysis (RE-CORD)	Conversion of five contaminated biomass samples
Pilot-scale pyrolysis (RE-CORD)	Conversion of two contaminated biomass samples, investigating oxidative and conventional slow pyrolysis. Pyrolyzed Sorghum and Miscanthus delivered to TUM-CES (Task 2.3).
Biomass and pyrolysis products characterization	Analytical results were made available to the other partners

 Table 29: Activities and achievements in Task 2.2.2.

During the reporting period RE-CORD contributed to two deliverables: **D2.1** Characterization of biomass materials and by-products, process considerations, balance of elements and recovery options - 1st version (leader: CERTH) and **D2.3** Pre-treatment options and contaminant separation as well as concentrated recovery (leader: TNO).

During the 2<sup>nd</sup> reporting period RE-CORD completed the experimental activities concerning the slow pyrolysis pretreatment of the contaminated biomasses, as foreseen by the Task 2.2.2.

Five contaminated biomass samples were converted at lab-scale and two were processed at pilot-scale, investigating conventional and oxidative slow pyrolysis.

The char obtained from the lab-scale pretreatment were characterized in terms of inorganic elements concentration and BET surface area.

Every pilot-scale pyrolysis product (char, aqueous phase, oil phase, permanent gas) was characterized and liquid and solid samples were shipped to WP2 partners.

**Torrefaction** of Sorghum and of Miscanthus (from the Lavrion site) was completed at pilot scale in RP2 at **TNO**, to generate solids for gasification testing.

Torrefaction of Sorghum was conducted at 280° C, resulting in a mass yield of 54.7%. Most of the heavy metals in the biomass remained in the torrefied solids. Some of the more volatile metals (Cd, Pb, Zn) were partially volatilized and released to the gas phase and therefore removed from the solids. For less volatile metals (AI, Fe), the metals were concentrated in the torrefied biomass in proportion to the mass lost. The higher heating value of the sorghum biomass increased from 17.4 MJ/kg (dry basis) in the feedstock to 21.6 MJ/kg (dry basis) in the torrefied material.

Torrefaction of Miscanthus (Lavrion site) was conducted at 285 °C, resulting in a mass yield of 56.5%. The analytical results of the material have not yet been completed at the end of RP2.

Conventional **lab-scale slow pyrolysis** (**RE-CORD**) was carried out on sorghum, miscanthus from Kozani, miscanthus from Lavrion, switchgrass and hemp specimens (**Error! Reference s ource not found.**37), which were provided by WP1 partners (1 kg each). Biochar samples were produced in a macro thermogravimetric analyser (LECO TGA 701) under nitrogen flow. The aim of these lab-scale experiments was to rapidly investigate the char yield, inorganic concentration and specific surface area at different reaction temperatures and residence times. Specifically, two temperatures (500 and 600 °C) and two residence times at that temperature (30 and 60 min) were adopted as operating conditions. Before the conversion experiments, the biomass specimen were characterized via proximate and ultimate analysis (Table 30) and inorganic elements concentration (Table 31).



Figure 38: Contaminated biomass samples; a) sorghum, b) miscanthus from Kozani, c) switchgrass, d) hemp, e) miscanthus from Lavrion.

Parameter	Sorghu m	Miscanthu s (Kozani)	Miscanthu s (Lavrion)	Switchgra ss	Hemp	U.M.
Volatiles	73.0	75.5	74.5	75.3	73.9	wt% d.b.
Ash content @ 550°C	9.0	7.9	5.9	8.5	8.1	wt% d.b.

Table 30: Contaminated biomass characterization.

Ash content @ 710°C	8.8	7.8	5.8	8.0	7.2	wt% d.b.
Fixed carbon	17.9	16.5	19.6	16.2	17.9	wt% d.b.
С	43.7	42.7	42.9	41.7	41.4	wt% d.b.
Н	5.6	6.0	6.1	5.9	5.9	wt% d.b.
Ν	0.9	0.3	0.4	0.3	0.9	wt% d.b.
S	0.2	0.2	0.1	0.1	0.2	wt% d.b.
0	40.7	42.9	44.6	43.4	43.5	wt% d.b.

Table	31: Main metal	elements	concentration	in biomass	specimens.	Values a	re in m	ig/kg	d.b.;
b.d.l.:	below detectio	n limit.							

Element	Sorghum	Miscanthus (Kozani)	Miscanthus (Lavrion)	Switchgrass	Hemp
AI	239	161	163	214	438
Cd	9	b.d.l.	3	b.d.l.	b.d.l.
Fe	235	210	149	311	438
Mn	71	92	114	59	104
Ni	b.d.l.	7	b.d.l.	7	b.d.l.
Pb	56	2	26	2	82
Zn	194	9	109	9	71

Figure 39 depicts a comparison among the results of the lab-scale pyrolysis of the investigated biomasses in terms of char yield and char specific surface (BET). All the char samples follow the same trends: with an increase in reaction severity the yield decreases while the BET surface increases. The latter parameter, however, shows a sharp increase when the reaction temperature is raised from 500 to 600 °C. It is observed that sorghum is the specie leading to the highest char yield, which is above 30 wt% d.b. for all the investigated conditions. Regarding the BET surface, at 500 °C the maximum value is obtained with switchgrass at 60 min (60 m2/g). At a reaction temperature of 600 °C, switchgrass and the two miscanthus samples show the highest values, ranging from 224 to 243 m2/g at 30 min and from 240 to 260 m2/g at 60 min. On the other hand, sorghum and hemp lead to lower values, i.e., 113 and 155 m2/g for sorghum and 49 and 70 m2/g for hemp.



Figure 39: Char yields and specific surface area comparison in lab-scale pyrolysis.

The inorganic concentration of every char sample was measured through ICP-OES after mineralization. These data were provided to WP3 partners for the modelling activities and allowed the selection of the operating conditions for the pilot-scale runs: 600 °C and 30 min were selected for the sorghum pyrolysis, while 600 °C and 60 min were selected for the

miscanthus (Lavrion) pyrolysis, as in these operating conditions the maximum concentration of contaminants was observed.

**Pilot scale pyrolysis** tests were performed in **RE-CORD**'s continuous pyrolysis reactor (SPYRO), whose condensation system was modified to be able to work under oxidative operation.

The aim of the pilot-scale experiments was the production of at least 10 kg of char from sorghum and miscanthus for its subsequent gasification. Char by conventional and oxidative



slow pyrolysis was produced for each biomass specimen. To obtain the target amount of char to be delivered to WP2 partners, several replicate tests were carried out. Before each replicate, the feedstock was oven-dried to ensure a correct evaluation of products yields.

Sorghum was the first biomass RE-CORD received (~ 50 kg) and its particle size and bulk density already met the required specification for feeding, i.e. particle size lower than 8 mm and bulk density higher than 150 kg/m<sup>3</sup>. On the other hand, the bulk density of the miscanthus (Lavrion) specimen (~60 kg received) was too low and in the first run the feeding was hindered by bridging in the feeding hopper. It was then decided to pelletize it (Figure 40), discarding the results from the first run.

Figure 40: Pelletized miscanthus (Lavrion) sample.

Table 32 reports the operating parameters adopted in the conventional and oxidative experimental runs. The equivalence ratio is defined as the ratio between the injected air and the air needed for complete combustion. The amount of air to be injected for reaching the desired equivalence ratio was calculated from the elemental composition of the feedstock. In each test, the first heating section was set to 150 °C in order to control the heating rate, but, being the process carried out in a continuous unit, the heating rate is governed by the screw velocity and by the heaters temperature, and resulted almost doubled with respect to the lab-scale TGA pyrolysis.

Table 32: Operating	conditions	selected for t	he pilot-scale	production tests.

Parameter	Conventional pyrolysis	Oxidative pyrolysis	U.M.
Equivalence ratio	0	0.06	-
Calculated Heating	40	41	°C/min
Rate			
Reaction temperature (set temperature of section 2 and 3 of reactor)	600	600	°C
Solids residence time	30 and 60	30 and 60	min

After each run, the char and the condensates were collected, and the latter were gravimetrically separated to obtain an aqueous and an oil phase. Table 33 reports the pyrolysis products yields from the pilot-scale experimental campaign.

Product yield (wt%) d.b.	Sorghum Convention al	Sorghum Oxidativ e	Miscanthus Convention al	Miscanthus Oxidative
Char	32.0	29.3	31.1	31.3
Aqueous phase	20.8	28.0	24.4	26.5
Oil phase	5.3	2.1	3.0	2.2
Gas	42.0	40.6	41.6	40.0

Table 33: Sorghum and miscanthus (Lavrion) slow pyrolysis yields.

Figure 41 shows the char samples obtained from the pilot-scale experimental campaign. It can be noted that the char from miscanthus partially retain the pelletized shape. In the following tables, the results from the characterization of the pyrolysis products are reported.



Figure 41: Char from a) sorghum conventional pyrolysis, b) sorghum oxidative pyrolysis, c) miscanthus (Lavrion) conventional pyrolysis, d) miscanthus (Lavrion) oxidative pyrolysis.

Parameter	Sorghum Conventional	Sorghum Oxidative	Miscanthus Conventional	Miscanthus Oxidative	U.M.		
Volatiles	9.9	9.9	6.9	6.8	wt% d.b.		
Ash content @ 550°C	25.9	25.7	19.8	20.3	wt% d.b.		
Ash content @ 710°C	25.4	25.1	19.7	20.2	wt% d.b.		
Fixed carbon	64.2	64.4	73.3	72.9	wt% d.b.		
С	68.4	68.0	74.5	74.1	wt% d.b.		
Н	1.7	1.7	1.7	1.6	wt% d.b.		
Ν	1.4	1.5	0.9	0.9	wt% d.b.		
S	0.4	0.5	0.1	0.2	wt% d.b.		
0	2.3	2.7	3.0	3.0	wt% d.b.		
Specific surface area	76	122	51	98	m²/g		

## Table 34: Properties of sorghum and Miscanthus (Lavrion) char samples.

Table 35: Concentration of main metal elements in sorghum char and liquid samples. Values are in mg/kg d.b.; b.d.l.: below detection limit.

Element	Conventional Char	Oxidative Char	Conventional Aqueous phase	Oxidative Aqueous phase	Conventional Oil phase	Oxidative Oil phase
AI	2131	903	b.d.l.	b.d.l.	2	9
Cd	b.d.l.	b.d.l.	b.d.l.	b.d.l.	54	74
Fe	1640	1324	b.d.l.	b.d.l.	22	b.d.l.
Mn	275	238	b.d.l.	b.d.l.	b.d.l.	2
Ni	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Pb	351	249	b.d.l.	b.d.l.	23	45
Zn	837	793	bdl	bdl	82	bdl

Table 36: Main metal elements concentration in Miscanthus (Lavrion) char and liquid samples. Values are in mg/kg d.b.; b.d.l.: below detection limit.

Element	Conventional Char	Oxidative Char	Conventional Aqueous phase	Oxidative Aqueous phase	Conventional Oil phase	Oxidative Oil phase
Al	1214	985	b.d.l.	b.d.l.	6	5
Cd	b.d.l.	b.d.l.	2	b.d.l.	12	55
Fe	1417	1170	b.d.l.	b.d.l.	7	21
Mn	374	330	b.d.l.	b.d.l.	0.4	3
Ni	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.

Pb	144	143	b.d.l.	b.d.l.	12	47
Zn	456	544	b.d.l.	b.d.l.	1	7

Pilot-scale conventional and oxidative runs produced char with similar proximate and ultimate analyses, but a higher specific surface value was observed in the oxidative case, although lower than that obtained in the lab-scale experiments. Generally, the inorganics concentrated in the char. The oil phase exhibited a higher concentration of metal contaminants with respect to the aqueous phase, whose inorganic element concentrations were mostly below the detection limit. The slow pyrolysis of sorghum and miscanthus from Lavrion yielded a permanent gas stream with very similar composition.

The volumetric composition of the gas species in the pyrolysis permanent gas was evaluated via an online Agilent microGC, whose sampling and calibration system were commissioned within the project. Generally, conventional pyrolysis produced a gas phase richer in hydrogen, while in the oxidative case, the share of CO and  $CO_2$  was higher.

# Interaction and integration between tasks and work packages

From the pilot-scale experiments, for each biomass specimen and for each regime of operation (conventional and oxidative):

- at least 5 kg of char were shipped to TUM for Task 2.3 Entrained flow gasification and gas cleaning
- at least 1 kg of char, 1 kg of biomass and hundreds of grams of oil and aqueous phase samples were delivered to CERTH for Task 2.1 Characterization of biomass materials and by-products, conversion process considerations, balance and recovery options of elements

Char samples were also shipped to TNO for TORWASH aqueous phase adsorption testing and the pyrolysis permanent gas compositions were shared with TUM to evaluate their potential in the fermentation process.

All the data collected from the experimental campaigns, together with scaled-up pyrolysis plant CAPEX, OPEX, layout and M&E balance, were shared with partners to help in modelling the value chains foreseen in Task 3.2 Modelling selected value chains.

**Deviations/obstacles**: No deviations or obstacles were observed during the 2<sup>nd</sup> reporting period.

D. no	Title	Leader	Delivery date (planned)	Delivery date (actual)
D2.3	Pre-treatment options and contaminant separation as well as concentrated recovery	TNO	M36	M36

M. no	Title	Leader	Delivery date (planned)	Delivery date (actual)
5	Low contaminant Feedstock (obtained by TORWASH)	TNO	M12	M22

**M5** had 10 months delay due to the M5 had to be postponed due the late harvesting of the biomass produced in GOLD fields. The field trials were established on fields from M11 (04/2022) to M13 (06/2022) and the harvesting started from mid of M17 (09/2022) and was completed by M20 (12/2022). The harvested biomass was sent to CRES for chipping and drying and the first packages started to be sent by M20 (12/2022) of the project. The milestone was achieved by M22, 02/2023.

# Task 2.3 Entrained flow gasification and gas cleaning

To better understand the heavy metal gasification behaviour, the phase transition from solid to gaseous is modelled within the GOLD project in Task 2.1.3. To validate the model and show

the actual fate of contaminations during gasification, work for Task 2.3 was divided into three subtasks, listed in Table 37. Activities and achievements of the 2<sup>nd</sup> reporting period are presented in Table 38.

Table 37: Task 2.3 breakdown						
Sub-task	Description	Leader	Duration	Status		
2.3.1	Basic experimental gasification character	ization	TUM-CES	M6-M12	Ongoing	
2.3.2	High temperature EFG performed with Ba	abiTER	TUM-CES	M13-M36	Ongoing	
2.3.3	High temperature EFG performed with BOOSTER		TUM-CES	M37-M48	Not started	
2.3.4	Gas cleaning for contaminant separation recovery		TUM-CES	M25-M48	Ongoing	
Table 38: A	ctivities and achievements in Task 2.3.1					
Activity		Achie	vement			
Basic exp character	perimental gasification	Fuel Analysis of raw and pretreated Sorghum				
		Probe preparation, grinding and handling behavior of pretreated Sorghum				
High temperature (entrained flow) gasification performed with WMR, ETC and BabiTER		Successful gasification of pretreated Sorghum				
Gas clear recoverv	ning for contaminant separation	First in	ndications o	n gas cleani	ng design	

During the 2<sup>nd</sup> reporting period, special effort was put into thermodynamic modelling and experimental gasification trials to validate the release behaviour of volatile heavy metals. First entrained flow gasification trials using pretreated Sorghum were conducted. ETV-ICP-OES is chosen as the standard method for measuring heavy metal release from contaminated biomass due to its versatility and productivity.

Material provision from WP2 partners: The pretreated Sorghum originated in Lavrion (AUA) was delivered to TUM in from RE-CORD and TNO. About 5 kg<sub>dry</sub> each of inert and oxidatively pyrolyzed char was delivered in May and June 2023 to TUM. In May 2023 TNO delivered also about 7 kg<sub>drv</sub> of torrefied and 5 kg<sub>drv</sub> of TORWASHed samples in September 2023.

As Switchgrass and Miscanthus from CRES from Kozani, where only provided in February 2024 in large quantities to TNO for TORWASH (25 kgdry each), they are not part of the gasification tests in this 2<sup>nd</sup> reporting period. Similarly, Miscanthus from 2023's AUA/Lavrion site was provided in late February 2024 at TNO for torrefaction and TORWASH (60-70 kgdrv), and at RE-CORD for pyrolysis (60-70 kgdrv), and will thus not be part of this report.

Entrained flow gasification and gas cleaning of the GOLD project investigate the WP2 process route 1 via entrained-flow gasification at high temperatures and moderate pressure and, after gas cleaning, the fermentation of the created synthesis gas in a bioreactor. The aim of this work is to predict and measure the fate of heavy metals and metalloids during gasification, determine syngas conditions and contamination after gasification and the resulting implications for gas cleaning before synthesis. As described in D2.4, it is expected that heavy metals and metalloids sublimate or react forming gaseous compounds in EFG eventually being enriched in [Ritz et al. 2024]:

- the bottom ash/slag in the gasification chamber, or
- the fly ash together with fine ash particles in the flue gas, or
- the flue gas and need to be removed in the gas cleaning system.

When heavy metals and metalloids are enriched in the bottom ash or slag, they are immobilized in a non-leachable vitrified form, which facilitates their management and disposal. The vitrification process essentially locks the contaminants into the solid matrix, reducing the risk of leaching into the environment. As a result, disposal of bottom ash or slag enriched with heavy metals and metalloids in non-leachable form is typically easier and safer compared to other forms of contamination. Proper handling and disposal methods remain important to ensure containment and prevent dispersion into the environment, but the inherent stability of the vitrified matrix minimizes the risk of environmental impact. Therefore, the enrichment of heavy metals and metalloids in bottom ash or slag is indeed a desired outcome in gasification processes aimed at managing these contaminants effectively. Regardless of the enrichment location, residues from downstream processes such as bottom ash, slag, fly ash, or captured contaminants need appropriate management, including storage, treatment, and disposal, to prevent environmental contamination.

Pretests to investigate the grinding behavior and handling (dmax <  $250\mu$ m and d $50 \approx 70\mu$ m), probe preparation (fuel and additive feeding) and physical and chemical characteristics of treated and untreated fuels were conducted between January and April 2023 (M21-M24).

Experimental trials are conducted using the gasification test rigs ETV, WMR (Task 2.3.1) and BabiTER (Task 2.3.2) at TUM-CES. All experimental test rigs are described in detail in D2.4 and the experimental plan is shown in Table 39. In short, the temperature-resolved release of the heavy metals Cd, Cr, Ni, Pb, and Zn from the biomasses is measured using ETV coupled with ICP-OES. For this purpose, the total heavy metal concentrations in the biomass samples are determined and the mass fraction in the gas phase over the temperature is measured in the ETV-ICP-OES system. The ETV-ICP-OES uses a novel developed method for the measurement of the release of the heavy metals cadmium (Cd), chromium (Cr), nickel (Ni), lead (Pb), and zinc (Zn). The first step is the calibration of the temperature and concentration, followed by the validation. ICP-OES and ETV experiments start from room temperature, where the sample in the ETV is heated with a heating rate of 20 °C/s to a temperature of 2400 °C, which is held for one minute. After a cooling phase of 50 seconds, the ETV is heated to 2400 °C again to avoid memory effects. The validation of the temperature and concentration are done twice before and after each measurement run. Each measurement is repeated five times to reduce the influence of inhomogeneities in the biomass.

Source	State	Quantity to be processed in kg <sub>dry</sub>	Date received	WMR	ETV	BabiTER
AUA	Raw	1	(11/2022)	-	Х	-
<b>RE-CORD</b>	Pyrolyzed inert	5	(05-06/23)	Х	Х	Х
RE-CORD	Pyrolyzed oxida.	5	(05-06/23)	Х	Х	х
TNO	TORWASHed	5	(10/23)	-*	Х	_**
TNO	Torrefied	7	(05/23)	Х	Х	Х

Table 39: Design of Experiment for Task 2.3 on gasification of contaminated Sorghum in 2<sup>nd</sup> reporting period.

\*due to limited time

\*\*due to challenging biomass handling

Experiments on the wire mesh reactor (WMR) were conducted at TUM-CES to analyze the reaction kinetics of gasification of feedstock under the EFG conditions, and the influence of released critical trace substances on subsequent gas purification. In addition, pretests to investigate the grinding behavior and handling ( $d_{max} < 250 \ \mu m$  and  $d_{50} \approx 70 \ \mu m$ ), probe preparation, fuel feeding, and physical and chemical characteristics of treated and untreated fuels were conducted. The WMR is used for the investigation of biomass devolatilization at high heating rates. In the GOLD project, additionally the residues of discrete measuring points at temperatures between 600 and 1200 °C are analyzed in the ICP-OES to measure the release of heavy metals. WMR experiments are conducted at atmospheric pressure with torrefied and the two types of pyrolyzed sorghum. The design of experiment is shown in Table 40. After each measuring point, the sample and mesh are dried again and weighed. Each measuring point is repeated at least five times and the mean volatile yield is calculated while neglecting the two values with the highest deviation from the median. In the case of oxidative pyrolyzed sorghum, measuring points at 600 °C with a volatile yield that above 10% of the

mean yield at 1000 °C are considered physically impossible and therefore neglected. All residues from the experiments at one measuring point are combined and the heavy-metal concentrations are measured using ICP-OES [Ritz et al. 2024].

Table 40: Experimental plan for Sor	hum WMR trials. T = torrefied (TNO), Po = oxidative- (RE-
CORD), Pi = inert pyrolyzed (RE-CO	D).

	Temperature in °C					
Residence time in s	600	800	1000	1200		
1	Т	Т	Т			
2	Т	Т	Т			
5	Т	Т	Т			
10	T, Po, Pi	T, Po, Pi	T, Po, Pi	T, Po, Pi		

To determine gasification kinetics, TUM-CES uses a Single First Order Reaction Model (SFOR) for the analysis of the volatile yield during gasification with only few parameters, based on the assumption of a first-order reaction. The SFOR assumes that the concentration of the volatiles  $c_v$  decreases in a linear correlation with increasing temperature. The reaction rate constant k of a first-order reaction is calculated using the Arrhenius equation. The pressure dependence of the volatile yield is neglected in this work. The combined influence of the temperature and residence time on the volatile yield  $Y_V(t, T)$  is:

$$Y_V(t,T) = Y_{V,\mathrm{T}_{\mathrm{set}}} + \left(Y_{V,\mathrm{T}_{\mathrm{max}}} - Y_{V,\mathrm{T}_{\mathrm{set}}}\right) \cdot \left(1 - e^{-\theta \cdot (T - T_{\mathrm{set}})}\right) \cdot \left(1 - \exp\left(-k_0 \cdot \left(e^{-\frac{E_A}{RT}}\right) \cdot t\right)\right)$$

where  $T_{max}$  is the highest investigated temperature,  $T_{set}$  is a set temperature smaller than  $T_{max}$ , R is the universal gas constant, and T is the temperature. The thermodynamic parameter  $\theta$  is fitted to experimental data by the method of the least square error and the kinetic parameters  $k_0$  and the activation energy  $E_A$  are calculated.

EFG experiments at atmospheric pressure are conducted with the Baby High Temperature Entrained Flow Reactor (BabiTER) at the Chair of Energy Systems. In GOLD WP2, N<sub>2</sub> and O<sub>2</sub> are used, and the amount of O<sub>2</sub> is adjusted so that a prior specified equivalence ratio is achieved in the reaction tube. Like in the WMR experiments, the residues from discrete measuring points, which are collected during the experiment with the sampling probe, are analyzed in the ICP-OES to measure the release of heavy metals. For each biomass, gasification trials are conducted at four temperatures between 800 and 1100 °C in 100°C steps. The sampling probe is set to a height so that the particles are collected 1 m below the start of the reaction tube corresponding to gas residence times of 2.5 s and 1.37 6s real residence time for particles until removal. The conversion is calculated using the ash-tracing method. The ash-tracing method is based on the assumption that the mass of the ash doesn't change during gasification. In addition, the BabiTER trials allow more detailed investigation of the biomass preparation, fuel feeding, handling (d<sub>max</sub> < 250 µm and d<sub>50</sub> ≈ 70 µm), and physical and chemical characteristics of treated and untreated fuels.

# Main results and achievements

The experimental work conducted in Task 2.3 during the 2<sup>nd</sup> reporting period aimed at investigating gasification kinetics and release behaviour of heavy metals during gasification of the supplied contaminated Sorghum in its different pretreatment states.

It should be noted, that major challenges were faced when feeding torrefied and TORWASHed material to the BabiTER test rig. Fuel is fed into the reaction tube through a dosing system at the top of the droptube reactor, ensuring a constant mass flow. However, when using torrefied or TORWASHed biomass, we encountered challenges with the dosing system due to the material's light and fluffy nature. It tended to stick to the funnel walls and block the channel, making it difficult to feed properly into the reactor tube and collect samples. Especially the TORWASHed material tends to agglomerate or form clumps, due to its physical properties, leading to blockages within the dosing system or reactor tube, impeding the flow of material and causing operational issues. Additionally, it may have a higher tendency to adhere to surfaces due to changes in its surface chemistry during pretreatment, exacerbating the

problem of material sticking to the walls of the funnel and reactor tube. These factors combined could contribute to the observed difficulties in feeding and processing torrefied and TORWASHed biomass in the gasification experiment. Consequently, no experimental results could be obtained for TORWASHed material in the BabiTER. This issue needs to be addressed to ensure smooth operation of the gasification process. A combination of preventive measures and operational adjustments is to be explored in the upcoming test campaigns including alternative methods for fuel feeding torrefied biomass into the reactor that minimize the risk of blockages. This could involve redesigning the dosing system to improve material flow and prevent clumping or sticking. This might include features such as improved vibration mechanisms promoting better material flow and preventing blockages.

# **Devolatilization during Gasification and SFOR Kinetics**

The temperature dependency and gasification kinetics are investigated for temperatures between 600 °C and 1200 °C in steps of 200 °C at atmospheric pressure, a heating rate of 1000 °K/s, and residence times between 1 and 10 s (see above). The parameters of the SFOR model are derived with the thermodynamic parameter  $\theta$  being fitted to experimental data by the method of the least square error and the kinetic parameters  $k_0$  and the activation energy  $E_A$  calculated (see above). The results for the fitting of gasification parameters are shown in Table 41.

 Table 41: Parameters of the Single First Order Reaction Model (SFOR) fit to data from WMR experiments of GOLD Sorghum from AUA.

Pretreatment method	θ	k₀ in s⁻¹	<i>EA</i> in kJ/mol	
Torrefied (TNO)	0.0125	779.99	48.012	
Pyrolyzed inert (RE-CORD)	0.005			
Pyrolyzed oxidative (RE-CORD)	0.0143			

The fitting of the SFOR, which are plotted in Figure 42 a) are calculated at 600 °C. The volatile yields at 1200 °C are neglected for the SFOR, as they are likely influenced by secondary pyrolysis reactions occurring at higher temperatures, which can't be predicted with a first-order reaction model. Therefore, 1000 °C is  $T_{max}$ . Further, the SFOR curve of oxidative pyrolyzed sorghum is assumed to have the same zero point as the curve of inert pyrolyzed sorghum to receive a physically reasonable curve.

For torrefied sorghum, the volatile yield increases from 44.3% at 60 °C to 58.4% at 800 °C and then remains on the same level for 1000 °C. At 1200 °C, the volatile yield is increased again to 67.8%. For inert pyrolyzed sorghum, the volatile yield is increased slowly between 600 ° and 1000 °C from 5.4% to 15.3%. The volatile yield at 1200 ° is 46.4% and therefore substantially higher than at 1000 °. For oxidative pyrolyzed sorghum, the volatile yield is constantly between 6% and 9% temperatures between 600 ° and 1000 °, while the volatile yield at 1200 ° is again substantially higher at 41.7%.



Figure 42: Fitted SFOR model dependency of the volatile yield on a) temperature for torrefied (TNO) and pyrolyzed sorghum (RE-CORD), b) residence time during devolatilization for torrefied sorghum (TNO) from AUA in WMR.

Results suggest that, for the pyrolyzed sorghum, almost all volatiles are released from the solid biomass structure during pretreatment already, while the volatile content in the torrefied sorghum is still high. Therefore, significant devolatilization is only observed for torrefied sorghum and the release of gases for the pyrolyzed sorghum is mainly due to the high heating rate. This is also why the volatile yield of the pyrolyzed sorghum shows only weak temperature dependence. The devolatilization of torrefied sorghum is finally completed at 800 °C. Yet, a big increase in volatile yield is observed from 1000 °C to 1200 °C for all biomasses. This is likely due to secondary pyrolysis reactions occurring at higher temperatures. The results for the kinetic parameters k<sub>0</sub> and E<sub>A</sub> are used to derive the dependency of the volatile yield on the residence time. Fitting the volatile yield over the residence time for torrefied sorghum for residence times between 1s and 10s in the base case at temperatures of 600 °C, 800 °C, and 1000 °C, at atmospheric pressure, and a heating rate of 1000 K/s, the curve fit shown in Figure 42 b) is obtained. The volatile yields at 600 ° and 80 °C are constant when the residence time is 2 s or higher. Values with a volatile yield that is more than 10% higher than the mean value at 10 s are considered physically impossible and therefore neglected. At 1000 °C, the volatile yield is constant at all residence times. This means that the devolatilization is completed after a residence time of 2 s at temperatures of 600 °C and 800 °C and after 1 s at a temperature of 1000 °C.

For torrefied sorghum, the devolatilization increases from 600 °C to 800 °C. At 800 °C, all volatiles are released from the sorghum, as the volatile content in torrefied sorghum on a dryand-ash-free (daf) basis is 57%. No further increase of the volatile yield is measured at 1000 °C. Cellulose and hemicellulose start to decompose at temperatures between 350 °C and 450 °C, which is why the volatile yield increases the most in the temperature range

between 400 °C and 800 C, as also observed in a previous study at the Chair of Energy Systems. The volatile content of pyrolyzed sorghum of only 12% (daf) shows that here, devolatilization already occurred during pretreatment. The release of a small fraction of volatiles during pyrolysis is likely influenced by the high heating rate. A significant increase of the volatile yield at temperatures of 1200 °C is observed for all biomasses and especially for pyrolyzed sorghum. Chemical bonds in the structure of the pretreated biomass, which are still stable at 1000 °C, seem to be activated and a release is observed. This behavior, however, follows different mechanisms and cannot be predicted with a model based on first-order reaction kinetics.

In entrained-flow gasification experiments of torrefied sorghum at 1100 °C, the conversion is 62% and 63%, respectively. In the gasification of inert pyrolyzed sorghum, conversions

between 21% at 800 C and 33% at 1100 C are achieved, while conversions between 26% at

900 C (29% at 800 °C) and 37% at 1100 C are achieved in the case of oxidative pyrolyzed sorghum. The conversions of the two types of pyrolyzed sorghum are lower than the conversion of torrefied sorghum due to the lower volatile and higher ash content. Furthermore, the conversion increases with increasing temperature, which indicates that complete conversion is not achieved at the lower temperatures.

## Heavy metal release behaviour in ETV, WMR and BabiTER

The elements Cd, Pb, and Zn are the volatile heavy metals and their release behavior is shown in Figure 43. Most of the Cd is released almost immediately at a temperature of 500 °C in the torrefied, TORWASHed, and raw sorghum. The volatilization of Cd in the case of the two types of pyrolyzed sorghum starts later at around 600 °C and takes on over a wider temperature range. Pb is entirely released quickly between 600 °C and 800 °C. The release of Zn also starts at a temperature of around 600 °C, but Zn is released over a wider temperature range compared to Pb. The release is especially slowed down between 1000 °C and 1500 °C, while most of the Zn has already been released from the biomasses at those temperatures. The release of heavy metals during pyrolysis is measured in this work by measuring their content in the char residues at discrete measuring points after devolatilization in the WMR. The release

of the volatile elements Cd, Pb, and Zn is proportional to the temperature. Around 40% of the Pb is released at 60 °C (0% in the case of inert pyrolyzed sorghum) and around 95% at 1200 °C. While less than 20% of the Zn are released at 600 °C, more than 80% are released at 1200 °C. The different biomasses show the same behavior for the release of Zn and, except for inert pyrolyzed sorghum where the release is delayed, for Pb. For Cd, the deviation of the different biomasses is bigger at lower temperatures. While 78% of the Cd in the torrefied sorghum are released at 600 °C, 0% are released from the inert pyrolyzed sorghum. At higher temperatures, all the Cd is released.

The BabiTER test rig at the TUM-CES is used for gasification experiments with torrefied, inert pyrolyzed, and oxidative pyrolyzed sorghum. The release of heavy metals during EFG is measured by measuring their content in solid samples that are withdrawn from the reaction zone with a sampling probe. The release of Pb and Zn occurs in the investigated temperature range. Pb is the only one of the volatile heavy metals where the different biomasses show significant deviations to each other. While just below 30% of the Pb for the inert pyrolyzed sorghum and around 56% for the oxidative pyrolyzed sorghum are released at temperatures of 800 °C and 900 °C, more than 50% is released at temperatures of 1000 °C and above in the case of inert pyrolyzed sorghum and more than 75% in the case of oxidative pyrolyzed sorghum. Around 55% of the Pb is released at a temperature of 1100 °C in the case of torrefied sorghum from TNO. For all investigated sorghum samples, less than 10% of the Zn is released at temperatures of 1000 °C and 1100 °C. Cd seems to be volatilized entirely in the investigated temperature range and the values below 100% lie within the inaccuracy of the measurement, especially in the ICP-OES due to the very low concentrations of Cd.

Cr and Ni show less volatile behavior in the ETV. Most of the Cr is released between 1500 °C and 1700 °C and most of the Ni between 1550 °C and 1750 °C. After that, their release is slower, and they are only entirely released at the final ETV temperature of 2400 °C.

In WMR, non-volatile elements are enriched in the char residue and no substantial release is observed. This can, for example, be seen for Cu, which is below the detection limit before WMR experiments, while its concentration in the residues is between 10 mg/kg and 69 mg/kg. The release of Mn is always around 0%. Some Ti is released but does not show any temperature dependence and is likely only due to the high heating rate and Ti concentration in the biomasses. However, Fe, Cr, and Ni cannot be measured with this method because the wire mesh material (stainless steel) contains those metals which are therefore enriched in the residue by abrasion of the mesh material.

In the BabiTER trials, non-volatile elements are enriched in the solid samples and no substantial release is observed for Cu, Cr, Fe, Ni, and Ti, while some Mn is released in the case of torrefied and inert pyrolyzed sorghum.







Figure 43: Results for gasification behaviour obtained with the different methods for the release of the volatile heavy metals (a) Pb, (b) Cd, and (c) Zn.

#### Summary and Expected Syngas Conditions from Pretreated Sorghum

The combination of the WMR and the BabiTER experimental trials provides valuable insights into the various gasification processes involved in the conversion of sorghum in EFG. For torrefied sorghum, devolatilization increases notably from 600 °C to 800 °C, with complete release of volatiles occurring at 800 °C due to the significant volatile content of torrefied sorghum at 57wt.%<sub>daf</sub>. The decomposition of cellulose and hemicellulose, occurring between 350 °C and 450 °C, leads to a substantial increase in volatile yield within the temperature range of 400 °C to 800 °C. Conversely, pyrolyzed sorghum exhibits a lower volatile content of only 12wt. %<sub>daf</sub>, suggesting devolatilization during pretreatment, possibly influenced by the rapid heating rate. An increase in volatile yield is observed at temperatures of 1200 °C across all biomasses. In BabiTER experiments, conversion rates of torrefied sorghum at 1100 °C are calculated to be 62% and 63% in two test campaigns, suggesting near-complete conversion of carbon to CO. In the gasification of inert pyrolyzed sorghum, conversions range between 21% at 800 °C and 33% at 1100 °C, while oxidative pyrolyzed sorghum yields conversions between 26% at 900 °C (29% at 800 °C) and 37% at 1100 °C. Notably, conversions of pyrolyzed sorghum are lower compared to torrefied sorghum due to differences in volatile and ash content. Conversion rates increase with temperature, indicating incomplete conversion at lower temperatures, potentially attributed to the formation of carbon dioxide and subsequent oxygen uptake by carbon atoms.

Syngas composition in terms of main substances CO, H<sub>2</sub>, and CO<sub>2</sub>, is a crucial aspect of syngas fermentation. As autotrophic CO conversion generates CO<sub>2</sub>, an ideal biomass-derived syngas would require as little CO<sub>2</sub> as possible. High CO<sub>2</sub> concentrations in syngas from EFG

mainly result from low product gas temperature at the end of the reactor (thermal losses and non-ideal quench geometry), unconverted biomass and generally poor rector design. An industrial EFG reactor would be almost CO<sub>2</sub> free. To achieve high conversion of CO<sub>2</sub> and H<sub>2</sub>, the  $H_2/CO_2$  ratio before fermentation must approach 2 for acetate and 3 for ethanol production. Thus, the ideal stoichiometric H<sub>2</sub>/CO ratio in the syngas for total conversion of both components in a bubble column or gas-lift bioreactor would be 2 for ethanol production, and 1 for acetate production. To estimate industrial-scale syngas compositions in terms of main components and close the mass balance for C, H, N, S from biomass-to-syngas, the biomassto-syngas model as explained in Task 2.1.3 is used. The model uses the minimization of Gibbs free energy to calculate gas phase chemical and phase equilibrium at given temperature and pressure. The feed stream to the gasifier model is based on the fuel analysis of the already pretreated biomass samples (torrefaction and TORWASH from TNO, inert and oxidative pyrolysis from RE-CORD). The EFG is scaled to 10 MW<sub>th</sub> to represent a feasible scale (Task 2.1.3), and O<sub>2</sub> requirements are calculated to reach T<sub>EFG</sub>=1400 °C. All feedstocks are gasified at an equivalence ratio around 0.26-0.28. For pyrolzed sorghum, a steam addition of 0.17 kg<sub>steam</sub>/kg<sub>biomass</sub> is necessary to ensure total conversion under EFG conditions. The resulting syngas is free of CO<sub>2</sub> and O<sub>2</sub> and shows a H<sub>2</sub>/CO ratio of about 0.5 for torrefied and TORWASHed sorghum, and about 0.25 for pyrolyzed sorghum. Figure 44 includes the resulting syngas composition after gasification and guench.0

Regarding the release of volatile heavy metals (Pb, Cd, Zn), experimental results from various methods demonstrate good agreement. For Pb, torrefied and oxidative pyrolyzed sorghum exhibit consistent release behavior, while inert pyrolyzed sorghum shows faster volatilization in the ETV compared to other methods. However, there is no significant difference in Pb release among different biomass types in the ETV, suggesting minimal influence of pretreatment on Pb release. Cd release occurs predominantly between 500 °C and 600 °C, with slower release observed in pyrolyzed sorghum due to changes in the chemical environment during pretreatment. In the BabiTER, Cd volatilization appears to be promoted by exothermic reactions in oxidative conditions, while background noise may affect measurement accuracy at lower concentrations. Zn release is observed mainly between 900 °C and 1200 °C, with some volatilization at lower temperatures possibly influenced by the reducing atmosphere. Slower release of Zn between 1100 °C and 1500 °C is attributed to the formation of stable compounds.

In summary, the experimental results obtained with the different methods show good agreement with each other and therefore validate each other. While the overall release behavior is the same for all methods, the volatilization tends to occur at slightly higher temperatures in the BabiTER. The mass fraction of the heavy elements in the gas phase is especially lower at high temperatures (1100 °C). This is likely due to the more oxidizing atmosphere in the BabiTER. The volatilization of Cd and Zn is restrained in an oxidizing atmosphere because, in the presence of oxygen, their oxides are formed. Cadmium oxide (CdO) and zinc oxide (ZnO) have much higher boiling points than Cd and Zn in elemental form. Usually, a more oxidative atmosphere promotes the volatilization of Pb, but the opposite effect can arise when Pb is bound in metal-matrix complexes. No release of the non-volatile heavy metals chromium (Cr) and nickel (Ni) was measured in the WMR or BabiTER in the respective investigated temperature range which coincides with the release in the ETV.

In conclusion, experimental and simulation results show that Cd, Pb, and Zn are entirely volatilized during entrained-flow gasification. The other heavy metals are rather non-volatile and are only partially released during gasification. Non-volatile elements start to recondense in the gasification chamber, and all heavy metals are entirely solidified in the water quench. Only very low levels of impurities are expected in the syngas after gasification, so that the requirements for the gas purification plant are rather low. The exact design of the gas cleaning is also heavily dependent on the gas fermentation's requirements.



Figure 44: Expected resulting syngas composition after gasification for 2023 sorghum samples collected from the AUA field in Lavrion (MB2 samples) and pretreated via TORWASH, torrefaction (both TNO), inert or oxidative pyrolysis (both RE-CORD).

Problem, delay or deviation: None

Corrective actions undertaken: None

D. no	Title	Leader	Delivery date (planned)	Delivery date (actual)
2.4	Process configurations, gas conditions and contamination content in gas and solid phase of entrained flow gasification and syngas cleaning	TUM	M34	M34

M. no	Title	Leader	Delivery date (planned)	Delivery date (actual)
6	Successful gasification to provide synthesis gas It was achieved in form of the expected syngas composition from industrial scale gasification of GOLD biomass to the Chair of Biochemical Engineering here at TUM in M24 according to plan [Dossow et al. 2023].	TUM	M24	M24

## References

[Dossow et al. 2023] Dossow, M.; Leuter, P.; Spliethoff, H. Fendt, S.: Process Modelling of Biofuel Production from Contaminated Biomass Through Entrained Flow Gasification and Syngas Fermentation. At 31<sup>st</sup> European Biomass Conference & Exhibition, in Bologna, Italy, 5<sup>th</sup> June 2023.

[Ritz et al. 2024] Ritz, M.; Dossow, M.; Mörtenkötter H., Spliethoff H., Fendt, S.: Experimental investigation of heavy metal release in entrained-flow gasification [submitted to Fuel]

## Task 2.4: Syngas fermentation (Leader: TUM-CBE, partners: TUM-CES, M25-M48)

**Objective:** To prove the syngas use in the newly developed fermentation, with specialized bacterial strains towards C2-C6 alcohols, that does not necessitate high pressures, thus lowering the EFG size requirements.

**Progress toward the objectives:** Work for Task 2.4 was divided into six subtasks; listed activities and achievements of the 2nd reporting period are presented in Table 42.

## Table 42: Activities and achievements in Task 2.4

Task	Activity	Achievement
2.4.1	Establishment of up to four microorganism-specific standardized gas fermentation processes with synthetic gas composition at well-defined reaction conditions (e.g., gas-liquid mass transfer rates, pH profiles, etc.) as reference.	completed
2.4.2	Establishment of a (continuous) lab-scale gas fermentation process at well-defined reaction conditions for efficient production of biofuels from real synthesis gases provided by TUM-CES and studies on long-term stability (few weeks).	ongoing
2.4.3	Selection of the best-performing acetogen for further studies.	completed
2.4.4	Studies of the microbial reference processes with increasing amounts of defined gas impurities based on findings from T2.2 and T2.3 to identify critical impurities and concentrations.	not started
2.4.5	Studies on the conversion of real synthesis gas or pyrolysis gas or combinations thereof provided by TUM-CES with the selected acetogen at reference conditions.	not started
2.4.6	Providing process-engineering data for further scale-up.	not started

Description of activities, main results and achievements Task 2.4.1 Establishment of up to four microorganism-specific standardized gas fermentation processes with synthetic gas composition at well-defined reaction conditions (e.g., gas-liquid mass transfer rates, pH profiles, etc.) as reference.

Acetogenic microorganisms can use the main components CO, CO<sub>2</sub>, and H<sub>2</sub> from biogenic syngas as substrates and convert them into organic acids and alcohols. Alcohols are favored over acids because they can be used as biofuels or platform chemicals.

Working with *Clostridia spp.* (*Clostridium autoethanogenum*, *Clostridium ljungdahlii*, *Clostridium ragsdalei*) had already been carried out at our chair in earlier research projects (Oliveira et al., 2022). They produce acetate, ethanol, and D-2-3-butanediol. As growth and alcohol formation by *C. ljungdahlii* was worse than the other *Clostridia*, it was decided to characterize the two most promising microorganisms (*C. autoethanogenum* and *C. ragsdalei*).

In the first investigations, the reaction temperature and pH were varied to observe their effect on biomass and product formation and find optimal reaction conditions. All batch processes were operated with continuous gassing in stirred tank bioreactors. The nutrients in the medium were provided at the beginning of the cultivation without adding any further during the process. Syngas was continuously dispersed in the fermentation medium with 0.083 vvm). The artificial syngas composition was derived from the gasification data of torrefied wood, according to Rückel et al. (2022). All processes were performed with a syngas composition of  $39.4\% N_2$ , 29.8% CO,  $22.0\% H_2$ , and  $8.9\% CO_2$ .

Table 43 shows the final concentrations of the batch processes performed with *C. ragsdalei* with varying pH (pH 5.5 – pH 6.0) and temperature ( $32^{\circ}C - 37^{\circ}C$ ). At  $37^{\circ}C$  and pH 6.0, the final acetate concentration was highest (4.62 g L<sup>-1</sup>) after 6 d of operation. At  $32^{\circ}C$  and the pH 5.5, the highest cell dry weight (CDW) concentration of 0.47 g L<sup>-1</sup> was achieved, and the final alcohol concentrations were at the maximum: 2.93 g L<sup>-1</sup> ethanol, and 0.42 g L<sup>-1</sup> D-2,3-butanediol, respectively.

Table 43: Maximal CDW and product concentrations achieved with C. ragsdalei in batch operated stirred tank bioreactors with continuous syngas gassing at varying combinations of temperature and pH

pH Temperature	рН 6.0 Т 37°С	рН 5.5 Т 37°С	рН 5.5 Т 32°С
CDW, g L <sup>-1</sup>	0.29	0.42	0.47
Acetate, g L <sup>-1</sup>	4.62	3.56	1.14
Ethanol, g L <sup>-1</sup>	0.45	1.72	2.93
D-2,3-butanediol, g L <sup>-1</sup>	0.29	0.24	0.42

Table 44 shows the final concentrations of the batch processes performed with *C. autoethanogenum* with varying pH and temperature. *C. autoethanogenum* showed the best performance at pH 6.0 and  $37^{\circ}$ C with respect to biomass and product formation after 6 d.

Table 44: Maximal CDW and product concentrations achieved with C. autoethanogenum in batch operated stirred tank bioreactors with continuous syngas gassing at varying combinations of temperature and pH

pH Temperature	рН 6.0 Т 37°С	рН 6.0 Т 32°С	рН 5.5 Т 37°С
CDW, g L <sup>-1</sup>	0.49-0.54	0.48	0.33
Acetate, g L <sup>-1</sup>	1.11-1.15	0.30	0.48
Ethanol, g L <sup>-1</sup>	2.62-2.77	2.47	1.80
D-2,3-butanediol, g L <sup>-1</sup>	0.31-0.32	0.26	0.20

*Task 2.4.2* Establishment of a (continuous) lab-scale gas fermentation process at welldefined reaction conditions for efficient production of biofuels from real synthesis gases provided by TUM-CES and studies on long-term stability (few weeks).

Due to the shown low added value for producing alcohols in batch processes, processes with high carbon conversions, high product concentrations, and high volumetric productivities (space-time yields), i.e., continuous processes, are required. However, since the growth rates in gas fermentation are low, the acetogenic microorganisms must be retained in a continuously

operated bioreactor (decoupling of the residence times). For this reason, work is being carried out to establish a continuous process with integrated cell retention.

A schematic setup of a continuous syngas fermentation process with cell retention is shown in Figure 45. As in the batch processes, a continuous syngas supply is provided. Additionally, a feed medium with a defined flow rate is conveyed via a pump into the reactor. To keep the liquid volume in the bioreactor constant, a second pump sucks the filtered medium (without cells) out of the reactor through an immersed microfiltration membrane. In this way, fresh medium is constantly supplied, and the used medium is removed continuously with the products, but the cells remain in the stirred tank bioreactor. Feeding and product removal are controlled gravimetrically.



Figure 45: Setup of continuously performed syngas fermentation processes with total cell retention (immersed microfiltration membrane).

Initial experiments with *C. autoethanogenum* and *C. ragsdalei* were carried out, as shown in Figure 46. The continuous process was started after an initial batch phase of ~ 27 h. The initial dilution rates D (feed volume flow divided by the reactor volume) were set to 4/3 of the maximum growth rate  $\mu_{max}$ .

Although a higher CDW concentration was achieved with *C. ragsdalei*, the product concentrations of acetate and ethanol showed oscillations, which does not indicate a stable operating state. It would have been expected that a stable operating state would be reached after 5 hydraulic resistance times  $\tau$ , i.e. after approx. 3.4 days after the start of the process. In addition, ethanol and D-2.3-butanediol concentrations were lower compared to the batch process. Higher stable product concentrations were achieved with *C. autoethanogenum* after 8 d (8.57g L<sup>-1</sup> acetate, 3.44 g L<sup>-1</sup> ethanol, and 0.45 g L<sup>-1</sup> D-2,3-butanediol).



Figure 46: Process performance of continuous syngas fermentation processes with total cell retention with C. autoethanogenum ( $\Box$ , pH 6.0 and 37°C) and C. ragsdalei ( $\blacklozenge$ , pH 5.5 and 32°C) and in stirred tank bioreactors with total cell retention and continuous gassing (390 mbar N<sub>2</sub>, 300 mbar CO, 220 mbar CO, 220 mbar H<sub>2</sub>, and 90 mbar CO<sub>2</sub>; F<sub>gas</sub> = 5 NL h<sup>-1</sup>; 1 L working volume). The gray shaded area indicates the initial batch phase.

During the following continuous syngas fermentation processes with cell retention (not shown here), the immersed microfiltration membrane repeatedly ruptured. The immersed hollow fiber membrane bundles (made of polysulfone) turned out to be not stable for long-term operation. Unfortunately, these hollow fiber membrane modules were no longer commercially available. A redesign of the immersed microfiltration unit membrane was performed based on robust sintered metal (delivery time above 3 months). Initial tests showed that the new membrane module works. However, the filtrate flow was reduced after 3 - 5 days of operation. A solution to this problem is still being worked on (back-flushing, increasing the membrane area, modification of the membrane surface, modification of the filtrate removal design, ...).

D. no	Title	Leader	Delivery date (planned)	Delivery date (actual)
M7	Fermentation to receive a liquid biofuel	тим	M32	M32

*Task 2.4.3.* Selection of the best-performing acetogen for further studies.

In batch processes, no significant difference in product formation was shown between *C. autoethanogenum* and *C. ragsdalei*. However, during the continuous process with total cell retention, *C. autoethangenum* showed improved process performance compared to *C. ragsdalei*. Based on these data, we decided to select *C. autoethanogenum* for further studies.

# *Task 2.4.4.* Studies of the microbial reference processes with increasing amounts of defined gas impurities based on findings from T2.2 and T2.3 to identify critical impurities and concentrations.

Not started yet. We currently do not have data on gas impurities from T2.2 and T2.3 (scheduled delivery date was December 2023).

# *Task 2.4.5* Studies on the conversion of real synthesis gas or pyrolysis gas or combinations thereof provided by TUM-CES with the selected acetogen at reference conditions.

Not started yet. No real synthesis gas has been made available to us so far (scheduled delivery date was December 2023). As an alternative, we are using an artificial syngas composition in analogy to syngas from torrefied wood, according to Rückel et al. (2022). The syngas composition comprises 39.4 % N<sub>2</sub>, 29.8 % CO, 22.0 % H<sub>2</sub> and 8.9 % CO<sub>2</sub>.

# *Task 2.4.6* Providing process-engineering data for further scale-up.

Not started yet.

**Problem, delay or deviation**: There are very small delays (see Task 2.4.4 and 2.4.5). The relevant project partners have already been made aware of this.

## Corrective actions undertaken: None

## References

Rückel A, Oppelt A, Leuter P, Johne P, Fendt S, Weuster-Botz D (2022): Conversion of syngas from entrained flow gasification of biogenic residues with *Clostridium carboxidivorans* and *Clostridium autoethanogenum*. *Fermentation* **8**: 465.

Oliveira L, Rückel A, Nordgauer L, Schlumprecht P, Hutter E, Weuster-Botz D (2022): Comparison of syngas-fermentation *Clostrida* in stirred-tank bioreactors and the effects of varing syngas impurities. *Microorganisms* **10**: 681.

# Task 2.5: High temperature autothermal pyrolysis and upgrading (Leader: UDES)

**Objective:** The purpose of this SOP is to provide a procedure that defines general guidelines to ensure proper operation of the pyrolysis facility. HDPE was used to simulate the one-stage catalytic pyrolysis + conversion of its products.

Work for Task 2.5 was divided into 3 subtasks (same titles with deliverables), listed in Table 40.

# Table 45: Task 2.5 breakdown

Sub-task	Description	Leader	Partners	Duration	Status
Task D2.7	AT Pyrolysis	UdeS		M1-M32	Ongoing
Task D2.8	Catalytic reforming or cracking	UdeS		M12-M36	Ongoing
Task D2.9	FTS	UdeS		M24-M48	Ongoing

Activities and achievements of the 2<sup>nd</sup> reporting period are presented in Table 46.

## Table 46: Activities and achievements in Task 2.5

Activity	Achievement
Autothermal pyrolysis commissioning and operation at kg-lab scale	Commissioning completed; first tests with residual waste streams; a first full mass balance available.
Dry catalytic reforming of pyrolysis surrogate gas with the Ni-UGSO and Ni-HAP catalysts	Optimization and full mass and energy balances with powder and pelletized catalysts at atmospheric and high-pressure regimes
Fischer-Tropsch Synthesis with a surrogate reformed pyrogas with new renewable materials- supported metallic catalysts in a 3-phase CST Reactor	Commissioning, protocol finalization and preliminary testing.
Another parallel task has been added to evaluate the possibility of using the metal-contaminated pyro- solids as adsorbents	

*Progress toward the objectives*: The pyrolysis plant is divided into 3 compartments: a) biomass feeding, b) reaction, and c) gas washing.

During the 2<sup>nd</sup> reporting period, special effort was put into

- Rendering operational the kg-lab scale autothermal pyrolyzer and achieve full mass balances and products characterization (pyrosolids, pyroliquids and pyrogases)
- Evaluate the efficiency of two types of catalysts in dry and steam reforming of a pyrogas surrogate. Parametric study over time-on-stream, O/C ratio and pressure.
- Commissioning and first FTS tests with a prechosen H2/CO ratio.
- Find whether heavy-metals-ladden pyrosolids can be used as adsorbents.

The overall picture. In the figure below we show the 4 sections (encircled) where we have the most important deliverables so far:



Figure 47: The main achievements of UdeS are the ones encircled.

# Summary of accomplishments

- Pyrolysis: Batch and ATP
  - Pure biomass representative of real contaminated biomass; switchgrass and willow are the species tested in Canada: CÉROM (https://cerom.qc.ca/) and Jardin botanique de Montréal are our collaborators (it was collected from an ancient mining site).
  - Optimal conditions determination at g-lab scale batch pyrolysis runs
- Artificial metals contamination of the pyrolysis solids and testing as adsorbents of 2nitrophenol and CO<sub>2</sub>.
  - Commissioning of the ATP and mass balances for yields in solid, liquid and gaseous products.
- Catalytic Reforming
  - Tests at dry reforming regime for the production of synthesis gas targeted towards FTS
  - o Use of methane as surrogate molecule
  - Use of catalyst in the form of powder and pellets (use of clay) at high T and various P.
- FTS
  - Unit commissioning and first runs with catalysts derived from renewable sources (HAP from eggs shells)
  - Use of CO+H<sub>2</sub> SG at various molar ratios.

Studied biomass Wood chip of	gatum Physical pre-treatment	<ol> <li>Washing with water.</li> <li>Drying in oven at 105°C.</li> <li>Grinding and sieving (≤1 mm)</li> </ol>
	Panicum virgatum	Wood chip of willow
pH	$5.37\pm0.10$	$6.12 \pm 0.11$
Ash content (wt %)	$1.4 \pm$	$3.2 \pm$
C (wt %)	$43.54\pm2.38$	$41.15\pm0.96$
S (wt %)	$0.1\pm0.003$	$0.14\pm0.053$
Cu (ppb)	34.8	105.8
Fe (ppb)	499.8	3726.2
Sb (ppb)	57.8	22



	Biomass	Ni (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Mg (mg/kg)	Ca (mg/kg)	Cu (mg/kg)	Al (mg/kg)	Sr (mg/kg)	Na (mg/kg)	K (mg/kg)
Roots (bassin)	RSB	21,60	101572,78	200,64	2097,13	5969,76	121,52	833,92	23,77	2882,11	9320,91
Perennial herbs	HVS	5,29	5827,94	89,84	1941,96	9485,38	37,19	85,54	36,11	474,38	16208,84
Leafs and stems	TF	15,30	1241,01	43,07	1536,80	9361,78	15,27	217,50	24,60	296,94	17761,03
Stems	тв	0,00	3573,14	872,71	1817,90	10756,10	20,67	44,96	35,27	1520,34	21013,61



Figure 48: Canadian biomasses from contaminated sites. Obtained by CÉROM and Jardin Botanique de Montréal.

Figure 49: Fixed-bed pyrolysis results with above biomasses (Cu-contaminated panicum virgatum biomass).

The conditions of Fixed-bed pyrolysis are : a) Temperature : 800°C, b) Under nitrogen atmosphere, c) Gas flow rate : 0.2 SLPM and d) Cu-contaminated biomass : 0.57wt.% of Cu



It was found that: a) the Cu presence improved biochar yields and decreased bio-oil yields, b) 90% of the Cu was retained in the solid phase and c) 2% of Cu was found in the bio-oil.

# **ATP Commissioning and first mass balance:** The mass balance composition of the products is: liquids (63%), gas (24%) and solids (13%).



Figure 51: Molar gas composition over time at the outlet of the reactor for both catalysts

# Table 47: Pyro liquids analysis with GC-MS (%wt)

Anthracene	11,6
7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	3,9
Naphthalene, 2-phenyl-	1,6
Fluoranthene	10,8
Pyrene	13,2
1,8-Diazacyclotetradecane-2,9-dione	5,9
7-Methyl-Z-tetradecen-1-ol acetate	1,5
1-Dodecanol, 3,7,11-trimethyl-	3,0
Benz[a]anthracene	2,9
Tetradecane, 2,6,10-trimethyl-	2,1
Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-ethyl-	3,7
Benzo[k]fluoranthene	4,2
Benzo[a]pyrene	2,9
Perylene	3,5



Figure 52: Catalytic performing

# Ni-UGSO catalyst pellets analysis for metals dispersion

- 2\*5 mm Ni-UGSO pellets (UGSO + Clay)
- Pellets have better dispersion of Ni in spinels
- Silicate-rich surface (MgO-SiO<sub>2</sub>-NiO).
- Higher availability of Lattice O<sub>2</sub> on the pellet.
- NiO/MgO s.s, enhances the dispersion & reduces average NiO crystallite size.





Figure 53: The pellets (1<sup>st</sup> row) and the metals mapping on the pellet (2<sup>nd</sup> row)



Figure 54: Performance of the catalyst

- Pellets performed better at higher pressure (5-10 atm)
- Lower ss is offset by better Ni dispersion
- Less coke formation over the pellet is attributed to silicate dispersion.
- The powder performs better at lower pressure (1 atm)



Figure 55: The SEM analysis validating better dispersion in pellets (bright spots are metallic species (Ni, Fe).



# FTS commissioning, protocol optimization and first results



t (min)	t (min) X <sub>co</sub>		Y <sub>C2-C4</sub>	Y <sub>C5+</sub>
	(%)	(%)	(%)	(%)
30	10,81	60	0,00	40,24
60	43,03	14	13,48	72,67
90	46,38	16	35,96	47,99
120	43,97	12	36,58	51,24
150	42,83	9	27,34	63,42
180	40,21	10	13,10	77,28
210	40,64	10	12,97	77,09
240	43,26	11	28,71	60,22
270	42,45	9	28,44	63,03
300	44,00	9	35,44	55 <i>,</i> 68

Table 48:	<b>Hydrocarbons</b>	selectivity	(6 h)
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Problem, delay or deviation: None

D. no	Title	Leader	Delivery date (planned)	Delivery date (actual)
2.7	ATP - Process configurations, conditions, products distribution, and quality and contamination content in all derived product phases): Commissioning completed; first tests with residual waste streams; a first full mass balance available	UdeS	M32	M32
2.8	CR&C - Process configurations, conditions, products distribution, and quality): Optimization and full mass and energy balances with powder and pelletized catalysts at atmospheric and high-pressure regimes	UdeS	M36	M36

M. no	Title	Leader	Delivery date (planned)	Delivery date (actual)
8	Commissioning of the BFB-ATP unit (delayed due to pilot (kg-kab) scale of the unit, biomass feeding proved more problematic than anticipated)	UdeS	M12	M26

9	BFB-ATP optimal operating conditions: mass and energy balances and HM fate evaluation	UdeS	M24	M30
11	Pyrolysis liquids catalytic cracking or hydrocracking): Replaced by reforming because cracking does not seem a convenient option	RECORD	M32	M32

Corrective actions undertaken: None

Key findings/achievements of the 1<sup>st</sup> reporting period are presented in the Box 2:

# 1<sup>st</sup> conversion route

- Establishment of a standardized protocol for the physical and chemical characterization of biomass samples from WP1. This protocol aims to ensure consistency, comparability, and reproducibility of results by aligning the methods used by each partner. As part of this effort, homogenization techniques, including particle size reduction and blending, were employed to create two homogenized samples of contaminated biomass for each species. All feedstock delivered by WP1 had been characterized (physical and chemical characterization).
- Development of simulation models predicting the fate of heavy metals and metalloids during gasification, and determining key performance indicators of the overall process. A thermodynamic model is used to estimate industrial-scale syngas compositions. The process model optimizes equipment interaction and overall design, increasing carbon efficiency to 40%.
- Pretreatment trials using GOLD feedstock. Trials using the feedstock of GOLD project had been carried where compared: TORWASH, slow pyrolysis and torrefaction. This activity is in progress. The results obtained so far for the simulation of the phase transition of the heavy metals and metalloids from the solid phase to the gas phase during EFG indicate that the release behavior of the heavy metals is similar in all investigated pretreatment methods. investigating gasification kinetics and release behaviour of heavy metals during gasification of the supplied contaminated Sorghum in its different pretreatment states.
- Special emphasis was given into thermodynamic modelling and experimental gasification trials to validate the release behaviour of volatile heavy metals. First entrained flow gasification trials using pretreated Sorghum were conducted. ETV-ICP-OES is chosen as the standard method for measuring heavy metal release from contaminated biomass due to its versatility and productivity. The major challenges were faced when feeding torrefied and TORWASHed material to the BabiTER test rig. Fuel is fed into the reaction tube through a dosing system at the top of the droptube reactor, ensuring a constant mass flow. However, when using torrefied or TORWASHed biomass, we encountered challenges with the dosing system due to the material's light and fluffy nature.
- Development a reproducible methodology to analyze biomass samples to be delivered to TUM in terms of composition. This analysis is crucial for determining the degree of contamination in the product gas depending on gasification process conditions. ICP-OES measurements on fuel, scrubber ash, and fly ash were conducted to specify remaining impurities in the syngas using contaminated biomass from other projects. These achievements mark significant progress in the study and bring the project closer to its goals.

# 2<sup>nd</sup> conversion route

- Rendering operational the kg-lab scale autothermal pyrolyzer and achievement of full mass balances and products characterization (pyrosolids, pyroliquids and pyrogases).
- Evaluation the efficiency of two types of catalysts in dry and steam reforming of a pyrogas surrogate. Parametric study over time-on-stream, O/C ratio and pressure.
- Commissioning and first FTS tests with a prechosen H2/CO ratio.
- Investigation on whether heavy-metals-ladden pyrosolids can be used as adsorbents.

# Work Package 3: Integrated sustainability assessment for bridging the gap

## Leader: RECORD; partners: ALL

Tasks	Title	Months	Leader	Participants	Status
3.1	Mapping selected contaminated lands and phytoremediation scenarios	1-36	WR	CRES, CTD, HUNAN, UdeS	On-going
3.2	Modelling selected value chains	6-36	RECORD	CRES, WR, AUA, TNO, TUM, UdeS, METE, IBFC, HUNAU, CTD	On-going
3.3	Integrated Sustainability Assessment	1-48	FCT	ICL, CRES, WR, RE-CORD	On-going
3.4	Task 3.4 Interpretation, strategy and recommendations	9-48	ICL	WR, FCT, CRES, RE-CORD	On-going

The main objective of WP3 is to carry out an integrated assessment to bridge the gap between the optimized phytoremediation solutions with energy crops (WP1) and the clean biofuel production with low ILUC risks (WP2). The specific objectives of WP3 were:

- To map the selected contaminated sites/lands of WP1 and develop scenarios, at European level, regarding the decontamination of polluted areas and the biomass potential, by using existing spatially explicit models.
- To set-up selected value chains by combining the selected contaminated sites, energy crops and conversion routes and to make a value-chains simulation model.
- To carry out an integrated sustainability assessment for the selected value chains including environmental, economic and social dimensions to provide an understanding of how largescale implementation of bioremediation activities in contaminated sites in combination with clean biofuel production can contribute the reaching of the SDGs.
- To develop, validate and analyse value chain, cross sector strategies between phytoremediation and clean biofuel production.

The work is being organized in four tasks. At the beginning the selected contaminated sites and their detailed characteristics will be mapped (Task 3.1) and this will be used to assess the upscale in potential of the pilot trial results of the selected energy crops (WP1). The mapping will be further translated into scenarios for Europe providing estimates of biomass and bioremediation cleaning up (amount of metals remediated) potentials. Biofuels production and the amount of metals recovered will be assessed in task 3.2, representing the full range of activities needed to produce biofuels and recovered metals (as co-products). Specific valuechains will be designed and analysed using a simulation model (developed for the project). The model will provide detailed representation of the whole chain setup in process flow charts, as well as the economic and logistical feasibility of the whole production chain (biomass and biofuel production in relation to land decontamination). An integrated sustainability assessment for the above-mentioned value-chains will be carried out including: LCA, s-LCA, LCC and a SWOT analysis (Task 3.3). In task 3.4 all the outcomes of the tasks 3.1-3.3 are integrated and translated into cross-sector strategies for phytoremediation and clean biofuel production. The strategies will analyse impacts and synergies for a number of global initiatives including Mission Innovation Challenge 4 and the Sustainable Development Goals.

## Task 3.1: Mapping selected contaminated lands and phytoremediation scenarios

**Objective:** To map the selected contaminated sites/lands of WP1 and develop scenarios, at European level, regarding the decontamination of polluted areas and the biomass potential, by using existing spatially explicit models

*Progress toward the objectives*: The activities performed so far in this task involve:

- 1. The mapping of the contaminated sites and their characteristics in the EU. This has resulted in the submission of Deliverable **3.1** (Extend location and contamination status and suitability for phytoremediation strategies of contaminated lands)
- 2. Development of approach to estimate the feedstock quantities that could be produced on these contaminated sites, predict how long it would take to remediate the soils, as well as, the relevant quantities of biofuel production possible.

# **Results and achievements**

Activity 1: Mapping contaminated sites and their characteristics

For the identification of areas affected by pollution a distinction was made between sites/ or rather areas affected by diffuse and by point source pollution:

1) **Diffuse pollution** (def. EEA: *Pollution* from widespread activities with no one discrete source, e.g. acid rain, pesticides, urban run-off, etc.)

alscrete source, e.g. acid rain, pesticides, urban run-on, e

2) **Point source pollution** (def. EPA: *Pollution from any single identifiable source* (e.g. *landfill, mine, industrial site*)

# Diffuse pollution

Diffuse pollution is ongoing in the EU and has already caused widespread emission of a range in pollutants including nutrients, organic pollutants and metals. Effects of diffuse pollution on water quality are well documented and effects of proximity pollution are known in various member states, however for soil pollution this is different. Current soil screening values (SSV's) are targeting point source pollution mostly whereas soils affected by diffuse pollution often do not exceed such SSVs. This does not imply that diffuse soil pollution poses no risk to the soil ecosystem or quality of food and fodder. A direct assessment of the current soil quality as affected by diffuse pollution is however not possible since SSVs currently in use are specific for individual member states. At EU level there is currently no agreed uniform screening level that can be used as a first approximation to allocate areas that need remediation. Therefore, in this project we did a risk assessment with a model that is applied based on specific risks in view of ecosystem health, food quality and water quality. This approach assumes that there is a connection between soil quality as expressed by relevant soil properties (for metals based on pH, organic matter, and clay) and the acceptable pollutant concentration at which the risk for either food, water or ecosystem is avoided (see Figure 57). The resulting regional critical concentrations in soil can be compared with actual concentrations to detect areas at risk.

> Soil properties (e.g. pH, soil org.mat., clay, oxides)



## Figure 57: Schematic approach of risk-based derivation of Soil Quality Standards

Critical concentrations of pollutants in soil can be related to critical concentrations in three environmental compartments: water, food and soil dwelling organisms. For each of these, three critical concentrations are available. For food, critical concentrations are based on WHO food quality criteria, for water critical concentrations based on drinking water criteria or aquatic organisms are available. For soil dwelling organisms critical concentrations in solution have been derived from laboratory studies for a large number of species. All of these can be converted to a corresponding critical concentration in soil that can be compared to current, measured concentrations in soil. For food and ecotoxicology the results are realistic in that the pollutant in the soil is in direct contact with either plant roots (uptake) or the soil dwelling organisms. For water quality the calculation is a worst-case approach since it would assume that water leaving the topsoil is in equilibrium with the groundwater. An alternative approach

for water is available but requires a substantial amount of both soil chemical and hydrological data both of which are not available at EU level.



Figure 58: Approach to calculate risk limits in soil in view of food safety (left) or ecotoxicity (right).

A major advantage of the risk-based approach as outlined in this chapter is that metal concentrations across member states can be compared using the same criteria considering specific risks for humans and the environment. Here risks are expressed in calculated critical concentrations in soil as related to the quality of food, drinking water and ecotoxicology (see Figure 58).

Maps of heavy metals are available for Pb. For Cu and Zn and have been used to construct spatially explicit maps at EU level. The calculation of critical concentrations of metals in soil beyond which the critical concentration in water or food is exceeded requires additional information on soil properties. Key properties include soil organic carbon, pH and clay content. Here we use the two largest databases currently available (LUCAS and SoilGrids) that do contain all required soil properties but do reveal however substantial differences in the spatial pattern and absolute level of soil carbon.

The differences in organic carbon led to markedly different critical concentrations for Cd, Cu and Pb. Most noticeable are the lower critical concentrations calculated based on the LUCAS database in Poland, Spain and part of Portugal and Italy. This also leads to differences in the level of exceedance at country level. In general, however, the exceedance risk of Cd critical concentrations appears to be limited as is the exceedance risk in view of ecotoxicology for Pb. For Cu and Zn the exceedance of the ecotoxicological critical concentrations is larger (see Figure 3). This is partly related to higher concentrations of Cu in areas in the Mediterranean countries and, for Zn, related to a combination of low pH and low soil carbon concentrations in among others Poland, parts of Spain and Portugal.

However, the difference in the exceedance when comparing results based on LUCAS data versus those based on SoilGrids suggests that these results need to be used with care (see Figure 59). Both uncertainty related to differences in basic soil properties as well as model uncertainty (not addressed further in this study) can lead to a substantial range in both the actual concentration of metals and soil carbon and also in the absolute level of the critical concentration.



Figure 59: Levels of exceedance of critical concentration of zink using Lucas and Soil grid soil data to asses it

Despite these shortcomings, the approach outlined here is a promising way to identify areas that are or can be at risk of pollution by the metals addressed in this study. It is however recommended to critically evaluate current soil databases to establish the reliability of maps derived from these databases. In addition, model uncertainty in many of the models used here can be reduced when more data become available. This specifically relates to models used to predict the concentration of metals in food. In contrast to data on soil, data on crop (product) quality and soils where these crops are grown are scarce. This is even more of an issue when considering many of the emerging contaminants that are or will become an issue in view of food safety.

## Point source pollution

Enquiry at JRC-ESDAC and consultation of the websites of EEA and Eurostat revealed that at present, there is no database of contaminated sites for Europe that carries spatially referenced information on area and contaminants. Because of lack of EU wide spatially explicit sources, another approach to mapping these contaminated sites was developed. In this study we we used data from Open Street Map based on properties of geographical objects, and to cross-check these areas with information on land cover and with recordings of contaminated sites in the literature and the internet. In addition, national registers of contaminated sites were also consulted for several countries in 2023, but with relatively little success. In addition polluted areas using other data than OpenStreetMap (OSM) was also applied particularly to land currently in use as agricultural land, that was previously used for irrigation with or treatment of wastewater, or for the disposal of sewage sludge.

The results of the contaminated sites identification show that the total area estimated in potentially contaminated sites due to military training activities, industrial activities, mining and landfills, of which less than 40% is sealed, amounts to 2,013,722 ha. This corresponds to 0.5% of the total area of the countries considered. In individual countries, the area of potentially contaminated sites identified on Open Street Map is at most 1% of the total surface area of the country. France, Germany and Spain have the largest total areas of all types of potentially contaminated sites, amounting to more than 150,000 ha in each of the countries.

The largest areas of potentially contaminated sites are in areas tagged on OSM as military sites (41%), industrial sites and brownfields (29%), quarries (25%) and landfills (4%). The land cover from CLC2018 in the considered OSM sites corresponded to the expected land cover for the larger part, i.e. forest and other semi-natural vegetation for military sites, industrial or
commercial units for industrial sites and brownfields, mineral extraction sites for quarries and dump sites for landfills. This supports the correct selection of the sites in OSM.

In sites where pollutants may occur, land cover consisting of densely built-up area, forest or other natural vegetation is considered unsuitable for phytoremediation as these types of land cover areas are either already vegetated by trees & shrubs or sealed by buildings and roads. This also applies to other land cover types unsuitable for cropping, such as beaches and dunes, bare rocks and water bodies. Land cover types in potentially contaminated sites with discontinuous urban fabric (e.g. mineral extraction sites) and with some form of agricultural land use are considered suitable for phytoremediation, provided that less than 40% of the area is artificially sealed (impervious). The total area of potentially contaminated sites with land cover types suitable for phytoremediation, and with less than 40% of the area sealed (impervious), amounts to 2,013,722 ha in the EU27 and UK. This area corresponds to 0.5% of the total surface area of these countries.

France, Germany, Spain and UK have the largest total areas of all types of potentially contaminated sites, amounting to more than 150,000 ha in each of the countries.

Land currently in use for agriculture covers between 7% (in military sites) and 20% (in landfills) of the area in potentially contaminated sites identified in OSM. These areas offer opportunities for phytoremediation through biomass cropping, because less effort is required for conversion of the land use than if the area would be covered by constructions or natural areas.

The Minerals4EU database features 42,731 mines in 22 EU Member States in 8 commodity groups considered of interest for phytoremediation. Of these, only 738 were found in proximity of potentially contaminated sites identified in Open Street Map. A large number of mines in the Minerals4EU database (20,137) was not identified in OSM, and of this number, only 204 are indicated as mines in the land cover class 'mineral extraction sites' in the Corine Land Cover database (class nr 7). These findings show that the databases with European coverage OSM and CLC2018 represent only a small part of the potentially contaminated sites, and that dedicated databases with spatial information on geographical objects associated with local contamination are required to map contaminated sites.

Commodities produced in mines, as specified per mine in the Minerals4EU database, were ranked according to the risk for human health and the possibility to reduce the risk in the site with biomass crops, and the likeliness of three modes of phytoremediation to manage the commodity. In 57% of the mines, commodities pose a high risk to human health and there is a need to remediate the contamination. For the commodities in this group phytoremediation might be possible to reduce the risk. In 40% of the mines, commodities do not pose a high risk for human health and the need to apply remediation is low.

Of the total of 20,708 mines observed in land cover classes considered relevant for phytoremediation, almost half (10,206) are located in areas with agricultural land use. These findings suggest a potential for options to use existing agricultural land in (former) mine areas for biomass crop production.

21% of the areas indicated as landfill in OSM is covered with some form of agricultural land, mainly by non-irrigated arable land and pastures, which may be relevant for phytoremediation using bioenergy crops, in case soil pollution is present. This requires an assessment at the level of these sites.

The total area of landfills in EU27 and UK on Open Street Map is 99,992 ha, overlapping with 88% of the total area of dump sites on CLC2018 (113,763 ha). This might suggest that not all landfills are identified in Open Street Map. However, there are also countries where the total area of polygons tagged as 'landfill' in Open Street Map is larger than the total area covered by dump sites on the CLC2018 map. Again, it confirms to the need to consult multiple spatial datasets for the purpose of mapping potentially polluted areas in or around landfills.

Brownfields may be considered a sub-set of industrial areas. In Open Street Map, 66,048 ha was tagged as both types of land use in the EU27 and UK, corresponding to 94% of the total

area of brownfields. For the generation of a map of potentially contaminated sites, the polygons tagged as industrial areas and brownfields on Open Street Map were therefore merged. This results in a total of 2,725,502 ha of industrial sites and brownfields, occurring in the EU27 plus the UK. Of this area 167,877 ha is in use by some form of agriculture (according to the overlay with CLC2018), which may be relevant for phytoremediation using bioenergy crops, in case soil pollution is present.

In the category of industrial sites, steel production sites with blast furnaces may deliver pollution risks through the emission of fine particles, but pollution of soils has not been demonstrated. It is however conceivable that vegetation might be used to stabilize particulate matter in the vicinity of the steel production sites and to prevent transport to other areas. 27 steel production sites with blast furnaces were mapped in the EU, with land cover in an area of 5 km around these sites. Considering only land cover types suitable for phytoremediation with <40% imperviousness, 60% of the area currently has land cover reflecting agricultural use. This might offer potential to deploy the area for stabilization of fine particulate matter by biomass crops.

Table 49: Total area (in ha) of potentially contaminated sites identified in Open Street Map, with land cover types relevant for phytoremediation and less than 40% imperviousness. Source data: OSM, CLC2018, HRL IMD2018.

Area (ha)	Type of potent	ially contamina				
Country	Military	Industrial &	Quarries	Landfills	Total	Total area
Austria	17 551	brownfields 4 157	8 / 23	027	area 31.058	8 387 900
Austria	17.551	4.137	0.423	927	31.058	0.307.900
Belgium	13.777	11.208	4.948	739	30.672	3.052.800
Bulgaria	9.973	17.400	30.418	2.462	60.253	11.037.000
Croatia	10.217	3.679	2.352	708	16.956	5.659.400
Czech Republic	42.335	14.581	21.100	2.504	80.520	7.886.800
Denmark	21.218	9.711	4.306	181	35.416	4.292.400
Estonia	8.538	3.733	7.523	3.163	22.957	4.522.700
Finland	48.932	13.971	14.586	3.844	81.333	33.844.000
France	126.163	78.260	55.948	10.164	270.535	63.318.660
Germany	118.826	65.857	84.051	18.652	287.386	35.737.600
Greece	15.373	5.904	25.319	2.325	48.921	13.204.900
Hungary	14.785	31.178	9.151	2.311	57.425	9.301.100
Ireland	2.253	4.924	8.605	821	16.603	6.979.700
Italia	36.462	43.963	37.393	5.967	123.785	30.207.300
Latvia	5.720	4.973	3.287	180	14.160	6.457.300
Lithuania	5.207	12.962	5.281	146	23.596	6.528.600
Luxembourg	21	355	197	201	774	258.600
Malta	10	55	280		345	31.540
Netherlands	11.026	19.076	810	783	31.695	4.154.000
Poland	56.571	44.248	36.234	11.003	148.056	31.267.900
Portugal	9.299	9.873	9.976	1.094	30.242	9.222.600
Romania	16.755	80.607	22.453	5.401	125.216	23.839.070
Slovakia	14.641	12.640	3.543	1.302	32.126	4.903.500
Slovenia	1.177	737	863	61	2.838	2.027.300
Spain	90.160	43.326	49.973	4.588	188.047	50.594.400
Sweden	39.404	17.848	10.261	2.051	69.564	43.857.400
United Kingdom	97.519	36.874	42.057	6.793	183.243	24.361.000
Total area	833.913	592.100	499.338	88.371	2.013.722	

# Activity 2: Approach to estimating biomass produced and biofuel potential and bioremediation time and potential

In this activity work has started on:

1) Making a partial analysis to estimates the potentials in EU of contaminated areas that could be remediated, feedstock quantities that could be produced, and the relevant amounts of biofuel production.

2) Make predictions of the rate at which pollutants are removed from soil and how long it would take to achieve specific target levels.

This work requires the integration of information generated in WP 1 and WP3 with the activities in WP3 (Figure 4).



Figure 60: Approach and WP links to mapping biomass and biofuel potentials from contaminated lands

The assessment of potentials of biomass and biofuels is strongly connected to upscaling results from WP1 on yields. However, the field trials are not providing sufficient information to upscale the potentials at EU wide level. So, in WP3 also additional information on yields and related contaminant uptakes is collected from literature and other studies. With this information the next step is now being prepared which is predicting the biomass yields and the **rate at which pollutants are removed from soil and how long it would take to achieve specific target levels.** For this the approach is followed presented in the diagram in Figure 61. Field trial information from WP1 will provide information on yields, pollutants uptake in combination with different soil and climate characteristics. Literature is reviewed to obtain more of this information. This is used to design the transfer model. This model is then applied spatially to the mapped information on diffuse pollution levels in the EU to come to final predictions of biomass potentials and pollution removal times. For the assessment of the biofuel potentials information is obtained from the WP2 activities on biomass to biofuel conversion rates.



Figure 61: Data and information sources for predicting rate of pollutant removals in time and place for diffuse pollutions.

*Problem, delay or deviation*: Deadline of Deliverable D3.1, originally set in M18, has been postponed to M24. There are 3 reasons for this:

- Obtaining access to certain JRC data from LUCAS on contaminants and also soil organic carbon from LUCAS 2018 in troublesome. We do not understand entirely why, but WR is also having this trouble within the context of the ETC-topic Centre land use. Even the EEA is not getting full access to data from LUCAS.
- 2) By extending the deadline we are able to also include a review of national data on contaminated sites
- 3) We preferred to collect internal comments from partners to further improve the report

*Corrective actions undertaken*: Some of the pollution concentration data were used from Gemas instead of from LUCAS.

D. no	Title	Leader	Delivery date (planned)	Delivery date (actual)
D3.1*	Extend location, contamination status, modelling and suitability for bioremediation strategies of contaminated lands (online tool).	WR	M18	M24

\*This deliverable will be updated in M44.

# Task 3.2: Modelling selected value chains

**Objective**: To set-up selected value chains by combining the selected contaminated sites, energy crops and conversion routes and to make a value-chains simulation model

#### Sub-task 3.2.1: Value chains configuration

**Objective:** Objective of this task is to select at least 16 complete value chains - that will represent selected case studies – from the combination of:

- the 4 crops (considering also the results of the various phyto-remediation techniques tested)
- the 8 contaminated sites (representing specific soils, types of pollution and climate conditions).
- the 2 conversion pathways (comprising also the three different possible solutions considered for pre-treatment in the EU process and the two proposed final conversion steps for the Canadian process)

**Progress toward the objectives**: Based on the preparatory work carried out during the first reporting period, a methodology for the **selection** of the most suitable and interesting Value Chains (VCs) was prepared.

**Specific selection criteria** were defined and discussed at several project's meeting, to reduce the number of value chains that will be further analysed and modeled in GOLD: from the total possible 165 combinations down to the selected 16 VCs.

15 VCs are related to EU countries and involve the 1<sup>st</sup> thermochemical conversion route. One more Value Chain is being developed, considering the 2<sup>nd</sup> conversion route that is being developed by UDES in Canada; it is modeled considering the use of locally sourced contaminated feedstock (switchgrass), further converted to liquid biofuels following the autothermal fluidized-bed pyrolysis conversion process.

Within this framework, CRES participated to the preparation and circulation of **questionnaires for WP1 and WP2 partners**, to gather qualitative and quantitative information on soil and crops characteristics, phyto-remediation strategies, cultivation inputs and costs and on process technologies.

# Main results, achievements

The methodology to narrow down the number of selected VCs was defined and applied to the network of crops, case studies (thus different soil types) and conversion processes. It considers a general Value Chain as composed by two main parts:

- The agricultural part: a combination of soil type, cultivated crop and treatment used; the selection criteria is the total amount of pollutants uptake in the biomass crop per hectare per year (g/ha/yr) and the outcome is the best performing (higher uptake) combination of crop and treatment for each soil type. The results are based on the five contaminated sites developed in Europe, since only for these case studies two full set of field data (related to two agricultural years) were made available by M32, while just one year field data were available for the Chinese case studies. The Indian case study started in only on M26 of the project, due to Indian partner replacement and couldn't provide data for this activity. Thus, five different combinations of soil, crop and treatment are provided.
- The biomass-to-biofuels conversion part: all the three combinations of pretreatments and final conversion process of the 1<sup>st</sup> conversion route (torrefaction, Torwash and slow-pyrolysis combined with gasification and syngas fermentation to ethanol) were considered for the evaluation, since each of them could provide specific advantages. Thus, three different combinations are provided as complete conversion pathways, from raw biomass to biofuel (and biochemicals).



Figure 62 below summarizes the methodological approach so far described:

#### Figure 62: Visual summary of the methodology developed for Value Chain selection

A set of spreadsheets were prepared, gathering data from WP1 partners on the yield and pollutants uptake of each cultivated crop (considering each type of treatment) in each test field, for the first two agronomical year. Such database was used to for the selection of the **best** 

performing combination of crop and treatment for each soil type, using the following methodology:

- All the rest being equal, the **best performing combination of crop and treatment** is the one that obtains the highest **total pollutants uptake (g/ha/yr)**, averaged across the two cultivation years.
- In cases of similar levels of **total pollutants uptake (g/ha/yr)**, average yield is considered, since it is the main economic driver and the enabler of higher biofuels production per ha.

The results are presented in the table below.

Table 50: Best performing combination of crops and treatments for each considered Case Study

Coco Study	Best performing	Averaged yield	Averaged total pollutants uptake (g/ha/yr)						
Case Sludy	crop + treatment	t/ha/yr (d.m.)	Pb	Zn	Ni	Cd	As	Sb	Cu
Italy	Sorghum - B2+M	18.0		985					149
France	Sorghum - Control	14.8	138	1,510		121			
Greece - Kozani	Sorghum -B2+M	30.0	2,521	12,198	26	746	23	3	
Greece - Lavrion	Sorghum -B2+M	21.7	1,665	6,585	24	473	41	18	
Poland	Sorghum -B2	21.1	145	4,370		277	3		

**Integrated and distributed solutions** for conversion process plants are being evaluated by Task 3.3, with the support of Task 3.2 model.

On December 2023 Deliverable D3.3 was submitted, providing an extended report on activities and outcomes.

D. no	Title	Leader	Delivery date (planned)	Delivery date (actual)
D3.3	Value chain configurations	CRES	M30	M32

D. no	Title	Leader	Delivery date (planned)	Delivery date (actual)
M15	Value-chains selection (it was achieved at the Bologna meeting; 8/6/23)	CRES	M20	M26
M18	Description of the value-chains to feed task 3.3	CRES	M24	M26

Problem, delay or deviation: No deviation or obstacles to report for T3.2.1

#### Corrective actions undertaken: None

# Sub-task 3.2.2: Modelling selected value chains (M12-36)

During the 2<sup>nd</sup> reporting period, the general model already developed has been tailored to the specific characteristics of the VCs; in order to do so, a data gathering campaign was conducted, using both surveys and direct interviews to WP1 and WP2 partners.

**Detailed questionnaires for WP1 and WP2 partners** have been prepared and circulated to gather qualitative and quantitative information on soil and crops characteristics, phytoremediation strategies, cultivation inputs and costs and on process technologies (i.e.: performance, costs, plant size, expected future developments, ...). Collected data is used as input for many WP3 Tasks activities, among which:

- Pollutants uptake modelling (T3.1),
- Value Chain description and Techno-Economic Analyses (T3.2, T3.3),
- Environmental Impact Assessment, LCA, S-LCA (T3.3).

The collected data was discussed and validated during an internal Workshop, carried out during Athens Project Meeting. Figure 63 below summarized the iterative process for data gathering, discussion and validation.



# Figure 63: Summary of the activities related to VCs data gathering through questionnaires circulation within WP1 and WP2 partners

The various phases of a value chain were modeled, following the overall VC structure reported in Figure 64 below. The **agricultural phase model** reports on crop yields, pollutants uptake and on the agricultural inputs needed (for costs and GHG emission evaluations) for each of the considered Case Study. The **conversion phase model** comprises all the evaluated conversion processes; it provides with mass and energy balances for different sizes of the plants, with biofuel yields and with economic data such as CAPEX and OPEX for successive techno-economic assessments. Meetings were organized with WP2 partners, and specifically CERTH, to define **expected pollutants fate** in the conversion processes.



# Figure 64: Overall structure of T3.2.2 VC model, highlighting inputs, outputs and section modules (section D is reported in purple)

A **basic logistics model** was developed - to be further developed by Task 3.1 – to support the evaluation of costs and environmental impacts, considering: a)The type and size of the mean of transportation, b) The distance of transportation and c) The type of payload (either raw biomass or intermediate bioenergy carrier).

## Main results, achievements

The survey conducted among WP1 partners regarded qualitative topics, needed to define the overall framework of the agricultural activity, such as:

- cultivation, harvesting and preprocessing methods used both in the case study and in a standard situation,
- biomass calendar availability in the considered Agro-Ecological Zone
- potential impacts on biodiversity
- regulation in place regarding soil and biomass contamination

The survey regarded also a quantitative assessment of data needed for VCs modeling and analysis (see Figure 65):

- Soil and site characterization, including the initial soil pollution levels
- Definition of the inputs needed in the various agricultural phases (cultivation, harvesting, eventual on-site pre-processing), such as diesel, fertilizers, pesticides, as well as the considered treatments (Mycorrhiza, Lonite, Siapton), and the related costs (where available)
- Harvested biomass characterization: yield, moisture level, pollutants uptake, for the two investigated agricultural years and for the various treatments used.

Generally, the answers were provided timely and when needed the surveys were integrated by face-to-face interviews on specific subjects of interest. Most of the requested data have been collected in and analyzed within the reporting period.

A similar approach was used also with WP2 partners, to model the conversion processes. The survey regarded topics such as plant typical mass and energy balance, expected size, current and expected TRL, economics (whenever publicly available, otherwise integrated with literature) and potential integration with external processes and activities. Whenever data on commercial scale processes was not directly available (i.e. as in the gasification + syngas fermentation case), additional research on existing literature on the topic was carried out. EU-based conversion pathways were modeled, and the outcome is being discussed with WP2 partners. Figure 66 reports some of the process factsheets prepared for a specific VC, showing the mass and energy flow structure and the main operating parameters considered, such as: *size of the plant, operating time in h/yr, intermediate bioenergy carrier / final biofuel yield, auxiliary power needed to operate the plant and financial and economic variables considered.* 

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#### Figure 65: Example of quantitative survey answered by WP1 partner



## Figure 66: Recap factsheets on modelled GOLD conversion processes

The model inputs and outputs were discussed with the other WP3 partners, that are using the model results for further analyses, such as:

- LCA and S-LCA assessment
- Sustainability assessment of the VCs towards SDGs.
- Techno-economic and environmental VCs assessment.
- General VCs optimization, i.e. in terms of total costs and thus considering also the logistics impacts. Under this perspective, the evaluated sizes of the intermediate process plants were tuned to match final conversion plant size, in order to evaluate both centralized and decentralized scenarios (see Error! Reference source not f ound. 67 below).



#### Figure 67: Description of the three possible logistics model for the biomass VC

**Deviations, obstacles and which was the mitigation plan:** No deviation or obstacles to report for T3.2.2

D. no	Title	Leader	Delivery date (planned)	Delivery date (actual)
M16	Setting the model for the value- chains	RECORD	M24	M26

# ► Task 3.3: Integrated Sustainability Assessment

**Section B of model** is dedicated to all the considered thermo-chemical conversion processes. It uses: economic data such as plant CAPEX and OPEX and their expected correlation with TRL; expected TRL evolution with time; mass and energy balances, including information on pollutants fate; GHG emissions and water use (if appropriate). It provides as outputs information on contaminants uptake in various process streams; biofuel/IBC overall yields; external energy requirements and, more in general, data on energy performance; data needed for environmental, LCA, S-LCA, LCC, SDGs performance assessment; expected Minimum Fuel/IBC Selling Price (MFSP) for a specific biomass price at the plant's gate.

**Section C of the model** is dedicated to the evaluation of the final use of IBCs and biofuels produced by the processes described in Section B. It provides as output data needed for environmental, LCA, S-LCA, LCC, SDGs performance assessment and allows for cost and performance comparison with either fossil or non-fossil reference products. Simplified mass and energy flows, as well as process models are prepared; main objective is to evaluate the impact of the new feedstock from GOLD VC on the process.

**Section D of the model** deals with logistics; it calculates logistics costs and environmental performances, depending on the distance between biomass production site(s) and conversion plant(s). It uses spatialized data to evaluate both centralized and decentralized solutions. Among the inputs there are logistic unitary costs and emissions, which depend on the type means of transportation, thus on the type of biomass, IBC or final product transported.

Moreover, inputs and constraints related to the conversion process from Section B are used, i.e. minimum/maximum plant size and the related plant costs and feedstock needs. Plant size define the corresponding area needed to fulfill feedstock needs; then, three different logistics model can be evaluated to find the optimal solution:

- **Single-plant centralized conversion process:** both pre-treatment and conversion units are in the same location, one unit covers the complete VC/the selected area.
- **Multi-plant centralized conversion process:** both pre-treatment and conversion units are in the same location, but several units are used for the complete VC/the selected area.
- Decentralized pre-treatment and centralized conversion process: several smaller pretreatment units are distributed across selected area, while the conversion process unit is bigger and possibly barycentrically located with respect to the pre-treatment units.

Figure 41 below summarizes the three different logistics model; barriers from contaminated material handling have to be evaluated.



#### Figure 68: Description of the three possible logistics model for the biomass VC

Figure 69 below reports preliminary results on modelling activity carried out on slow-pyrolysis pre-treatment plant from RE-CORD. An Excel-based model has been prepared for the calculation of mass and energy balances of the plant; the model for the evaluation of the fate of the contaminants is currently under definition, while preliminary tests on polluted biomass are being carried out.



Figure 69: Slow pyrolysis Spyro plant process diagram (a), simplified mass and energy flow chart (b) and techno-economic analysis model spreadsheet (c)

Problem, delay or deviation: No deviation or obstacles to report for T3.2.1

Corrective actions undertaken: None

# Task 3.3: Integrated Sustainability Assessment

**Objective**: To carry out an integrated sustainability assessment for the selected value chains including environmental, economic and social dimensions to provide an understanding of how large-scale implementation of bioremediation activities in contaminated sites in combination with clean biofuel production can contribute the reaching of the SDGs.

# Sub-task 3.3.1 - System boundaries and settings (M1-M12)

The aim of Task 3.3 - Integrated Sustainability Assessment, is to perform an integrated sustainability assessment for selected value chains taken from the GOLD project, including the environmental, economic and social dimensions of sustainability. Indeed, the implementation of the selected value chains proposed by the GOLD project can have significant impacts on environment, economy and society. As a result, it is a major aim of WP3 to maximise the impact of GOLD through provision of objective information regarding all important sustainability aspects (covering environment, society and economy) of the value chains using scientific, transparent and reproducible methodologies. Modelling techniques such as life cycle assessment (LCA), life cycle costing (LCC), social life cycle assessment (S-LCA) and SWOT analysis will be used to determine the impacts on sustainability, followed by integration (Figure 70). Interpretation of the results obtained in this assessment will allow to identify the implications from the solutions proposed (the most promising value chains) from a

consequential perspective, including cost effective analysis and the key-sustainability indicators. Information retained will allow identifying which parameters are of particular relevance and which options for improvement exist to feed in task 3.4 (Interpretation, strategy and recommendations). Sustainability assessment is a comprehensive topic which can be interpreted and applied in different ways depending on the project goals.



Figure 70: Life Cycle Sustainability Assessment (LCSA), a combination of methods to evaluate environmental (LCA), economic (LCC) and social impacts (S-LCA) across the whole life cycle of products. [adapted from Contactica. https://contactica.es/en/]

In this 2<sup>nd</sup> reporting period Deliverable 3.5 - Setting and definitions for the integrated sustainability assessment - 1st version, and D3.6 - Setting and definitions for the integrated sustainability assessment - final version, were successfully submitted, respectively D3.5 on 09.12.2022 and D3.6 on 04.07.2023. Both deliverables, D3.5 and D3.6 correspond to the description of work of task 3.3 Integrated Sustainability Assessment, which is part of WP3 - Integrated sustainability assessment for bridging the gap of the project GOLD, and establishes the settings and definitions that will be used by several tasks of WP3 that will be studying the sustainability of the different value chains selected from the GOLD project, to guarantee a consistent evaluation throughout the assessment. D3.5 report – 1st version of "Setting and definitions for the integrated sustainability assessment", was concluded in December 2022. The final report (D3.6), concluded in the beginning of July 2023, is the final version of "Setting and definitions for the integrated sustainability assessment" and was based on D3.5 and on the discussions that were held in the meeting of the Gold Project, in Bologna, in June 2023.

Figure 71 shows the Integration of task 3.3 in WP3 and how the "Setting and definitions for the integrated sustainability assessment" will be the support to other sub-tasks within task 3.3.



Figure 71: Integration of task 3.3 in WP3 (SWOT: Strengths, weaknesses, opportunities, threats)

#### Main results, achievements

In the task, the definition of all system boundaries and settings such as geographical and timerelated coverage and the setting of reference systems (conventional-fossil based reference systems and biomass-based), was presented. As the GOLD project works on many different aspects of industrial crop cultivation techniques to improve the phytoremediation action, and with different processing options, to retrieve contaminants, along with the production of biobased products and/or bioenergy, since the obtained products and co-products will be suitable for various applications, different value chains from GOLD project should be analysed. In the assessment, a cradle-to-grave approach will be applied and to each selected value chain, all stages, cultivation, harvesting, pre-treatment, processing, end-of-life treatment and final disposal, will be evaluated. The conventional reference systems shall represent the conventional value chain that would most likely be replaced first, due to economic and political boundary conditions when additional bio-based products as suggested by the GOLD approach will be used. Within the GOLD project, the conventional reference systems will be specified in task 3.2 within the selection of GOLD value chains and the gualitative description of the most appropriate technologies for conversion into promising intermediate and end products. The cropping systems can be also compared with conventional soil treatment systems, to understand the impact of the phytoremediation action. Geographical coverage for the sustainability assessment is focused on European countries, and the differing growing conditions, yield potentials and cultivation practices in Europe will be taken into account. Considering the immature state of the production of bio-based products from contaminated land, the year 2030 is set as a reference, so that a more representative picture of the investigated system's potential to achieve the goals can be achieved. Within the GOLD project, three reference units can be applied. In the case of the biomass used as biofuel, a typical output-related functional unit could be the provision of 1 MJ of fuel energy. If the focus is set on the input, 1 ton oven-dry biomass could be used as reference unit. As land is a main factor limiting the production of bio-based products in Europe, referencing the results to 1 hectare is also a suitable functional unit to be applied in the GOLD project. Identification of the environmental burdens, the economic benefits and the social welfare along the different individual processes or life cycle steps will be recognized and mitigation or minimization options will be named. Ultimately, the integrated sustainable assessment will provide info on the findings of the GOLD project to key stakeholders, i.e. regional authorities and policy makers, industrial and RTD establishments, farmers cooperatives, governmental bodies, among others, and will alert the recipients on which policies should be developed.

The conventional reference systems shall represent the conventional value chain that would most likely be replaced first, due to economic and political boundary conditions when additional bio-based products as suggested by the GOLD approach will be used (Figure 72).



Figure 72: Sustainability assessment within the GOLD project. The GOLD bio-based products are compared to conventional reference products, both along the whole life cycle

Within the GOLD project, the conventional reference systems will be specified in task 3.2 within

the selection of GOLD value chains and the qualitative description of the most appropriate technologies for conversion into promising intermediate and end products. In the report it was identified that the cropping systems can be also compared with conventional soil treatment systems, to understand the impact of the phytoremediation action (Figure 73).



# Figure 73: Sustainability assessment within the GOLD project. The GOLD phytoremediation actions are compared to conventional remediation processes, both along the whole life cycle.

# Problem, delay or deviation:

The Deliverable **D3.6**, that was scheduled for M24, this presented a delay from month 24 to month 26. This delay was due to the fact that the yearly meeting of the GOLD project took place in the beginning of June 2023 (M26). During this meeting, discussions that were held, feed the final version of D3.6, that was submitted in the beginning of July 2023. This delay did not preclude any problems in terms of the planning of remaining project activities related with Task 3.3.

# Corrective actions undertaken: None

D. no	Title	Leader	Delivery date (planned)	Delivery date (actual)
D3.6	Setting and definitions for the integrated sustainability assessment - Final version	FCT	M24	M26

# Sub-task 3.3.2- Environmental assessment (M13-M42)

# Activities carried out in the 2<sup>nd</sup> reporting period

FCT NOVA is carrying out the D3.7 - Environmental impacts associated with the value chains. This deliverable is schedule to M42, and is in progress based on the definition of the selected value chains, on results obtained from WP1 and WP2 and on info provided from Task 3.2. This study will include the life cycle environmental impact assessment (LCEIA) of the cultivation of the four crops studied in the GOLD project (miscanthus, switchgrass, biomass sorghum and industrial hemp), that evaluates the local and site-specific environmental impacts associated with the cultivation of these lignocellulosic crops in contaminated soils. This is being conducted addressing local environmental impacts with a generic (life-cycle) approach, which are not yet being considered in state-of-the-art LCAs. It covers impacts such as on fauna and flora, on soil and on water and uses elements from an environmental impact assessment (EIA), a standardized methodology for analyzing the potential environmental impact of proposed projects. The study on LCEIA is being finalized based on the data from 1st years of the project. It will be updated until M42 with new data from WP1. The study will include also LCA, which will address the environmental aspects and potential environmental impacts of the selected value chains products throughout its life cycle, following the guidelines of ISO 14040/14044.

**Main results, achievements:** The study on LCEIA s being applied to the cultivation phase of the four different lignocellulosic crops in contaminated soils of Europe, using environmental impact assessment (EIA) protocols. Different categories are being studied: fertilizers and pesticides related emissions, impact on soil and water resources and biological and landscape diversity. Each of these categories comprises different indicators, e.g. erosion, nutrient status, etc, which are being evaluated in a quantitative manner. A qualitative scoring is being used when there is a shortage of quantitative data. In this qualitative assessment, each crop and process is scored for a set of pertinent parameters, through expert judgment and literature review. In the study, we analysed the behavier of the different crops in the contaminated soils and also the behaviour of the crops when treated with Mycorrhiza (M), Biostimulants (protein hydrolysates, B1; Fulvic/humic acids, B2), or combined systems (M x B).

The analysis of the results taken from WP1, show that yields are affected by the level of contamination in the soil, but that treatments applied can improve those yields. The reduction in yield affect parameters related with the sustainability impact studies (Figure 74).

# ↓ Yields

- $\downarrow$  GHG emissions savings
- Chemical composition
  - increment of [N, P, K, etc] in the biomass
  - the plants may not reach a mature status
- Iand use to obtain the same energy output
- $\uparrow$  need for fertilizers per unit land
- I shelter for animals
- ↑ energy production costs
- GHG emissions reduction costs

#### Figure 74: Effects of lower yields on parameters related with the sustainability impact studies.

In terms of parameters related with fertilizer and pesticides related emissions, impact on water resources, and impacts related with biodiversity and landscape, show that there are differences among the different crops being studied. The perennial grasses (miscanthus and switchgrass) presented better results due to the perennial character of the crops. Less need on fertilizers and water, higher cover of soil, improves the environmental output of those crops, compared with hemp and sorghum. Yet, crop management options can be applied to reduce the impacts related cropping systems (namely those related with fertilizers and pesticides application). Impacts on soil are the most interesting to study, once the outputs can bring new vision of how to perform phytomanagement options. Indeed, introducing a vegetative crop in a contaminated soil bring several opportunities related with the soil quality (Figure 75).

# *Opportunities...Soil quality*

- → Introduction of a vegetative cover
  - ⇒ reduction of erosion potential
  - ⇒ organic matter incorporation in the soil
    - ⇒ soil structure/SOM improvement
    - $\Rightarrow$  carbon sequestration
  - Phytoremediation

⇔

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restoration of soil properties

Figure 75: Effects of lower yields on parameters related with the sustainability impact studies.

Figure 76 shows the opportunities linked with soil quality when crops, such as the perennial grasses, miscanthus and switchgrass, are cultivated in contaminated soils.



Figure 76: Opportunities linked with soil quality when crops, such as the perennial grasses, miscanthus and switchgrass, are cultivated in contaminated soils.

As observed in Figure 77, when comparing the effect of the production of miscanthus and switchgrass in contaminated soils with the soil without vegetation, it is possible to see that the impact is being reduced. This way, the incorporation of a vegetative crop contributes to the reduction of impacts related with soil quality, namely, pH, SOM, structure, remediation and waste generation, and erosion. In terms of erosion, miscanthus even presents a better result than switchgrass due (Figure 14) to the amount of underground biomass being produced.



Figure 77 shows the impact of certain treatments in the soil quality index.

Figure 77: Impact of certain treatments in the soil quality index

**Deviations, obstacles, mitigation plan:** Regarding the work related with D3.7 - Environmental impacts associated with the value chains, there is no deviation from the workplan.

## Sub-task 3.3.3 - Life-Cycle-Analysis (M13-M42)

Life-Cycle-Analysis (Leader: ICL, partners: FCT) M13-M42 In the Life Cycle Cost assessment (LCC) the costs will be determined for value chains whose configuration has been economically optimised. Key performance indicators (KPI) will be estimated for each value chain, such as costs and profitability. KPIs will be compared to a baseline where degraded lands would remain unused and where fuels/energy commodities would come from fossil (LCC).

In the Social life cycle assessment (S-LCA), a life cycle inventory for selected S-LCA indicators (e.g. number of jobs created) linked to impact categories (e.g. local employment) related to the main stakeholder groups (worker, consumer, local community, society and value chain actors)

will be evaluated, along with the dimension related with the restoration of the contaminated land.

These sub-tasks focus on the social and economic analysis of the value chains. The Value Chains will be partially aggregated into groups with specific similarities. These Value chains will be assessed comparing them with baselines where the land undergoes conventional remediation (i.e. dig and dump); also against fossil fuels production and use.

The deliverables have been delayed due to a change in staff at Imperial College but this will be submitted by Month 24.

# Activities during the 2<sup>nd</sup> reporting period

The economic assessment will aim at providing an estimate of project costs for the supply chains giving an idea of profitability and whether the proposal is viable enough for a more detailed assessment to be carried out (see Hall, 2019 for full description and analysis). As with the other assessments, options will be considered with different levels of complexity and cost, and product markets. The main activity has been focused on finalising the methodology described below and gathering the data from WP1 and 2.

The economic assessment will be carried out at two levels. Firstly, a microeconomic assessment undertaken to provide a Life Cycle Costing (LCC) considering capital and operating costs over the projected lifetime of the production plant. A sensitivity analysis will be conducted focusing on the selected countries.

A database will be set for the economic analysis.

The LCC will be assessed developing supply chain optimization models.

Supply chain optimization methods based on Mixed Integer Programming (MIP) are powerful in design of industrial systems since they can support the identification of cost-efficient (or most profitable) configurations and operations. These methods have been widely used for the improvement existing industrial system configurations, for the design of totally new infrastructures, as well as for the integration of novel technologies into existing systems.

The design of biofuel systems is a key application of supply chain optimization methods. In fact, this requires the optimization across each value chain step to have them working cooperatively and optimally in the geographical, political, and social context where the system will be operating. Research on modelling and optimization of biofuel supply chain has focused on first generation (Akgul, Shah, and Papageorgiou 2012; Kostin et al. 2012), second generation (Giarola, Zamboni, and Bezzo 2012; Panteli, Giarola, and Shah 2018; Dunnett, Adjiman, and Shah 2008; Neill et al. 2022), and hybrid biofuels.

The major controversies in the scale-up of biofuels have come from direct or indirect competition in the use of lands, otherwise allocated to food and feed crops. It has become of paramount importance for preserving food security, maintaining the destination of agricultural areas for food/feed uses (avoiding direct land use change), but also to reduce a diverse allocation of land as a side effect of land exploitation for biofuels (avoiding indirect land use change). Biofuels can be produced from feedstocks that avoid food and feed crop displacement through (i) yield increases due to improved agricultural practices or (ii) cultivation on areas not previously used for crop production, for example, unused, abandoned or severely degraded land or (iii) combining cover crop rotations with biomass feedstock production (Panoutsou et al., 2022). Recently, Dauda et al. (2024) proposed an optimization model for low-indirect land use change biofuels, focusing on yield enhancement and crop rotation.

In this project, a supply chain optimization model will be developed for the optimal design of 5 value chains, for the identification of the best performing configurations optimizing biofuel production at a minimum cost or at a maximum profit.

A mixed integer linear programming model for biofuel production with the purpose of identifying the most efficient production routes. The model will incorporate:

- crop availability, seasonality, as well as provision costs
- crop mass loss
- storage constraints and costs
- technological route yields, capital costs, and operating costs
- product and by-product market.

In particular, the inputs to the value chain model include a set of crops/crops sequence to be planted, a set of available land, fertilizer consumption, price of crops, feedstock production cost, crop yield, feedstock conversion technological types, feedstock conversion costs, feedstock conversion yields (into biofuel, by-product, and aggregate pollutants), biofuel price, by-product price.

The model output will be the design of the optimal value chain configuration, which includes

- intermediate, biofuel, and by-product rates
- feedstock rates
- amount of feedstock stored
- amount of intermediate stored
- amount of feedstock transported from crop sites to intermediate conversion sites
- amount of intermediate transported from intermediate to final conversion sites
- number, size, and location of intermediate conversion plants
- number, size, and location of final product conversion plants
- amount of land used
- average feedstock transport distance
- average intermediate transport distance
- total system cost with breakdown by value chain echelon
- total system profit
- total greenhouse gas emissions with a breakdown by value chain echelon

The value chain is composed of

- land phyto-remediation
- feedstock provision, transport, and storage
- feedstock conversion and pollutant segregation
- biofuel use

A schematic is represented in Figure 78. The methodology will be based on data obtained from the case study.



## Figure 78: Value chain schematic

Although the data will be obtained from the case studies, the model will not include just the case study area, but will focus on the surrounding area of each identified case study. Logistics will be modelled considering abstract configurations, as shown in Figure 79. Priority will be given to a decentralised pre-treatment configuration.



Figure 79: Possible logistics models

# Case study approach

The capabilities of the proposed systematic approaches were demonstrated using industrial case studies as a reference, aiming to facilitate market uptake of European feedstocks. Five European case studies will be modelled

- AUA Lavrion, located near a mining/metallurgical site, with presence of contaminants such as Pb, Zn, Cd, Ni, As
- CRES Kozani, located near a lignite mining, with presence of contaminants such as Ni
- UNIBO Chiarini area, with presence of contaminants such as Zinc (Zn), Nikel (Ni), Lead (Pb), Tin (Sb)
- UMCS Lublin, located near a waste deposit with presence of contaminants such as Zn, Pb, Cd, As
- JUNIA Metaleurope, a former smelter site contaminated mostly by Cd, Pb and Zn

The sites are located as shown in **Error! Reference source not found.** The value chain approach will consider a bigger area surrounding the selected case studies, to support the biofuel production plant operation. The approach to the modelling of logistics will be more abstract rather than being a detailed mapping of the logistical nodes.



Figure 80: Site mapping

Different methods are being used to assess them considering the social Life Cycle assessment. The SLCA framework is based on four phases of the LCA ISO standard (ISO, 2006). The Goal and Scope and Interpretation stages correspond to those used in LCA, whilst the inventory stage is based on a stakeholder approach that incorporates impact categories, subcategories, and indicators (Figure 81), where a stakeholder category comprises a cluster of social actors that have shared interests due to their proximate relationship to the product system being assessed (UNEP/SETAC, 2009).

Stakeholder categories	Impact categories	Subcategories	Inv. indicators	Inventory data
Workers	Human rights			
Local community	Working conditions			
Society	Health and safety			
Consumers	Cultural heritage			
Value chain actors	Governance			
	Socio-economic repercussions			

Figure 81: Stakeholders and Impact Categories (UNEP/SETAC, 2009)

A variety of methodologies and frameworks have been developed for social sustainability assessment based on SCLA, but none is universally accepted (Reitinger et al., 2011; Benoît et al., 2013; de Luca 2015; Fortier et al., 2019). SLCA is still evolving and can be used on its own or in combination with other techniques. Given the limitations of current SLCA methodologies, the approach used for the social assessment of BioMates draws from SIA and SLCA, combining elements to provide a more comprehensive and robust analysis, as employed in previous research (Diaz-Chavez, 2013; 2014; Diaz-Chavez et al. 2016; Diaz-Chavez and Evans, 2021). The approach is illustrated in Figure 82.



Figure 82: Adapted SCLA and SIA (Diaz-Chavez, 2014; Diaz-Chavez et al., 2016)

From the steps common to SLCA, a direct link can be drawn with different techniques, such as, for instance, mapping stakeholders, creating a baseline (i.e., inventory), and identifying and assessing the impacts. Examples of social, economic and policy issues that can be assessed in the context of BioMates are shown in Figure 83. Selection of indicators is being conducted.



Figure 83: Examples of social, economic and policy issues that can be assessed in the context of BioMates

# Key variables and sustainability indicators

#### A matrix for the final assessment will be elaborated to assess criteria and indicators.

No	Parameter	Characteristics/ criteria	Assessment Level	Supply chain stage	Data type and source
1	Restoration of ecosystems/soil	Incentives and barriers	EU/National	Feedstock	Qualitative Literature Survey Workshop
2	Identification of	Producers	National	All	Qualitative
	stakeholders	Regulators	Local		Desk search

	along the supply chain	Business Traders			Project partners
3	Policies and regulations	International National Regional Local	National International	All	Qualitative Literature Policy documents
4	Potential biorefinery location/logistic	Availability of feedstock	National Local	Feedstock Transport Storage Biorefinery	Qualitative Literature Project partners
5	Land (use/tenure)	<ul> <li>Availability in EU</li> <li>Ownership and rights</li> </ul>	National	Feedstock	Quantitative Indicators FAOSTAT EUROSTAT
6	Community participation	Community acceptance of: • Biorefinery feedstocks, processes, products • Other involvement	National Local	Feedstock Transport Storage Biorefinery	Quantitative Survey Qualitative Workshop
7	Quality of life	Improvement of quality of life Improvement of livelihood Improvement of socio-economic conditions	National Local	N/A (General)	Quantitative EUROSTAT
8	Rural development and Infrastructure	<ul><li> Roads</li><li> Sanitation</li><li> Water</li></ul>	National Local	Feedstock Transport Storage Biorefinery	Qualitative SHDB
9	Job creation and wages	<ul> <li>Labour (harvesting; collection of residues)</li> <li>Jobs created (biorefinery&amp; transportation)</li> <li>Wages paid according to national/regional regulations (minimum wage)</li> </ul>	National Local	Feedstock Transport Storage Biorefinery	Quantitative Indicators EUROSTAT FAOSTAT ILOSTAT SHDB
10	Gender equity	Inclusion of women	National	Feedstock Transport Storage Biorefinery	Quantitative Qualitative EUROSTAT SHDB
11	Labour conditions	<ul><li>ILO conventions and human rights including:</li><li>Child labour</li><li>Right to organise</li><li>Forced labour</li></ul>	National	Feedstock Transport Storage Biorefinery	Quantitative Qualitative ILOSTAT SHDB
12	Health and safety	Compliance with health and safety regulations	National Local	Feedstock Transport Storage	Qualitative Literature SHDB

				Biorefinery	
13	Competition with other sectors	Competition and negative impacts on other industries and sectors	National Local	Feedstock Intermediate and end products	Qualitative Literature

LCA analyses the effects that a product or process will have on the environment. It provides information about the efficiency of the production and areas for improvement and encompasses all stages in the product's life cycle (e.g., extraction of raw materials, processing, transportation, use, disposal). It requires data about the initial product, as wells data on the full life cycle of all other materials used in making the product (which also applies to green procurement). SLCA, in turn, requires collection of additional data relating to organisational issues along the chain (UNEP-SETAC, 2009; Diaz-Chavez and Evans, 2021) (see figure 84).



The SHDB will be used to complement the characterisation of the countries where the supply chains have been identified and to provide a 'combined social hotspot index' for these countries, as explained below. According to the UNEP-SETAC (in Norris and Norris, 2013), 'hotspots are the elementary processes in a region or situation that may seem problematic, where social issues are at risk or, conversely, opportunities exist'. Conceived for use in SLCA, the SHDB is a tool allows to identify hotspots or potential risks in supply chains in specific economic sectors at country level, based on potential social impacts. It is an extended input/output Life Cycle Inventory database providing a solution to enable the modelling of product systems and the assessment of potential social impacts (Norris and Norris, 2015). The potential social impacts of activities in specified economic sectors at country level can be identified through a range of indicators that are used to measure the risk levels associated with social issues, highlight an opportunity to address them (SHDB, 2021).

For the current analysis using the HSDB, the sectors analysed at National Level included:

- Cereal grans nec (sorghum)
- Fibre crops (Miscanthus, hemp and switchgrass)
- Electricity
- Chemicals

Figure 85 shows the result of the overall assessment (risks) for all the selected countries of the GOLD project. Preliminary results are shown in the next figures.

Labor Rights and Decent Work	🛑 Health & Safety	Society
Governance	Community	
(France) Cereal grains nec		
듵 (Greece) Cereal grains nec		
📕 (Italy) Cereal grains nec		
(Poland) Cereal grains nec		
Labor Rights and Decent Work	Health & Safety	Society
Governance	Community	
(France) Plant-based fibers		
(Greece) Plant-based fibers		
(Italy) Plant-based fibers		
(Poland) Plant-based fibers		

### Figure 85: Social hotspot Index (Source: HSDB, 2024)

Specifically, on preliminary results, some of the indicators selected for the analysis include labour risks (Figure 86), particularly on occupational risks as per figure 87.

# Labour risks

Issue	Country specific sector	Risk level
Overall risk occupational	(France) Cereal grains nec	
toxics & hazards	(Greece) Cereal grains nec	
	📕 📕 (Italy) Cereal grains nec	
	(Poland) Cereal grains nec	
Occupational noise related	(France) Cereal grains nec	
risk	😐 (Greece) Cereal grains nec	
	📕 📕 (Italy) Cereal grains nec	
	(Poland) Cereal grains nec	

#### Figure 86: Labour risks (Source: HSDB, 2024)

## Smallholders versus commercial farms (only agriculture sectors)

Overall risk related to (agri) smallholders	<ul> <li>(France) Cereal grains nec</li> <li>(Greece) Cereal grains nec</li> </ul>	
	(Italy) Cereal grains nec	
	<ul> <li>(Poland) Cereal grains nec</li> </ul>	
Percentage of family-owned	(France) Cereal grains nec	
farms in country	Greece) Cereal grains nec	
	(Italy) Cereal grains nec	
	(Poland) Cereal grains pec	
Dereentage of commercially		
owned farms in country		
,		
	(Italy) Cereal grains nec	
	(Poland) Cereal grains nec	
Smallholdings Land % < x	(France) Cereal grains pec	
hectares	(Greece) Cereal grains nec	
	(Reland) Coroal grains nee	
Smallholdings Land % > ×	(France) Cereal grains nec	
hectares	(Greece) Cereal grains nec	
	(Italy) Cereal grains nec	
	(Reland) Coroal grains nee	
	(Poland) Cereal grains nec	

Figure 87: Smallholders versus commercial farms (only agriculture sectors) (Source: HSDB, 2024)

**Future work includes**: a) Stakeholder mapping, b) Policy assessment, c) Other sectors to be analysed and d) selected indicators

**Stakeholder mapping:** Various methodologies exist for stakeholder mapping (e.g., UNEP/SETAC, 2009). Stakeholder selection should be comprehensive and include those at the production level (NGOs, farmers, other civil organisations), industry, consumers, society at large and any other value chain actors. This will be linked to activities in WP4 Task 4.1.

#### Main results, achievements

In this reporting period we can confirm that there has been advance in the subtasks 33.4 on techno-economic assessment and socio-economic assessments. Gathering of data from WP1-2 has been done through WP3 coordination and supply value chains set up. In addition, with the meeting In April 2024 in Athens.

# Deviations, obstacles and which was the mitigation plan: There are currently no deviations for this subtask.

## Problem, delay or deviation: None

## **Task 3.4: Task 3.4 Interpretation, strategy and recommendations**

*Objective*: To develop, validate and analyse value chain, cross sector strategies between phytoremediation and clean biofuel production.

**Progress toward the objectives**: The aim of the task is to develop, validate and analyse value chain, cross sector strategies between phytoremediation and clean biofuel production. The strategies will be developed at local, national European and interregional level (Europe, China, India, Canada)

A policy assessment and the overall interpretation of the analysis will be conducted. The assessment focuses on the most relevant instruments to GOLD to highlight how they may enable, boost or hinder the scaling up of the GOLD concept to full commercial ventures.

The recommendations will be made once all the analysis has been performed (economic, environmental, social and policy). This assessment will include four components as shown in Figure 88.

Analysis & direction	Setting the strategic agendas	Design future implementation strategies	Perform an impact assessment (w/SDG)
<ul> <li>Advantages of value chains for rehabilitation of degraded land</li> <li>biomass production through phytoremediation strategies</li> <li>efficient and innovative biofuel conversion pathways</li> <li>market infrastructures</li> <li>rural and economic development</li> <li>political and institutional frameworks</li> </ul>	<ul> <li>value chains, rationalise strategic needs (under research, technical, policy and institutional terms)</li> <li>ensure that any future interventions are well integrated into national and international planning and initiatives.</li> <li>Stakeholders participation for challenges and gaps</li> <li>Performance indicators aligned with SDGs</li> </ul>	<ul> <li>create 'future' concepts that will be tailored to local capacity and requirements</li> <li>Concepts that support the mobilisation of domestic, resource efficient biofuel value chains from degraded land through phytoremediation strategies</li> </ul>	<ul> <li>integrate the information generated in Tasks 3.1-3.3</li> <li>translate into the relevant SDG indicators and link them with EU policy and challenges</li> </ul>

Figure 88: Components for assessment of recommendations.



Emphasis is given to the links with SDGs and other international goals such as the ESG. The impact assessment has considered the results for WP1-3 and the synergies and challenges they involve. This has moved to consider strategic thinking analysis. Some indicators have been selected for this analysis and systems thinking to be able to link SDGs with policies. An example of the links is provided in Figure 89. The network of supply chains within GOLD will be connected with the SDGs and with the policy assessment.

Figure 89: Network of goals, systemic view (Mohr, 2016).

#### Deviations, obstacles and which was the mitigation plan

The work started in Month 20 to accommodate the final selection of value chains from the previous tasks in WP3. This will also allow the project team to capitalize on the recent regulatory updates from the Renewable Energy Directive and embed the project analysis and findings within the context of the ongoing policy debates in the European Union and at international level. An additional policy on Nature restoration has been considered but it was also delayed to be passed at the Parliament in 2024.

This delay is not expected to impact the final delivery of the planned deliverables.

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# Key findings/achievements of the 2<sup>nd</sup> reporting period are presented in the Box 3:

- Mapping and characterization of the EU contaminated sites, using existing data sources. A risk-based framework was prepared as basis for mapping and selection of target areas where diffuse pollution levels are above the thresholds related to specific endpoints (based on food quality, water quality and ecotoxicology) and their relevant critical limits. The modelling of diffuse pollution was implemented for four main, widespread pollutants: cadmium (Cd), lead (Pb), Copper (Cu) and Zinc (Zn). This work was continued and approach to estimating biomass produced and biofuel potential and bioremediation time and potential has been initiated.
- A framework for the selection of the most suitable and interesting Value Chains (VCs) has been prepared. A literature review for existing biomass-to-X value chain models has been carried out, together with an analysis of ongoing and concluded projects related to the topic. A preliminary selection of VCs, alternative in terms of final use a of the biomass from phyto-remediation activities, has been defined (i.e. syngas for Direct Reduced Iron (DRI) steel production, biochar as partial replacement for PCI in BF steelmaking). A general VC structure has been defined, and the model prepared accordingly. Questionnaires for WP1 and WP2 partners are being prepared and are under finalization phase, to gather qualitative and quantitative information. A total number of 16 value chains have been selected that are being modelling.
- The settings and definitions that will be used for the sustainability of the different VCs were finalised, to guarantee a consistent evaluation throughout the assessment. Moreover, the sustainability assessment has been improved in the 2<sup>nd</sup> reporting with emphasis on key variables and sustainability indicators.

# Work Package 4: Dissemination and communication

# Leaders: ETA; partners: ALL

Tasks	Title	Months	Leader	Participants	Status
4.1	Stakeholders mapping, dissemination and communication plan	1-48	ETA	All partners	On -going

4.2	Visual identity and development of dissemination materials	1-3	ΕΤΑ		Completed
4.3	Online presence		ETA	All partners	On-going
4.4	Events	1-48	ETA	All partners	On -going
4.5	Publications	1-48	ETA	All partners	On -going
4.6	Demo and open days	1-48	ETA	All partners	On -going

The specific objectives of WP4 are as follows:

- To define a detailed dissemination strategy and a set of promotional and dissemination materials that will lead to the successful dissemination of project activities and results.
- To widely disseminate the project activities and results at national, European and international level, ensuring sustainability of the project outcomes after its end.
- To engage with stakeholders through a number of targeted events at regional and EU level.

The KPIs for dissemination and communication are presented below.

Activity	Implementation	Audience	Impact	KPIs
Website	www.GOLD_h2020.eu	Open to all	Improve visibility	The website
Social media	LinkedIn, Facebook & Twitter	Open to all	Improve visibility of GOLD and its results	Relevant account
Webinars	4 sessions on weekly intervals	Students, relevant stakeholders	Improve knowledge transfer to stakeholders	4 webinars; >25 participants /webinar
Links with relevant organisations, websites, etc.	European Technology Platforms, organisations, NGO, etc.	GOLD & relevant stakeholders	Improve public awareness	>10 links
Open workshops/days	To be organised in large exhibitions for agriculture.	Open to the society; relevant stakeholders	Improve GOLD visibility of and public awareness	At least 3
Promotional publications	Leaflets, newsletters, brochures, etc.	Stakeholders and media	Improve GOLD visibility	20-50 (publications)
Demo days	Prior of after the technical meetings	GOLD & stakeholders	Knowledge transfer to stakeholders	At least 4
Open access papers	Articles in journals, proceedings, books, etc.	Scientists	Improve visibility to the scientists society	>10 (publications)
Other scientific publications	Articles in journals, proceedings, books, etc.	Scientists	Improve visibility to the scientific society	>20 (publications)
Presentations to conferences, etc.	Plenary, oral and/or poster presentations	Relevant stakeholders	Scientists, companies, etc.	20-50 (publications)
Brokerage event in Brussels	Growing energy crops for phytoremediation and biofuel production	Relevant stakeholders	Public awareness & multi- stakeholders dialogue	150 participants
Videos	1 general plus videos from activities, etc.	All relevant stakeholders	Improve visibility; transfer knowledge	>5

#### Table 51: KPIs for GOLD dissemination and communication

# Progress towards objectives and KPIs:

In the second reporting period (M19-36) WP4, with the contribution of all project partners, has made significant progress towards the objectives listed above firstly by creating a project identity with various channels of dissemination such as website, social media, and appearances at relevant conferences.

	g the repetting		
Activity	KPI	M18 Progress	M36 Progress
Website	The website	Online and active from M4	Achieved in RP1
Social media	Relevant account	Pages created and regularly updated on LinkedIn, Twitter, and Facebook	Achieved in RP1
Webinars	4 webinars; >25 participants/ webinar	1st Webinar planned for March 2023	1 <sup>st</sup> Webinar held on 15 <sup>th</sup> March 2023 (>100 participants). 2 <sup>nd</sup> Webinar / hybrid conference held on 13 <sup>th</sup> March 2024 (c.200 participants).
Links with relevant organisations, etc.	>10 links	Links made with H2020 project: CERESiS & Phy2Climate	Links made with University of Texas.
Open workshops/days	At least 3	1 online workshop – EUBCE, 9 <sup>th</sup> June 2022.	2 <sup>nd</sup> one day conference (hybrid) held on 13 <sup>th</sup> March 2024 (c.200 participants).
Promotional publications	20-50 (publications)	12 News posts on Project website	18 News posts on Project website
Demo days	At least 4	1 field trip day – Lille, France, 29 <sup>th</sup> June 2022.	1 Site Visit: Bologna, Italy, 9 June 2023
Open access papers	>10 (publications)	1 published by USherbrooke, Canada	5 total published papers
Other scientific publications	>20 (publications)	6 publications	21 website posts
Presentations at conferences, etc.	20-50 (publications)	15 presentations at conferences in the first period.	34 total presentations in second period
Brokerage event in Brussels	150 (participants)	Planned for M46-48	Planned for M47 – at TNO or TUM
Videos	>5	8 videos on project YouTube channel	7 videos on project YouTube channel

Table 52: KPIs during the 1<sup>st</sup> reporting period

# Task 4.1: Stakeholders' mapping, dissemination and communication plan

**Progress toward the objectives**: The GOLD Webinars and Events interim report **(D4.5)** was submitted in M24. This report reports on the EUBCE 2022 Online workshop, and the 1st project webinar 'Phytoremediation with energy crops for biofuel production'. For each of the events the report summarises the preparation process, a summary of the event including speakers and content, and the conclusions of the event including the number of participants etc.

The Dissemination and Communication plan – Update 2 (D4.4) was submitted in M36, which includes an updated time plan with some further details on specific activities planned for the final 12 months of the project. The upcoming activities include webinars, conferences and events, short videos, scientific publications, ongoing activities such as the website and social media presence, the final event, and the final project booklet.

# Results and achievements: D4.1 and D4.3

D. no	Title	Leader	Delivery date (planned)	Delivery date (actual)
D4.4	Dissemination and Communication Plan – Update 2	ETA	M36	M36
D4.5	Webinars and Events interim report	ETA	M24	M24

D. no	Title	Leader	Delivery date (planned)	Delivery date (actual)
M19	Projects events	ETA	M24	M24
M20	Stakeholders' mapping	ETA	M20	M20

# **Task 4.2: Visual identity and development of dissemination materials**

**Progress toward the objectives**: The GOLD Visual Identity and branding kit was completed and shared in RP1, there were no updates during RP2. The consortium continued to be used the project branding for reporting and events.

#### Problem, delay or deviation: None

Corrective actions undertaken: None

## ►T4.3 Online presence

**Progress toward the objectives**: The GOLD website is among the one of the most strategic communication and dissemination means of the project. To ensure the highest possible visibility to the GOLD goals and results, the project website is accessible with an intuitive URL: https://www.gold-h2020.eu/ The website went live in M4. During this second reporting period the following statistics were collected:

- Website: 18 News posts
- 2 x Project Newsletters
- YouTube Channel: 7 new videos, 663 total views, 15 subscribers
- LinkedIn Page: 678 Followers, Content: 582 Reactions // 26 Comments // 38 Reposts

Results and achievements: The online presence of GOLD (Figures 90).

G GOLD +	B2BOLDER CAMPAIGNS"
GOLD Project H2020         Closing the gap between phytoremediation solutions on growing energy crops on polluted lands & clean biofuel production         Renewable Energy Semiconductor Manufacturing - 678 followers - 11-50 employees         Maurizo & 457 other connections follow this page         Image: About Posts Jobs People	Pages people also viewed         EBIO H2020 Project         Reneable Dreny Semiconductor         Mandaturing         Windrawing         Windrawing         Connections failure this page         ✓ Following
About GOLD is a R&I project aiming to grow energy crops on contaminated sites and produce sustainable biofuels without indirect land use change, removing soil pollutants and bringing those lands back to agriculture. This project has received funding from the European Union's Horizon 2020 Researc see more	GreenMeUp Project Services for Renewable Energy 703 followers Marchiol & 108 other connections follow this page ✓ Following
Show all details → Page posts ( ) GOLD Project H2020 GOLD Project H2020 GOLD Project H2020	Re-CORD Reserch Services 1,473 followers Mapric & 16 other connections work here ✓ Following
services     services	Show all →



Figure 90: Online presence of GOLD project

Problem, delay or deviation: None

Corrective actions undertaken: None

# ►T4.4: Events

**Progress toward the objectives**: On the 13th March 2024 project GOLD hosted a one-day international workshop in Athens, Greece (Figure 87). The workshop was a huge success, not only was the day started with a keynote speech from the European Commission's Dr. Maria Georgiadou, but we welcomed a full conference room with international delegates from Europe, India, China, USA, and Canada, and online the event reached even more countries around the word, nearly 200 people were part of the live online and in person audience.

During RP2 GOLD was presented at 50 events including conferences and workshops, counting all partners, some online and some in person.



Figure 91: View of the GOLD workshop in Athens on 13th of March 2024.

Apart from this workshop GOLD supported the organisation of a workshop entitled "Production of Low ILUC risks feedstock" that was organished by BIKE. In this event 67 participants participated onsite, while more than 100 persons had been registered to join online.



Figure 92: View of the BIKE workshop in Thessaloniki on 30<sup>th</sup> of March 2023, supported by GOLD workshop.

A parallel event was organished in EUBCE2023 in Bologna on 6<sup>th</sup> of June 2023 entitled "Clean advanced biofuels production from contaminated land" where the three sister projects: GOLD, Phy2Climate and CERESiS presented and compared their main findings.

# Problem, delay or deviation: None

#### Corrective actions undertaken: None

# ►T4.5: Publications

**Progress toward the objectives**: The second project press release was issued on the 10th April 2024 titled "Bridging the Gap Between Phytoremediation & Advanced Biofuels with Decision Making Tools" and shared with ETAs 'media' mailing list.

Four scientific papers have been published:

- Catalytic routes for upgrading pyrolysis oil derived from biomass
- Hydrothermal conversion of Cu-laden biomass to one-step doped hydrochar used as a potential adsorbent for 2-nitrophenol removal
- Mixotrophic Syngas Conversion Enables the Production of meso-2,3-butanediol with Clostridium autoethanogenum
- Plant testing with hemp and miscanthus to assess phytomanagement options including biostimulants and mycorrhizae on a metal-contaminated soil to provide biomass for sustainable biofuel production

Also, for almost all of the above-mentioned event's abstracts, posters, and presentations have been published in the proceedings.

# Problem, delay or deviation: None

# Corrective actions undertaken: None

# ► T4.6 Demo and open days

**Progress toward the objectives**: One demo day was held for the consortium as part of the consortium meeting held in Bologna, Italy, 8 -9 June 2023. The GOLD project team met for the second time in person at The University of Bologna, 8-9 June 2023. The first part of the meeting, commencing in the afternoon of the 8th of June, consisted of individual Work Package presentations. On Friday 9th June the University of Bologna kindly hosted the consortium at the trial site Chiarini 2, on the outskirts of Bologna, to the west. This site has a long history of contaminative use with records dating back to post World War II when the site was used as an illegal dumping ground for industry and craft workshops that were present in the area. The site visit video can be viewed here: GOLD: <a href="https://youtu.be/0XOHddDBFLs">https://youtu.be/0XOHddDBFLs</a>



Figure 93: View of the GOLD demo day on 10<sup>th</sup> of June 2023 in Bologna.

Problem, delay or deviation: None

Corrective actions undertaken: None

# Work Package 5: Coordination and management

# Leaders: CRES; partners: ALL

Tasks	Title	Months	Leader	Participants	Status
5.1	Project coordination & management	1-48	CRES	ALL	On-going
5.2	General Assembly	1-48	CRES	ALL	On-going
5.3	International Advisory board	1-48	CRES	ALL	On-going
5.4	Editorial Board	1-48	CRES	ALL	On-going
5.5	Data Management and exploitation of the results	1-48	CRES	ALL	On-going
5.6	Ethics requirements	1-48	CRES	ALL	On-going

# Task 5.1: Project coordination & management

**Progress toward the objectives**: The coordination of the project is being accomplished through technical meetings held regularly, with respect to the project planning and timetable. Special attention was given to the preparation of the kick-off meeting. All WP leaders (in close collaboration with the Task leaders of their WPs) as appointed in the project outline, developed

protocols (or action plan) and updated time schedules, which were discussed, finalized and accepted by all partners during the kick-off meeting. The WP leaders ensures that the accepted protocol (or action plan) is realistic and will lead to the collection of high quality, up-to-date data. Possible adjustment to the predicted time schedule may be required, depending on the approved project starting date. At the kick-off meeting the WP leaders apart from the protocol (or the action plan) had to present in detail the resources (reports from completed projects, ongoing research actives and sites, international literature, etc.) that they will use as a base to run efficiently their WPs.

**Results and achievements**: In the 2<sup>nd</sup> reporting period two physical meetings had been organised; the 1<sup>st</sup> was carried out in the view of EUBCE23 conference in Bologna on 8<sup>th</sup> and 9<sup>th</sup> of June 2023 and the 2<sup>nd</sup> on 14<sup>th</sup> of March 2024 in Athens/Greece. The first meeting was combined with a demo day on UNIBO field trials (8/6/23) and the second followed the GOLD workshop organised on 13<sup>th</sup> of March 2024.



Figure 94: View of the GOLD demo day on 10<sup>th</sup> of June 2023 in Bologna.

Problem, delay or de viation: None Corrective actions undertaken: None



Figure 95: View of the GOLD demo day on 10<sup>th</sup> of June 2023 in Bologna.

# Task 5.2: General Assembly

**Progress toward the objectives**: The General Assembly is the decision-making body of the project is composed by one representative per partner and will be chaired by the project coordinator. The general assembly will ensure the successful operation of the project according to the timetable, the protocols, the milestones and the deliverables. The General Assembly will be in charge of the operational management of all activities of the project and re-orientation whenever necessary, budget revision, incorporation of new contractors, measures towards defaulting partners. It will integrate recommendations from the Intellectual Property Use and Dissemination Committee and survey ethical and gender issues. The General Assembly will meet regularly (every 9 months), while skype meetings will be organised in the intervals between the technical meetings among the work package leader and the coordinator to ensure the smooth operation of the project.

**Results and achievements**: In the 2<sup>nd</sup> reporting period two physical meetings had been organised; the 1<sup>st</sup> was carried out in the view of EUBCE23 conference in Bologna on 8<sup>th</sup> and 9<sup>th</sup> of June 2023 and the 2<sup>nd</sup> on 14<sup>th</sup> of March 2024 in Athens/Greece. The first meeting was combined with a demo day on UNIBO field trials (8/6/23) and the second followed the GOLD workshop organised on 13<sup>th</sup> of March 2024.

## Problem, delay or deviation: None

## Corrective actions undertaken: None

# Task 5.3: International Advisory board

**Progress toward the objectives**: An international Advisory Board (Europe, USA, Brazil, Africa and Australia) has been set up consisted on 6 experts on phytoremediation, environmental engineering, advanced biofuels, sustainability issues, SDGs and cost analysis. The members of the board will join up to two project meetings combined with dissemination events and will have a consulting role. They will sign confidentiality agreements before the project initiation. Their signed letters of commitment were presented in the proposal ANNEX.

**Results and achievements**: During the 2<sup>nd</sup> reporting period one member of the international advisory board (Prof. Alan Baker) was invited to the workshop carried out in Athens on 13<sup>th</sup> of March 2024.

#### Problem, delay or deviation: None

#### Corrective actions undertaken: None

# Task 5.4: Editorial Board

**Progress toward the objectives**: The editorial board is a body that is responsible for the GOLD publications (scientific and promotional ones). It consists of the coordinator (CRES); UNIBO & ETA. The editorial board is led by the coordinator (CRES). Dr. Andrea Monti (UNIBO) is responsible for the scientific publications (scientific articles, special issues, book chapters, open access journals, etc.) due to his deep experience to act as an editor (Guest Editor in BioFPR, Wiley). ETA is responsible for the promotional publications (practice abstracts, roadmaps, posters, leaflets, procures, booklets, fact sheets, newsletters, etc.) that is a key element of the project.

**Results and achievements**: During the 2<sup>nd</sup> reporting period the consortium were collaborated in the development of common publications as presented in WP4. More publications have been planned by the end of 2024.

#### Problem, delay or deviation: None

#### Corrective actions undertaken: None.

# Task 5.5: Data management plan

**Progress toward the objectives**: Under this task the project's Data Management Plan (DMP) had to be developed, outlining how research data will be collected, processed or generated within the project; what methodology and standards will be adopted; whether and how this data will be shared and/or made open; and how this data will be curated and preserved during and after the project. The DMP aims to ensure that GOLD activities are compliant with the H2020 Open Access policy and the recommendations of the Open Research Data pilot. The DMP will furthermore explain how the project will be connected with the EIP-Agri, as well as the European thematic aggregator of agINFRA in order to disseminate its research outcomes to the relevant European and global channels (such as OpenAIRE). Under this task an Open Access Support Pack will be developed translating the generic H2020 requirements and recommendations into specific guidelines and advice that can be applied in the project. The application of the DMP by all GOLD partners will be monitored under this task.

**Results and achievements**: The 1<sup>st</sup> version of DMP (<u>**D5.6**</u>) was prepared by M9 and will be updated and finalised by M48.

# Problem, delay or deviation: None

Corrective actions undertaken: None.
### 1.3 Impact

## **1.3.1 Specific impact**

Impact 1 GOLD will create a win-win situation by bringing polluted land back to agricultural production through cost reduction and improved phytoremediation

The food vs fuel competition is a long-lasting topic for debate. The new Directive for biofuels (RED II) is going to put an end to this issue since the biofuel production from food crops will gradually decline starting from 2023 and at the same time the production of biofuels with low ILUC risks from growing non-food crops on unused, abandoned or severely degraded land will be promoted (advanced biofuels). Soil contamination is a global issue and phytoremediation has been developed as an environmentally friendly approach with a low ecological footprint that can be used for both organic and inorganic pollutants.

Phytoremediation is a relatively cheap, non-invasive and publicly acceptable technology that uses plants to remove contaminants from soil or to render them harmless. Phytoremediation is more effective and economically viable when: (i) it is applied in large areas with low to medium concentrations of pollutants so that phytotoxicity on plant remains low and plants can grow, (ii) the crops used produce high added-value biomass providing a revenue, (iii) the site is in unused/abandoned arable land and agricultural practices and mechanization can be applied. The possibility to combine phytoremediation with the production of biomass with a high economic value seems very promising since a double target may be achieved. The harvested biomass can be used as feedstock for bioenergy purposes, and concurrently, plants are decontaminating the soil. In this way, marginal or degraded soils that cannot be given over for food production will be exploited and upgraded, the energy targets of RED II will be supported, new jobs will be created, local farmers will have the possibility to maintain and/or increase their income, and the development of rural areas will be reinforced. In GOLD optimised and low-cost phytoremediation solutions will be tested, such as mycorrhiza and biostimulants on high selected high yielding energy crops. Cost-effective and sustainable value chains will be developed and analysed in order to achieve optimised win-win solutions.

In GOLD optimized phytoremediation solutions are being developed as the outcome of the combinations "**contaminated sites X energy crops X phytoremediation practices**" that will be studied in EU and non-EU countries. In particular, the phytoremediation solutions per crop are organized as follows:

Miscanthus	CRES-GR, AUA-GR, UNIBO-IT, YNCREA-IT, UMCS-PL, CTD-IN, HUNAU-CN
Biomass Sorghum	CRES-GR, AUA-GR, UNIBO-IT, YNCREA-IT, UMCS-PL, CTD-IN
Industrial hemp	AUA-GR, UNIBO-IT, YNCREA-IT, UMCS-PL, CTD-IN, IBFC-CN
Switchgrass	CRES-GR, HUNAU-CN
Kenaf	IBFC-CN, CRES-GR
Sunn hemp	CRES-GR

Although four high yielding lignocellulosic crops had been selected for GOLD two more had been added; kenaf and sunn hemp with quite promising results. Land decontamination in GOLD will be based in the case of inorganic pollutants on the metal(loid)s uptake in the produced biomass, and in the case of organic pollutants on their decrease in the soil. In both cases of contamination, the biomass yields and quality will also be considered, since the produced biomass will be used for clean biofuels with low ILUC. The best performed phytoremediation solutions will be selected for replication in other sites having similar contamination problems and climatic conditions.

The above-mentioned phytoremediation solutions have been combined with the two conversion routes and 16 value chains will be selected (D3.3, Figure 96), modelled and analysed in terms of cost and sustainability in order win-win situations for both biofuels production and decontamination of the polluted lands to be created. For these a further

replicability analysis will be done to understand upscaling options, economic and, logistical feasibility and potential larger scale environmental and economic. These wider scale evaluations will be exploited and translated in strategies and recommendations to be developed for the application of the "phytoremediation/biofuel production" combination achieving both environmental and socio-economic gains as contributions towards the relevant SDGs (Impact 3).



#### Figure 96: Selected value chains for GOLD purposes.

**Optimize the innovative and promising technology of phytoremediation using energy crops under field conditions:** GOLD project develops practical information about the cultivation of miscanthus, switchgrass, sorghum and hemp in polluted sites. It will contribute to the remediation and restoration of the depressed areas of the experimental fields and of other similar to them. Most certainly, GOLD solutions can be implemented at local, regional, national and -in some cases- at EU and International level.

*Mitigate the exposure route for the intake of contaminants by humans:* The local population of the polluted sites is exposed to multiple hazardous pollution sources. Therefore, developing, presenting and promoting the GOLD green technology is an important step of improvement, and will be a valuable guide to mitigate the exposure route for the intake of contaminants by humans.

These GOLD Green technologies are also developed to stimulate the ecological functions of those degraded lands and outline a path towards rehabilitated ecosystems. They may favour the restoration of a range of ecological functions and ecosystem services such as habitat for microbial and animal communities, C sequestration, biogeochemical cycles of elements and organic matter. They may also offer in a larger scale the opportunities for a landscape restoration in areas that are quite often barren of vegetation.

**Contribute to the wellbeing of local population:** The wellbeing of the local communities will be increased, and an additional income for local farmers and population will be developed. In addition, new job opportunities will be created, along with new knowledge and new skills for young people. On the same time, the area of its economy will be revitalized with the increased added value of the cultivated energy crops.

**Entrepreneurship and formation of new market**. The project will stimulate the development of innovative entrepreneurship by exploiting the biomass of the energy crop for the production of clean biofuels. In addition, GOLD will increase the availability of domestic raw materials and the ability to be used in new emerging markets. Diversify the panel of cultivable species in these marginal lands and encourage the implementation of new entrepreneurship using the produced biomass

Knowledge creation and sharing among researchers and the industry: Enhancing the production of new knowledge in the field of phytoremediation and biofuel production will fuel

the research effort of enterprises and strengthen their cooperation with educational and research bodies. This will subsequently encourage the development of innovative solutions.

*Knowledge sharing amongst rural stakeholders*: Knowledge sharing will be systematically taking place. Farmers will gain insights on how they can create/improve their business models and by participating in the GOLD dissemination and knowledge sharing events.

**Optimization of the value chain**: The economic analysis, environmental and social impact assessment will offer greater visibility across the selected value chains and will ensure a full package of lessons learned and optimal operations. The methodology followed to measure sustainability as described in WP3 is expected to set a good example for other similar projects to follow, due to its holistic view and systematic life cycle thinking.

**Public policy**: Science- and evidence-based knowledge and information will be created that can be used in setting-up a coherent policy framework and utilization. In general, public stakeholders are less reluctant to adopt such new concept when demonstration case studies at field scale are proved success stories

**Progressive Climate change and C sequestration**: The increasing use of fossil fuels over the last decades is still contributing to the progressive climate change leading more frequently to unexpected events (e.g., heatwaves, storms and flooding, erosion, long drought and fires, etc.). Production of renewable, biofuels, notably on marginal (contaminated) land, with low N fertilization to avoid denitrification, is obviously helping to counteract the GHG emissions and cropping renewable biomass to sequester a part of plant residues and rhizodeposition allowing to progressively improve humification and C sequestration<sup>i</sup>. Moreover, perennial grasses and woody crops established at (peri)urban areas on to-be-remediated brownfield can capture small particles and evapotranspiration, which counteract diffuse pollution, clean air and quench heat islands in summer. Such phytomanagement options can also act to limit large-scale impacts on recharge and groundwater levels aggravated by climate change.

# Impact 2 GOLD produces clean biofuels with low ILUC from selected energy crops grown on contaminated lands

In GOLD, two conversion routes have been selected in order the polluted biomass to be converted to clean liquid biofuels and the contaminants to be collected in a concentrated form. The contaminants will be metal(loid)s and will be found in the feedstock produced in contaminated soils with inorganic pollutants. The biomass produced in soils contaminated with organic pollutants is considered as clean. The first criterion for the selection of an appropriate conversion route was the possibility to collect the contaminants in a concentrated form. The 1<sup>st</sup> route is based on entrained flow gasification combined with fermentation and the 2<sup>nd</sup> on autothermal pyrolysis combined with FT synthesis. In the 1<sup>st</sup> route the feedstock will be pretreated (using three options: Torwash technology, torrefaction and slow pyrolysis), while in the 2<sup>nd</sup> route no special pretreatment will be included. The 1<sup>st</sup> route will be developed by the EU partners using feedstock produced in European contaminated lands, while the 2<sup>nd</sup> will be developed by the Canadian partner using feedstock from switchgrass that will be grown in a contaminated site with inorganic pollutants in Canada. Synergies between the two routes have been planned in terms of Torwash technology, of entrained flow gasification and fermentation process.

# Impact 3 GOLD promotes the international collaboration towards the innovation mission challenge on biofuels

GOLD has been designed to promote the international collaboration towards Mission Innovation Challenge 4 on advanced biofuels. Thus, three partners outside EU and key members of the Mission innovation have been included having key roles throughout the value chains; 3 in the growing of energy crops for phytoremediation purposes and one on the conversion of the polluted biomass to clean biofuels, while collecting the contaminants in a concentrated form. The three non-EU partners participate in GOLD at three levels: a) carry out research in the area of their expertise, b) develop synergies with the EU partners in the area of their expertise and, finally, c) participate in the design, evaluation and selection of the best value-chains (as win-win situations in terms of phytoremediation, biomass production, clean biofuels production, cost and sustainability efficiency towards the SDGs).

Impact 4 GOLD concept, through the developed optimized phytoremediation strategies/solutions, contributes to several sustainable development goals (SDGs) beyond the Energy is anticipated

GOLD is directly linked to eight of the SDGs, namely: SDG2: Zero hunger; SDG3: Good health and well-being, SDG6: Clean water & Sanitation, SGD7: Affordable and clean energy; SGD8: Decent work and economic growth, SDG9: Industry innovation and infrastructure, SDG12: Responsible Consumption and Production; SDG13: Climate Action and SDG15: Life on Land. In table 23 is presented the SDGs related to GOLD and the indicators to measure potential impacts from the 'GOLD' research in WP3.

# Table 53: Challenges that GOLD will address (in italics) and their relevance to policy and SDGs

Value chain EU policy mechanism	15 LIFE AND	Land use (8 sites in EU MS, India & China)	12 CONCIMUENTIAN AND PRODUCTION Biomass Producti	on (4	7 AFFORDABLE AND CLEANENERGY	Conversion (2 conversion routes)
<ul> <li>Soil Thematic Strategy         <ul> <li>soil protection COM</li> <li>(2006) 231</li> </ul> </li> <li>Progress in         <ul> <li>management of</li> <li>contaminated sites -</li> <li>LSI 003</li> </ul> </li> </ul>	<ul> <li>Restore through crops</li> <li>Prevent preserv</li> <li>Impact degrada pH, nut</li> </ul>	humic acids ad in Torwash ogy as ulants				
<ul> <li>Standards for soil improvers (CEN- TC223)</li> <li>Standards for fertilizers and liming materials (CEN-TC260)</li> <li>Directive for sustainable use of pesticides 128/EC</li> <li>Nitrates Directive 676/EEC</li> </ul>	<ul> <li>Low input agricultural management and less intensive cropping practices</li> <li>Apply nutrients only in periods of crop growth, under suitable climactic conditions</li> <li>Use resistant/tolerant cultivars/hybrids</li> <li>Practices and measures to prevent water pollution from nitrates (WP1)</li> <li>Emissions to soil and water (fertilizers, pesticides)(WP3)</li> </ul>					
<ul> <li>Habitat Directive 92/43/EEC</li> <li>Bird Directive 2009/147/EC</li> <li>Natura 2000</li> </ul>	<ul> <li>Decrease</li> <li>Impact related aggress allelopa abunda species color) (1</li> </ul>	se soil biodiver on Biodiversity to managemer siveness, native thy of the chos nce and divers ) and Landsca WP3)				
<ul> <li>Water framework Directive 2000/60/EC</li> </ul>	<ul> <li>Improve groundwater pollution (WP1)</li> <li>Impact on water resources (depletion, hydrology) (WP3)</li> </ul>					
• RED II	Sustainable biomass supply through phytoremediation (WP1,3)     Analysis for technologies up for low IL biofuels (WF					

	Improve biomass
Fuel quality directive	processing into biofuel
2009/30/EC	quality purification
	(WP2)

Table 54: Impact of GOLD project supporting the targets and indicators of SDGs.

SDG	Targets & Indicators	Impact of	GOLD in support of SDGs			
Land use	<ul> <li>15.3: By 2030, combat desertification, restore degraded land and soil, including land affected by desertification, drought and floods, strive to achieve a land degradation-neutral world</li> <li>15.3.1: Proportion of land that is degraded over total land area</li> </ul>	<ul> <li>Proposed innovative phytoremediation strategies and optimised solutions will support the restoration of degraded/contaminated lands and soils<sup>ii,iii,iv,v,vi</sup></li> <li>Cultivating polluted soils with energy crops will support th reduction of desertification and floods by increasing vegetation cover and thus reducing erosion and surface runoffs, decreasing contaminant transportation to other clean areas, reducing leaching to the groundwater, increasing soil organic matter and carbon sequestration, promoting soil biodiversity, protecting soil structure, etc. vii,viii,ix, x</li> <li>Mapping contaminated lands, applying the INTEGRATOF model, projecting the long-term changes in contaminant levels in soil, providing estimates of the regional, Nationa and EU production capacity of biomass to be used for biofuel production and releasing a Decision Support System will help Governments and stakeholders to make this SDG target a reality<sup>xii,xii</sup></li> </ul>				
Biomass productio n 12 RESPONSIBLE CONSUMPTION AND PRODUCTION	<ul> <li>12.2: By 2030, achieve t sustainable manage efficient use of natu resources</li> <li>12.2.1: Material footprint footprint per capita, material footprint per</li> </ul>	he ement and ral t, material and er GDP	<ul> <li>Cultivating energy crops in contaminated lands following a low input management will reduce the material and ecological footprint of the produced biomass<sup>xiii,xiv</sup></li> <li>The production of clean water (for recycling), humic acids, etc. from the proposed biomass conversion routes will reduce the material footprint of the supply chain<sup>XV</sup></li> </ul>			
Conversi 7 AFFORDABLE AND CLEAN ENERGY	<ul> <li>7.1: By 2030, ensure un access to affordable and modern energy</li> <li>7.1.2: Proportion of popu primary reliance on and technology</li> <li>7.2: By 2030, increase s the share of renewa in the global energy</li> <li>7.2.1: Renewable energy the total final energy consumption</li> </ul>	iversal e, reliable services ulation with clean fuels substantially able energy mix y share in y	<ul> <li>Production of clean fuels from biomas harvested on contaminated lands under remediation and the use of GOLD innovativ conversion technologies will support the increase of the proportion of the populatio with primary reliance on clean fuels an technology.</li> <li>By exploiting only 1/3 of the 650000 ha of the well-defined contaminated sites of EU<sup>xvi</sup> by the GOLD selected energy crops, and taking as their mean yield the worst scenario of the 10 t/ha, GOLD will provide approx. 2.2 millior tonnes of feedstock for clean biofuel production and thus, increasing renewable energy share in the total final energy consumption.</li> </ul>			
Horizontal, across value chains (SDG 2, 6,	<ul> <li>2.4 By 2030, ensure sus systems &amp; impleme practices that increat production, that help that strengthen capa climate change, ext flooding &amp; other dist progressively impro</li> <li>2.4.1: Proportion of agrid productive and sust</li> </ul>	tainable food nt resilient ag ase productiv o maintain ec acity for adap reme weathe asters and th ve land & soi cultural area ainable agric	<ul> <li>By producing feedstock for biofuels from contaminated land under on-going remediation, useful agricultural land will be released for food and feed production.</li> <li>GOLD final outcomes will support the restoration of contaminated land for agricultural uses. Most certainly</li> </ul>			

8, 9, 13) 2 <sup>ZERO</sup> HUNGER			prior an assessment and monitoring of residual risks will have to be done to evaluate if any pollutant linkages may remain.
3 GOOD HEALTH AND WELL-BEING	<ul> <li>3.4 By 2030, reduce by one third p from non-communicable disea prevention and treatment and health and well-being</li> <li>3.4.1 Mortality rate attributed to ca disease, cancer, diabetes or o disease</li> <li>3.9 By 2030, substantially reduce deaths and illnesses from haz and air, water and soil pollutio</li> <li>3.9.1 Mortality rate attributed to ho ambient air pollution</li> <li>3.9.2 Mortality rate attributed to ur sanitation and lack of hygiene Water, Sanitation and Hygien services)</li> <li>3.9.3 Mortality rate attributed to ur</li> </ul>	premature mortality ases through promote mental rdiovascular chronic respiratory the number of cardous chemicals on and contaminat busehold and asafe water, unsafe (exposure to uns e for All (WASH) intentional poison	<ul> <li>Proposed innovative phytoremediation strategies and optimised solutions will support the restoration of degraded/contaminated lands and soils, contributing to reduce the exposure to hazardous chemicals and to contaminated groundwater and soil, bringing benefits in terms of human health<sup>xvii</sup></li> <li>The use of harvested biomass for clean biofuel production will support the reduce to further educe co-emitted air pollutants, bringing cobenefits for air quality and to come for the solution state of the exposure to harvested biomass for clean biofuel production will support the reduce co-emitted air pollutants, bringing cobenefits for air quality and the mediate the solution of t</li></ul>
6 CLEAN WATER AND SANITATION	<ul> <li>6.3: By 2030, improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals &amp; materials, halving the proportion of untreated wastewater &amp; substantially increasing recycling safe reuse</li> <li>6.3.2: Proportion of bodies of water with good ambient water quality</li> </ul>	premediation strategies and ions will reduce leaching of ollutants, and will improve the rmation /dissipation, and/or f organic compounds in soil and ion of contaminated sites and of ts that possibly threat the ground s (useful for drinking water irrigation) will stimulate the f strategies and recommendations ion of 'phytoremediation/biofuel nbination achieving both and socio-economic gains <sup>xx</sup>	
8 DECENT WORK AND ECONOMIC GROWTH	<ul> <li>8.4: Improve progressively, throug resource efficiency in consum production &amp; endeavour to de economic growth from environ degradation, in accordance w framework of programmes on consumption &amp; production, wi countries taking the lead</li> <li>8.4.1: Material footprint, material footprint</li> </ul>	<ul> <li>The low input agricultural practices that will be applied in the cultivation of the selected energy crops in contaminated sites will reduce the material and ecological footprint (see also SDG 12)</li> <li>Increasing the number of jobs in crop production, logistics, conversion and distribution of biofuels.</li> </ul>	

		<ul> <li>Additional income for local farmers and population will be developed.</li> </ul>
9 INDUSTRY, INNOVATION AND INFRASTRUCTURE	<ul> <li>9.2: Promote inclusive and sustainable industrialization and, by 2030, significantly raise industry's share of employment and gross domestic product, in line with national circumstances, and double its share in least developed countries</li> <li>9.4: By 2030, upgrade infrastructure and retrofit industries to make them sustainable, with increased resource-use efficiency and greater adoption of clean and environmentally sound technologies and industrial processes, with all countries taking action in accordance with their respective capabilities</li> </ul>	<ul> <li>Assess the GHG emissions avoided due to biofuel production on contaminated lands under remediation/phytomanagement</li> <li>Development of innovative entrepreneurship by exploiting the biomass of the energy crop for the production of clean biofuels.</li> <li>Apply a framework for supply and value chain analyses of the three pillars of sustainability (environment, economy and society), performing detailed analysis for the selected contaminated site- conversion technology- and business- based systems and provide recommendations for future policy and market development.</li> <li>Prospects of job creation for women, men and young people, both within their family farms and along the supply chain of the produced biofuel</li> <li>Increase the availability of domestic raw materials and the ability to be used in new emerging markets.</li> </ul>
13 climate Action	<ul> <li>13.2: Integrate climate change measures into national policies, strategies and planning</li> <li>13.b: Promote mechanisms for raising capacity for effective climate change-related planning and management</li> <li>13.b.1: Number of least developed countries that are receiving specialized support, and amount o support, including finance, technology and capacity-building.</li> </ul>	<ul> <li>Promoting the cultivation of energy crops in unused/abandoned contaminated areas facilitates the long-term locking-up of carbon and new sequestration</li> <li>The use of harvested biomass for clean biofuel production will support the reduction of greenhouse gas emissions<sup>xxi</sup>, <sup>xxii</sup></li> <li>The cultivation of 2nd-generation energy crops in EU will decrease the biofuel import from least developed countries, decreasing their land use changes (rain</li> </ul>

### **General impacts**

The specific impacts are related to energy, environment and agricultural targets. Issues that should be discussed are: **RED II, Green Deal, sustainable development goals (SDGs), Climate change, bioeconomy and GAP after 2020**.

**Renewable Energy Directive (REDII)**<sup>xxiii</sup>- emphasises the role of biofuels<sup>xxiv</sup>, bioliquids and biomass fuels<sup>xxv</sup> but at the same time takes a more targeted approach to ensure Indirect Land Use Change (ILUC) impacts associated with conventional pathways are reduced. After the 31st December 2023 biofuels, bioliquids and biomass fuels produced from food or feed crops - for which a significant expansion of the production area into land with high carbon stock is observed<sup>xxvi</sup> - will gradually decrease to zero by 2030. In this context, the Directive also sets national limits at Member States' 2019 levels for the period 2021 – 2023. These limits will affect the biofuel quantities that can be counted towards the overall national share of renewables and the share of renewables in transport. Member States will still be able to import and use fuels affected by the limits, but they will not be able to consider them as renewable energy or count them for their renewable energy targets. The Directive also introduces another concept, aimed to contribute to the 14% target: the Low-ILUC risk biofuels, bioliquids and biomass fuels that, however, need to be certified as low ILUC risk. These will therefore represent one of the main options to maintain current shares and further develop the sustainable biofuels market potential in Europe from 2023 onwards, especially in sectors with limited short-term

alternatives as aviation, heavy duty and maritime. The low ILUC risk status is so far defined by the Commission Delegated Regulation (EU) 2019/807 of 13 March 2019<sup>xxvii</sup> supplementing Directive (EU) 2018/2001. This states that low ILUC risk biofuels, bioliquids and biomass fuels are those:

 'that are produced under circumstances that avoid ILUC effects, by virtue of having been cultivated on "unused, abandoned or severely degraded land"xxviii (the selected highyielding lignocellulosic energy crops proposed by GOLD)

**Green Deal** - is a new growth strategy that aims to transform EU into a fair and prosperous society, with a modern, resource-efficient and competitive economy where there are no net emissions of greenhouse gases in 2050 and where economic growth is decoupled from resource use. <u>GOLD will provide the knowledge on solutions that can tackle the targets imposed by this EU new vision (no net emissions of GG in 2050 and economic growth decoupled from resource use), based on chains of energy crops for biofuels with low ILUC risks. Namely, based on the project findings, valuable knowledge will be collected regarding optimised value-chains for biofuel production by selected energy crops grown on contaminated lands, land decontamination projections, and how the socio-economic and environmental-related challenges of the optimised value-chains will be in line with the Commission's strategy to implement the United Nation's 2030 Agenda and the Sustainable Development Goals for 2030.</u>

## 2 Update of the plan for exploitation and dissemination of result (if applicable)

An updated version has been updated during the 2<sup>nd</sup> reporting period and it was uploaded in the participants' portal (D4.4).

### **3** Update of the data management plan (if applicable)

An updated version has been planned for M48.

# 4 Follow-up of recommendations and comments from previous review(s) (if applicable)

Not applicable

### 5 Deviations from Annex 1 and Annex 2 (if applicable)

No deviations have been monitored in the  $2^{nd}$  reporting period.

### 5.1 Tasks

- Milestones 5 and 8 although planned for the 1<sup>st</sup> reporting period they both achieved in the 2<sup>nd</sup> reporting period.
- Milestone 5 had to be postponed due the late harvesting of the biomass produced in GOLD fields. The field trials established on fields from M11 to M13 and the harvesting started from mid of M17 and completed in M20. The harvested biomass was sent to CRES for chipping and drying and the first packages started to be sent in M20 of the project.
- Milestone 8 it was initially planned for M9 (in the proposal) that was January 2022. In the portal, by mistake was written M2. There was an issue with the preheating protocol due to a lower combustion chamber of the ATP unit but it is now resolved. Also, the flare for the full operation will be officially certified and operational up until September. The ATP will be fully operational in fall 2023. However, the FTS and the reforming parts of the work with surrogate reactants are more advanced than scheduled.

### 5.2 Use of resources

In table 55 the use of the resources per partner is presented. In table 56 it is presented the person months per WP and person.

			U.S. C.S. C.S. C.S. C.S. C.S. C.S. C.S.				_
				Adjustment		Total costs	Remaining
	Partners	Budget	Costs period 1	for period 1	Costs period 2	claimed	budget
1	CRES	330000	75670,20		119009,05	194679,25	135320,75
2	AUA	249375	65482,49		100735,2	166217,69	83157,31
3	TUM	498750	56192,10		198584,55	254776,65	243973,35
4	RECORD	195250	72132,99		72834,76	144967,75	50282,25
	POLITO	40000	4908,45		15203,25	20111,70	19888,30
5	ETA	195000	38467,30		74138,3	112605,60	82394,40
6	UMCS	182500	36786,78		96848,57	133635,35	48864,65
7	TNO	283875	8519,08		162497,33	171016,41	112858,59
8	CERTH	208750	0,00		91598,40	91598,40	117151,60
9	UNIBO	185125	80090,80		82149,19	162239,99	22885,01
10	INRAE	65000	32721,34		14055,68	46777,02	18222,98
11	JUNIA	166075	0,00	68919,10	87739,96	156659,06	9415,94
12	FCT	73750	27121,44		14207,99	41329,43	32420,57
13	ICL	136250	0,00		51078,98	51078,98	85171,02
14	WR	141375	38980,70		57585,8	96566,50	44808,50
15	METE	48875	26918,29		14055,68	40973,97	7901,03
	Total	2999950	563991,96		1252322,69	1885233,75	1114716,25

 Table 55: Use of the resources during the 2<sup>nd</sup> reporting period

### Table 56: Use of the person months during the 2<sup>nd</sup> reporting period

									Mean person	Mean person
	Partners	WP1	WP2	WP3	WP4	WP5	TOTAL	Budget	cost (actual)	cost (DoA)
1	CRES	8,00	0,00	1,00	2,00	9,40	20,40	48692,75	2386,90	3500,00
2	AUA	18,09	0,00	3,40	0,40	0,42	22,31	57490,27	2576,88	3750,00
3	тим	0,00	22,72	0,50	0,20	0,20	23,62	131027,94	5547,33	6800,00
4	RECORD	0,00	6,27	0,87	0,42	0,56	8,12	45588,14	5614,30	3760,14
	POLITO	0,00	0,00	4,56	0,00	0,00	4,56	12162,6	2667,24	2461,54
5	ETA	0,00	0,00	0,00	11,69	1,00	12,69	45931,45	3619,50	4000,00
6	UMCS	20,95	0,00	0,00	0,80	0,85	22,60	33083,81	1463,89	3000,00
7	TNO	0,00	10,74	0,79	0,69	0,17	12,39	92554,06	7470,06	8824,24
8	CERTH	0,00	27,54	4,73	0,21	0,45	32,93	66241,17	2011,58	3500,00
9	UNIBO	14,28	0,00	0,00	0,93	1,40	16,61	50327,99	3029,98	4100,00
10	INRAE	0,59	0,00	0,00	0,09	0,06	0,74	9236,84	12482,22	7500,00
11	JUNIA	13,97	0,00	0,00	6,23	0,00	20,20	92161,91	4562,47	6900,00
12	FCT	0,85	0,00	0,36	0,18	0,15	1,54	8914,99	5788,95	3461,54
13	ICL	0,00	0,00	4,60	0,00	0,00	4,60	38831,15	8441,55	9142,86
14	WR	1,47	0,00	6,27	0,41	0,55	8,70	40562,2	4662,32	8341,67
15	METE	2,50	0,00	0,00	0,00	0,00	2,50	8557,47	3422,99	3325,00
	Total	80,70	67,27	27,08	24,25	15,21	214,51	781364,74		

**Junia (former YNCREA)** didn't submit on time the expenses of the 1<sup>st</sup> reporting period and thus in the 2<sup>nd</sup> reporting period submitted two reports; a report for the 2<sup>nd</sup> period and an adjustment form for the 1<sup>st</sup> reporting period.

Table 57: Deviation in personnel costs during the 2<sup>nd</sup> reporting period

Partner	Deviations on personnel costs		Justification			
CRES	Deviation of the average rates for personnel costs declared for RP2 (-31,80%)	During had lov been p 1 <sup>st</sup> repo 2 <sup>nd</sup> rep	During the 2 <sup>nd</sup> reporting period the personnel that was involved ad lower personnel costs compared to the personnel that had een planned during the GA. This deviation was larger in the <sup>st</sup> reporting period (48%) and it was partially corrected in the <sup>nd</sup> reporting period			
AUA	Deviation of the D average rates for m personnel costs tr		During the 2 <sup>nd</sup> reporting period, as it was in the 1 <sup>st</sup> , the najority of the person months spent was for work on field rials where PhD students had been involved. Thus, the			

	declared for RP2 (-		mean person costs were 31.28% lower than planned in DoA.				
тим	Deviation of th	he averac	During the 2 <sup>nd</sup> reporting period the personnel that				
. •	rates for perso	sonnel costs		was involved had lower personnel costs compared to			
	declared for R	RP2 (-18.4	12%)	the personnel that had been planned during the GA.			
RECORD	Deviation of th	he D	uring	the 2 <sup>nd</sup> reporting period the personnel that was involved			
	average rates	for ha	br had lower personnel costs compared to the personnel that I				
	personnel cos	sts be	en p	lanned during the GA. This deviation was mainly for the			
	declared for R	RP2 w	work under WP2 (blomass pretreatment) where young				
Uni-Lublin	(-49%)			sis had been involved to accomplished it.			
	the average	for an ex	nerie	enced staff. However, during the grant realization the			
	rates for	tasks we	ere m	ainly performed by a PhD student that had by far (about			
	personnel	60-70%)	lowe	er salary. The person in charge from UMCS has trained			
	costs	the PhD	stud	ent to run the research activities. Due to lack of			
	declared for	experien	ice, t	he PhD student worked more time and she will need			
	RP2 (-	more pe	rson	months (for lower rates) to carry out the planned			
	51.12%)	activities		al person months had been asked from 26.5 to increase			
		to 46) wi	thout	t changing our budget for personnel.			
CERTH	Deviation of th	ne	Dur	ing the 2 <sup>nd</sup> reporting period the personnel that was			
	average rates	for	invo	blved had lower personnel costs compared to the			
	personnel cos	sts	per	sonnel that had been planned during the GA. It should			
	declared for R	RP2 (-	be r	noted the majority of the person months was devoted to			
	42.50%)	The ave	tasi	(2.1)			
UNIBO	the average	was an e	estim	ate that reflected the situation at the time of the			
	rates for	proposa	l. The	e role and level of seniority of the members of the			
	personnel	UNIBO r	resea	arch group indicated in the proposal has led to a higher			
	costs	average	pers	onnel cost.			
	declared for	The ave	The average rate for personnel costs declared in RP1, 3029.98 €,				
	RP2 (- 26 10%)	reflects the current situation and is related to:					
	20.1078)	the project from UNIBO research unit:					
		the willingness to foster the participation of younger researchers in					
		order to support their career development at the University;					
		the ne	the need to rationalize the contribution of senior researchers with				
		releva	nt sci	ientific expertise engaging younger researchers, placed			
		side by	y side	e to senior researchers, with resulting a lower average			
INRAE	Deviation of th	he averac	ie	During the 2 <sup>nd</sup> reporting period only one person from			
	rates for perso	onnel cos	ts I	INRAE participated in GOLD and this person was senior			
	declared for R	RP2		export that means that had high monthly rate compared			
	(+66.42%)		1	to the mean one declared in the Grant agreement.			
JUNIA	Deviation of th	he averag	je   l	During the 2 <sup>nd</sup> reporting period the personnel that was			
(Iormer Vocrea)	declared for R			nersonnel that had been planned during the GA. The			
moreaj	33 88%)	(1 2 (-		majority of the person months was used for the field			
	00.00707		1	trials in WP1.			
UNL	Deviation of th	ne	The s	salaries of the permanent personnel increased due to			
	average rates	for	caree	er promotion, and also because the post doc (temporary			
	personnel cos	Sts	personnel) was nired at the end of the 2 <sup>nd</sup> reporting period				
	(+67.24%)		planned				
WR	Deviation of th	veviation of the During the 2 <sup>nd</sup> reporting period the personnel that was					
	average rates for			ved had lower personnel costs compared to the			
	personnel cos	sts	personnel that had been planned during the GA. It should be				
	declared for R	RP1 (- 🛛 i	noted the majority of the person months was devoted to task				
	44%)		3.1.				

### CTD participation in GOLD during the 2<sup>nd</sup> periodic report

CTD replaced the work of IITD. Due to the late replacement of the IITD the work with CTD started later than planned and thus the field work will be replaced with pot trials to speed up the procedure. The activities of CTD will be reported in the 3<sup>rd</sup> reporting period.

#### 5.2.1 Unforeseen subcontracting (if applicable)

No unforeseen subcontracting is reported in this period.

### **5.2.1 Unforeseen subcontracting (if applicable)**

No unforeseen third parties are involved in the project.

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<sup>xxii</sup> Schmidt T, Fernando AL, Monti A, Rettenmaier N (2015) Life Cycle Assessment of Bioenergy and Bio-Based Products from Perennial Grasses Cultivated on Marginal Land in the Mediterranean Region, BioEnergy Research, 8, 1548-1561, https://doi.org/10.1007/s12155-015-9691-1

xxiii https://ec.europa.eu/jrc/en/jec/renewable-energy-recast-2030-red-ii

xxiv Biofuels" as defined in RED

xxv Biomass fuels" is a new term introduced in REDII, for gaseous and solid fuels produced from biomass

xxvi https://ec.europa.eu/transparency/regdoc/rep/3/2019/EN/C-2019-2055-F1-EN-ANNEX-1-PART-1.PDF

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- <sup>xxviii</sup> "Severely degraded land' means land that, for a significant period of time, has either been significantly salinated or presented significantly low organic matter content and has been severely eroded."