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Chapter

Biorefinery for Rehabilitation of Heavy Metals Polluted Areas

Teodor Vintila, Eniko Gaspar, Maria Mihaela Antofie, Luca Magagnin, Adina Berbecea and Isidora Radulov

Abstract

Biorefinery applied in heavy metals polluted lands proposed here describes a process starting from soil (polluted and unfit for food and feed production) and solar energy stored in carbohydrates (regarded here as a solar energy carrier) to deliver liquid and gaseous biofuels, green building block chemicals for the market and return the rest of the matter (not delivered to the market) as fertilizer and soil improver, extracting the heavy metals from the polluted soil for safe reuse and remediating the land to sustainably deliver resources in a circular bioeconomy. The circular economy proposed in this chapter offers a novel approach to land rehabilitation by investigating the opportunity for economic value creation as an integral part of a rehabilitation strategy and production of biomaterials and biofuels as renewable energy carriers. The case study approached here can be developed in a complete circular biorefinery process and value chain enabling the use of heavy metals polluted lands for production of renewable energy and biomaterials and at the same time serve as a means of rehabilitation of contaminated lands. This biotechnology can be transferred and adapted in other areas improper for food/feed production due to contamination human industrial activity.

Keywords: biofuels, biorefinery, circular bioeconomy, Copsa mica, heavy metals, pollution, soil remediation

1. Introduction

In recent years, agricultural use of the anaerobic digestate as organic fertilizer has aroused extensive public criticism due to its increased heavy metal (HM) contents, [1, 2]. Consequently, some novel approaches are developed to treat organic materials and avoid the negative effect of HMs to environment [3, 4]. Comparing with the fresh crops, their biogas residues after anaerobic digestion retained main fibrous texture which is essential for soil texture and fertility. On the other hand, organic materials such as digestate, manure, compost, have been reported to effectively reduce the availability of heavy metals in contaminated soils. This effect can be explained by the enhanced contents of organic matter in amended soil associated with the improvement of the biological, microbiological and biochemical properties of contaminated soils amended with organic materials [5, 6]. Organic amendments decreased

significantly metal availability in soil, due to the binding of metals to organic matter as metal-organic complexes. The addition of 45 t ha^{-1} of organic amendments dry matter, led to an increase biomass yield in a mix of perennial grasses and straw cereals, belonging to the Leguminosae (*Trifolium pratense*) and Gramineae family (*Dactylis glomerata*, *Lolium perenne*, *Agropyron repens*), cultivated in polluted area of Copsa Mica (Romania). The contents of Cd and Pb in plants treated with organic amendments were significantly decreased [7]. The Pb concentrations in plants from field treatments with organic amendments were below the threshold for green fodder (40 mg kg^{-1}) according with Directive 2002/32/EC on undesirable substances in animal feed [8]. Administration of organic materials as amendments to contaminated soils is used in many cases with in order to improve soil fertility, improve vegetation on polluted lands and decrease availability of toxic substances for the plants cultivated on marginal lands [9, 10]. The addition of organic amendments to contaminated soils can affect bioavailability of heavy metals by forming metal oxides or carbonates associated with organic matter, which reduce the bioavailable forms to more stable fractions [11]. In addition to these effects, organic amendments are known to improve other soil characteristics such as water and nutrient holding capacities or aeration in the soil particles.

Sorghum crop is selected in this work as a tool with multiple purpose. It is applied as a green cover for un-used, or not-properly used polluted soil; being a robust, drought tolerant and low-demanding for nutrients plant, can deliver important yields of biomass and sugars for industrial purpose; intensive cultivation can be a tool to extract pollutants from soil; residues generated along cascade biorefining of sorghum biomass are regarded as heavy metals carriers, which can be delivered by the biorefinery in concentrated form.

The proposed circular approach proposed in this work consists in processing sorghum crop in cascade. Biorefinery will primarily process sugars to liquid biofuels-biochemicals and sorghum crops harvested from the HM polluted area (high or low polluted) is considered as feedstock for an industrial scale biorefinery. The harvested biomass (highly polluted and low polluted) from the envisaged area is used as feedstock in biorefinery for liquid biofuels, anaerobic digestion and thermal decomposition (pyrolysis or combustion) applied in cascade:

Biorefinery – Anaerobic digestion – Thermal decomposition

Thermal decomposition (combustion-pyrolysis) is performed to concentrate HM from digestate obtained by processing biomass from very polluted areas, primarily envisaged to carry HM in high concentration.

The aim of this work is to design a truly circular production process for bioenergy production that simultaneous serves as a contaminated land rehabilitation strategy. Thus, our approach will provide a means to address past wrong doings, yield a new opportunity for already polluted lands to be used sustainably and offer an example of how value chains can be made self-sustainable.

In our approach, we start from the paradigm “*considering the plants as the greenest battery able to accumulate and store solar energy, simultaneously delivering organic matter as feedstock for bio-based economy and cure the environment*”. It all starts with unique and wonderful ability of the photo-autotrophic living organisms (plants) to convert CO_2 , H_2O and sun energy (by simultaneously emitting free O_2) into $\text{C}_6\text{H}_{12}\text{O}_6$ (simple sugars)– the molecule used as basic energy source in all living organisms and consequently the main energy carrier in bio-based economy. Plants have also the ability to grow in a wide range of environments, including those affected by humans, and can therefore re-introduce “lost” molecules in natural cycles. We just need to understand

how to harness these organisms, their metabolism and to find them the right place in a sustainable bioeconomy.

Circular bioeconomy is about integration and inter-connection. We propose to connect several processes and technologies in a comprehensive, sustainable and circular bioeconomic value chain with the objective to offer a method of biological remediation of environment affected by humans that integrates a complete biorefinery of plants to deliver products and eco-service at the same time by smart management of bioresources.

2. Concept of remediating biorefinery

We propose a study case using a sugary plant – *sweet sorghum* as feedstock for a biorefinery and remediating tool – delivering sugars for bioethanol, lignocellulose for second generation biofuels and for biogas to capture residual energy. This crop is considered here as a tool to extract heavy metals (HM) from an industrially polluted area, where the main pollutants are Cd, Pb, Cu and Zn. The area heavily polluted in the proximity of the heavy metals' smelter stretches on around 22,000 ha (the surface polluted by lead according to previous research [12, 13]) and pollution radially decreases. From this point of view, we divided the studied area in two categories: “heavily polluted” and “lightly polluted”. Crop from both categories will be used as feedstock in biorefinery where it is converted to liquid biofuels and biochemicals. The by-products resulting from this process carry organic matter, energy and pollutants (HM). These by-products can contain HM in a wide range of concentrations depending on the soil used to grow the crop.

Both lightly polluted and heavily polluted biomass (by-products) are sent to anaerobic digestion (AD) to continue this way the biorefinery of the feedstock and to deliver more energy (gaseous biofuel - biogas) and to continue decomposition of the vegetal organic complex structures. After AD process, the obtained digestate is separated in liquid and solid fraction, which will contain HM in varying concentrations. The solid fraction containing HM above legal limits, is sent to combustion/pyrolysis. The ash/char is used to extract metals in concentrated form and re-delivered to metals industry. The solid fraction containing HM within legal limits, is used as soil improver and immobilizer for lightly polluted soil, this way gradually returning polluted soil back to produce edible crops. From the liquid fraction, nitrogen is extracted to obtain two types of products: nitrogen organic fertilizers and liquid digestate rich in other elements (P, K, S). This way eutrophication by using N-rich digestate to improve soil quality is avoided. Liquid digestate containing HM above legal limits, is sent to extraction of metals and the resulted digestate is returned back to soil. **Figure 1** displays the overall concept of the circular remediating biorefinery described here.

By this concept of circular remediating biorefinery we intend to develop a new approach for biorefining agricultural feedstock, addressing as case study/main feedstock the biomass obtained in marginal lands with reference to industrially polluted areas that take into consideration not only the economy related to the biorefinery products but also to create a complete value and social chain that will allow agriculture to bloom again in polluted areas.

By implementing our concept, we intend to develop a complete circular biorefinery including remediation technologies (more specific: phytoremediation, immobilization and phytoextraction, applied in two main scenarios) of heavy metals contaminated land using as feedstock carbohydrates (regarded here as solar

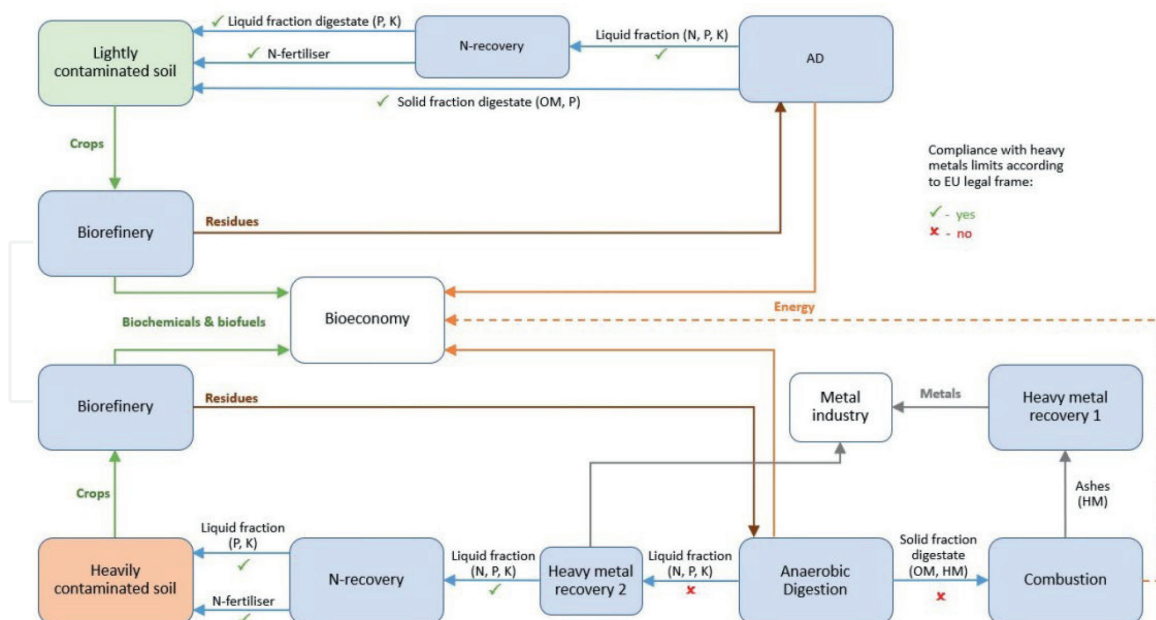


Figure 1.
Scheme of the circular remediating biorefinery concept.

energy carriers). The biorefinery will convert feedstock to green energy and a range of biochemicals, (ethanol, lactic acid for PLA etc) regarded as biofuels and green building block chemicals for the market. Other part of the feedstock is returned as fertilizer and soil improver, while residues containing metals in concentrated form are extracted for safe use.

“Circular Remediating biorefinery” developed here will bridge the gap between phytoremediation strategies and clean biofuel production in a sustainable and optimum manner, using and simultaneously remediating the contaminated land to sustainably deliver resources for bioeconomy - as case study- to be transferred and adapted in other areas with land improper for food/feed production.

3. Polluted area of Copsa Mica – Romania, as case study

Copsa Mica (see **Figure 2**) has for decades been known as “the most polluted town in Europe”. The main pollutants identified in this area were cadmium, copper, lead and zinc. Moreover, this city was presented in Blacksmith Institute and Green Cross Switzerland Report 2012 - “World’s Worst Polluted Places” [15] as examples of high cadmium pollution. In Romania there are some critical areas in terms of heavy metal pollution (Baia Mare, Zlatna, Moldova Noua, Coșșa Mică). Of these, Coșșa Mică area presents the highest risk of interception of heavy metals through locally produced local food, due to the large abundance of agrosystems in the structure of local socio-ecological systems. The Copsa Mica polluted area can be defined as the surface of land where the pollutant content in the top level of the soil (upper 20 cm) exceeds the alert thresholds defined by Romanian legislation. According to Vrinceanu and Lacatusu [12, 13], this polluted area covers 7040 ha where zinc content in soil is over 300 mg/kg; 10,320 ha of land where cadmium content in soil is over 3 mg/kg, or 22,565 ha where the lead content in soil exceed 50 mg/kg.

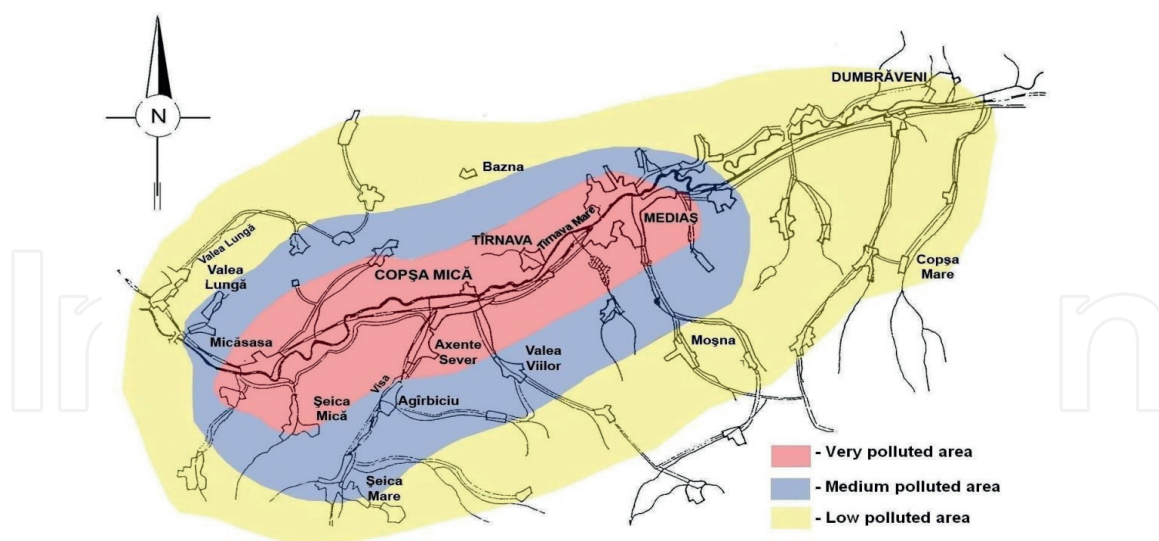


Figure 2.
Polluted area of Copsa mica (adaptation after: Barbu Horia, Lucian Blaga University of Sibiu [14]).

In Copsa Mica, the amount of Pb and Cd in vegetable samples exceeded the maximum permissible limits in carrots (median concentration 0.32 mg/kg for Pb and Cd) and in yellow onions (median concentration 0.24 mg/kg for Cd).

The European Commission has recently set new maximum levels for Cd and Pb in a range of food products to improve public health protection, with these measures entering into force from Aug. 30th 2021. Such actions aim to further reduce the presence of carcinogenic contaminants in food and make healthy food more accessible — a key aim of Europe's Beating Cancer Plan. Examples of these thresholds include 0.030 milligram per kilogram wet weight (ppm WT) for Cd and 0.10 ppm WT for Pb in stem vegetables; 0.10 ppm WT for Cd and 0.10 ppm WT for Pb in root and tuber vegetables (EU Regulations/2021 [16, 17]). In the case study area, the daily TM intake rates via local vegetable consumption are well above these values, more precisely 2 to 4 times higher for Pb and 5 to 10 times higher for Cd; yielding potential adverse public health effects [18]. Even after 10 years of ceasing production of the nonferrous smelter (production was ceased in 2009), the HM contents in the soil and plants are high inside the polluted area [7]. Such soils, or those with various other components that can be absorbed by crop plants and endanger public health, are recommended for use in the production of non-food crops, ideal for obtaining biomass to be used as a raw material in biorefinery.

Chronic effects in human health mainly result from exposure to low levels of cadmium and are represented by chronic obstructive diseases of the lungs and the renal system. There may also be effects on the cardiovascular and bone system. The fetus, young children, and pregnant women are unanimously recognized as sensitive populations with increased risk of developing adverse effects in chronic exposure to lead, including relatively low concentrations. Another indicator influenced by chronic lead exposure is somatic development, the height and weight can be changed, in the sense of growth delay, of about 1–1.5 years [19].

Over the decades, many options to clean the soils polluted with heavy metals have been considered. Taking into account the problems posed by top layer removal and replacement, chemical washing and many other “hard” methods, “gentle remediation” options have been explored.

Phytoextraction, using plants that can accumulate large amounts of potentially toxic metals in their above ground parts was proposed by (Gosh and Singh, 2005) as a feasible option, but the proposed plants (*Thlaspi caerulescens*, *Brassica juncea*, *Ipomoea carnea*, *Datura innoxia*, *Phragmites karka* etc), either were exotic in Europe, raise cultivation problems, deliver small yields in terms of feedstock (carbohydrates, biomass) for biorefinery and/or concerns about their invasive potential. On the other hand, common European plants with high productivity have a small metal accumulation capacity [20]. Even several remediation attempts in Copsa Mica area have applied, none of them have been proven particularly successful [21–24] and the local community and farmers have adopted coping strategies, looking for other crops with a low uptake of heavy metals (i.e. excluders, as defined by Baker [25]) (**Figures 3 and 4**).

An important research focused on bioremediation of polluted soil in Copsa Mica area is *The RECARE project funded by the European Commission FP7 Programme, ENV.2013.6.2–4 ‘Sustainable land care in Europe’. EU grant agreement: 603498*. The research in this project regarding Copsa Mica case was focused on immobilization of these pollutants using different types of inorganic additives, such as zeolitic tuff, bentonite, volcanic tuff, and organic materials such as biosolids, cattle manure [26]. Although the situation is well documented, and there have been some attempts to remediate these soils, until now, no feasible solution for the decontamination of this large region has been found.

When phytoextraction is approached, important attention is dedicated to plants able to accumulate a particular metal from soil with higher efficiency compared with other plants. These plants are defined as hyperaccumulator plants and can accumulate metals in high concentration in some of their tissues - 100-fold or 1000-fold when compared to other plants growing in that soil. The bad news is that such plants are relatively rare, are endemic only in scattered areas around the world, are less adaptive



Figure 3.
Area in vicinity of heavy metals smelter.



Figure 4. *Miscanthus giganteus* (left) and sweet sorghum (right) cultivated on polluted soil in Copsa mica area.

to the polluted areas where they need to be cultivated and the number of known species are low - less than four hundred species identified for as little as eight polluting metals [27]. The good news is that heavy metals can be extracted by very common plants, even they do not have ability to accumulate metal in high concentrations in their tissues as hyperaccumulator plants. If we take into account plants that produce high amounts of biomass per hectare of land, such as corn (*Zea mays*), sorghum (*Sorghum bicolor*), alfalfa (*Medicago sativa* L.) cup plant (*Silphium perfoliatum*) [27] or sunflower (*Helianthus annuus* L.) [28], the quantity of metals extracted from soil by plants producing high yields even containing lower concentrations of metals, can be more important than quantity of metals extracted by low yielding hyperaccumulator plants. Large quantity of biomass produced by such crops can remove higher amount of metals from the polluted soil even at lower concentrations of metal within the plants compared with low quantity of biomass with high concentrations of metal produced by hyperaccumulator plants [27].

Even high levels of heavy metals have been found in edible plants in the polluted area, people continue to farming and to produce food. There are farms producing different types of crops, cattle, chicken and other animal farms. There is no constraining regarding farming in the polluted area. The people are not informed regarding the risks. Still, in the polluted area there are land owners avoiding cultivation of edible plants. There are several hectares of *Miscanthus giganteus* as energy crops. Sweet sorghum has been cultivated as well, as trials in a former research projects, obtaining high yields: 60–100 to/ha of fresh mater, or up to 35 to/ha of biomass dry matter. **Figure 4** is an example of *Miscanthus giganteus* cultures adopted by local land owners to use the polluted soil for energy purpose.

Although is generally accepted that phytoremediation of metals from contaminated soil is possible and several plants have the ability to extract the pollutants from soil [29], the utilization of the biomass containing heavy metals raise important questions. Several approaches for disposal of metals containing biomass include decaying, thermal decomposition including burning or pyrolysis, chemical extraction, or even recovery of precious and semiprecious metals - called phytomining [30]. These technologies applied for processing polluted biomass generates wastes. For example, in

the process of thermal decomposition by pyrolysis of heavy metals polluted biomass, almost all metals accumulate in the char, while by burning, metals can be found both in flue gasses and ash. Consequently, questions are raising regarding disposal of the heavy metals contaminated byproducts/residues such as char or ash. An attractive alternative approach to use heavy metal-polluted soils is to produce sugars crops and high-yielding biomass crops such as sweet sorghum. Sugars extracted from such crops can be converted in biorefineries to a wide range of biochemical; the organic residues resulted in biorefinery to be digested for production of biogas and digestate and to return this digestate in the same polluted soil as a fertilizer. By this circular bioeconomy approach, heavy metals can be confined in the polluted area and the risks of disposal of contaminated residues and further disperse the pollutants is eliminated.

Plant biomass can be used for different energy-recovery techniques, such as anaerobic digestion, incineration, gasification and liquid biofuels production. It is important to be sure that the metal burden, toxic metals such as Cd, in plant biomass will not affect biofuels production [31]. So, it is essential to assess these effects of metals concentrations on biofuels production systems and the design of biotechnological processes (ethanol fermentation, anaerobic digestion for biogas production etc). Moreover, selecting suitable plants is essential, as species accumulating high concentrations of pollution may raise difficulties in conversion processes [31].

Sweet sorghum has been chosen by our team for bioremediation/biorefinery application. This type of plant biomass could be used to supplement the metals needed in fermentation systems and anaerobic digester, contributing to the implementation of circular economic strategies and closing the loop in resource utilization chain.

Why sweet sorghum has been chosen for this study case? Sweet sorghum can be an important source of fermentable sugars for industrial biotechnology. A wide range of bioproducts for industrial, pharmaceutical or agricultural use can be obtained by microbial fermentation processes (alcohols, organic acids, amino acids, proteins, antibiotics, etc.). Sweet sorghum is an annual plant with a short production cycle and can be harvested after about 140–150 days of cultivation. The optimal seeding season is at the end of April - beginning of May and the harvesting can be done in September-October. It can be cultivated as secondary or precursor crops in combination with other short-cycle plants (for example triticale from early spring to June, followed by sweet sorghum for biofuels production). In classical biogas production technology, sugars in sorghum stems are converted in lactic acid during ensiling and by this the biomass is preserved until anaerobic digestion for biogas production.

Several studies indicates a variety of advantages of sorghum bicolor (L.) Moench over other sugar and starchy crops, which make this plant a highly studied energy crop [32]. Exhibiting high tolerance to draught, both sweet and grain sorghum varieties produce high yields even under a wide range of environmental conditions. More than that, studies demonstrates that sorghum can be cultivated on marginal lands and require low inputs [33–35]. In the context of climate change adaptation, temperatures and higher atmospheric level of CO₂ may beneficially affect sorghum crops in terms of a higher biomass yield. Sorghum cultures have been previously applied in *phytoextraction* experiments in polluted areas [36–38] and our own research results [39] indicated sweet sorghum as a good alternative for utilizing land polluted by heavy metals for bioethanol production, which would not only avoid food-fuel competition issues, but also provide way forward for land that is uncultivated due to human pollution.

Compared to other energy crops, sorghum has a global potential, being one of the most variable plants in terms of genetic resources, making breeding and development of new cultivars, adapted to different climate zones around the globe, easier [40].

Crops	Corn (for grains)		Sugar beet		Sweet sorghum	
Fresh mass (ton/ha)	20 (\approx 30–50% moisture)		50 (\approx 75–80% moisture)		60 (\approx 60–65% moisture)	
Products	Grains	Stalks	Sugar	Press cake	Sugar	Bagasse
(ton/ha) \approx	9	9	8	20	6	30
Ethanol (ton/ha) \approx	2.5	—	5	—	3	—
Methane (m ³ /ha)	—	750	—	1200	—	2500
(MWh/ha)*	20.6	7.5	41.2	12	24.8	25
1st + 2nd gen (MWh/ha)	28		53		50	
Climate change, (drought)	Sensitive to drought, production dramatically affected		Very sensitive to drought, production dramatically affected		Resilient to drought, high production in hot summer 40–60 MWh/ha	
Technological advantages	Low cost, long term and easy storage of main energy carrier (starch)		Direct conversion of main energy carrier - sugar (no hydrolysis phase)		Direct conversion of main energy carrier - sugar (no hydrolysis phase); availability of high energy content lignocellulose (bagasse)	
Technological disadvantages	Hydrolysis of starch (added costs); difficult storage of high moisture stalks (too dry for ensilage, too moist for baling); large surface to cover for harvest and transport of stalks		Seasonal production, loss of sugar during storage of beets, sorghum stalks; difficult to storage beets cake and sorghum bagasse; high costs, energy intensive technology for sugar concentration and refining. Problems solved by patented innovation 131,499 /2021 [41]			

*1 kg EtOH = 8.25 kWh; 1 m³ methane = 10 kWh.

Table 1.
 Relevant features of application of three main crops cultivable in European climate conditions.

Calculations show that sorghum can be comparable and, in some cases, competitive to sugar cane and corn in terms of sugar and bioethanol output per hectare (**Table 1**), while requiring much less water [42–45].

In this work we propose an integrated process in cascade using as feedstock sorghum biomass produced on heavy metals polluted soil (15 km distance from the smelter – the core of polluted area) having as objective soil remediation. Preliminary results obtained in lab scale [39] recommended sorghum as a crop able to grow on polluted soil and to provide readily fermentable sugars by juice extraction. In this research, metals concentration in sorghum juice are between 0.5 and 1.0 mg·kg⁻¹ for Pb and between 22.7 and 86.2 mg·kg⁻¹ for Zn, while Cd and Cu are not detected. When bagasse resulted after juice extraction is analyzed, the concentration of heavy metals increase as bagasses are pretreated - the average metals levels found in the thermo-chemically pretreated biomass were higher than those in the unpretreated biomass. Concentrations of all four analyzed metals increased after pretreatment: Cd from 3.60 to 4.03 mg·kg⁻¹, Cu from 15.57 to 25.56 mg·kg⁻¹, Pb from 11.24 to

19.38 mg·kg⁻¹ and Zn from 123.50 to 134.19 mg·kg⁻¹. These increased values after pre-treatments indicates higher availability of free metals after decomposition of lignocellulosic complex. More than that, the fate of metals was tracked in the biorefinery of bagasse to produce second generation bioethanol and after distillation, portions of Cu and Pb were found in the distilled ethanol, while Cd and Zn remained in vinasse.

In order to define “highly polluted biomass” and “low polluted biomass”, we refer to the European legal frame [46, 47]. In this EU legal frame are defined the highest levels of heavy metals accepted in products used as fertilizers and soil improvers (Table 2). Assuming that the concentration of metals increases in the solid part of the biomass along cascade processing (regarded as by-products in biorefinery) during treatments (juice pressing, hydrolysis, anaerobic digestion), we expect higher concentration of heavy metals to be found in digestate than in the raw material (sorghum biomass). According to European legal frame above mentioned, contaminants must not exceed the following limit values:

In this respect and according to previous research [39], in average Cd is the main pollutant found in sorghum in the area selected as study case – average concentration of 5 mg/kg dry matter of sorghum biomass, while lead is found in average concentration of 20 mg/kg (under the limit of 120 mg/kg in EU legislation). It is expected to harvest sorghum biomass containing higher concentrations of cadmium and lead closer to smelter and lower in low polluted areas (blue and yellow on the map, Figure 2). When the limit of Cd < 1,5 mg/kg DM (EU threshold for fertilizer) is regarded here to define low polluted biomass, the surface delivering very polluted biomass in the map from Figure 2 includes red and blue zones.

Respecting the above-mentioned legal frame, we propose to developed a new approach for biorefining agricultural feedstock, addressing as case study/main feedstock the biomass obtained from an energetic crop cultivated in marginal lands with reference to industrially polluted areas that take into consideration not only the economy related to the biorefinery products but also to deliver an integrated soil remediation system and create a complete value and social environment that will allow agriculture to bloom again in the selected area.

Regarding extraction of metals from biorefinery by-products, ashes/chars obtained through combustion/pyrolysis of solid digestate fraction can be considered as renewable secondary sources for the recovery of heavy metals. These ashes are usually classified as hazardous material due to their high content of toxic metals and soluble components. The most widespread leaching method is acidic leaching using strong mineral acids as many metal compounds have high solubility at low pH.

Metal	In soil improver, mg/kg dry matter	In organic fertilizer, mg/kg dry matter
cadmium (Cd)	2	1.5
hexavalent chromium (Cr VI)	2	2
mercury (Hg)	1	1
nickel (Ni)	50	50
lead (Pb)	120	120
inorganic arsenic (As)	40	40

Table 2. Highest levels of heavy metals accepted in products used as fertilizers and soil improvers according to EU legal framework.

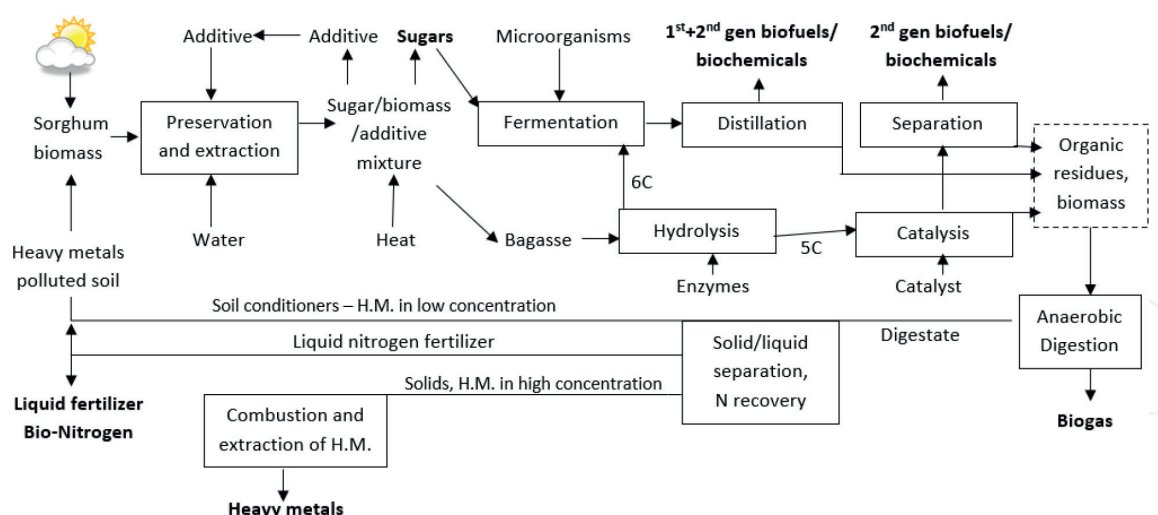


Figure 5.
 Draft of the proposed circular bioeconomy.

However, due to the alkalinity of the ash large amounts of acid are needed. This problem can be overcome by alternative leaching media (especially organic acids obtained in biorefinery) in order to favor the achievement of high efficiency in the dissolution and in the electrowinning of heavy metals. In this respect, the biorefinery can be an important provider for metals industry. Firstly, redistributing back “lost metals” extracted by plants and delivered through biorefinery by-products and secondly, providing catalysts for metals extraction. Organic acids can be produced in biorefinery by fermentation of sugars and delivered to industry to prepare leaching media for dissolution and in the electrowinning of heavy metals. This can be another aspect of circular (bio)economy proposed here. The schematic approach of the proposed circular economy is presented in **Figure 5**.

4. Preservation and extraction of sugars from biomass for biorefinery

There are numerous research results indicating sweet sorghum as one of the best crops for biofuels industry. Still, industrial exploitation of sorghum cultures as an energy carrier is inhibited by a short harvesting period in temperate regions (1–2 months in Romania) and storage challenges leading either to high costs (in either processing or storage facilities) or high losses of fermentable sugar [48, 49]. Apart from tropical climates where there is a minimum of two harvests a year of sugar cane, the production of biofuels from sugary plants in other part of the world (and in particular in Europe) does not allow processing cycles on an annual basis. This means that the entire production capacity of the plants is not exploited, with the consequent problems of scale economy that penalize these types of feedstock in Europe for bioethanol production. In North America market corn is widely used since this type of feedstock (corn grains) can be stored for long periods and the full capacity of the plant is fulfilled on annual basis. In Europe this approach is not considered environmentally friendly due to the large soil and water usage for non-food application. On the other hand, pretreatments of lignocellulose matrices have not yet exploited their full potential in order to be competitive with bioethanol produced in Brazil and North America.

The main disadvantage is the impossibility of preserving the sugar-containing sorghum crop throughout the year without losing the sugar content accumulated in

sorghum stems. Having a considerable moisture content (30–35%), sugar sorghum biomass is easily colonized by microorganisms, which consume sugars and cause the degradation of biomass. Classical ensiling (by lactic bacteria) has the same effect of sugar consumption, and drying of the biomass and preservation in dried form until processing is an alternative that cannot be applied on an industrial scale due to high energy inputs and storage costs. Therefore, the main bottleneck in using sweet sorghum as feedstock in biorefinery is preservation of sugar content in the biomass to be available around the year as feedstock for biorefinery.

Without preservation of sugars, the processing of sweet sorghum biomass would resemble sugar-beet processing: high capacity processing within a short period of time to minimize loss of sugars contained in the biomass. Processing facilities have large capacity and are only operated for a short period. This classical approach makes the process expensive due to high cost of capital per outputs unit. Furthermore, current sugar extraction technologies involve pressing the sorghum stalks (sometimes hydrated by the addition of water) and the harvesting of the sugar-containing juice. This process extracts only part of the sugar content stored in the sorghum biomass; the rest of the sugars remain in the bagasse. Sugars left in the bagasse are lost shortly after pressing by microbial proliferation. Incomplete use of sugars from sugar-containing biomass results in a much lower energy balance, reflected in a low degree of sustainability, low economic efficiency and higher carbon footprint.

Laboratory studies made by BUAS team have validated analytical predictions regarding sugars preservation and extraction from sorghum biomass and sugar beet. The analysis was carried out in small scale batches preserved during periods of over 12 months and the whole biorefinery of biomass was carried out in laboratory equipment. This technology, patented by BUAS Timisoara, is registered to Romanian Office for Inventions and Marks (OSIM) under the title “*PROCESS FOR BIOREFINING OF SUGAR YIELDING PLANTS WITH CONSERVATION AND EXTRACTION OF SUGARS FOR PRODUCTION OF BIOFUELS AND OTHER BIOPRODUCTS*”, Patent no. 131499/2021 [41]. Recently, at the global “Climate Launchpad” event - the world’s largest green business ideas competition, the invention reached the world semifinal and won the 1st place at national Climate Launchpad final in Romania.

The innovation of our approach lies in:

The use of a sorghum pre-treatment approach, proved at laboratory-scale (TRL3), consisting of preservation of sorghum biomass containing sugars for several months, more than one year, to make possible the use of sweet sorghum crops as feedstock for biofuels and biochemicals. The preservation of the main energy carrier (sugar) in the plants is the main criterion in considering a certain crop as feedstock for biorefinery. The patent developed a process of preservation of sugars in sorghum biomass by additivated ensilage, using a cost effective, recoverable, produced in situ additive. In traditional ensiling techniques, the sugars are lost by fermentation and transformed into organic acids such as lactic acid.

The invention has triple effect: (1) preservation of sugars, (2) extraction of sugars and (3) release of cellulose from lignocellulosic complex and access of cellulolytic enzymes to hydrolyse cellulose to glucose.

The advantages of the pre-treatment method can be found on three levels:

- Firstly, this method preserves sugars in the biomass for year around, improve extraction and releasing the sugars from biomass resulting in higher sugar yields and energy yields on the surface of land and the possibility to produce sweet

juice for fermentation on an ongoing basis; reducing the required pressing capacity and hence investment costs.

- Secondly and perhaps more importantly, during preservation period of the sugar-containing biomass by this original process, the chemical structure of lignocellulosic biomass is affected, facilitating the access of enzymes for hydrolysis of cellulose, this way excluding conventional methods of thermal-chemical pretreatment (alkaline/steam).
- And last, but not least, the economy of the complete biorefinery is much improved by lower capital expenditures, since smaller factories can be installed to process the same amount of biomass which currently have to be processed by large capacity refineries in short time, exclusively in the cold season, to prevent sugar lost by natural decaying. The economically-improved complete biorefinery is made possible by the original preserving process since first generation technologies can be directly linked to second generation biofuels and biochemicals and to anaerobic digestion which closes the loop of the circular economy.

In order to protect patent priority, data regarding sugars extraction and preservation have not yet been published.

By chaining the three main processes: (1) alcoholic fermentation of sugars extracted from sweet sorghum (2) enzymatic hydrolysis and fermentation of bagasse results after extraction of sugars and (3) anaerobic digestion of waste resulted after hydrolysis and fermentation for biogas production, total energy production is maximized (see **Table 3**), and the digestate returns to soil as organic fertilizer.

In order to increase technology readiness level (TRL), the pre-treatment process will be tested at pilot scale, and coupled with down-stream pressing, hydrolysis and fermentation to produce amounts of bioethanol and biochemicals in sufficient amounts to prove higher TRL. More than that, modeling of environmental impact and energy balance, profitability and costs need to be assessed to support transferability of project results from research to industrial application. Equipment located in University of Life Science from Timisoara, part of the pilot scale biorefinery, will be used to fulfill these objectives. **Figure 6** summarizes the innovative processes of preservation and biorefinery of sugary plants.

Circular bioeconomy proposed here integrate several technologies such as energy crops production, extraction of sugars, biorefinery, anaerobic digestion and remediation of heavy metals polluted soil. The concept can be summarized as follows.

Sweet sorghum harvested from highly and low polluted area is sent to preservation phase. In order to make sugars available for biorefinery around the year, the innovative technology for preservation of sugar containing biomass is proposed. In the next phase of the integrated circular bioeconomy, the extracted sugars are converted to first generation biofuels & biochemicals and the resulted lignocellulosic portion of the biomass is converted to second generation biofuels & biochemicals. The by-products generated in biofuels technology (bagasse, thin stillage, vinasse etc) are converted by anaerobic digestion to biogas (for bio-electricity or bio-methane) and digestate. From this phase, the bioeconomy will follow two paths:

- a. Digestate containing high concentration of pollutants (over the limits according to EU legal frame) is sent to combustion and to extraction of heavy metals. In

	Process	1st gen. Ethanol, (kJ·kg ⁻¹ biomass D.M.)	2nd gen. Ethanol, (kJ·kg ⁻¹ D.M.)	Biogas (kJ·kg ⁻¹ biomass D.M.)	Integrated process, cumulated energy production (kJ·kg ⁻¹ biomass D.M.)
A	Solid State Fermentation of sugar containing ensiled biomass	6522	0	7236	13,758
B	Hydrolysis and fermentation of bagasse resulted from (A)	6522	913	5256	12,691
C	Pretreatment, hydrolysis and fermentation of bagasse resulted from (A)	6522	1696	2149	10,367
D	Fermentation of freshly harvested juice, without ensilage	804	0	9000	9804
E	Fermentation of juice harvested from ensiled bagasse resulted from (D)	3996	0	14,400	18,396
F	Fermentation of juice (single extraction) from ensiled biomass	9343	0	5940	15,283
G	Hydrolysis and fermentation of bagasse resulted from (F)	9343	7500	3679	20,522
H	Fermentation of juice (multi- stage extraction) from ensiled biomass	16,620	0	4932	21,552
I	Hydrolysis and fermentation of bagasse resulted from (H)	16,620	2857	5904	25,381

Table 3.

Energy production by several processes applied in laboratory scale for biorefinery of sweet sorghum preserved by original preservation method.

industrial scale application, it is envisaged to deliver the heavy metals containing ash back to the smelter responsible for dispersion of pollutants in the area.

- b. The digestate containing low concentration of pollutants (between the limits according to EU legal frame) is used as soil improver to remediate, improve soil characteristics and to immobilize heavy metals inside the polluted area.

According with results from previous studies carried out in experimental field from Copsa Mica [26] the addition of organic amendments enhances the formation of stable complexes with organic compounds, improving the heavy metals immobilization processes in soil and leads to a decreasing of metals available amounts in soil. By addition of organic solids such as digestate resulted from AD of biorefinery by-products, it is foreseen to immobilize important part of pollutants (heavy metals), this way allowing the cultivation of edible crops at least in the low polluted area. Previous studies [7] indicated important rates of immobilization in polluted area due to the addition of organic fertilizer (digested plants) in the ranges of 38–40% of extractable Cd, 77–83% of extractable Pb and 43–47% of extractable Zn. Addition of organic residues will have significant effects on metal accumulation in biomass

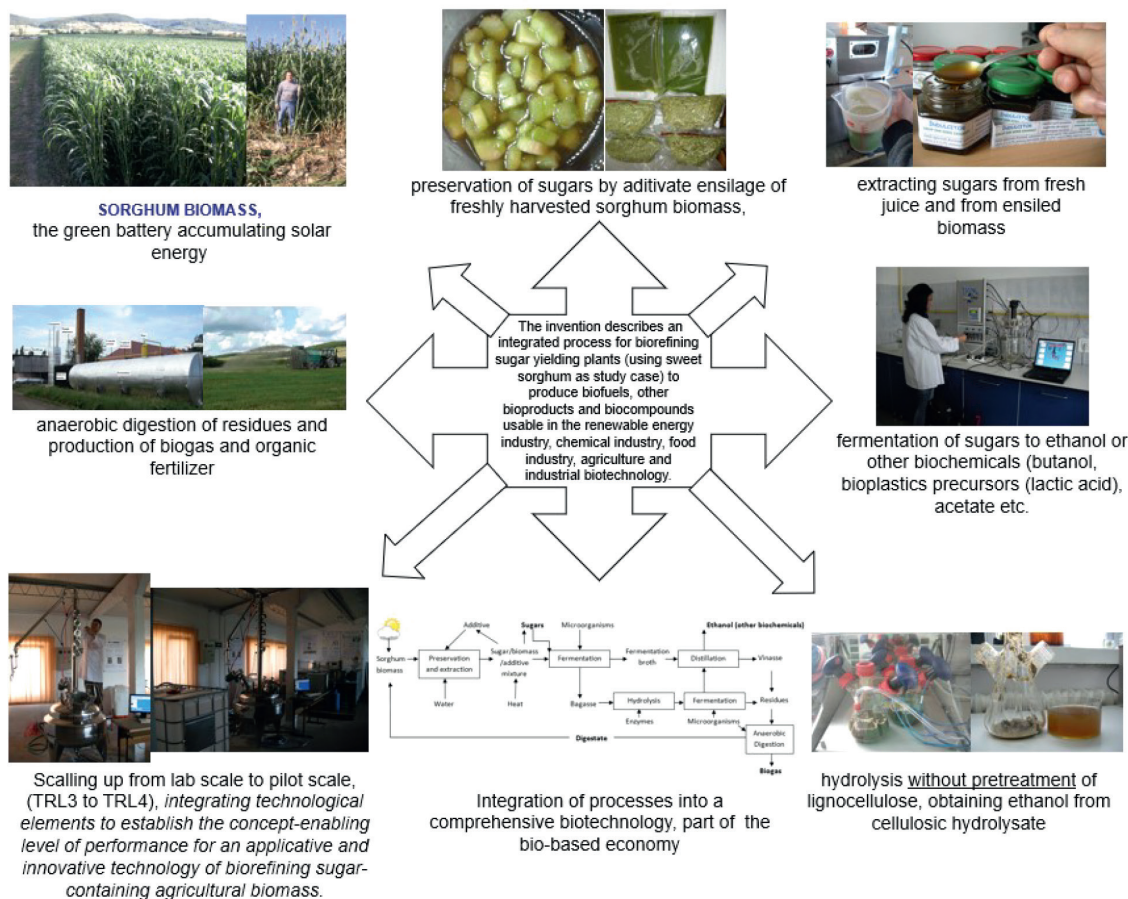


Figure 6.
 Summary of innovative process of preservation and biorefinery of sugary plants.

and the contents of pollutants in plants will significantly decrease. The target is to reach below the threshold for green fodder (40 mg kg^{-1}) according with EU legislation on undesirable substances in animal feed [8]. Also, by reducing metal toxicity and improving soil fertility, the application of organic amendments, will result in the development of a permanent vegetation cover in non-arable land of polluted area. Development of a dense plant cover can halt erosion and thus prevent pollutants from spreading to other areas.

Particular outcome is envisaged in low polluted area, where application of digestate for immobilization of metals can restore the agriculture lands for food and feed production in shorter time frame, improving social attractiveness of the area and consolidating social acceptance of the biorefinery-bioenergy-remediation circular economy in polluted areas.

Summarizing, the overall methodology proposed here consists of the following main aspects to be approached:

- Production of sugar crops (sweet sorghum) while assessing the effects of organic fertilizers and improvers (liquid nitrogen and digestate) on soil quality, crops production and quality and degree of pollution in HM polluted area;
- Application of the innovative process consisting of preservation of sugars by ensiling the freshly harvested biomass in the presence of a preservation additive, which simultaneously preserves the sugars, pretreat biomass and enhances the yields regarding sugars extraction;

- Fermentation of extracted sugars to produce ethanol/lactate as biofuel and bio-based building block chemicals, hydrolysis of cellulose (approaching additional pretreatments in relation to additivated ensiling regarded as pretreatment here), fermentation of hexoses and pentoses from hydrolysate to produce second generation biofuels/biochemicals;
- Treatment of by-products generated in previous stages by anaerobic digestion to obtain biogas and digestate to be used as soil conditioner and organic fertilizer, pyrolysis of highly polluted by-products (solid digestate) to provide bioenergy and treatment of ash by electro-chemical techniques to extract heavy metals in concentrated form.

5. Sustainability of the proposed biorefinery

The sustainability of biofuels production has been widely addressed in former projects and actions and shared among the chain actors which accepted the technologies through the technical, logistic, economic, financial, energetic, environmental and administrative aspects. Consequently, the main market players have been encouraged to start up new entrepreneurship to increase the economic competitiveness and at the same time the environmental sustainability of biofuels. The challenges in the biofuels market are to enhance raw material diversification, decentralization of the production and sustainability of biofuels (mainly as GHGs saving). The circular economy proposed here regarding the production of biofuels and other products in a biorefinery approach using sweet sorghum (as case study crop) and in the same time to cure the environment (polluted areas) contributes to address the current debates on land use and sustainability and to facilitate and promote a well-informed and balanced attitude among decision makers and the general public.

In order to better evaluate the impact of our circular biorefinery approach in the case study area, let us have an insight look on two possible scenarios to use local bioresources for biofuels production, considering *50,000 tons commercial scale ethanol biorefinery*. This is not approached as part of this research in this project, it can be considered a possible future scenario. This impact scenario is not restricted exclusively to the industrial polluted area, it can be extrapolated in general as circular bioeconomy approach.

Scenario 1: consider recuperation of lignocellulosic agricultural by-products and their conversion to second generation biofuels (ethanol).

Previous own laboratory results, in concordance with other published data indicate an average production potential of 200–250 ml ethanol per 1 kg of agricultural residual biomass (wheat straw and corn stover). *The question raised is: what are the potentials in different regions to provide agricultural residues for a 50,000 tons commercial scale lignocellulosic ethanol biorefinery?* We assume that half of an entire region straw production can be harvested from the fields and transported to the biorefinery.

Table 4 shows the comparison of the average production of grains (main products) and straw (by-products) of the most used energy crops as well as the proportion of main products/by-products.

Sustainable harvesting of straw from the field, without affecting the humus content of the soil, generally depends on local climate and soil conditions. As a general rule, according to the scientific analysis of the above cited authors, up to 40% of the available straw can be harvested from the field for energy production, without

Crop	Average grains production, t/ha	Average straw production, t/ha	Grain – straw rate
Wheat	6.5	5.2	1: 0.8
Corn	6.8	8.9	1: 1.3
Sunflower	2.5	10.2	1: 4.1
Soy	3.5	2.3	1: 0.6
Rape	3.5	10.1	1: 2.9

(Source: *Energie aus Biomasse* [50])

Table 4.
 Proportion of main products/by-products in energy crops.

damaging the quality of the soil. This important fact is respected in all related projects and business plans.

Assessing regions with large agricultural areas and regions with lower agricultural productions, the availability in space of the by-products to be delivered to a 50,000 tones capacity second-generation biorefinery differs. In our calculations, the surface needed to provide the feedstock necessary for the biorefinery is around 5000 km², more specific $\geq 70 \times 70$ km is need to be covered to harvest the agricultural residues for biofuels production in agricultural areas with high crops productions (such as western Romanian planes). As for forestry and hilly regions, such as center Romania (case study polluted area), in average 34,000 km² can provide similar quantity of feedstock as in intensive agricultural areas.

When calculating ethanol yields per surface of cultivated land, data in **Table 5** are obtained, as the average ethanol potential for two of the main crops in Romania.

According to this approach, to provide feedstock for a 50,000 tons commercial scale lignocellulosic ethanol biorefinery, needs harvesting of wheat straw and corn stover from $\approx 88,000$ hectares. The resulted numbers are generated from a theoretical potential analysis approach. Still, even if more criteria are introduced in the potential study, the main conclusions does not change, namely: if the approach is to produce ethanol exclusively from agricultural residues, large surfaces of land are needed. The biomass need to be harvested from large surfaces and transported long distances.

Scenario 2: consider using marginal lands, or areas improper for edible crops for biorefinery converting sweet sorghum as feedstock.

In our research, in laboratory and pilot scale trials, we obtained 3–4 tons of ethanol / hectare of sweet sorghum by fermentation of sweet juice harvested from sorghum stems and around 3 tons of lignocellulosic ethanol from sorghum bagasse resulted after juice extraction. This is a total amount of 6–7 tons of ethanol/hectare of sweet sorghum.

Biomass	Grains average production, t/ha	Proportion grains-straw	Straw average production, t/ha	40% available for biofuels	Ethanol, L/ha
Wheat	6.5	1:0.8	5,2	2.08	416
Corn	6.8	1:1.3	8,9	3.56	712
Average:					564

Table 5.
 Average ethanol potential for two of the main crops.

Another scenario, proved by our team in laboratory scale is fermentation of sweet sorghum juice to lactic acid. Yields obtained in lactic acid fermentation indicate that 5 tons of lactate can be produced by lactic fermentation of sweet juice obtained from one hectare of sweet sorghum. This can be converted in biodegradable bioplastic PLA, replacing plastic waste generated by 360 Romanians/year. If bagasse is anaerobically digested, the BMP preliminary assays indicate an average of 6000 m³ of methane potential from bagasse resulted from one hectare of sorghum.

If we consider that one hectare of sweet sorghum crop yields 6 tons of ethanol (from sugars + cellulosic ethanol), 50,000 tons ethanol biorefinery can be operated using as feedstock the sweet sorghum crops cultivated on \approx 8000–9000 hectares. This is around 10% from the surface to be covered to transport the by-products for second-generation biorefinery in the first scenario.

In our case study, the total area considered as polluted is 50 x 20 km, meaning around 100,000 hectares. Approximately 30% is agricultural land, which totalize around 30,000 ha. The total surface of the farmers associated in GAL Podișul Mediașului (association in Copsa Mica polluted area) is approximately 25,000 ha arable land. If 30% of the total agricultural area is cultivated with energy crops, a biorefinery can count on 10,000 ha of total crops production as feedstock to produce biofuels and other chemical building blocks (a biorefinery 50,000 L ethanol capacity relying on sweet sorghum needs around 8000–9000 ha). If the biorefinery is located in the centre of the polluted area, the maximum distance to transport the feedstock is 20 km.

Consequently, comparing the efforts to gather feedstock in the two above scenarios, the balance indicates the scenario 2 as the most attractive.

The system proposed to be developed in the polluted area consists of:

- One "flexible" lignocellulose/sugar to ethanol biorefinery. The main feedstock: sugar crops from polluted area, such as non-food crops (to not interfere with food sector). Example of non-food crop: sweet sorghum. Problem regarding the preservation of sugars in the biomass around the year is solved by "*PROCESS FOR BIOREFINING OF SUGAR YIELDING PLANTS WITH CONSERVATION AND EXTRACTION OF SUGARS FOR PRODUCTION OF BIOFUELS AND OTHER BIOPRODUCTS*" [41].
- Several biogas plants in the proximity of the biorefinery. The total capacity of biogas plants to collaborate with ethanol biorefinery is flexible, but ideally is 5 MWe installed power to serve 50,000 tones/year ethanol biorefinery with sugar and part of the lignocellulosic biomass. More clearly is a picture of the biorefinery collaborating with five one-MWe biogas plants (**Figure 7**).

Biorefinery uses as feedstock: (a) syrup extracted from sweet sorghum grown in polluted area and (b) lignocellulose (sorghum bagasse, other biomass from polluted area). The process can be multiple: production of first and second generation biofuels or building block chemicals. The residual lignin resulted after second generation biorefinery, originating from biomass grown in the highly polluted area (red zone), containing high concentration of heavy metals is pyrolysed. The char containing heavy metals is sent to the local smelter to extract metals simultaneously with the extraction process from mineral ores.

Biorefinery can have installed on-site biogas plant. The large storage capacities for preservation of sugar plants, the large volume of digesters for A.D. does not allow

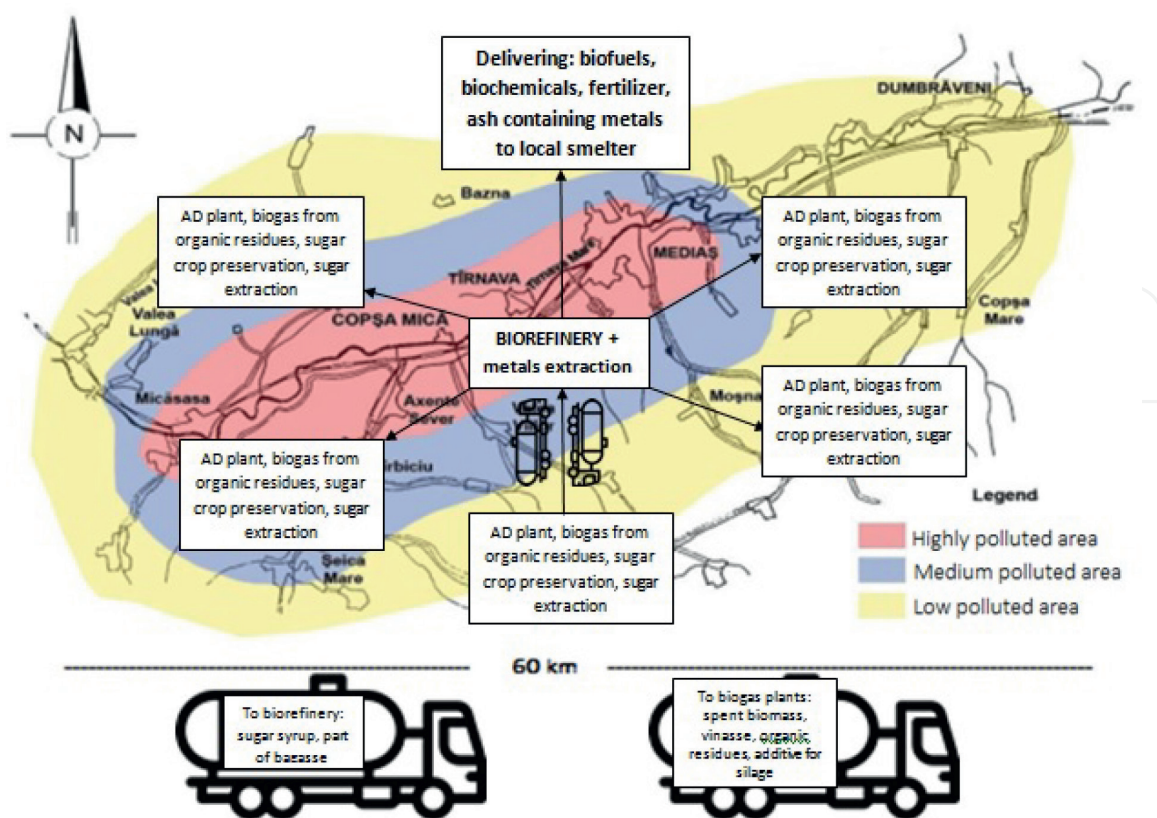


Figure 7.
 System proposed to be developed in polluted area.

construction of such a large surface industrial facility [51, 52]. Therefore, it is recommended to outsource the storage of sugar plants connected to biogas technology in agricultural area (on-farm biogas plants).

The on-farm biogas plants are upgraded with the followings:

- Storage capacities for preservation of sugar containing biomass (sweet sorghum, sugar beet).
- Roller press to harvest sweet juice from preserved sugar plants.
- Evaporation equipment (operated by waste heat from biogas CHP unit plus part of the biogas) to concentrate the sweet juice from Brix 16–18 (obtainable in local climate conditions of sweet sorghum crops) to Brix 50 or higher; concomitantly, the preservation additive is recovered by distillation and stored on-site for preservation of the next harvest.

Description of the system operation, in general lines.

A trading system will be developed between the biorefinery and biogas plants (Figure 7):

- Biorefinery provide equipment needed to upgrade the biogas plants to be able to deliver sugar syrup (storage facilities, preservative chemical, press for harvesting sweet juice, evaporation equipment). Biorefinery provide as well a part of the spent biomass resulted after ethanol production process (containing

low concentration of metals); vinasse resulted after distillation and other organic residues that can be used as feedstock for anaerobic digestion in biogas production.

- Biorefinery will adjust the production process according to a yearly plan agreed with biogas plants. For example, in cold season, when the electricity needs are higher, the energy from biogas will be dedicated to CHP unit. In this period, the ethanol production will be based mainly on residual lignocellulosic biomass. In warm season, part of the energy of biogas is used to produce syrup. The syrup will be added in biorefinery to the cellulosic hydrolysate, this way the ethanol production is much increased.
- Biogas plants provide to biorefinery the sugar syrup when situation on biofuels and biochemicals is favorable and when energy needs in the grid are covered by other sources. The sweet juice need to be concentrated to lower the transport costs and carbon emissions associated to transport. For production of syrup, part of the energy of the biogas produced on-site is dedicated to this process.
- Biogas plants can use the bagasse resulted after extraction of sweet juice to produce biogas (case of biomass containing low concentration of heavy metals), or can sell it to biorefinery for production of lignocellulosic ethanol, to be incinerated and sent for extraction of heavy metals (the highly polluted biomass obtained in the core of the polluted area - red zone).
- In case of deficit in energy grid, or other criteria recommending production of higher amount of electric energy, the biogas plant is operated to ensure electricity production of CHP unit at full capacity.
- Another scenario regarding flexibility consists of biogas plants equipped with biogas upgrading technology and delivering of biomethane. In this case, the biomethane can be compressed and liquefied to be used as second-generation biofuel. Biomethane can be also injected into the grid, can be stored in national storage system and used in thermo-power plants in case of deficit in electricity (instead of importing natural gas). The trading system with biorefinery is similar as in biogas plants + CHP technology.

6. Conclusions

To summarize, in our scenario, biomass containing sugars is stored around-the-year and sugar is extracted on daily basis. Sugar is converted in biorefinery to biofuels/biochemicals. Bagasse is converted to second generation biofuels/biochemicals and the by-products are sent to AD. The highly polluted solid digestate is pyrolysed to obtain process heat and the char is sent to local smelter for metal extraction. The highly polluted liquid digestate is sent to smelter for metals extraction. By-products containing low concentrations of pollutants are digested to obtain biomethane. The digestate containing low concentration of metals (within legal limits) is returned in the soil to maintain fertility and to immobilize heavy metals.

The whole biorefinery approach is an innovative aspect and can be adapted to other cases of polluted areas, to be remediated for production of edible crops for

food and feed. To note that crops containing pollutants within legal limits are subject to be used for food sector, while polluted bioresources are subject to biorefinery for non-food products. The main impacts of the circular bioeconomy developed here are foreseen to be materialized in the following directions:

- **Environment**, by remediation of polluted areas and contribution to climate neutrality through the proposed innovative bioremediating farming system, decreasing Greenhouse Gases (GHG) emissions through cascading use of bioresources;
- **Human health**, by redirecting polluted lands from producing contaminated food responsible for degradation of public health to the production of materials which contributes to the improvement of public health (biofuels and biochemical that replace fossil based materials and fuels currently produced by a polluting industry);
- **Economy**, developing an interconnected agro-industrial system based on smart management of main resources (sun, water and soil) by optimization of agricultural feedstock production in the emerging circular bioeconomy and delivering bio-based goods and services for a healthy and sustainable human society;
- **Social dimension**, improving quality of life in communities from polluted areas as social distribution of environmental quality is unequal, and often biased against poorer or socially excluded groups which are more likely to live in areas of poorer environmental quality than other groups.

Regarding the impact of the biorefinery on soil remediation (environment), the addition of immobilizing amendments is a promising and suitable technique for remediation of contaminated soils even if the total content of contaminants is not decreased. Organic amendments like, manure, compost, bio-solids and bio-solids compost may effectively reduce the availability of HM due to its high content of organic matter and improve the biochemical properties of contaminated soils. Immobilized in the soil, the pollution poses much less of a threat to e.g. groundwater, organisms in the soil or uptake by crops.

All the previous impacts converge into one important impact: food security (integrating health, environment, economy and society). Circular bioeconomy is meant to be one of the tools needed by today's society to improve food security and decrease pollution and impact of human activities on the environment.

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Author details

Teodor Vintila^{1*}, Eniko Gaspar², Maria Mihaela Antofie², Luca Magagnin³, Adina Berbecea¹ and Isidora Radulov¹


1 University of Life Science “King Mihai I” from Timișoara, Romania

2 “Lucian Blaga” University of Sibiu, Romania

3 Polytechnic University of Milan, Italy

*Address all correspondence to: tvintila@animalsci-tm.ro

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