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# Greenhouse Residues' Potential for Biogas Production

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**Abstract:** Agricultural residues are intensively evaluated as potential feedstocks for biogas plants. Vegetable crops generate massive residues during and at the end of their growing seasons. A greenhouse facility in Greece, Thrace Greenhouses S.A., generates 7000–8000 t per year of residual green biomass, resulting from the hydroponic cultivation of tomatoes and cucumbers on 170,000 $m^2$ of land from February to November. The crop residues included leaves, suckers, and stalks. The biochemical methane potential (BMP) estimation was realized on samples taken in March, May, and August, as well as at the end of cultivation (November). Suckers, leaves, and stalks of both plants yielded a range of 221–357, 210–296, and 225–250 NL $kg^{-1}$ VS, respectively. *t*-test statistical analysis showed that the BMP of the leaves and suckers were statistically different for tomato and cucumber plants. The BMP of stalks was lower than the other residue types except for the tomato leaves. The diauxic behavior of the specifi'1c methane production curves indicated that the two-phase Gompertz model (TGM) was the most suitable. The model fitting showed that leaves and suckers, in spite of having a higher BMP than the stalks, exhibited a lower maximum specific methane production rate constant than the stalks during the first phase, which may indicate the presence of inhibitory or slowly biodegradable compounds in leaves and suckers in comparison to the stalks.

**Keywords:** anaerobic digestion; biochemical methane potential; crop residues; greenhouse residues; Gompertz model

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## 1. Introduction

Currently, the energy crisis is dominant due to the growing population and the total dependence of human civilization on depleting mineral resources. Therefore, the interest of scientists has been focused on developing environmentally friendly technologies using renewable energy sources. The gross electricity production in the EU was driven by renewable energy sources in 2020 (1086 TWh), surpassing the electricity produced from all fossil fuels (1012 TWh) [1]. It is a fact that the electricity from renewables doubled from 2000 to 2020, reaching a 39% share of the total electricity produced in 2021 in the EU [1]. However, the electricity production from biogas has remained a small fraction of renewable electrical energy (5–6%) from 2011 to 2021, while the share in electricity coming from hydroelectric plants decreased from 87% to 34.5%, and the energy from wind and solar photovoltaic systems has increased from 4.9% to 36.6% and 0.0% to 12.8%, respectively, from 2000 to 2021 [1].

The relatively high costs of biogas power generation compared to wind and solar photovoltaic energy systems may limit the further development of the biogas sector. On the other hand, biogas plants are more flexible to operate. Wherever heat off-take is available, an additional energy source (waste heat) can be exploited [2]. The vast opportunities of exploiting biomethane from biogas upgrading are expected to boost the biogas sector. It is recognized that although the combined biogas and biomethane share in the global bioenergy demand is approximately 5% (in 2018), they are the rapidly growing bioenergy sectors, and they are expected to reach a 12% share according to the Stated Policies Scenario

(STEPS), and a 20% share according to the Sustainable Development Scenario SDS (STEPS), by 2040 [2].

There is a variety of feedstocks (usually referred to as biomass) which can be used for biogas production. The municipal biomass consists of domestic organic waste, green waste, such as grass from parks and gardens, and sewage sludge. The agro-industrial sector produces agricultural residues (crop residues left in the field after harvesting, such as stems, stalks, leaves, or residues during crop processing) and industrial wastes from food/fruit manufacturing, mainly peels and oil cakes [3]. In addition, biomass also includes livestock waste (manure), energy crops, and wood processing waste (wood chips, wood logs). Recently, plant biomass has been used for energy production. Approximately 5 billion hectares are estimated to be used for agricultural production worldwide [4], generating large quantities of plant residues. In Greece, there were more than 63,000 hectares cultivated for vegetable production in 2019, according to the Hellenic Statistical Authority [5], most of which produce vast amounts of residues in the form of leaves and stems.

Each year, agricultural residues are disposed of by incineration, land application (mulching, composting), and landfilling [6]. The common practice of burning the residual biomass in the fields releases particulate matter, carbon dioxide ($CO_2$), carbon monoxide (CO), sulfur oxides (SOx), nitrogen oxides (NOx), ammonia ($NH_3$), volatile organic compounds (VOC), and non-methane hydrocarbons (NMHC) [7,8], causing acid rain and environmental pollution. In addition, it introduces toxic compounds, such as polycyclic aromatic hydrocarbons (PAHs) and phenols, into the atmosphere [9,10]. These pollutants create smog, which is dangerous for public health. Moreover, leaving the agricultural residues in the fields for a herd of grazing animals might be a good option, but it should be done in an organized way [11,12]. The exploitation of agricultural residues via anaerobic digestion becomes popular since, besides energy, the digestate from anaerobic digesters treating agricultural residues can be used as a growing medium or nutrient solution within novel cultivation schemes [13]; however, issues such as the environmental and economic cost of transfer and processing may surpass any benefit from valorizing this type of renewable resource [14,15]. Therefore, the sustainable management of all of these crop residues becomes mandatory.

Except for anaerobic digestion, processing methods applied to biomass for energy recovery are pyrolysis, gasification, and combustion. The main disadvantages of combustion, pyrolysis, and gasification are the high cost of the processes due to the high energy consumption in order to achieve the high temperatures [16], the high investment cost, and the operational cost to make these technologies environmentally safe due to the atmospheric pollution induced. In the case of biomass with high moisture (e.g., leaves and suckers from vegetable crops), the energy required is even higher, rendering this option unsuitable. Contrary to the thermal methods, anaerobic digestion is suitable for wet and biodegradable organic material (such as vegetable residues). Other advantages are the low energy consumption, low sludge output, and high organic load [17,18], as well as the potential to remove or convert $CO_2$ to $CH_4$ and produce a methane-rich gas mixture (biomethane) that resembles natural gas [19]. According to the European Union Biogas Barometer, there are 17.4 thousand active anaerobic digestion plants in Europe [14,20]. In addition, 367.0 upgraded biomethane units are in operation, enabling the production of biofuels together with electricity and heat. More than 70% of biogas plants are farm-based due to important incentive policies (mainly applied in Germany, Austria, and Italy) [21]. In 2019, 49 biogas plants were in operation in Greece [22], producing 73.6 MW of electrical power, more than half of which (ca. 40 MW) came from landfills and sewage treatment plants [23].

Depending on the characteristics of the crop residues and their composition, a pretreatment method may be required before anaerobic digestion to improve biogas production. Pretreatment is especially needed if the feeding waste consists of lignocellulose. Distracting the recalcitrant structure of lignocellulosic material enhances the accessibility of cellulose enzymes [24,25]. However, there is no such problem with crop residues from greenhouse crops such as tomatoes and cucumbers, as these residues mainly contain leaves. According to Szilágyi et al. [26], tomato waste (tomato stems and leaves) has relatively lower lignin and hemicellulose content than other plant waste, such as corn stover. Since fruits and vegetables are characterized by low cellulose, hemicellulose, and lignin content [27,28], the hydrolytic process is not a limiting factor, and a high VS content with a low TS content results in rapid hydrolysis [29].

The utilization of energy crops for biogas production is not sustainable. According to Banaszuk et al. and Prochnow et al. [30,31], expanded cultivation of energy crops leads to loss of biodiversity and increased competition for the land area for food and fodder. In many countries, the current biogas production system is based on feedstock from energy crop production, requiring significant financial and energy costs [32]. On the other hand, the organic wastes and residues from agriculture are preferable for biogas production due to their characteristics (wet, bulky) and low economic value compared to energy crops [33].

Several studies have been conducted to investigate the utilization of various types of tomato waste, such as those from groceries, local marketplaces or restaurants [34–38], processing plants [39,40], tomato sauce [41], and tomato puree [42]. Nevertheless, there are few reports on using vegetable residues' green parts. For example, Li et al. [43] reported that tomato residues, including stalks, leaves, and residual tomatoes, could serve as good co-substrates for dairy manure and corn stover, provide balanced nutrients, and increase biogas yields. Another study [44] suggests that tomato branches/stems are potential feedstocks for biogas production but no more than rotten or green tomatoes. Due to its lignin content, the BMP of tomato branches/stems was half of the BMP of rotten or green tomatoes. Furthermore, Oleszek et al. [45] proved that the methane fermentation of fresh tomato and cucumber residues from the greenhouse is energy efficient. More specifically, they showed that conversion of greenhouse residues to biogas is a sustainable disposal option since it provides heat and carbon dioxide after biogas combustion for the greenhouse needs. In the same line, Jagadabhi et al. [46] stated that greenhouses could use their crop residues for biogas production and, in turn, meet their energy demand. Gioulounta et al. [47] evaluated the potential of tomatoes' and cucumbers' leaves and suckers generated in a greenhouse to provide energy autonomy to the greenhouse via a CHP unit combined with a battery system. The hybrid renewable energy system could partially cover the facility's energy demands.

Generally, much of the tomato plant remains unused during traditional or greenhouse cultivation, harvesting, and industrial processing, resulting in a large amount of waste (peels, seeds, stems, leaves), including even the whole vegetable if damaged, reaching 473,989 tons in 2017 in Mexico [48]. Furthermore, this type of waste is generated seasonally just after harvesting, meaning that a large amount of waste is accumulated quickly [48]. Studies on biogas production from tomato and cucumber crop residues are limited to wastes from industrial processing or from green parts of the plant that are uprooted at the end of the growing season (such as stems), which, in addition to the plant, may have fruits. On the other hand, many leaves and stems are removed during the growing season, especially in hydroponic greenhouses [47], since the regular removal of leaves and suckers is necessary to promote plant growth. Therefore, there is a massive production of biomass throughout the cultivating period. Designating this type of residue for feed for gazing animals in neighboring fields is the currently practiced option, but it should be done in an organized way to avoid possible environmental impacts such as gas emissions or nitrogenous compound leaching [49]. The alternative option for energy production is studied in this paper, which aims to evaluate the methane potential of the various types of waste biomass generated during the hydroponic cultivation of tomatoes and cucumbers in a greenhouse and its variation in time. The study also involves a detailed recording of the waste mass generated within a year. In this way, an accurate estimate of the annual methane production can be made.

## 2. Materials and Methods

### 2.1. Substrate Collection and Pretreatment

Three different parts (leaves, suckers, and stalks) of the cucumber (*Cucumis sativus*) and tomato plant (*Solanum lycopersicum*) were collected separately from the Thrace Greenhouses S.A. located in "New Erasmio" of Xanthi in Greece. Thrace Greenhouses S.A. produce tomatoes and cucumbers using the hydroponic method in a 14-hectare facility. During cultivating, leaves and suckers (part of the plant having a rigorous vertical growth on the plant's stalk) are removed regularly to promote plant and vegetable growth. The stalks are a considerable part of the biomass when the plant is removed, which occurs twice a year for the cucumbers and once yearly for the tomatoes.

In the present study, samples of leaves and suckers were collected in March, May, and August, and samples of stalks were collected in November. After collection, each part of the residual biomass was chopped down to about 0.1–2 mm and dried at 57 °C in an oven (MMM-Verticell). Then, each substrate was sieved through a series of sieves from 1.7 mm to 0.15 mm to determine the particle size distribution (Table 1). A total of 7–20% of the biomass was larger than 1.7 mm, and 20–30% was smaller than 0.15%, leaving roughly 60% within the range of 0.15 to 1.7 mm.

**Table 1.** Particle size distribution of residual biomass.

| Sieve Diameter (mm) | T.L. (%) | T.S. (%) | T.St. (%) | C.L. (%) | C.S. (%) | C.St. (%) |
|---|---|---|---|---|---|---|
| >1.7 | 12.32 | 16.29 | 22.52 | 16.99 | 7.35 | 23.21 |
| 1.7–1.4 | 5.63 | 6.72 | 9.35 | 2.68 | 6 | 5.46 |
| 1.4–1 | 10.98 | 11.81 | 10.81 | 5.1 | 14.53 | 10.52 |
| 1–0.85 | 4.61 | 4.7 | 2.22 | 2.42 | 5.94 | 5.97 |
| 0.85–0.71 | 5.46 | 5.33 | 6.5 | 2.9 | 7.08 | 3.23 |
| 0.71–0.6 | 3.71 | 3.81 | 4.73 | 2.5 | 5.13 | 4.79 |
| 0.6–0.5 | 5.21 | 5.05 | 3.68 | 4.05 | 6.76 | 6.49 |
| 0.5–0.25 | 13.98 | 12.97 | 13.88 | 14.6 | 15.3 | 12.93 |
| 0.25–0.15 | 9.62 | 9.34 | 9.97 | 15.12 | 6.91 | 8.25 |
| <0.15 | 28.47 | 23.98 | 16.33 | 33.64 | 25.02 | 19.16 |

T.S.: Tomato Suckers, T.L.: Tomato Leaves, T.St.: Tomato Stalks, C.S.: Cucumber Suckers, C.L.: Cucumber Leaves, C.St.: Cucumber Stalks.

### 2.2. Analysis

The protocols included in the Standard Methods [50] were followed for the determination of the total solids (TS), the volatile solids (VS), the chemical oxygen demand (COD), the total Kjeldahl Nitrogen (TKN), and the total phosphorous. The TS and the organic matter expressed in terms of VS were determined by drying at 105 °C to remove the humidity and igniting to constant weight at 550 °C in a muffle furnace. Total COD was measured on the samples after pretreatment using the open reflux method. TKN was measured by digestion, ammonia distillation, and titration. Total phosphorus was determined by applying the persulfate digestion method followed by the stannous chloride method. The lignin content was evaluated according to Laboratory Analytical Procedure (LAP) [51] using extraction with water and ethanol, autoclaving, and filtering to evaluate acid-insoluble lignin, as well as measuring the acid-soluble lignin on a UV–Visible spectrophotometer.

### 2.3. BMP Test

The inoculum was collected from a biogas plant in "Avato" of Xanthi in Greece, mainly treating cattle manure, chicken manure, and energy crops. After collection, the inoculum was sieved through a 2 mm mesh sieve to remove the large particles. The BMP test was conducted in 250 mL and 200 mL working volume vessels. Each vessel was inoculated with approximately 152 mL of the biogas plant's inoculum containing 4.12 g VS, and 2.06 g VS of the substrate was added to keep the ratio of substrate/inoculum (S/I) at 1:2 on a VS basis [52]. Each substrate was studied in triplicate, along with the blank tests in which no substrate was added. The reactors were flushed with a gaseous mixture of $N_2/CO_2$ (80/20) for two minutes, sealed with a rubber stopper, and placed on a magnetic stirrer (rpm) in an incubator for about 40 days at a constant temperature of 37 ± 1 °C. The headspace of each vessel was connected with a NaOH trap to absorb the $CO_2$ of the produced biogas (Figure 1). The remaining gas after absorption was the $CH_4$, which displaced an equivalent volume of the NaOH aqueous solution of the trap. The displaced volume was recorded daily. The volume of the $CH_4$ was expressed at standard conditions of temperature and pressure (STP) after subtracting the $CH_4$ produced from the blank tests and was divided by the substrate VS added.

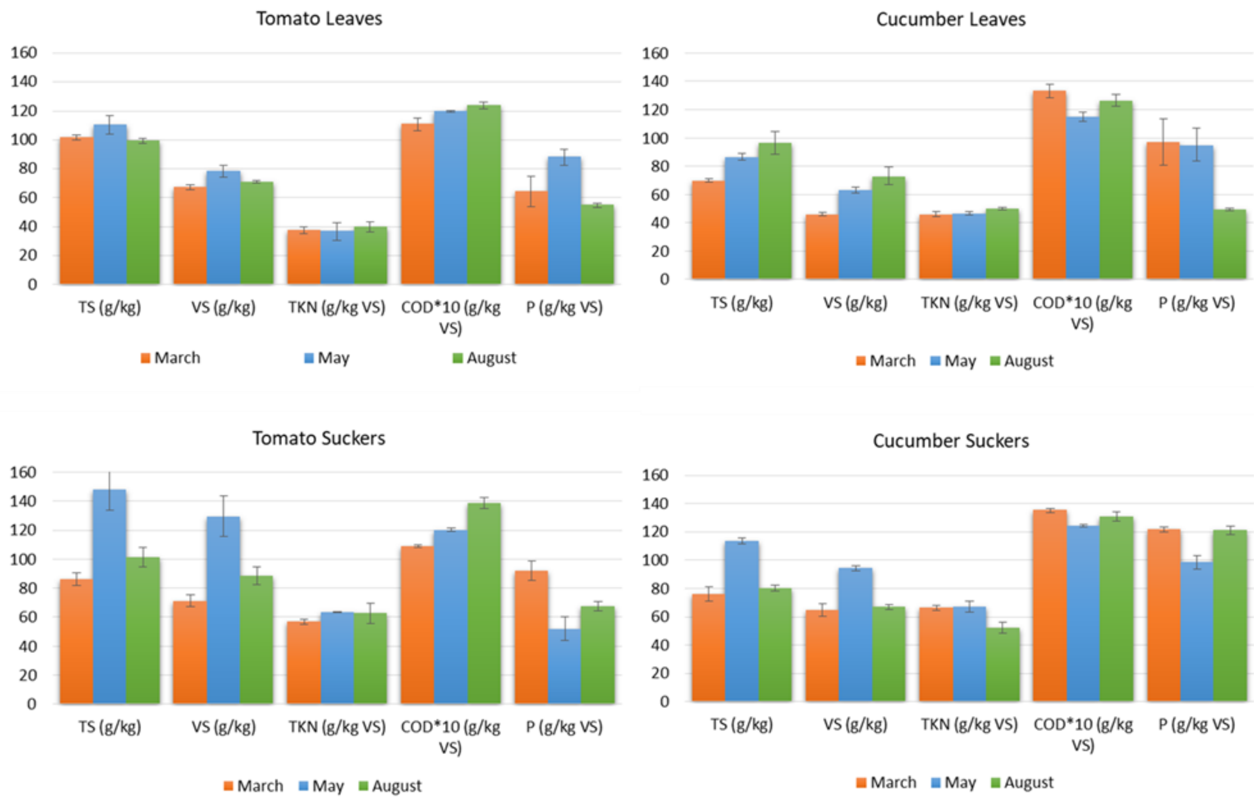



**Figure 1.** Variation of leave and sucker characteristics in time.

### *2.4. Statistics and Model Evaluation*

The average values of all characteristics, BMP values, and kinetic parameters were compared using the one-way ANOVA test at a 95% confidence level. If a statistically significant difference was indicated, a pairwise *t*-test was performed. All statistical analysis was performed using the Microsoft Excel statistics tool. The modelling of the BMP curves was based on the modified Gompertz model (MGM). A two-phase Gompertz model (TGM) for methane production in batch anaerobic systems with diauxic behavior was applied to improve the simulation [53]. TGM sums the two-phase cumulative biogas or methane production according to Equation (1):

$$y = \left(A_1 \exp\left\{-exp\left(\frac{\mu_{mi}\, e}{A_1}(\lambda_1 - t) + 1\right)\right\}\right) + \left(A_2 \exp\left\{-exp\left(\frac{\mu_{mi}\, e}{A_2}(\lambda_2 - t) + 1\right)\right\}\right) \quad (1)$$

where $A_i$ (L kg$^{-1}$ VS) is the biogas or methane in each phase, $\mu_{mi}$ is the maximum specific biogas or methane production rate constant in each phase (L kg$^{-1}$ VS d$^{-1}$), $e$ is Euler's number, $\lambda_i$ is the lag time (d) of each phase, and $t$ is the time (d). The parameters were estimated using the solver of the Microsoft Excel software v365. The goodness of fit was assessed by, besides the correlation coefficient (R2), the Nash–Sutcliffe efficiency (NSE) and percent bias (PBIAS) in all TGMs, according to Equations (2) and (3), respectively:

$$NSE = 1 - \frac{\sum_{i=1}^{n}\left(Y_{exp,i} - Y_{m,i}\right)^2}{\sum_{i=1}^{n}\left(Y_{exp,i} - \overline{Y_{exp}}\right)^2} \quad (2)$$

$$PBIAS = \frac{\sum_{i=1}^{n}\left(Y_{exp,i} - Y_{m,i}\right)}{\sum_{i=1}^{n}\left(Y_{exp,i}\right)} \times 100 \quad (3)$$

where $n$ is the total number of data points, $Y_{exp}$ is the experimental value, $Y_m$ is the model value, and $i$ is the number of the datum (i.e., 1, 2, 3, ... , $n$).

## 3. Results

### 3.1. Physicochemical Characteristics

The characteristics per residue type (tomato leaves and suckers and cucumber leaves and suckers) along the three sampling times are shown in Figure 1. The TS content of the leaves was not statistically different over time, except for the cucumber leaves in March, which seemed different from the samples taken in May ($p$ = 0.012) and August ($p$ = 0.042). The suckers seemed to be drier in May; however, the TS of the samples in May did not differ statistically from the samples in August ($p$ = 0.052) but differed from the samples in March ($p$ = 0.028) in the case of tomato sucker. In the case of the cucumber suckers, there was a statistical difference between the samples of May and August ($p$ = 0.004) and between May and March ($p$ = 0.010). The same trend in the variation was observed in the VS content of all types of biomass.

The TKN content was statistically the same in time in most cases ($p$ = 0.063 to 0.916), except for the samples taken in March and May for the tomato suckers ($p$ = 0.013) and in March and August for the cucumber suckers ($p$ = 0.010). On the contrary, the COD content was statistically different in most cases; tomato leaves and suckers increased their COD content from March to August, while the cucumber leaves and suckers had lower COD in May and statistically similar COD in March and August ($p$ = 0.082 and $p$ = 0.096 for leaves and suckers, respectively). It should be noted that the tomatoes were planted in February and remained until the end of the season (October), while the cucumbers were planted twice (in January and June). Therefore, the plants were younger in March or August than in May. The phosphorus content of the samples in time was statistically the same only in some cases, that is, between March and August ($p$ = 0.255) for the tomato leaves, between March and May ($p$ = 0.871) for the cucumber leaves, and between March and August ($p$ = 0.813) for the cucumber suckers. In all other cases, there was a significant statistical difference within the same type of plant residue, but no safe conclusion can be drawn regarding how the plant maturity phase or temperature correlate with the P content of the leaves and suckers for each crop. For example, the leaves of tomato seemed to be richer in P during May, while the leaves of cucumber had the highest P content in March and May. Moreover, suckers of tomatoes had the highest P concentration in March, while the suckers of cucumbers contained the highest P in March and August. On the other hand, the cultivation practice applied with respect to fertilization, which could affect the P content, did not change during these months. More frequent sampling events within March, May, and August could reveal the variance of P content in these months accurately.

Averaging the values of each parameter within the same residue type resulted in a high standard deviation in the cases for which significant differences in time were noted (Table 2). For example, the TS and VS content of suckers, which were much higher in the samples taken in May, had a standard deviation of 20–30% of the mean value. The same applied to the cucumber leaves with a higher TS content in the samples of August. As a result of the high standard deviation, there were no statistically significant differences in the TS content of the various residues (except for tomato leaves being drier than the cucumber leaves, $p$ = 0.007). The VS content followed the same trend.

**Table 2.** Mean values and standard deviations of the physicochemical characteristics of the residual biomass.

| | T.L. | T.S. | T.St. | C.L. | C.S. | C.St. |
|---|---|---|---|---|---|---|
| Humidity (%) | 89.6 ± 0.6 | 88.8 ± 3 | 85.8 ± 1.7 | 91.6 ± 1.3 | 91 ± 1.9 | 92.3 ± 2.8 |
| TS (% FM) | 10.4 ± 0.6 | 11.2 ± 3 | 14.2 ± 1.7 | 8.4 ± 1.3 | 9 ± 1.9 | 7.7 ± 2.8 |
| VS (% TS) | 69.5 ± 2.6 | 85.9 ± 2.5 | 86.1 ± 1.4 | 71.6 ± 4.3 | 83.8 ± 1 | 81.3 ± 0.5 |
| COD (g $kg^{-1}$ VS) | 1179 ± 64 | 1239 ± 129 | 1215 ± 7 | 1251 ± 83 | 1304 ± 49 | 1157 ± 14 |
| TKN (g $kg^{-1}$ VS) | 38 ± 3.9 | 60.4 ± 4.5 | 11.7 ± 0.5 | 47.3 ± 2.1 | 62.6 ± 7.4 | 15.3 ± 1.2 |
| P (g $kg^{-1}$ VS) | 69.1 ± 16 | 70.5 ± 18 | 26.8 ± 0.5 | 80.5 ± 25.4 | 110.9 ± 18 | 47.5 ± 5 |
| Acid Insoluble Acid-insoluble lignin (% e.f.s.) | | | 10 ± 1.1 | | | 10.1 ± 1.4 |
| Acid-soluble lignin (%e.f.s.) | | | n.d. | | | 16.4 ± 0.6 |

T.S.: Tomato Suckers, T.L.: Tomato Leaves, T.St.: Tomato Stalks C.S.: Cucumber Suckers, C.L.: Cucumber Leaves, C.St.: Cucumber Stalks TS: Total Solids, FM: Fresh Matter, VS: Volatile Solids, e.f.s.: extractive free solids, n.d.: not determined.

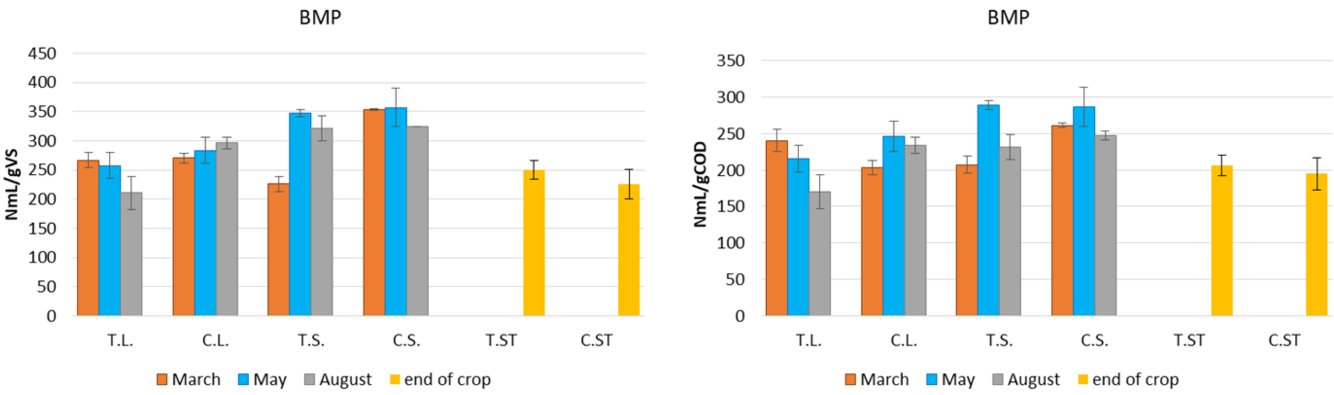
The COD content had a low standard deviation (except for the tomato suckers being the richer in COD in the samples of August). As a result, the comparison of the means revealed that the tomato leaves had a lower COD content. However, it was not statistically different from the COD content of the tomato suckers, which had a higher standard deviation ($p = 0.178$). Similarly, the TKN content had a low standard deviation (4–10% of the mean value) and most values were statistically different ($p < 0.05$). Suckers were richer in TKN than leaves, but tomato and cucumber suckers had statistically the same TKN content ($p = 0.516$). On the contrary, the high standard deviation of the P content (23–32% of the mean values) equated the values, except for the P content of the cucumber suckers, which was statistically different from all the other types of residues.

The whole tomato plants were removed in November, and the same occurred for the cucumber plants in June and November. As a result, the residue from these activities differed from the type of biomass removed daily (leaves and suckers) since it contained the stalks. Tomato and cucumber stalks were statistically different in all of their characteristics. The stalks of tomatoes seemed drier and higher in COD content than the cucumber stalks, while the TKN and P content were higher in the cucumber stalks (Table 2). However, the TS, VS, and COD content of the stalks was generally comparable to the other types of residues (leaves and suckers), but the TKN and P contents of both stalk types were lower than the leaves and suckers.

Lignin was determined in all residue types, but it was found only in the stalks. The acid-insoluble lignin content on an extractives free basis of the two stalk types was not statistically different ($p = 0.897$). However, it was 10% in both tomato and cucumber stalks. Acid-soluble lignin on an extractives free basis was also determined for cucumber stalks and was about 16%.

### *3.2. BMP Evaluation*

The BMP varied between 210 and 357 NmL $g^{-1}$ VS or 170 and 289 NmL $g^{-1}$ COD (Figure 2). There is no correlation between the time of sampling (March, May, August, end of crop), the type of residue (leaves, suckers, stalks), and the plant (tomato, cucumber) with the BMP, either expressed per g of VS or g of COD. Comparing the maximum yield of 350 NmL of $CH_4$ per g of COD consumed with the BMP values expressed in terms of g COD (Figure 2) reveals the high anaerobic biodegradability of the various residue types (up to 82%). In all cases, the suckers had the highest methane yield compared to the leaves and stalks of the two plants. The highest yield expressed per VS was found in cucumber suckers (357.1 ± 33.8 NmL $CH_4$ $g^{-1}$ VS), while tomato suckers had the highest yield when expressed per FM. These results were consistent with the chemical analysis, where the VS and COD content of the suckers were higher for both plants, while tomato leaves were the lowest in content (Table 3). Specifically, the methane potential of tomato suckers was 23.3% higher than their leaves, and was 21.1% in the cucumber's case. In total, the methane yield of the cucumber's residues was 16.6% higher than the total yield of the tomatoes.




(**a**) (**b**)

**Figure 2.** BMP of the various residue types along time expressed in g VS (**a**) or g COD (**b**).

**Table 3.** Annual production of residual biomass in Thrace Greenhouses S.A in tons of fresh matter (FM).

| Tons | January | February | March | April | May | June | July | August | September | October | November | December | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| T.S. | 0 | 0 | 27 | 264 | 346 | 437 | 458 | 360 | 275 | 339 | 127 | 0 | 2633 |
| T.L. | 0 | 0 | 7 | 66 | 86 | 109 | 115 | 90 | 69 | 85 | 32 | 0 | 658 |
| T.St. | | | | | | | | | | | 425.7 | | 426 |
| C.S. | 8 | 264 | 500 | 625 | 495 | 155 | 213 | 471 | 317 | 149 | 74 | 0 | 3272 |
| C.L. | 1 | 47 | 88 | 110 | 87 | 27 | 38 | 83 | 56 | 26 | 13 | 0 | 577 |
| C.St. | | | | | | 113 | | | | | 113 | | 225 |
| Total | 9 | 311 | 622 | 1065 | 1015 | 841 | 823 | 1004 | 718 | 600 | 672 | 0 | 7567 |

By eliminating the seasonality factor from the evaluation of the BMP, all BMP values were taken into account per residue type and averaged (Figure 3a). The null hypothesis of all BMPs being equal was rejected at a 95% level ($p = 1.8 \times 10^{-6}$) according to the one-way analysis of variance (ANOVA) test. By performing a *t*-test pairwise, it was found that the BMP of the leaves was statistically different from the BMP of the suckers ($p = 0.027$ and $p = 9.3 \times 10^{-5}$ for the tomatoes and cucumbers, respectively). The BMP of the cucumber leaves was statistically different from the BMP of the tomato leaves ($p = 0.0058$), but this was not the case for the BMP of the cucumber and tomato suckers ($p = 0.081$). By comparing the leaves/suckers with the stalks, it was found that the BMP of the tomato suckers and the cucumber leaves and suckers was statistically different from the BMP of the stalks ($p < 0.05$). Only the BMP of the tomato leaves and tomato and cucumber stalks were statistically similar. Finally, no statistical difference was recorded for the BMP between the tomato and cucumber stalks ($p = 0.804$).

Although the BMP expressed per mass of VS indicates that these residues are promising feedstocks in a biogas plant, the low TS content (or high moisture content) results in a low energy density expressed as NL of methane per kg of fresh matter (Figure 3b). Therefore, transferring the fresh residue biomass to a central biogas plant would be economically and environmentally unsustainable, while generating biogas on-site would be an attractive alternative. Gioulounta et al. [47] concluded that exploiting the plant residues (leaves and suckers) of a hydroponic greenhouse for energy production via a combined heat and power (CHP) engine and managing the energy supply via a hybrid CHP battery system could partially cover the facility's energy demands. Furthermore, incorporating the biomass from the removal of the whole plant would increase the total biomass and contribute to increasing the autonomy level of the energy management system.

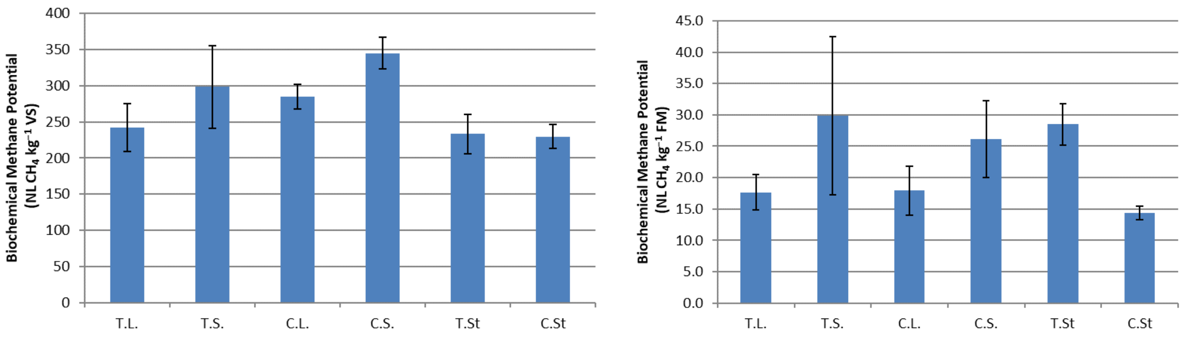



**Figure 3.** Average values of BMP per residue type expressed in terms of (**a**) mass of VS and (**b**) mass of fresh matter (FM).

Therefore, a detailed recording of the quantities of all types of residues removed per month in the hydroponic greenhouse was conducted per month (Table 3). During December, the greenhouse was prepared for the next crop season. Cucumbers were planted first (in January and February), and tomatoes were planted in March. The cucumbers were renewed at the end of May and the beginning of June; therefore, the whole crop plant was removed (recorded as "stalk" in Tables 1 and 2). Both plants (tomatoes and cucumbers) were removed in November when the crop season was over. Therefore, the leaves and suckers were generated at a rate corresponding to the stage of crop growth. The highest amount of biomass was recorded between April and August, with a slight decline in June and July because of the cucumber replantation.

The maximum methane production per month was calculated based on the BMP of each residual biomass type (Figure 3b) and their quantity (Table 3). Following the trend of the amount of biomass, the highest methane production was expected between April, May, and August (Figure 4). However, since the tomato plants were removed massively in November, there was a considerable quantity of residues (tomato stalks) available having a high BMP compared to the BMP of leaves (Figure 3b).

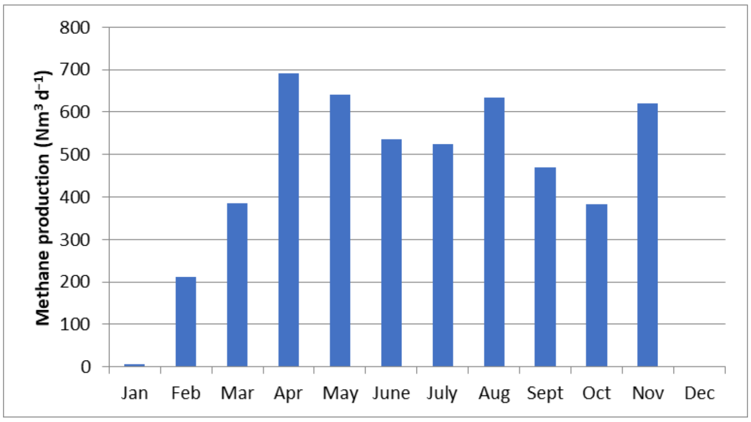



**Figure 4.** Methane production of residual biomass.

### *3.3. BMP Simulation*

The BMP test is performed in batch reactors using an inoculum of microorganisms suitable to degrade the substrate added for evaluation anaerobically. The typical sources of inoculum are anaerobic digesters treating sewage sludge or a variety of substrates (e.g., energy crops, food wastes, manures, etc.) so that the microorganisms contained in the inoculum are well adapted to a variety of organic matter. In this way, the initial lag phase, which is typical in microbial growth, is minimized. However, it cannot be diminished since the microorganisms need a particular amount of time to adapt to the conditions of a new environment when exposed to a specific substrate. Since biogas production is assumed to be proportional to the microorganisms' growth, the Gompertz model or the MGM, developed to fit growth data, are frequently used. However, a two-phase biogas production is often observed, which includes a temporal cease or slowdown of the biogas after start-up and a subsequent resumption of the production at a lower rate most times. This "diauxic type" of biogas or methane production can be attributed to various reasons, including the degradation of readily biodegradable and difficult-to-degrade substrates. In this case, the MGM cannot accurately fit the experimental data. Therefore, a TGM has been proposed to estimate the lag time, the methane production, and the maximum specific growth production rate at the two phases. Since most BMP tests in the present study exhibited this type of profile (Supplementary Materials, Figures S1–S5), the TGM (Equation (1)) was applied to fit the experimental data and compare the model parameter values for each biomass type studied.

The model's goodness of fit was evaluated based on the NSE and PBIAS coefficients. The NSE coefficient represents the residual over the experimental variance [54], while the PBIAS coefficient expresses the average tendency of the model to overestimate or underestimate the experimental data [55]. The model fitting was evaluated according to the limits set in literature [56]. In all cases, the NSE was close to 1, and PBIAS was close to 0, (Tables S1–S5) indicating a very good fit.

In all cases, the first lag time constant was close to zero, meaning that there was readily biodegradable organic matter which yielded the highest portion of the BMP (more than 50% of the methane was obtained until the first plateau, as indicated via A1 compared to the sum of $A_1$ and $A_2$), except for the cucumber suckers collected in August. When both lag time constants were close, there was no apparent diauxic behavior; however, MGM did not fit the data well. It is evident that the slope of the methane production rate curve was initially high and then decreased long before it reached a plateau, indicating the need to use a TGM. Comparisons of the kinetic parameters for the same type of biomass during the different sampling times showed that no tendency for different kinetics could be identified. For example, the parameter $\mu_{max1}$ was lower in the May samples for tomato leaves but higher for tomato suckers and cucumber leaves, while no statistical difference can be identified for $\mu_{max2}$.

Comparing the maximum specific methane production rate constants for the different types of biomass showed that the tomato suckers were degraded faster during the first phase (23.9 ± 4.9 NL $kg^{-1}$ VS $d^{-1}$). At the same time, there was no statistical difference in the μmax1 for the other biomass types (15.4 ± 6.2, 16. ±6.0, 19.1 ± 4.9 NL $kg^{-1}$ VS $d^{-1}$ for the tomato leaves, cucumber leaves, and suckers, respectively). Regarding the $\mu_{max2}$, it was lower for the tomato leaves and suckers (3.7 ± 1.9 and 4.6 ± 3.5 NL $kg^{-1}$ VS $d^{-1}$, respectively) than for the cucumber leaves and suckers (12.8 ± 4.1 and 12.9 ± 3.5 NL $kg^{-1}$ VS $d^{-1}$, respectively). There was no statistical difference for $\mu_{max2}$ between leaves and suckers for the same vegetable (tomato or cucumber). In most cases, the maximum specific methane production rate of the first phase was higher than the second phase (for tomato leaves and suckers and cucumber suckers), which agrees with the assumption that the organic matter of the biomass consists of readily biodegradable (e.g., dissolved sugars) and more difficult-to-biodegrade compounds (e.g., macromolecules in particulate form, which need more time to break down to monomers). The rapid uptake of the easily biodegradable organic matter yields the methane faster, which is showed by a higher incline in the accumulated methane curve. Another reason for the lower maximum specific methane production rate of the second phase might be the production of a metabolite with inhibiting properties. In the case of the cucumber leaves, there was a statistical difference between the two kinetic constants ($p$ = 0.23).

Finally, the simulation of the BMP tests conducted on the stalks showed higher kinetics than the leaves and suckers (except for the tomato stalks, which had no statistical difference from the tomato suckers) concerning the $\mu_{max1}$. Moreover, tomato stalks seemed to be degraded slower than cucumber stalks (29.6 ± 5.9 and 47.9 ± 5.7 NL $kg^{-1}$ VS $d^{-1}$, respectively and $p$ = 0.002). Concerning the $\mu_{max2}$, it was much lower than $\mu_{max1}$, and its value for the tomato stalks was higher than for the cucumber stalks (4.6 ± 0.2 and 2.9 ± 0.7 NL $kg^{-1}$ VS $d^{-1}$, respectively, and $p$ = 0.002).

## 4. Discussion

Most studies involving biogas production from vegetable residues concern either the lignocellulosic part of the plant or peels, pomace, and rotten vegetables. However, only a few have concentrated on the leaves and suckers. In the present study, the BMP of tomato residues (leaves, suckers, and stalks) was averaged at 242.0 ± 33.1, 298.3 ± 56.9, and 233.1 ± 27.2 NL $CH_4$ $kg^{-1}$ VS, respectively, while the BMP of cucumber residues (leaves, suckers, and stalks) was averaged at 284.9 ± 17.4, 344.9 ± 21.9, and 229.6 ± 16.8 NL $CH_4$ $kg^{-1}$ VS, respectively (Figure 3a). The averages were calculated from the BMP of all samples taken throughout the cultivating season. Statistical comparisons showed that the leaves yielded lower methane than the suckers for each crop. There was no difference between the BMP of suckers from tomatoes or cucumbers, but a statistical difference was found for the BMP of leaves between the two crops. The stalks of both crops yielded lower methane than leaves and suckers, except for the tomato leaves, which exhibited similar BMP as the stalks. It should be noted that the BMP of the tomato leaves collected in March was lower than all other samples and caused a high variance of the average calculated for the BMP of tomato leaves throughout the cultivating season. Finally, there was no statistical difference in the BMP between the tomato and cucumber stalks.

As shown in the following discussion, the tomato and cucumber crop residues' BMP determined in the present work lie at the higher range of values reported in the literature for the tomato and cucumber, as well as for other vegetable crop residues.

The BMP values are similar to what Oleszek et al. [45] determined by using a mixture of stems, leaves, and stalks at fresh or ensiled conditions as residues from tomato and cucumber plants taken from a greenhouse of the University of Life Sciences in Lublin. The fresh and ensiled tomato biomass yielded 301 ± 5 L $CH_4$ $kg^{-1}$ VS and 238 ± 7 L $CH_4$ $kg^{-1}$ VS, respectively, while the fresh and ensiled cucumber biomass yielded 280 ± 5 L $CH_4$ $kg^{-1}$ VS and 166 ± 4 L $CH_4$ $kg^{-1}$ VS, respectively. The fresh residues used in their study and the leaves and suckers used in the present study had a similar BMP, but the stalks of both plants in the present study yielded a lower methane value. The TS content of the fresh residues in the study of Oleszek et al. (10.77 ± 1.11 and 17.42 ± 0.54%), the VS content (74.70 ± 7.17% TS and 81.97 ± 0.41% TS), and the TKN content (4.38 ± 0.16 and 3.47 ± 0.13% TS) for cucumber and tomato fresh residues, respectively, were at similar levels with the results of the present work (Table 2), except for the tomato residues, which were drier (17.42 ± 0.54%) in the study of Oleszek et al. [45]. Moreover, the net heat energy production corresponding to the methane produced was evaluated according to Oleszek et al. [45], who accounted a 20% utilization of the heat for heating the digester. The obtainable heat energy ranges from 4.84 (tomato leaves) to 8.32 (cucumber suckers) MJ $kg^{-1}$ TS and can be compared to the low heat calorific value of tomato and cucumber residues (12.60 ± 0.47 and 11.12 ± 0.53 MJ $kg^{-1}$ TS, respectively) as determined in [45].

Li et al. [57] reported lower yields, 124 ± 6 L $CH_4$ $kg^{-1}$ VS from tomato (*Lycopersicon esculentum* Mill.) crop residues and 118 ± 5 L $CH_4$ $kg^{-1}$ VS from cucumber (*Cucumis sativus* L.) crop residues from a greenhouse in China. The BMP vessels were not mixed continuously, which may have affected the yield. The residues included stems, vines, residual fruit, and leaves, which were drier (higher TS content of tomato and cucumber residues at 17.5 ± 0.1 and 21.9 ± 0.1%, respectively) than in the present work (7.7–14.2 ± 0.6–3%). The VS content of cucumber residues (75.7% TS) was similar to the results of the present study (71.6–83.8% TS), but, as regards the tomato residues, the VS content (82.9% TS) was between the VS of the leaves (69.5% TS) and the suckers and stalks (85.9–86.1% TS) of the present study.

Almeida et al. [44] found a lower methane yield of 140 L $CH_4$ $kg^{-1}$ VS from tomato branches (*Solanum lycopersicum*) collected from a private farm in Portugal. Tomato branches had similar VS content (80 ± 0.3% TS), higher COD (1592 ± 73 g $kg^{-1}$ VS), TKN (33.68 ± 0.99 g $kg^{-1}$ TS), and insoluble lignin (13.83 ± 0.59% TS) compared to that found in the tomato stalks of the present study (86.1 ± 1.4% TS, 1215 ± 7 g $kg^{-1}$ VS, 11.7 ± 0.5 g $kg^{-1}$ VS and 10 ± 1.1% on an extractive free solid basis, respectively). Manual stirring and/or the higher lignin content may have been responsible for the lower methane yield.

Gunaseelan et al. [58] tested the biochemical methane potential of about 54 fruits and vegetables from a vegetable market in India, including leaves and stems of the coriander plant, cabbage, cauliflower, and leaves of turnip, garden beet, and carrot. The VS content of coriander (80% TS in leaves and 85.7% TS in stems), cauliflower (82% TS in leaves and 87.1% TS in stems), turnip (84.4% TS in leaves), and beet (81.4% TS in leaves) was close to the VS of most residues in the present study (81.3–86.1% TS), except for the cabbage (91.2% TS in leaves and 91.8% TS in stems) and carrot (93.1% TS in leaves), in which the VS content was higher. The lowest methane yield was found in cauliflower leaves (190 L $CH_4$ $kg^{-1}$ VS), garden beet leaves (231 L $CH_4$ $kg^{-1}$ VS), and carrot leaves (241 L $CH_4$ $kg^{-1}$ VS), while the highest methane yield was obtained from coriander leaves (325 L $CH_4$ $kg^{-1}$ VS), cauliflower stems (331 L $CH_4$ $kg^{-1}$ VS), and turnip leaves (314 L $CH_4$ $kg^{-1}$ VS).

Aravani et al. [59] determined that the lignin content of tomato stalks was 6.49 ± 0.93%, very close to 10 ± 1.1% determined as acid-insoluble lignin in the present work. Although Aravani et al. found this material fibrous and did not proceed further with evaluating its BMP, tomato stalks yielded 233.1 ± 27.2 NL $CH_4$ $kg^{-1}$ VS in the present work.

The diauxic growth lag phase for the biogas production from the agricultural residues indicates the presence of two main fractions of organic matter, which degrade at a different rate [60,61], or an inhibitory factor, which slows down the process [62]. In most cases of this study, the methane production was faster at the beginning of the BMP test, and, afterwards, it slowed down until the final plateau. Even if the first plateau was not evident during methane production (from the stalks, for example) (Figure S5), the change in the BMP curve slope indicated there were fast and slow degrading compounds in the substrates, which the MGM cannot predict. Moreover, the methane production from the stalks occurred at a higher initial rate than the other residues, which is not compatible with the fact that the stalks contained lignin, while there was no lignin in the leaves and the suckers. It is possible that there are compounds in the leaves and suckers which may have an inhibitory effect. For example, it has recently been found that tomato leaf extracts exhibit antimicrobial properties [63,64], which may also slow the anaerobic digestion process.

## 5. Conclusions

Tomato and cucumber residues are produced massively from hydroponic greenhouses throughout the cultivating period starting from January and ending in November, especially from April to August. The primary part of residues consists of leaves and suckers, while the whole plant (consisting mainly of stalks) is removed at the end of the cultivating season. The BMP of tomato residues was assessed to be 242.0 ± 33.1, 298.3 ± 56.9, and 233.1 ± 27.2 NL $CH_4$ $kg^{-1}$ VS for leaves, suckers, and stalks, respectively, while the BMP of cucumber residues was found to be 284.9 ± 17.4, 344.9 ± 21.9, and 229.6 ± 16.8 NL $CH_4$ $kg^{-1}$ VS for the leaves, suckers, and stalks, respectively. Fitting the BMP curves with the two-phase modified Gompetz model showed that a diauxic methane production occurred. The methane production was at a higher rate in the first than in the second phase, suggesting a readily biodegradable fraction in the biomass. Moreover, it is worthwhile to mention that the methane produced from the stalks took place faster in the first phase, although the stalks are considered less biodegradable due to their lignin content. Therefore, there may be inhibitory compounds in the leaves and suckers that slow the process but do not limit the ultimate methane yield.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app13095445/s1, Figure S1: Replicate BMP curves of samples from tomato leaves; Table S1: Parameter values of the TGM fitting the BMP curves of samples from tomato leaves; Figure S2: Replicate BMP curves of samples from tomato suckers; Table S2: Parameter values of the TGM fitting the BMP curves of samples from tomato suckers; Figure S3: Replicate BMP curves of samples from cucumber leaves; Table S3: Parameter values of the TGM fitting the BMP curves of samples from cucumber leaves; Figure S4: Replicate BMP curves of samples from cucumber suckers; Table S4: Parameter values of the TGM fitting the BMP curves of samples from cucumber suckers; Figure S5: Replicate BMP curves of samples from tomato and cucumber stalks after removal of the whole plant; Table S5: Parameter values of the TGM fitting the BMP curves of samples from tomato and cucumber stalks after removal of the whole plant.

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