Principles of circular economy applied to energy plants in culture. The correlation of soil quality with the valuation potential of willow by-products.

Gabriela Vlăsceanu[1,*], *Floarea* Nicolae[1], *Nicole* Petculescu[1], and *Marian* Nicolae[1]

[1]Bioterra University, Gârlei 81 street, district 1, Bucharest, Romania

Abstract. Energy plants are used for biomass products such as wood chips (pellets) or working wood (OSB boards). For this purpose, you can cultivate willow (*Salix alba*), artichoke, elephant grass, Chinese reed, energetic hybrid poplars, canary grass, giant cane, and oil tree (source of biodiesel). The study aims, by analyzing the quality of the soil correlated with the composition of the energetic willow bark, to highlight the potential for the valorization of the by-products. In this study, the soil fertility of some Romanian energy willow crops was compared with chernozem with a high input of humus from the Natural Meadow Reserve of Slobozia Mare, Moldavia. Through the analysis of the bark (plant by-product), the determination of salicin from the dry extract, the aqueous extract, and a compressed mixture was sought. Reported to the main macronutrients and pH, the soil of the energy willow crops in Romania is qualitatively similar to Moldavia. Although willow is cultivated primarily as an energy plant (biomass for pellets, biodiesel), if the conditions of the culture area are monitored, the waste represented by the easily removable bark can be utilized because it contains salicin in concentrations that, depending on the area.

1. Introduction

The European Commission defines the notion of a circular economy in which "the value of products and materials is maintained as much as possible; waste and resource use are minimized, and when a product reaches the end of its life, it is used again to create an additional value; this can bring major economic benefits, contributing to innovation, economic growth, and job creation". The EU's transition to a circular economy will reduce pressure on natural resources and create sustainable growth and jobs. Material flow management is understood in the circular economy in two forms: *biological nutrients*, designed to re-enter the biosphere without risk to rebuild natural capital, and *technical nutrients*, designed to circulate with maximum qualities and without entering the biosphere. Thus, the EU supports agriculture according to the legal framework (Common Agricultural Policy) through the development of energy plant crops, which are eligible for both direct payment schemes from European funds and national aid. As measures of local interest, the use of heat sources based on biomass and the development of biogas production and distribution systems, at the community level, are encouraged.

Currently, in Romania, different energy plants can be cultivated both for the production of biomass in the form of chips (for pellets) and as woodwork (for the production of OSB boards). For this purpose, you can cultivate willow (*Salix alba*), artichoke (*Cynara carduncul*us), elephant grass (*Miscanthu*s), Chinese reed (G*iganteus*), energetic hybrid poplars, canary grass (*Phalaris canariensis*), giant cane, oil tree (Jatropha, which through processing, gives an oil from which biodiesel is produced). [1,2,3,4]

The quality of the products and by-products is also found in the proper management of the cultivated soil, in order to obtain ecological products, aiming for an adequate conversion. The dynamic study aims a comparison of the quality of the soil from ecological greenhouse-field areas in Romania, compared to humus-type soil from a nature reserve in the Republic of Moldova, known as one of the most ecological in Eastern Europe. Fertility is the most important soil property necessary for the development of vegetation. To determine soil fertility, specific parameters are analyzed, namely macronutrients (N, P, K, S, Ca, Mg), micronutrients (Co, Cu, Zn, Mo), pH, and humus intake.

The eco-energetic willow develops a stem and thick branches, from which you can obtain a mince with a small percentage of bark, a criterion increasingly demanded by pelletizing or briquette factories. [5,6]

The bark, which comes off easily, can be exploited by the production of methanol, as a source of cellulose, in the manufacture of standardized products from willow bark in the form of dry extract, aqueous extract, glycerol-hydroalcoholic extract, tablet, or just a compression mixture, with real effects on health. [7]

The study aims, through the analysis of soil quality, to highlight the potential of valorization of eco-energetic willow by-products.

* Corresponding author: ga.vlasceanu@yahoo.com

2. Materials and methods

2.1. Soil analysis

In the study, the soil fertility of an ecologically certified greenhouse-field area in Romania (zone A) was compared with chernozem with a high input of humus from the Meadow Natural Reserve in Slobozia Mare, Republic of Moldova (zone B).

The study was carried out in the laboratories of the Ecological University of Bucharest. 5 samples were collected from area A and 5 samples from the territory of the natural reserve, in the southeast (area B); all samples were extracted from a depth of 20 cm. The content of major macronutrients (N, P, K) and pH were analyzed.

2.1.1. Determination of mineral nitrogen

The NO_3 reduction method was used in the presence of sulfanilic acid and naphthylamine.

The pink color, of different intensities, was highlighted by colorimetric analysis.

2.1.2. Determination of inorganic phosphorus

Was used the method of reducing phosphomolybdic acid with $SnCl_2$, with the appearance of a dark blue color of different intensities.

2.1.3. Determination of potassium

The analysis was based on the reaction with magnesium dipicrylaminate in an acidic medium (HCl), when a red-orange-yellow color appears, which can be analyzed colorimetrically.

2.1.4. Deter8,5mination of pH

Made by comparing colors. (Fig. 1)

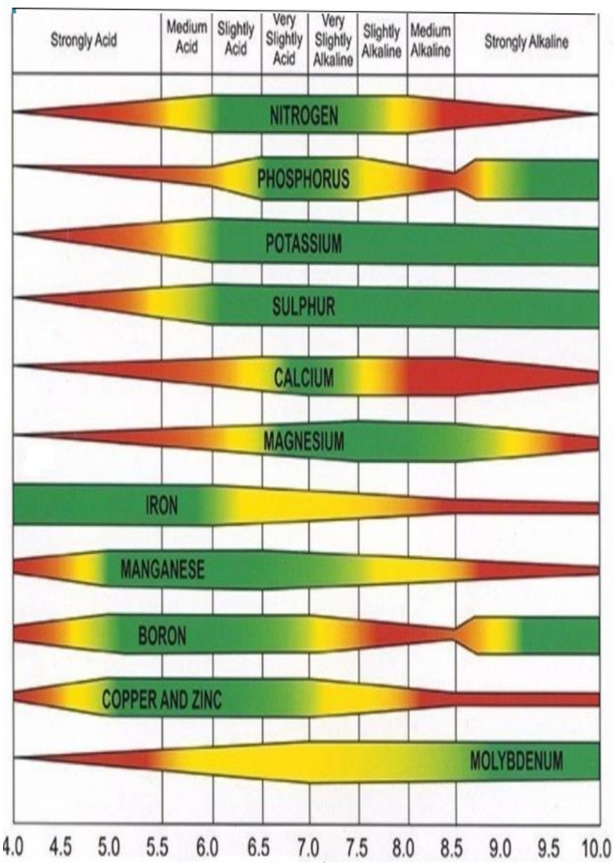

Figure. 1. Colorimetric determination of pH
https://agrobiznes.md

2.2. Determination of salicin by analyzing the bark (a vegetable by-product from the processing of eco-energetic willow), extracts, and compressing powders based on *Salicys cortex*.

2.2.1. Bark analysis

The bark and branches of young and mature white willow trees (*Salix alba*) were harvested in June (the optimal period of maturity). The samples were manually separated, dried and ground. The working parameters were the following: plant material - brought to an advanced degree of shredding; extraction method - maceration; the extraction solvent – purified water; extraction temperature – room temperature; extract concentration – 10% (g plant/mL water); extraction time – 24 hours.

The following equipment was used for the preparation of the raw material: analytical balance Partner AS 310.R2; Biovita-DEH600D plant dryer; laboratory mill Retch GM 200; Retch AS 200 Basic sieve machine.

To prepare the samples to be analyzed, were used the following equipment: ultrasonic bath Elmasonic P180 H; Julabo TW8 water bath; centrifuge Ortoalresa 21 R; rotavapor Buchi R-300 EL, equipped with water bath B-300 Base, vacuum pump V-300 and chiller with recirculation F-308; thermobalance VWR MB 160;

thermoreactor WTW CR 3200; Milli-Q Direct 8 water purification system

The quality of the bark was analyzed by determination of the content of salicylic derivatives, expressed in salicin, according to the European Pharmacopoeia (EF), current edition, "SALICIS CORTEX" monograph, by liquid chromatography (3 samples, area: Breaza, Furculesti, Gheorghieni).

The NIST spectra library was available for the peaks corresponding to the chromatographically analyzed compounds.

2.2.2. Analysis of extracts

A 1:8 plant:solvent ratio was kept constant during the experiment. Water bath reflux extraction was performed at a temperature of 60°C for 60 minutes

The salicin aqueous extract was determined according to EF, by thin-layer chromatography (TLC).

2.2.3. Analysis of powders

The determination of the content of active principles (salicin) in the dry and pulverized plant material was carried out by quantitative analysis, depending on the subsequent specific solubility of the compounds.

To compress mixture and salicin tablets were determined according to EF, by liquid chromatography.

3. Results and discussions

3.1. Soil analysis

The analytical values obtained in the experimental laboratory of the Ecological University of Bucharest were interpreted in accordance with the limits of soil nutrient levels established on the basis of legislation and standards in force, highlighting qualitative similarities between the two types of soil analyzed.

The evaluation of the content of main macronutrients was done based on OG MAPPM no. 756/1997 regarding the evaluation of environmental pollution specific to soils with less sensitive use. Law no. 74/2019 regarding the management of potentially contaminated sites and those contaminated and GEO no. 92/2021 regarding the waste regime. (Fig. 2, 3, 4).[8]

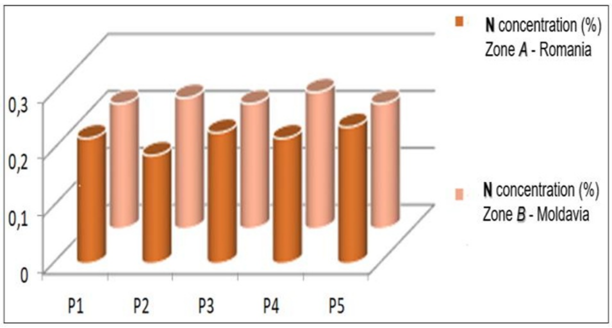

Figure 2. Graphical comparison of Nitrogen (total N) values in the soil– *EUB Lab. Res* [9]

It is observed that 4 of the 5 samples (from Romania) analyzed comparatively are similar in terms of percentage nitrogen content (less P_2 from Romania), compared to the N levels in the soil samples from the Republic of Moldova).

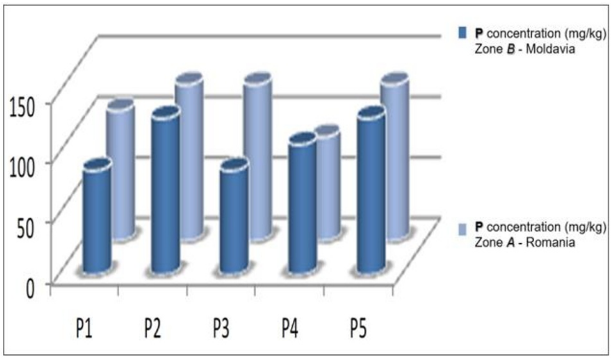

Figure 3. Graphical comparison of Phosphorus (mobile P) values in the soil– *EUB Lab. Res* [9]

Among the 5 comparatively analyzed samples, 3 are similar in percentage phosphorus content (less P_1 and P_3 from Romania), compared to the P levels in the soil samples from the Republic of Moldova).

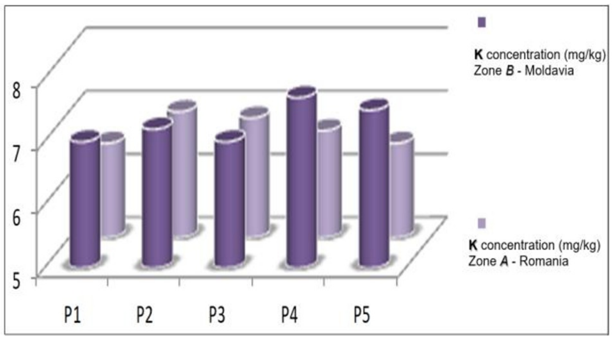

Figure 4. Graphical comparison of the values of Potassium (mobile K) in the soil– *EUB Lab. Res* [9]

All 5 samples from Romania showed similar potassium content (P_2 and P_3 from Romania), or much higher (P_1, P_4, P_5 from Romania), compared to the K levels in the soil samples from the Republic of Moldova).

3.2. Determination of salicin

3.2.1. Determination of salicin in the bark

White willow bark is the main source of salicin and other salicylic derivatives – salicortin, 2'-O-acetylsalicortin and tremulacin – compounds similar in structure to aspirin (acetylsalicylic acid), often white willow being referred to as "vegetable aspirin". Salicin, through enzymatic hydrolysis induced by emulsin and diastase, splits into glucose and saligenin, also known as o-oxybenzyl alcohol or saligenol. Saligenin in turn produces, through oxidation, salicylic acid, with notable analgesic, antipyretic and antirheumatic properties, thus achieving a gradual, prolonged effect. Also, the tannins present in the

 https://doi.org/10.1051/e3sconf/202343604004

willow bark have a tonic, astringent, coagulant and slightly hemostatic action (Assessment Report on Salicis Cortex (Willow Bark) and Herbal Preparation(S) thereof with Well-Established Use and Traditional Use. Doc.Ref.: EMEA/HMPC/295337/2007, 2009). (Fig. 5, 6, 7, Table 1)

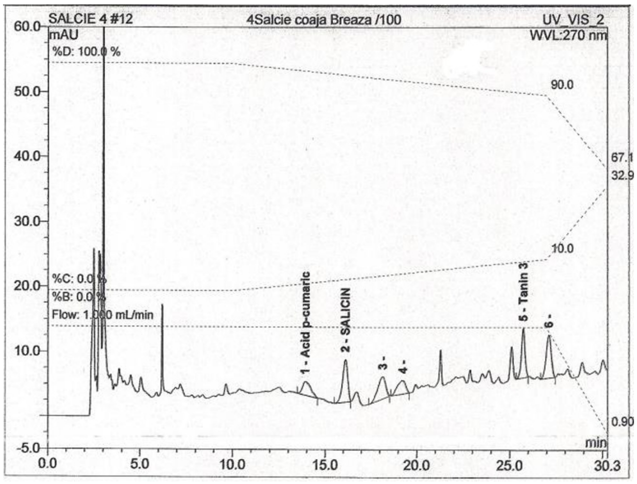

Figure 5. Salicilin determination in *Salix cortex* - Breaza

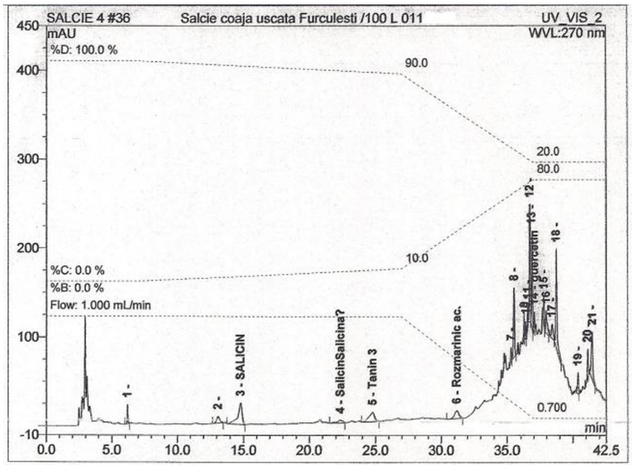

Figure 6. Salicilin determination in *Salix cortex* – Furculesti

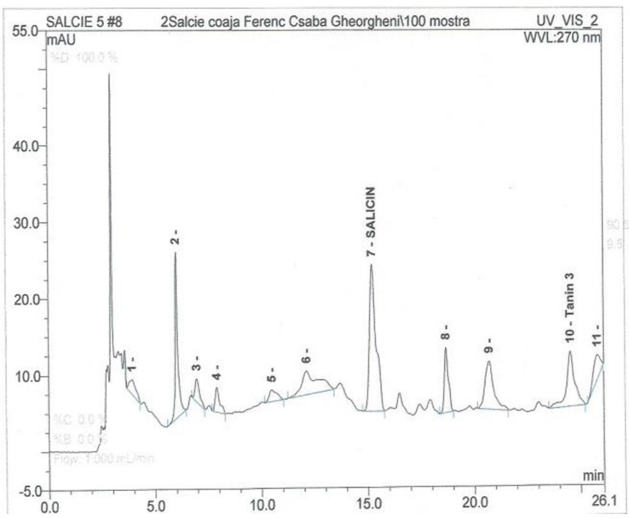

Figure 7. Salicilin determination in *Salix cortex* – Ghiorghieni

The dosage is not valid if the resolutions between the peaks corresponding to *salicin* and *picein* and between the peaks corresponding to *picein* and *resorcinol* are not at least 1.5

Table 1. Salicin content determined in dry willow bark

Cultivation/harvesting area	Content in salicin %
1_Breaza	**0.50**
2_Furculesti	**1.70**
3_Georghieni	**1.26**

The quality of its back expressed in salicin, for all 3 samples, the only corresponding one being the one from Furculesti, with a salicin content > 1.5%.

3.2.2. Determination of salicin in extracts

In extracts (dry, aqueous) from willow bark, salicin was determined according to E.F., by subtle layer chromatography (TLC). (Fig. 8, 9).

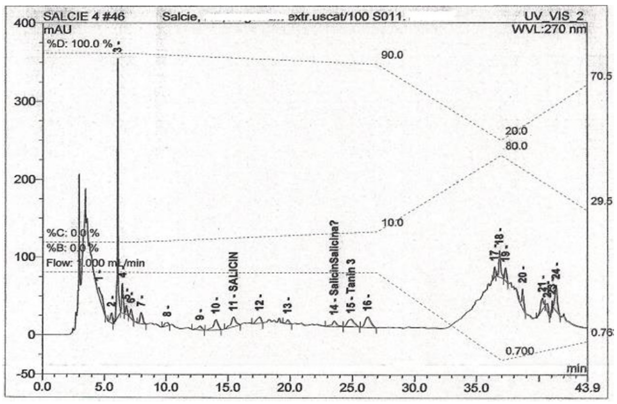

Figure 8. Salicilin determination in the dry extract

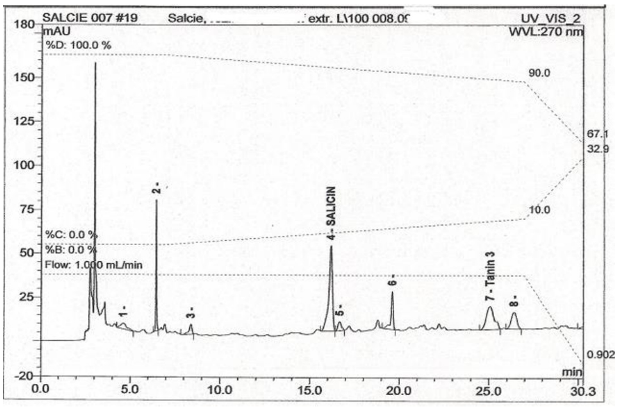

Figure 9. Salicilin determination in the aqueous extract

The chromatogram obtained with the *reference solution* shows in the middle third a red-violet spot determined by salicin. In the chromatogram obtained with the *test solution*, the spot determined by *salicin* is clear and more intense, and above it, another spot determined by *salicortin* or *2'-O-acetyl salicortin*. Other yellow, blue, or brown spots may appear in both chromatograms.

3.2.3. Determination of salicin in the compressed mixture and in tablets

Sallicin was determined according to EF, by liquid chromatography. (Fig. 10, 11).

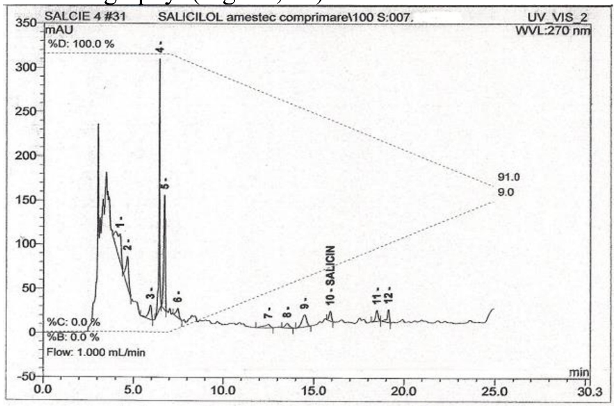

Figure 10. Determination of salicin in the compressed mixture

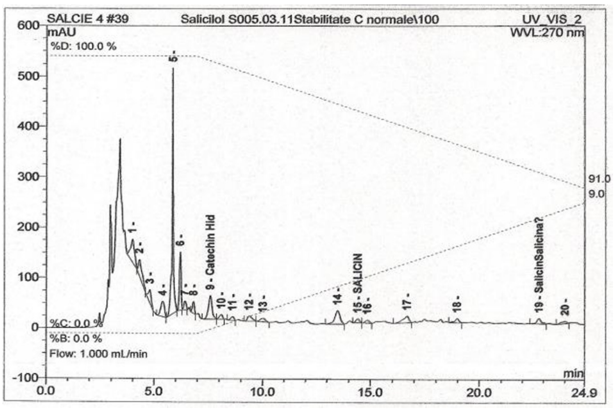

Figure 11. Determination of salicin in the tablet

Compared to the technical specifications, all analyzed samples: dry extract, aqueous extract, compression mixture, and stabilized tablet fell within the parameters from the point of view of the quantitative content of salicin, being declared compliant products (Table 2).

Table 2. Salicin content in the analyzed samples

The sample analyzed	Content min. salicin % in the technical specification	Content in salicin % determined
Dry extract	0.15	**1.10**
Aqueous extract	0.25	**1.09**
Compression mixture	0.17	**0.28**
Tablet	1.00	**1.86**

Various extraction methods and extraction conditions were compared to obtain extracts rich in salicylic derivatives, but also other polyphenolic compounds, with an effect in relieving joint and muscle discomfort. The dry extract proved to be the most concentrated in salicin.

4. Conclusions

From the point of view of the main macronutrients (N, P, K) and pH, the soil in area A (greenhouse-field ecological certification, from Romania) is qualitatively similar to that in the Slobozia Mare Nature Reserve – the Republic of Moldova, recognized as one of the most ecological in Eastern Europe.

Although willow is cultivated primarily as an energy plant (biomass for pellets, biodiesel), if the ecological conditions of the cultivation area are monitored, the waste represented by the easily removable bark can be utilized because it contains salicin in concentrations that, depending on the area, correspond to or they even exceed the limits imposed by the European Pharmacopoeia.

The exploitation of ecological willow bark (as a by-product) consists in obtaining dry extracts, aqueous extracts, compression mixtures, or tablets with large amounts of salicin, which guarantees beneficial effects on health.

According to the specialized documentation, a good source of salicylic derivatives proved to be the young willow bark, having the highest concentration in the compounds of interest. The willow bark residue resulting from the extraction can be further used for the additional extraction of active principles (microwave treatment is more effective than ultrasound - at 150°C an additional 8.7% salicin was extracted - vs. the amount extracted from plant material not subject to extraction). [10]

It follows that the healthy effects of willow bark (which has been chromatographically demonstrated to contain high concentrations of salicin) will be demonstrated through case studies and clinical trials.

References

1. V. Dragusanu, A. Lunguleasa, C. Spirchez, Forests **14**, 1134 (2023)
2. J.M. Wilkinson, E.J. Evans, P.E. Bilsborrow, C. Wright, W.O. Wewison, D.J. Pilbeam, Biomass Bioenergy **31**, 469 (2007).
3. M. Mleczek, P. Rutowski, I. Rissman, Z. Kaczmarek, P. Golinski, K. Szentner, K. Strazynska, A. Stachowiak, Biomass Bioen. **34**, 1410 (2010)
4. B.Z. Amichev, R.D. Hangs, K.G.J. van Ress, Biomass En.**35**, 473 (2011)
5. W. Stelte, J.K. Holm, A.R. Sanadi, S. Barsberg, J. Ahrenfeldt, U.B. Henriksen, Biomass Bioen. **35**, 910 (2011)
6. Rebina Agrar. (2022) (Available online: *https://balkangreenenergynews.com/energy-willow-salix-viminalis-biomass-where-you-want-it/*)
7. M. Shara, S. Stohs., Phytother. Res. **29**, 1112 (2015)

https://doi.org/10.1051/e3sconf/202343604004

8. O.G. MAPPM nr.756/1997. Environmental pollution assessment specific to less sensitive soils (in Romanian) (1997)
9. Ecological University of Bucharest, *Data files.* Laboratory results (2012-2022)
10. https://docs.upb.ro/content/uploads/2022/04/REZUMAT-TEZA_Neagu_RO.pdf (2020)