



Biomethanation of invasive water hyacinth from eutrophic waters as a post weed management practice in the Dominican Republic: a developing country

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Abstract

Anaerobic digestion of water hyacinth (*Pontederia crassipes* Mart.) from eutrophic water bodies could be a sustainable post weed management practice to generate bioenergy. Comparative analyses of the water quality, physicochemical characteristics, and biomethanation kinetics of water hyacinth from two sites with different water types (brackish versus freshwater) in the Ozama river, Dominican Republic, were conducted. Also, the energy produced from the anaerobic digestion and that consumed in harvesting was estimated. The highest non-structural components in the form of protein ($18.8 \pm 1.9\%$) and extractives ($26.4 \pm 0.1\%$) were found in brackish water hyacinth, whereas that from freshwater had the highest amount of holocellulose ($41.2 \pm 2.8\%$). Indicators of plant productivity, i.e., chlorophyll *b* and bulk density, were more than 30% higher in brackish than in freshwater hyacinth. The methane production rate in the digestion of water hyacinth from brackish water ($22.5 \text{ N. L/kg VS}_{\text{added}} \cdot \text{day}$) was twice that from freshwater ($10.0 \text{ N. L/kg VS}_{\text{added}} \cdot \text{day}$). The higher nutrient content in the brackish water could have influenced the superior performance of water hyacinth from that source compared with that from freshwater. Overall, the maximum methane potential of the Ozama river water hyacinth was $399.2 \pm 32.2 \text{ N. L CH}_4/\text{kg VS}_{\text{added}}$. The estimated energy produced per ton of fresh biomass was 846.5 MJ, but only 57.9 MJ would be required for mechanical harvesting. The biomethanation of water hyacinth can mitigate weed management costs in developing countries.

Keywords Eutrophication · *Eichhornia crassipes* · Anaerobic digestion · Chemical composition · Biomethane · Chlorophyll · Brackish water · Kinetics

Introduction

Water hyacinth (*Pontederia crassipes* Mart.), formerly *Eichhornia crassipes* (Mart.) Solms (Pellegrini et al. 2018), is one of the most noxious and invasive aquatic plants threatening the water quality of tropical and subtropical ecosystems. The capacity of this plant to reproduce sexually and asexually leads to high growth rates and the formation of large floating mats. As a result, water bodies affected by water hyacinth

have lower oxygen and high organic debris contents. Decaying biomass has detrimental effects on rivers such as acceleration of eutrophication and unpleasant taste of water and odor due to oxygen depletion (Jones 2001; Hronich et al. 2008; Gettys et al. 2009). Increased eutrophication and reduced light penetration due to the dense mats can be lethal to fish and other plant species. Invasions by aquatic weeds have also been linked to increases in human water-related diseases (Jones 2001; Chamier et al. 2012). The proliferation of water hyacinth in rivers and its detrimental impact on the ecosystems require sustainable weed management practices.

The reduction of costs associated with weed management has the potential to contribute to the sustainability of environmental protection practices. In high-income countries, millions of dollars are expended annually to prevent harbors from aquatic weed invasions. California Bay-Delta paid \$46.852 million on herbicidal treatments to control invasive weeds between 2013 and 2016 (Jetter and Nes 2018). In developing countries, high costs can limit the application of

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environmental management practices. Therefore, sustainable and cost-effective methods for weed control are needed. Herbicides (e.g., diquat, ioxynil + 2,4-D-isooctyl) can be as effective as manual and mechanical harvesting but are linked to higher operational costs (Alimi and Akinyemiju 1990). The use of chemical methods to eliminate water hyacinth from water bodies is five times less cost-effective than biological, mechanical, and integrated methods (Wyk and Wilgen 2002). However, the mechanical removal of weeds is connected to high disposal costs. Some methods that have been considered for facilitating and reducing disposal expenses are energy consuming such as fluidizing, dewatering, and combustion (Livermore et al. 1971). Integrating the mechanical harvesting of water hyacinth with the bioprocessing of the biomass could reduce the harvesting and weed disposal costs by generating valuable products.

Ozama river, an important water body in the Dominican Republic that is used for fishing, urban, industrial, recreational, and agricultural activities, has been invaded by water hyacinth. Previous reports on the water condition of the river along Santo Domingo showed turbidity ranging from 5.0 to 12.0 NTU; 10–35 $\mu\text{g/L}$ of chlorophyll-*a*; 0.4–4.0 mg/L dissolved oxygen (DO); and salinity levels ranging from 0.1 to 2.5 PSU (Miño et al. 2011). Water hyacinth has been identified as the main macrophyte associated with the high nutrient contamination of the river due to plant debris sedimentation (Salas and Martino 1988). Corrective measures were applied recently to mitigate the eutrophication of the water through the mechanical harvesting of the weed (Gavilán 2018). After removal, the plant biomass could serve as a feedstock for the generation of valuable products, which would potentially contribute to the sustainability of environmental protection practices by reducing the costs associated with weed management, a key factor in developing countries.

The biomethanation of water hyacinth from contaminated rivers in developing countries could be a sustainable weed management practice since the pollutants accumulated in the biomass can be digested or immobilized during anaerobic digestion while generating bioenergy. Water hyacinth has phytoremediation properties targeting heavy metals, and organic and inorganic compounds such as sulfates, phosphates, nitrates, nitrites, ammonia, phenols, and formaldehyde (Wolverton and McKown 1976; Mahmood et al. 2010; Moyo et al. 2013; Gong et al. 2018; Ting et al. 2018; Melignani 2019; Shirinpur-valadi et al. 2019). Cultivation of water hyacinth in contaminated waters and subsequent harvesting of the biomass increased DO, and decreased total dissolved solids (TDS), chemical oxygen demand (COD), biological oxygen demand (BOD), phosphorous, and nitrogen in the water (Saha et al. 2017; Edwige et al. 2018; Sekar and Ansari 2018; Zhang et al. 2019). Anaerobic digestion could be a sustainable process for the treatment of water hyacinth after phytoremediation of contaminated waters. Many

xenobiotics including monoaromatic and polyaromatic substances with or without chloro substitutes can be degraded or dechlorinated by anaerobic mixed cultures (Gallert and Winter 2005). Aquatic plants have also been identified as one of the most promising feedstocks for anaerobic digestion due to their high water content and low indigestible organic matter (Wellinger et al. 2013). The implementation of this technology in rural areas has potential dual benefits for producing renewable energy and treating organic wastes (Radu et al. 2017). In addition, biogas could one day be used as fuel for aquatic harvesters (Angelidaki et al. 2018).

The success of integrating the management of water hyacinth using physical removal and biomethanation methods requires understanding the impact of the up-taken compounds on the bioconversion process. Monitoring chlorophyll levels helps to estimate the effect these compounds (e.g., formaldehyde) have on photosynthesis efficiency and macrophyte bioproductivity, which are necessary for phytoremediation proficiency (Lagepinto et al. 2008; Pavlović et al. 2014; Gong et al. 2018). Progressive drought and nutrient stress decreased chlorophyll content in water hyacinth and consequently compromised the photosynthetic activity of the plants (Venter et al. 2017). TDS are organic solutes and salt ions that can act as stress agents for water hyacinth and be detrimental for anaerobic digestion when they accumulate in the plant biomass. Within 6 days, water hyacinth is able to remove up to 55% of TDS from waters containing 4500 mg/L TDS (Sekar and Ansari 2018). However, high concentrations of chloride salts (i.e., 4–10 g/L) in feedstock for anaerobic digestion have an inhibitory effect on biomethane production (McCarty and McKinney 1961; Feijoo and Soto 1995). Reports of the effect of TDS on water hyacinth growth are variable. When plants were cultivated in high TDS waters (i.e., sewage), larger leaves were observed than when cultivated in distilled, tap, and lake waters (Daddy et al. 2002). In contrast, a reduction in plant size and chlorophyll production due to high TDS was reported by other authors (Sekar and Ansari 2018).

The water quality and composition of the water hyacinth from areas with different characteristics need to be accounted for when considering anaerobic digestion as post weed management practice. The performance of the bioconversion processes such as anaerobic digestion depends on the feedstock composition, which is influenced by growth conditions (Angelidaki and Sanders 2004; Agblevor and Pereira 2013). In the Dominican Republic, two sites (La Ciénaga and El Naranjo), with different water types, TDS loads, and demographic characteristics within the Ozama river are being affected by water hyacinth growth. La Ciénaga (brackish water) and El Naranjo (freshwater) are 1.5 km and 23.14 km north of the Caribbean Sea, respectively. The TDS of freshwater like that from El Naranjo is below 1000 ppm, whereas estuaries or brackish water like that from La Ciénaga have between 1000 and 35,000 ppm of TDS (Swenson and Baldwin 1965). La Ciénaga is a dense low-income area of Santo Domingo city

characterized by numerous informal settlements on the riverbank while El Naranjo is a low populated rural area located in the peripheries of Santo Domingo. The anthropogenic contamination at La Ciénaga is higher than at El Naranjo. The Ozama river carries solid waste, raw sewage, industrial discharges, and pestilential odor along La Ciénaga (Chantada 1991; Edelman 2019). These differences between La Ciénaga and El Naranjo could impact the water hyacinth characteristics and bimethanation performance.

The energy generated through the anaerobic digestion of water hyacinth from eutrophic rivers can mitigate the costs associated with weed harvesting, making this process more sustainable in developing countries such as the Dominican Republic. In the present work, the water quality of the Ozama river at La Ciénaga and El Naranjo was evaluated. The physicochemical characteristics including bioproductivity indicators (chlorophyll, and density) and the bimethanation kinetics of the water hyacinth from La Ciénaga and El Naranjo were compared. Additionally, the energy produced by the anaerobic digestion of water hyacinth from the Ozama river was compared with the energy required to mechanically harvest the plant from eutrophic rivers.

Materials and methods

Study sites and water quality

Samples of water hyacinth were collected from two sites: El Naranjo (18° 34' 27.2" N 69°47' 09.9" W) and La Ciénaga (18° 29' 21.8" N 69° 52' 57.4" W) within Ozama River. The sampling sites were 21.64 km apart along the river. The water type at El Naranjo is freshwater, whereas the water at La Ciénaga is brackish. The water quality (temperature, pH, DO, salinity, nitrates, and TDS) was measured in situ during harvesting using YSI DSSPro (YSI Incorporated, Yellow Springs OH, USA). TDS and nitrate measurements were repeated the following year after harvesting. Because only one site per water type was sampled, caution must be used when interpreting the data.

Biomass harvesting and preparation

About 10 kg of freshwater hyacinth biomass was manually harvested from each site and knives were used to discard the roots. The leafy biomass was washed with tap water, ground using Power Pro 2 Model FP 1510 (Black and Decker, Towson, MD, USA), and placed on shelves to dry at ambient conditions for 3 weeks at the Specialized Institute of Higher Studies Loyola (San Cristobal, Dominican Republic). The air-dried ground biomass was stored and shipped to Utah State University. The rest of the preparation was conducted as described by ASTM E 1757-01. The biomass was milled with a

Thomas-Wiley Laboratory Mill Model 4 (Thomas Scientific, Swedesboro, NJ, USA) equipped with a 2-mm mesh.

Photosynthetic pigments

For the determination of chlorophyll-*a* (C_a) and chlorophyll-*b* (C_b), 0.5 g of prepared biomass was placed in test tubes with 80% acetone (10 mL) and vortexed for 5 min. The absorbance of the supernatant was taken at 470, 646, and 663 nm using a DR5000 Hach UV-Vis spectrophotometer (Hach Company, Loveland, CO, USA). Pigment content was calculated using Lichtenthaler (1987) equations. Based on previous research, chlorophyll content measurements using air-dried biomass do not differ from those using fresh biomass (Roshanak et al. 2016). The procedure was conducted in triplicates for each biomass type.

Density

Bulk volume (VB) of air-dried biomass (180–850 μm) was determined using three graduated cylinders according to the methods outlined by Mani et al. (2008). The biomass was poured to the containers from a 300-mm height measured from the bottom of the container. The procedure was conducted four times for each biomass type.

Proximate analysis

The analyses were conducted in triplicate using a TGA-Q500 (TA Instruments, New Castle, DE, USA) according to previous works (García et al. 2013; de Jong and Van Ommen 2015). The samples (20 mg) were heated at a rate of 10 °C/min using nitrogen at 60 mL/min as the carrier gas. At 600 °C, the carrier gas was changed to oxygen instead of nitrogen to allow fixed carbon combustion up to 700 °C. Equations (1)–(3) were used for the determination of volatile solids (VS), fixed carbon (FC), and total ash content (ASH).

$$\%VS = ((W_{T=190^\circ C} - W_{T=550^\circ}) \times 100\%) / W_{T=190^\circ C} \quad (1)$$

$$\%FC = ((W_{T=600^\circ C} - W_{T=700^\circ}) \times 100\%) / W_{T=190^\circ C} \quad (2)$$

$$\%ASH = (W_{T=700^\circ C} \times 100\%) / W_{T=190^\circ C} \quad (3)$$

Ultimate analysis

The organic elemental analysis (CHNSO) was conducted using FLASH 2000 Organic Elemental Analyzer (Thermo Fisher Scientific, Waltham, MA, USA). The oxygen content was calculated as the residual mass after accounting for CHNS and ash content. The experiment was performed with four replicate per site.

Summative analysis

The moisture content was determined using the IR-60 infrared moisture analyzer (Denver Instruments, Bohemia, NY, USA) as described in ASTM E-1756-08, Test Method B. The total extractives were determined via sequential extraction using ethanol/toluene mixture (1:2), 95% ethanol, and deionized water. For the extractions, ASTM E1690-08 was followed and the BUCHI 011 rotavapor equipped with a BUCHI 461 water bath used (BUCHI AG, Fawil, Switzerland). The ash content was determined using a Thermo Scientific Lindberg/Blue M furnace (Thermo Fisher Scientific, Waltham, MA, USA), following ASTM E 1755-01. The non-extractable ash was the inorganic material in the biomass after extractives removal. The extractable ash was the difference between the total ash (on a whole dry basis, see the “[Proximate analysis](#)” section) and the non-extractable ash. The protein content was estimated using the nitrogen conversion factor (NF = 6.25).

The carbohydrates and acid-insoluble lignin were determined in six replicate following ASTM E 1758-01 and in triplicate using ASTM E1721 methods, respectively. For lignin combustion, 475 °C instead of 575 °C was used, for a 20-h period. The monosaccharides were measured using LC-10AT, equipped with a RID-10A (Shimadzu Corp., Kyoto, Japan). The sample was injected at 0.40 mL/min and passed through a BP-800Pb column (Benson Polymeric, Reno, NV, USA) at 80 °C for separation. Monosaccharides were determined for six replicate per site. Cellulose was calculated from glucose, assuming that 90% of the monomers came from the digested polymer and 10% from hemicellulose (Deka et al. 2018). The rest of the sugar monomers were derived from hemicellulose.

Extractable salts

To assess the type of chloride salts accumulated in the biomass, the water hyacinth extractives (see the “[Density](#)” section) were analyzed with a FEI Quanta FEG 650 scanning electron microscopy (SEM) (FEI Company Oregon, USA). The instrument was equipped with an Oxford energy dispersive X-ray spectrometer (EDS) with X-Max detector (Oxford Instruments, Abingdon, UK).

Inorganic elemental analysis

For the total inorganic elemental composition, 2.0 g of water hyacinth ash from each site was acid digested according to EPA 3050 and analyzed using ICP-AES by the Utah State University Analytical lab (USUAL), Logan, UT, USA. The results of the duplicate samples were reported on dry ash basis.

Anaerobic digestion

The biochemical methane potential (BMP) of water hyacinth was determined following the guidelines in Holliger et al. (2016). The inoculum used was anaerobic sludge from a mesophilic wastewater plant (North Davis Sewer District, Syracuse, UT, USA). The sludge had 2.3 ± 0.08 % total solids, 62.4 ± 1.9 VS% (1.4 ± 1.12 % VS on a dry basis), and pH 7.8 ± 0.07 . The standard anaerobic medium was prepared as reported by Angelidaki et al. (2009) but without the addition of resazurin. Since there was no a priori evidence of the presence of nutrients on the feedstock or inoculum, anaerobic media were added to the reactors. The biodegradation reactions took place in 200-mL amber serum bottles containing 1.2 g of water hyacinth mixed with 50 mL of anaerobic medium and 50 mL of sludge. The negative control contained the anaerobic medium and sludge without the biomass. The experimental units had 2.365% total solids and the feed to inoculum ratio (F/I) was 1.0. The triplicated samples and negative control had 1.445 g and 0.725 g of total VS, respectively. The bottles were incubated inside a reciprocal shaking water bath, Precision Model 50 (American Laboratory Trading, East Lyme, CT, USA) at 38.0 ± 1.0 °C.

The original assay (Group 1) was reproduced (Group 2) in duplicate for both water hyacinth types using the residual anaerobic sludge from Group 1 as inoculum.

Gas measurement

The produced gas was measured via volume displacement using a lubricated glass syringe every 48–72 h and analyzed using the Agilent 490 Micro (Group 1) and Agilent 7890B (Group 2) Gas Chromatographs (Agilent Technologies, Santa Clara, CA, USA). The measured volume (V) was converted to normal volume (V_0) through Eq. (4), where $T_0 = 273.15$ K and $P_0 = 101,325$ Pa. The barometric pressure (P) and temperature (T) during the gas measurements were 86 kPa and 300 K, on average.

$$V_0 = (V \times P \times T_0) / (P_0 \times T) \quad (4)$$

The accumulated methane volume was reported per mass of VS added to the systems. The normalized volume of methane produced by the negative control, which is the inoculum without VS added, was subtracted from all the experimental units to eliminate the methane due to inoculum substrate residues. When using the present method (Group 1), the biochemical methane potential of amorphous cellulose was 395.3 N.L CH₄/kg VS added, which is 95.4% of the theoretical value (i.e., 414 N.L CH₄/kg VS).

Modified Gompertz equation

The modified Gompertz model for the batch anaerobic digestion assumes that methane production follows the microbial growth pattern, and is appropriate for batch systems (Kafle and Chen 2016). In the model (Eq. (5)), W [N.L CH₄/kg VS added] is the accumulated methane produced as a function of time, A [N. L CH₄/kg VS added] is the maximum methane produced, K_z [N. L CH₄/Kg VS added × day] is the absolute growth rate, and T_{lag} [days] is the lag time. The doubling time (T_d) was calculated from the model.

$$W(t) = A \times \text{EXP}(-\text{EXP}((e \times k_z/A) \times (T_{lag}-t) + 1)) \quad (5)$$

The $W(t)$ curves of each replicate were fitted using the data analysis add on “Solver” in Microsoft Excel 2010. The resulting kinetic parameters of the replicates were analyzed statistically (see the “Statistical analysis” section).

Energy assessment

The operational characteristics associated with harvesting water hyacinth were calculated from previous studies with harvesting rates up to 9.3 t/h, (Bryant 1969). However, rates up to 34.55 t/h have been recorded for mixed aquatic plants using similar equipment (Smith 1984). The operative costs considered in this study were due to diesel fuel consumption (10–15 L/h) of aquatic harvesters with middle load capacity, i.e., 2.5 t/load (Julong 2018). Equations (6) and (7) were used to estimate the energy consumed (E_c [MJ/t_{biomass}]) in harvesting and energy produced (E_p [MJ/t_{biomass}]) from anaerobic digestion of fresh biomass. FC [L/h] is the fuel consumption per machine operation time, assumed to be 15, and HR [$t_{biomass}/h$] is the harvesting rate, assumed to be 10. The higher heating values (HHV) are 38.6 MJ/L diesel and 0.0398 MJ/L CH₄. BMP [L CH₄/kg VS] is expressed on a fresh biomass basis under the assumption that the water content of the harvested biomass is 91% (Akendo et al. 2008). The BMP value is the models’ mean on the anaerobic digestion of water hyacinth from the Ozama river.

$$E_c = (FC/HR) \times \text{HHV}_{\text{fuel}} \quad (6)$$

$$E_p = \text{BMP} \times (1000\text{kg}/t) \times (\text{VS}/100) \times (\text{TS}/100) \\ \times \text{HHV}_{\text{CH}_4} \quad (7)$$

Statistical analysis

The comparison between the characteristics (photosynthetic pigments, density, extractable salts, proximate analysis, ultimate analysis, inorganic element, and summative analysis) of water hyacinth from La Ciénaga and El Naranjo, and the

methane percentage in the produced biogas (%CH₄), were made using the Welch’s unpaired t test (www.graphpad.com). The two populations were assumed to be independent, normally distributed and unequal variances. The variability of the data was reported as the standard deviation of the mean (mean ± SD).

The kinetics from the fitted modified Gompertz model were compared using analysis of variance (ANOVA) in R Studio (version 3.6.1). The factors and levels considered for the analysis were as follows: (i) water source (El Naranjo, La Ciénaga) as treatment factor and (ii) Group (1, 2) as a blocking factor. The responses analyzed in ANOVA were the kinetic parameters (A , K_d , T_{lag} , T_d).

Results

Water quality

At the time of harvesting, the water temperature and pH at El Naranjo (freshwater) were 26.4 °C and 7.13, and 28.1 °C and 7.11 at La Ciénaga (brackish water). The salinity was 0.09 ppT and 1.23 ppT at El Naranjo and La Ciénaga, respectively. DO in El Naranjo was 2.50 mg/L and 1.37 mg/L at La Ciénaga. The nitrate content in La Ciénaga ranged from 11.76 to 17.33 mg/L NO₃⁻, and from 2.6 to 4.5 mg/L NO₃⁻ in El Naranjo 1 year between harvesting. Similarly, the TDS was between 122 and 640 mg/L in El Naranjo, and between 1550 and 3028 mg/L in La Ciénaga.

Photosynthetic pigments

The chlorophyll- a (C_a) and chlorophyll- b (C_b) contents in water hyacinth from El Naranjo were 0.48 ± 0.01 mg C_a/g and 0.68 ± 0.02 mg C_b/g (1.16 ± 0.02 mg C_{a+b} g), while those from La Ciénaga were 0.46 ± 0.01 mg C_a/g and 0.89 ± 0.03 mg C_b/g (1.35 ± 0.04 mg/g C_{a+b}). The chlorophyll a/b ratios were 0.5 and 0.7 for the water hyacinth from La Ciénaga and El Naranjo, respectively. The total chlorophyll (C_{a+b}) was higher ($p = 0.018$) in the biomass from La Ciénaga due to a higher ($p = 0.002$) chlorophyll- b content. However, the chlorophyll a/b ratio was lower ($p = 0.008$) in the water hyacinth from La Ciénaga than in that from El Naranjo.

Density

The bulk density of the biomass from La Ciénaga (0.219 ± 0.03 g/L) was higher ($p = 0.004$) than that from El Naranjo (0.114 ± 0.003 g/L).

Proximate analysis

The values of proximate analysis of water hyacinth (VS, FC, ASH) showed no difference ($p > 0.057$; Table 1) between La Ciénaga and El Naranjo. The water hyacinth from the Ozama river had 57.9 to 60.6% VS, 19.3 to 20.5% FC, and around 20% ASH on a dry weight basis.

Ultimate analysis (CHNSO)

There was no difference ($p > 0.1840$; Table 1) in the carbon, hydrogen, and sulfur contents of the water hyacinth from La Ciénaga and El Naranjo. In contrast, the nitrogen and oxygen contents in the biomass from the two sites were different ($p < 0.0001$, and $p = 0.03$, respectively). The sulfur content for all samples was below the detection limit (i.e., 100 ppm).

Summative analysis

The percentages of structural components in the biomass from El Naranjo ($45.3 \pm 2.38\%$ w/w) were higher ($p = 0.03$) than that from La Ciénaga ($34.7 \pm 5.3\%$ w/w).

Structural components

The amount of holocellulose in the water hyacinth from El Naranjo ($41.3 \pm 1.18\%$ w/w) was higher ($p = 0.046$, Table 1) than in that from La Ciénaga ($32.1 \pm 1.7\%$ w/w). All the monosaccharides were higher ($p < 0.01$) in the biomass from El Naranjo compared with that from La Ciénaga. However, the percentage of pentoses within the total monosaccharide content was not different ($p = 0.31$) between the water hyacinth from El Naranjo ($28.6 \pm 2.2\%$) and La Ciénaga ($27.3 \pm 2.0\%$). The main monosaccharides in La Ciénaga and El Naranjo's water hyacinth were glucose ($21.6 \pm 0.5\%$ and $27.0 \pm 1.4\%$), arabinose ($5.3 \pm 0.2\%$ and $7.5 \pm 0.5\%$), xylose ($3.5 \pm 0.5\%$ and $4.3 \pm 0.4\%$), and galactose ($1.8 \pm 0.1\%$ and $2.5 \pm 0.2\%$), in that order. Mannose was under the detection limit. The content of acid-insoluble lignin in the water hyacinth from El Naranjo was higher ($p = 0.03$, Table 1) than in that from La Ciénaga.

Non-structural components

The amounts of protein and extractives in the biomass from La Ciénaga were higher ($p = 0.02$, and $p = 0.002$, respectively; Table 1) than those from El Naranjo. Similarly, the extractable ash in the biomass from La Ciénaga ($13.6 \pm 0.3\%$ w/w) was higher ($p = 0.01$) than in that from El Naranjo ($9.8 \pm 0.7\%$ w/w).

Table 1 Mean \pm SD values of proximate and ultimate analyses, and composition of water hyacinth from the Ozama river. The ash from the biomass composition was determined after extractives removal, i.e., non-extractable ash. Results are reported on a dry weight basis

	Proximate analysis % (w/w)			Ultimate analysis (% w/w)					Composition (% w/w)					
	Volatiles (VS)	Fixed carbon (FC)	Total ash (ASH)	C	H	N	O	C/N	Cellulose	Hemi-cellulose	Lignin	Ash ¹	Protein	Extractives
El Naranjo (freshwater)	59.9 \pm 0.7 ^a	19.9 \pm 0.2 ^a	20.3 \pm 0.6 ^a	38.5 \pm 1.0 ^a	3.9 \pm 0.2 ^a	1.8 \pm 0.2 ^a	35.6 \pm 2.0 ^a	21.4	24.5 \pm 1.2 ^a	16.8 \pm 1.5 ^a	4.0 \pm 0.1 ^a	10.5 \pm 0.1 ^a	9.8 \pm 0.7 ^a	17.3 \pm 0.2 ^a
La Ciénaga (brackish)	58.4 \pm 0.5 ^a	19.9 \pm 0.6 ^a	21.7 \pm 0.1 ^a	39.4 \pm 0.4 ^a	4.0 \pm 0.2 ^a	3.7 \pm 0.1 ^b	31.3 \pm 0.8 ^b	10.5	19.5 \pm 0.5 ^b	12.6 \pm 1.2 ^b	3.6 \pm 0.1 ^b	8.1 \pm 0.2 ^b	18.8 \pm 1.9 ^b	26.4 \pm 0.1 ^b

Ash: ¹ The non-extractable ash, determined after extractives removal

^{a,b} Different letters within each column indicate a significant difference between sites for Welch's unpaired *t* test (alpha = 0.05)

Extractable salts

The salt clusters in the extractives from La Ciénaga were larger than in those from El Naranjo (Fig. 1). The map sum spectrum for the salt ions in the biomass from the water at La Ciénaga was 18.6 ± 0.1 wt% Cl, 9.7 ± 0.1 wt% K, 4.1 ± 0.0 wt% Na, and 1.4 ± 0.0 wt% Mg; and from El Naranjo was 6.6 ± 0.1 wt% Cl, 1.7 ± 0.0 wt% Mg, 1.1 ± 0.0 wt% Na, and 0.7 ± 0.1 wt% K. The total chloride ion (wt%) in the extractives from La Ciénaga (33.8 ± 0.2 wt%) water hyacinth was higher ($p = 0.0001$) than that from El Naranjo (10.7 ± 0.2 wt%). The results suggest that the main extractable salts from La Ciénaga and El Naranjo biomass were KCl and $MgCl_2$, respectively. However, the spectra for Mg (Fig. 1) show that most of the element is not tied to Cl, which indicates that the element might be present as Mg^{+2} or $MgCO_3$.

Inorganic elemental analysis

The total content of Na and Mg in the water hyacinth from La Ciénaga is higher ($p < 0.013$, Table 2) than that from El Naranjo. Similarly, phosphorus in water hyacinth from La Ciénaga was twice higher ($p = 0.009$) than that from El Naranjo. However, the biomass from El Naranjo had higher ($p < 0.02$) content of metals (i.e., Fe, Al, Co, As, Cr, Co) than that from La Ciénaga.

Anaerobic biodegradation

The methane yield from the water hyacinth at La Ciénaga (452.2 ± 51.5 N. L CH_4 /kg VS_{added}) was higher ($p = 0.044$; Fig. 2a) and El Naranjo (387.2 ± 10.9 N. L CH_4 /kg VS_{added}). Similarly, the methane production rate (K_z) of water hyacinth from La Ciénaga was higher ($p = 0.0004$, Table 3) than that from El Naranjo. However, there was no difference ($p = 0.134$, Table 3) between the estimated maximum methane potential (A) of the biomass from both sites (399.2 ± 32.2 N. L CH_4 /kg VS_{added}). In general, the estimated lag phase of the anaerobic digestion from the Ozama river biomass was below 1 day (Table 3). The doubling time (T_d) was two times higher for the anaerobic digestion of water hyacinth from El Naranjo than that from La Ciénaga.

During the first 10 days of digestion, the CH_4 in Group 2 ($68.2 \pm 4.1\%$ CH_4), which was set up using adapted inoculum,

was higher ($p = 0.0001$) than in Group 1 ($40.0 \pm 14.9\%$ CH_4). After 10 days of digestion, the % CH_4 was higher ($p = 0.0001$, Fig. 2b) for the water hyacinth from la Ciénaga ($67.0 \pm 2.5\%$ CH_4) than for that from El Naranjo ($61.9 \pm 4.7\%$ CH_4).

Energy assessment

The amount of energy (MJ/t fresh biomass) produced via anaerobic digestion of water hyacinth from the Ozama river was more than 10 times that required for harvesting (Table 4).

Discussion

Eutrophication of the Ozama river

Dissolved oxygen, phosphorus, and total nitrogen are the most effective parameters in the determination of the water quality index and eutrophication level of estuaries (Wang et al. 2019). The nitrate content at La Ciénaga was three times higher than at El Naranjo (the “Water quality” section) during harvesting and a year after. Also, water hyacinth from La Ciénaga (Table 2) contained higher phosphorus than the water hyacinth from El Naranjo, which suggests higher available phosphorus in La Ciénaga water. Thus, the water from La Ciénaga is more eutrophic than the water from El Naranjo, which might be due to the anthropogenic activities surrounding that site. Similarly, the higher heavy metal content in the water hyacinth from El Naranjo (Table 2) suggests a higher content of metals in the water that is attributed to the salinity barrier that is present near the site (Parayil et al. 2006).

Chemical composition of water hyacinth

Results from the organic elemental analysis of water hyacinth from the Ozama river are comparable with those from previous studies on tropical water bodies with similar water conditions. For instance, the organic elemental composition of water hyacinth from Indian fresh eutrophic water bodies was 40.3% carbon, 34.0% oxygen, 1.51% nitrogen, 4.6% hydrogen, and non-detected sulfur (Vaz 2016). Similarly, the monosaccharide content (the “Structural

Fig. 1 SEM-EDX images of Na, Cl, K, and Mg in ethanol extractives of water hyacinth from a La Ciénaga (brackish water) and b El Naranjo (freshwater)

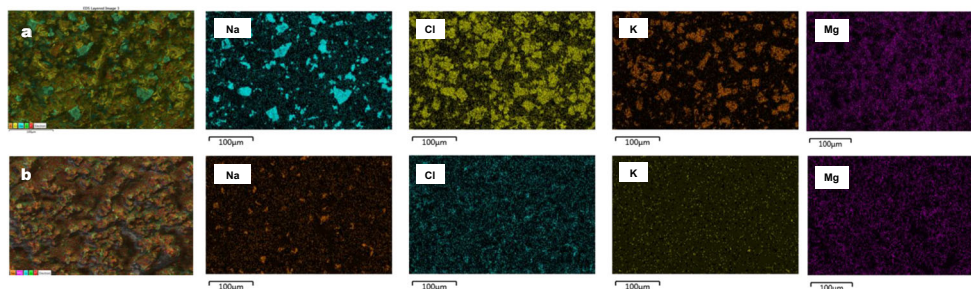


Table 2 Inorganic elements in water hyacinth from Ozama river. The values are on a dry ash basis

	Macronutrients (% w/w)					Micronutrients (% w/w)				
	Ca	K	Mg	P	S	Fe	Mn	Al	Na	Si
El Naranjo (Freshwater)	11.3 ± 0.6 ^a	17.9 ± 2.0 ^a	1.3 ± 0.1 ^a	0.9 ± 0.06 ^a	0.3 ± 0.09 ^a	1.2 ± 0.04 ^a	0.3 ± 0.01 ^a	1.73 ± 0.06 ^a	0.65 ± 0.2 ^a	1.3 ± 0.3 ^a
La Ciénaga (Brackish)	7.2 ± 0.5 ^b	21.9 ± 1.1 ^a	3.1 ± 0.2 ^b	3.1 ± 0.3 ^b	1.0 ± 0.04 ^b	0.2 ± 0.02 ^b	0.2 ± 0.01 ^b	0.18 ± 0.01 ^b	2.2 ± 0.03 ^b	0.79 ± 0.04 ^a
Heavy metals (mg/kg)										
	Cu	Ni	Mo	Co	Zn	As	Cd	Cr		
El Naranjo (Freshwater)	54.3 ± 5.2 ^a	37.8 ± 19.1 ^a	5.5 ± 3.0 ^a	7.6 ± 0.1 ^a	114.3 ± 7.5 ^a	1.9 ± 0.03 ^a	0.4 ± 0.1 ^a	26.1 ± 0.1 ^a		
La Ciénaga (Brackish)	41.0 ± 2.6 ^a	23.9 ± 12.7 ^b	2.8 ± 1.0 ^a	2.2 ± 0.04 ^b	142.5 ± 22.0 ^a	0.19 ± 0.2 ^b	<0.05 ^a	7.3 ± 0.3 ^b		

^{a,b} Different letters within each column indicate a significant difference between sites for Welch's unpaired *t* test (alpha = 0.05)

components” section) is in concordance with previous works in water hyacinth (Ahn et al. 2012; Xia et al. 2013; Cheng and Zhong 2014), where arabinose was the dominant hemicellulose monomer. However, our results differ from most herbaceous biomass feedstocks and from the water hyacinth found in other tropical regions where xylose has been reported as the main hemicellulose sugar (Nigam 2002; Lin et al. 2015).

The higher amount of lignocellulose in the biomass from El Naranjo (freshwater) than that from La Ciénaga (brackish water) is related to the salinity content in the biomass. The larger salt clusters in the extractives (the “Extractable salts” section) and the higher Na content (Table 2) in the water hyacinth from La Ciénaga suggest higher salt content in the biomass. The increase of water salinity during plant irrigation decreases the content of lignocellulosic components in *Salicornia* sp. (Cybulska et al. 2014). Also, the higher amount of nitrogen available during growth is related to lower cellulose content in plants (Etter 1972). The protein content in biomass from La Ciénaga is almost two times higher than in biomass from El Naranjo due to the higher content of nitrogen available in the more eutrophic waters.

Productivity indicators

The indicators of productivity (e.g., photosynthetic activity, density) in water hyacinth did not suggest lower performance in the growth of the species from brackish waters. The photosynthetic activity (i.e., chlorophyll levels) of water hyacinth was not compromised as a result of accumulated NaCl and KCl ions (Fig. 1, the “Extractable salts” section) after growing in water containing TDS levels up to 3000 mg/L. The amount of total chlorophyll (the “Photosynthetic pigments” section) was 15% higher in the biomass from brackish than in that from freshwaters. The value of chlorophyll a/b ratio for the water hyacinth from both sites was very low, which indicates that the specimens from El Naranjo and La Ciénaga exposed and adapted to low light environments (Givnish 1988). Thus, the concentration of TDS in the biomass did not affect the survival mechanism of the species. Similarly, biomass from the brackish waters showed greater bulk density than that from freshwaters, resulting in higher biomass yield (wt%) per growth area. In anaerobic digestion, denser feedstock has been linked to better degradation performance (Wang et al. 2016). The suggested higher performance in the productivity of water hyacinth from the brackish water at La Ciénaga could be due to the higher eutrophication compared with the freshwater.

Biomethanation of water hyacinth

Anaerobic digestion of water hyacinth from La Ciénaga was not compromised by the higher salt content in the biomass (the “Extractable salts” section) when compared with that from El Naranjo. Studies have shown that low levels of NaCl promote the hydrolysis and acidification steps of

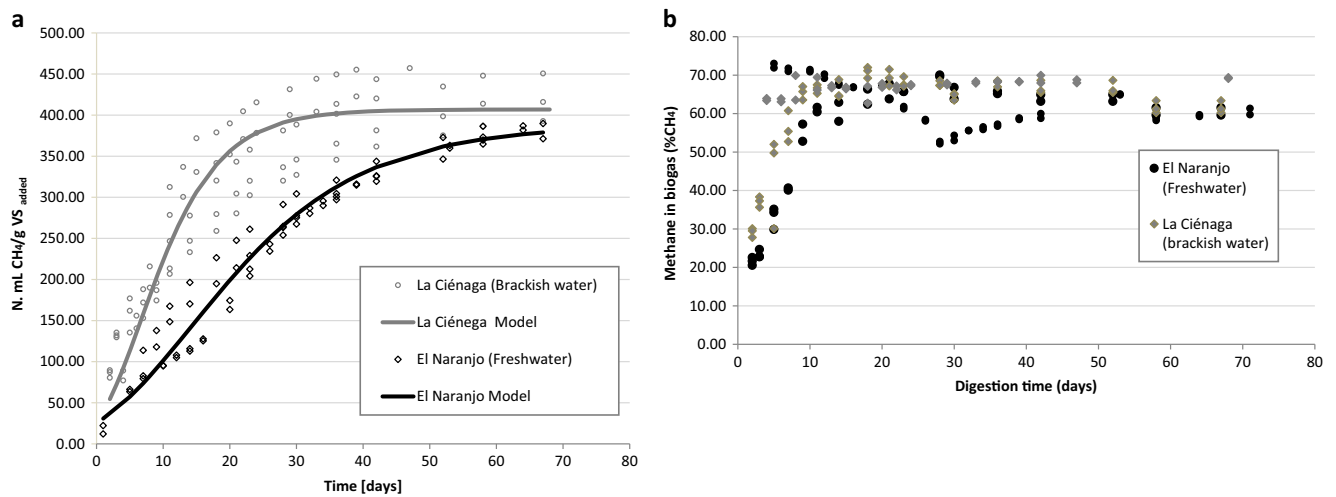


Fig. 2 Biochemical methane potential of water hyacinth from La Ciénaga (brackish waters) and El Naranjo (fresh water) within Ozama River, Dominican Republic: **a** Methane production curves and the fitted modified Gompertz models and **b** percentage of methane in the biogas

anaerobic digestion, but inhibit the methanogens (Zhao et al. 2017). The Gompertz model for the anaerobic digestion of water hyacinth from La Ciénaga estimated a biomethane potential that was not significantly different from that from El Naranjo, but the production rate was higher (the “[Anaerobic biodegradation](#)” section). Similarly, the methane yield of water hyacinth from La Ciénaga was higher and the stationary phase was reached sooner than that from El Naranjo (Fig. 2a). Thus, water hyacinth from La Ciénaga brackish water was as effective as or superior to that from El Naranjo freshwater.

During the first 10 days of digestion, the methane percentage in the biogas was higher when adapted anaerobic sludge was used as inoculum. After 10 days, the percentage of methane in the biogas from La Ciénaga biomass was higher than that from El Naranjo. The higher methane in the biogas from La Ciénaga water hyacinth can be attributed to the buffering capacity of high nitrogen levels in the biomass. The higher biomethanation rate of water hyacinth from La Ciénaga can be attributed to the low content of structural components in this biomass compared with that from El Naranjo since biopolymers are more difficult to digest than non-structural compounds.

Potential inhibitions from feedstock

The high nitrogen content of water hyacinth from the Ozama river can have beneficial or inhibitory effects on anaerobic digestion. When nitrogen is converted into ammonia, it acts as an alkaline agent that neutralizes the volatile acids produced by fermentative bacteria and hence reduces inhibition of methanogens. However, excessive ammonia can be toxic to the microbial community when enough acid is not produced to neutralize it. The recommended C/N ratio in feedstocks for steady anaerobic digestion is between 10 and 45 in the hydrolysis step and between 20 to 30 during methanogenesis (Wellinger et al. 2013). However, water hyacinth from La Ciénaga had a theoretical methanogenic hindrance (i.e., C/N 10.5) that was not observed in our study. This could be explained by the higher content of phosphorus in the water hyacinth (Table 2). Gil et al. (2019) reported that the highest proportion of methane in the biogas occurred when both nitrogen and phosphorus in the feedstock were high.

Phosphates or precipitates of cations such as magnesium and calcium also contribute to the buffer capacity of anaerobic digestion (de Jong and Van Ommen 2015). However, calcium might

Table 3 Kinetic parameters from the modified Gompertz model for the biomethanation of water hyacinth from the Ozama river. A is the maximum methane produced, K_z is the methane production rate, T_{lag} is

Parameter	La Ciénaga (brackish water)	El Naranjo (freshwater)
A [N. L CH ₄ /kg VS added]	408.5	389.8
K_z [N. L CH ₄ /kg VS added · day]	22.5	10.0
T_{lag} [day]	0.0	0.0
T_d [day]	9.1	19.5
RMSE [N. L CH ₄ /kg VS added]	4.6	4.03
R^2	0.886	0.901

the lag time, and T_d is the doubling time. RMSE is the root mean square error, and R^2 is the variation of the measurements explained by the model

Table 4 Estimated energy consumed in mechanical harvesting of water hyacinth, and energy produced by the anaerobic digestion of the weed. FC is the fuel consumption per machine operation time, HR is the

harvesting rate, and BMP is the mean of the biochemical methane potential from the Ozama river

	Parameters	Value	Energy (MJ/t biomass)
Consumption	FC [L/h]	15	$E_c = 57.9$
	HR [t biomass/h]	10	
	HHV diesel [MJ/L]	38.6	
Production	BMP mean [L CH ₄ /kg VS]	399.2	$E_p = 846.5$
	HHV methane [MJ/L]	0.0398	
	VS mean [%]	59.2	

also act as a microbiological inhibitor when present in quantities higher than 2.5 g/L (Ahn et al. 2006). The sulfur in biomass for biochemical conversion processes is unfavorable. The inorganic content of sulfur in the ash of water hyacinth from the Ozama river ranged from 0.28 to 1.00% on dry biomass basis. Concentrations of sulfur over 9 mM have an inhibition effect on the degradation of cellulose in the hydrolysis step (Khan and Trottier 1978). Also, sulfur in the form of sulfate is chosen as an electron acceptor for organic carbon oxidation in the anaerobic digestion leading to its reduction to H₂S, which is detrimental to human health and to the environment (de Jong and Van Ommen 2015).

Some of the micronutrients that are essential for the growth of anaerobes are Ni, Co, Mo, Fe, and Se for methanogens, and Zn, Cu, and Mn for hydrolytic bacteria; however, certain heavy metals have a negative effect on anaerobic digestion when their concentrations exceeded 40 mg/L Cu, 20 mg/L Cd, 150 mg/L Zn, 10 mg/L Ni, 340 mg/L Pb, and 100 mg/L Cr (Wellinger et al. 2013). Water hyacinth from El Naranjo has higher heavy metal content than that from La Ciénaga (Table 2). This might explain the higher doubling time on the anaerobic digestion of El Naranjo (the “[Anaerobic biodegradation](#)” section). The micronutrients and heavy metals in water hyacinth need to be accounted for in the design of bio-conversion processes to minimize the negative effect that some elements might have on the system performance.

Energy assessment

The estimated amount of energy required for mechanical harvesting water hyacinth was less than 7% of the produced energy due to methane. However, energy requirements for processing and pre-treating the water hyacinth prior to anaerobic digestion, and to maintain the temperature of the digester, have not been considered. Large-scale studies using unprocessed instead of ground biomass, cow manure instead of supplemented anaerobic sludge, and the lowest instead of the highest end of mesophilic temperature range are required to accurately assess the revenue from this post weed management practice. For the scale-up of the technology, several modifications of the current process will have to be done for cost-effectiveness, including inoculum selection

and acclimatization, feed to inoculum ratio, and biogas upgrading. Biological methods for biogas upgrading offer great potential, high feasibility, and low operational difficulty, which are important to reduce downstream processing costs (Angelidaki et al. 2018). Biogas upgrading for the use of methane as a transportation fuel in the harvesting equipment could be the next step for a sustainable weed management cycle in eutrophic rivers.

Conclusion

The anaerobic digestion of residual water hyacinth harvested from eutrophic rivers contributes to the sustainability of the weed management practices conducted by environmental agencies in developing countries. The modified Gompertz model estimated a biochemical methane potential of 399.2 ± 32.2 N. L CH₄/kg VS_{added} for water hyacinth from the Ozama river. The methane production rate when digesting the water hyacinth from brackish water doubled that from freshwater. The doubling time for the anaerobic digestion of freshwater was twice that from brackish waters. The lower performance of freshwater hyacinth during anaerobic digestion is related to its higher content of recalcitrant lignocellulose. The differences in the characteristics of the water hyacinth from both water types were linked to the nutrients in the water source. The brackish water was more eutrophic than that from freshwater. The water hyacinth collected from the Ozama river, to mitigate the effect of the macrophyte debris on the water bodies, could be anaerobically digested to produce more than 10 times the energy consumed in the mechanical harvesting.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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