Evaluation of Sargassum Recycling Options through Risk-Based Approaches

(DRAFT)

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With Arsenic Speciation by

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LIST OF ABBREVIATIONS AND ACRONYMS

ABS	Dermal absorption fraction
AF	Skin adherence factor
ANOVA	Analysis of variance
As	Arsenic
As(III)	Arsenic in the +3 oxidation state (arsenite)
As(V)	Arsenic in the +5 oxidation state (arsenate)
AsB	Arsenobetaine
AsC	Arsenocholine
AsH_3	Arsine
AT	Averaging time
ATSDR	Agency for Toxic Substances and Disease Registry
BW	Body weight
CARDI	Caribbean Agricultural Research and Development Institute
CFHF	Conservation, Food & Health Foundation
CRM	Certified reference material
CSF	Cancer slope factor
DERM	Miami-Dade County Department of Environmental Resource Management
DL	Detection limit
DMA	Dimethylarsinic acid (DMA(III), DMA(V))
ED	Exposure duration
EF	Exposure frequency
ET	Exposure time
F.A.C.	Florida Administrative Code
FDEP	Florida Department of Environmental Protection
FIU	Florida International University
FL	Florida
GWCTL	Groundwater Cleanup Target Level
HCSHWM	Hinkley Center for Solid and Hazardous Waste Management
HI	Hazard index
HPLC	High performance liquid chromatography
HQ	Hazard quotient
IARC	International Agency for Research on Cancer
ICP-MS	Inductively coupled plasma mass spectrometry
ILCR	Incremental lifetime cancer risk
IR	Ingestion (intake) rate
IRIS	Integrated Risk Information System
IUR	Inhalation unit risk
MMA	Monomethylarsonic acid (MMA(III), MMA(V))
MRL	Minimum risk level
ND	Non-detect
NCHS	National Center for Health Statistics
NIOSH	National Institute for Occupational Safety and Health
NRC	National Research Council
OSHA	Occupational Safety and Health Administration
PEF	Particulate emission factor
PI	Principal Investigator

LIST OF ABBREVIATIONS AND ACRONYMS (con'd)

RAGS	Risk Assessment Guidance for Superfund
RBA	Relative bioavailability
RfC	Reference concentration
RfD	Reference dose
RFP	Request for Proposal
RSMAES	Rosenstiel School of Marine, Atmospheric, and Earth Science
SA	Skin surface area
SCTL	Soil Cleanup Target Level
SOP	Standard operating procedure
SPLP	Synthetic Precipitation Leaching Procedure
SWCTL	Surface Water Cleanup Target Level
TAG	Technical Awareness Group
TMAO	Trimethylarsine oxide
UF	University of Florida
UF/IFAS	University of Florida Institute of Food and Agricultural Sciences
UM	University of Miami
US EPA	United States Environmental Protection Agency
UWI	University of the West Indies

UNITS OF MEASURE

%	Percent, parts per hundred
°C	Degrees Celsius
cm	Centimeter
g	Gram
h	Hour
kg	Kilogram
L	Liter
m	Meter
m^3	Cubic meter
mg	Milligram
mg/kg	Milligram per kilogram
min	Minute
mL	Milliliter
mm	Millimeter
ng	Nanogram
nm	Nanometer
rpm	Revolutions per minute
µg	Microgram
µg/L	Microgram per liter
$\mu g/m^3$	Microgram per cubic meter
µm	Micrometer (micron)

EXECUTIVE SUMMARY

Sargassum's high arsenic concentrations have raised concerns about health impacts when repurposed for potential beneficial uses. Potential health impacts depend upon the speciation or specific chemical form of the arsenic, with inorganic forms more toxic than organic forms. The goal of this study is to assess the risk of arsenic from Sargassum in different recycling scenarios. Specifically, the objectives of this study are to: evaluate arsenic levels (total and speciation) in products made from recycled Sargassum (compost, biochar, biogas) (**Study 1**), and to use this information to determine risks to humans from environmental exposures (**Study 2**).

Study 1. Total and species distributions of arsenic in sargassum recycling products

This study evaluated total arsenic concentrations and speciation in products derived from recycled sargassum, including compost, biochar, and biogas, to provide data for assessing arsenic risks from these materials. Additionally, the study evaluated two additional categories of sargassum, fresh and dry, as baseline references of sargassum under natural beach conditions. All sample types were analyzed for arsenic in their "raw" form (as a solid except for the substrate for biogas) and in their "environmental" form. Environmental forms, which represent possible arsenic releases from the recycled products, were assessed through the Synthetic Precipitation Leaching Procedure (SPLP) for all evaluated categories except for biogas for which the liquid digestate and gas samples were analyzed instead. Results revealed that biochar retained the highest total arsenic concentrations in the solid phase, with arsenate (As^V) as the dominant species, yet exhibited minimal arsenic leaching (<1%) by SPLP. Compost and dry sargassum showed moderate leachability and a broader distribution of arsenic species, including small fractions of lower toxicity organoarsenicals such as dimethylarsinic acid (DMA^V) and arsenobetaine. Fresh sargassum exhibited the highest leachability, with over 50% of total arsenic mobilized into solution, primarily as As^V. Arsine gas, a highly toxic form of arsenic, was the predominant form of arsenic in biogas. These findings demonstrated that arsenic mobility and toxicity vary significantly across recycled waste management scenarios.

Study 2. Evaluation of sargassum recycling options through risk-based approaches

This study quantified non-cancer and lifetime cancer risks across recreational and occupational exposure scenarios, with the integration of arsenic speciation data where possible. Oral, dermal, and inhalation pathways were evaluated. Monte Carlo simulation was applied to characterize variability and uncertainty in exposure conditions. Results indicate non-cancer risks were below risk threshold values for all scenarios, although more research is needed to evaluate the biogas recycling scenario due to the release of highly toxic arsine gas. For the cancer disease endpoint, the highest-risk group corresponded to recreational beach users, with mean total lifetime cancer risks on the order of 10^{-5}, exceeding all occupational scenarios. Across all scenarios assessing cancer risk, oral exposure was the dominant contributor, with dermal exposure contributing secondarily and inhalation representing a minor pathway. However, the dermal pathway also merits additional study due to the partitioning of arsenic in sargassum towards DMA(V), which is known to pass the skin barrier to a greater extent than inorganic forms of arsenic. Studies are needed to evaluate skin uptake of arsenic from sargassum. Overall results suggest that reducing direct contact with sargassum in recreational settings and implementing appropriate controls (use of personal protective equipment and filtration of arsine gas) during handling processed sargassum products are critical for minimizing exposure. Overall, this study provides a preliminary assessment that informs public health decision-making and sustainable management strategies for sargassum in affected regions.

Overall, results from both studies indicate that arsenic concentrations and species are similar among

different recycling scenarios (dominated by As(V)) with the exception of biogas which produces arsine gas. Arsenic cancer risks from occupational exposure during recycling were lower than risks associated with lifetime exposure to natural beach strandings of sargassum. Although occupational settings result in longer contact with sargassum, we assume that workers are fully clothed reducing dermal exposure risks primarily to hands, whereas recreational exposures impact a larger proportion of the body due to the assumption of a greater amount of exposed skin. As a result, personal protection is important to reduce cancer risks for occupational recycling. Efforts are also needed to reduce arsenic exposures during natural beach strandings by raising awareness and developing management strategies to handle excessive sargassum inundations that are impacting areas bordering the western Atlantic Ocean, especially Florida, the Gulf Coast, eastern Mexico, and the Caribbean.

CHAPTER I

INTRODUCTION & OBJECTIVES

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This chapter focuses the introduction (Section I.1) and the project objectives (Section I.2) for this study.

I.1 Introduction

Sargassum, a floating macroalgae, increasingly inundates the shores of Florida and the Caribbean, with strandings expected to grow more frequent due to climate and oceanographic factors. Accumulations occur mainly in the spring and summer months, and their large and staggered volumes are difficult for municipalities to manage. During major strandings the material is often sent to landfill, which is costly and runs counter to sustainability goals, since sargassum is an algal material with potential value that can be repurposed locally.

Sargassum can be recycled into several products. As compost, it enriches soils with nutrients and supports healthier plant growth. As biochar, produced through controlled pyrolysis, it can improve soil structure, water retention, and nutrient availability while sequestering carbon. As a feedstock for biogas, through anaerobic digestion, it offers an alternative to conventional fossil fuels. Together these routes reframe stranded sargassum as a resource consistent with a circular-economy approach.

The central obstacle to reuse is arsenic. Sargassum bioaccumulates arsenic from seawater, and the health implications of that arsenic depend on its chemical form, with inorganic species generally more toxic than most organic forms. Regulatory guideline levels are written for total arsenic and do not distinguish among species. At the outset of this project, the arsenic content and speciation of recycled sargassum products, and the human-health risks of exposure to those products relative to leaving sargassum on the beach, had not been characterized. This report addresses those gaps through two phases of work.

I.2 Objectives

This project addresses the juxtaposition of the potential value of sargassum recycling against the potential toxicity of the arsenic contained in recycled products. The objectives were to:

1. Evaluate arsenic levels, including total concentrations and speciation, in products made from recycled sargassum (compost, biochar, and biogas), with fresh and dried sargassum measured as controls (Chapter II).
2. Use the results of that arsenic analysis to assess non-cancer and cancer health risks from potential exposure to the sargassum products, including a baseline case of leaving sargassum on the beach to decompose (Chapter III).

CHAPTER II

Evaluation of Total and Species Distributions of Arsenic in Sargassum Recycling Products

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II.1 Introduction

Sargassum inundations, caused by the holopelagic brown macroalgae species *Sargassum fluitans* and *Sargassum natans* (herein referred to as "sargassum"), have escalated across the Atlantic Basin, impacting coastlines from the US eastern seaboard to West Africa (Johns et al., 2020; Wang et al., 2019) with its frequency expected to rise due to climate and oceanographic factors (Tomenchok et al., 2021). Caribbean countries and the Mexican Yucatan Peninsula have been particularly impacted due to their proximity to a massive new source of oceanic sargassum found in the tropical Atlantic called the Great Atlantic Sargassum Belt (GASB) (LaPointe et al., 2025; Wang et al., 2019). This new source and its overwhelming quantities have prompted opportunities for valorization of this material via recycling (Olguin-Maciel et al., 2022; Farghali et al. 2023).

Recycling sargassum as compost has the advantage of reducing the mass of the sargassum by up to 90% and concentrating nutrients through natural degradation under aerobic conditions (Abdool-Ghany et al. 2023b). This nutrient-rich compost, in turn, can be utilized to enhance soil fertility, promoting healthier plant growth, and contributing to overall ecosystem health especially for areas in need of soil amendments. For example, the geology of many islands of the Caribbean are devoid of rich organic soils due to typical karst limestone geology (Mylroie et al., 2022). Sargassum compost can in turn serve as an organic rich amendment to existing soils to enhance crop growth promoting sustainability through local reliance on food sources.

Recycling sargassum as biochar also has its potential advantages. Biochar, a form of charcoal produced by a controlled pyrolysis process, has been recognized for its ability to enhance soil structure, water retention, and nutrient availability (Lehmann & Joseph, 2015). The incorporation of sargassum-derived biochar into agricultural practices could not only improve crop yields but also mitigate the impacts of climate change by capturing and storing carbon in the soil (Poo et al., 2017).

In addition to compost and biochar, sargassum has emerged as a promising candidate for biogas production (Salgado-Hernandez et al., 2023), especially when combined with additional feedstocks (Castro et al., 2022). Through advanced processing techniques such as anaerobic digestion or bioconversion, sargassum can be transformed into biogas, providing an alternative to conventional fossil fuels. This not only addresses the need for cleaner energy sources but also reduces the reliance on finite fossil fuel reserves, contributing to a more sustainable energy landscape (Thompson et al., 2021).

In contrast to its recycling potential, sargassum does have a negative side. Sargassum is known to contain high levels of heavy metals (Devault et al., 2021; Devault et al., 2020; Dassié et al., 2021; Gobert et al., 2022); it is known to bioaccumulate arsenic. Brown algae, such as sargassum, are known to absorb arsenic from their environment via two mechanisms, uptake (McGillicuddy et al., 2023) and surface adsorption (Rodríguez-Martínez et al., 2020). Uptake occurs because arsenate (As^V) has the same structure as phosphate and in low-phosphate environments enters cells via phosphate nutrient transporters (McGillicuddy et al., 2023; Rodríguez-Martínez et al., 2020). Surface adsorption also contributes, with

arsenic binding to functional groups like carboxyl and hydroxyl sites on the algal surface (Dassié et al., 2021). As a result of the multiple bioaccumulation pathways, the levels of arsenic in sargassum are high.

When sargassum strands on shore it can potentially release arsenic back into the environment (Volesky & Holan, 1995; Abdool-Ghany et al. 2026a,b). Studies across the Caribbean and Gulf of Mexico report arsenic in stranded sargassum ranging from 2 to 172 mg/kg (Rodríguez et al., 2020, Cipolloni et al., 2022). Globally, arsenic concentrations in pelagic sargassum extend beyond this range, with levels in the greater Atlantic Ocean reaching 300 mg/kg due to bioaccumulation in nutrient-poor waters (Rodríguez-Martínez et al., 2020; McGillicuddy et al., 2023). These diverse concentrations underscore the need for region-specific management strategies to mitigate arsenic-related risks from sargassum strandings.

One of the main concerns associated with arsenic is its toxicity. To assess health risks, regulatory guideline levels are put in place for the land application of recycled products. In the US, one common recycled product that is land applied is biosolids (produced from the digestion of organic sludge from wastewater treatment plants). The regulatory guideline level for arsenic in biosolids in land-applied materials is 41 mg/kg with a ceiling of 75 mg/kg (US EPA 1993). In Florida, guideline levels for arsenic are lower through defined Soil Cleanup Target Levels (SCTLs) which are used to assess safety for the land application of recycled materials. The Florida arsenic SCTL for residential applications is 2.1 mg/kg and for industrial applications is 12 mg/kg (FDEP 2005). Of note is that these guideline levels specify total arsenic concentrations. However, it is well known that the toxicity of arsenic varies with speciation.

Speciation is dictated by the oxidation states of arsenic, usually as either +3 (III) or +5 (V), and also found as -3 under reducing conditions. Arsenic can exist in inorganic forms (bound to oxygen and hydrogen only), methylated forms (containing CH_3 methyl groups), or in complex organic compounds. In its methylated form, it can include one methyl group (monomethyl or MMAs), two methyl groups (dimethyl or DMAs), or three methyl groups (trimethyl or TMAs). Arsenic can also volatilize as a gas (e.g., arsine gas, AsH_3), through the action of either microorganisms or heat. In general, arsenic toxicity depends on both its oxidation state and degree of methylation. The highly reduced gaseous arsine form (arsenic in the 3 oxidation state) is highly toxic. In its positive trivalent form (As in the +3 oxidation state, As^{III}) it is also considered highly toxic but less toxic than arsine but more toxic and mobile than its oxidized pentavalent (+5) form, As^{V} (Khan et al., 2006; Stýblo et al., 2022). In contrast, arsenobetaine (AsB) and arsenocholine (AsC), which commonly occur in marine organisms within complex organic compounds, are regarded as non-toxic end products of arsenic biotransformation (Di et al., 2019). As shown in the right panel of Figure II.1, toxicity generally decreases in the order arsine (AsH_3) > monomethylarsenite (MMA^{III}) > dimethylarsenite (DMA^{III}) > inorganic arsenite (As^{III}) > arsenate (As^{V}) > methylated pentavalent species (MMA^{V}, DMA^{V}) > $TMA^{V}O$ > organically bound forms found in biota, AsB and AsC (U.S. EPA, 2014). Biotransformation pathways, including methylation, demethylation, oxidation, and reduction, govern the interconversion among these species in environmental matrices. For example, DMA^{V} can undergo microbial demethylation to MMA^{V}, which can then further degrade to inorganic As^{V}, or conversely, As^{V} can be methylated to MMA^{V} and DMA^{V}. These transformations are influenced by redox conditions, microbial presence, and soil properties, all of which affect arsenic mobility and toxicity. Despite extensive work on arsenic speciation in soils and aquatic systems, no prior studies have evaluated arsenic species in sargassum compost or other recycled byproducts. Three recent studies have examined As^{III} and As^{V} (Alleyne et al., 2023) and additional species (Abdool-Ghany et al., 2026b, Devault et al. 2022) in beached sargassum, but not in recycled derivatives such as compost, biochar, or biogas.

This study aimed to address the information gap in understanding arsenic species in recycled sargassum products. The objective of the current study was to measure total arsenic concentrations and speciation in

compost, biochar, and biogas made from sargassum in efforts to better understand the arsenic risks from products made from sargassum. To provide a basis of comparison, the arsenic concentrations in these recycled options were compared against the natural environmental conditions of sargassum (as freshly stranded or dry). By analyzing both the total quantity and arsenic species, the research provides preliminary information needed to establish risks of each recycling method, in comparison to risks associated with natural environmental conditions.

II.2 Methods

A total of five sargassum categories were evaluated. These included the two natural conditions (fresh and dry sargassum) and three recycling options (compost, biochar, and biogas). For each category we defined the samples as raw or environmental (Figure II.1).

In this study, "raw form" refers to unprocessed, solid forms of the recycled material, or the feedstock for the biogas system. These include fresh and dry sargassum, composted sargassum, biochar derived from sargassum, and the biogas substrate (input feedstock). The “raw” form reflects the total arsenic content present in each material matrix, without extraction, leaching, or simulation of environmental conditions.

The “environmental” forms refer to samples processed from the raw form, which represents the portion of arsenic that is released to the environment, and thus more relevant to human or ecological exposure. This includes leachates from fresh sargassum, dry sargassum, compost and biochar, plus unfiltered and filtered biogas and biogas digestate (anaerobic digestion byproduct).

Four of the five categories were evaluated using the same splits of freshly stranded sargassum (fresh and dry sargassum, compost and biochar). Upon preparation of each of these four sargassum categories, the solid samples were then subjected to SPLP analysis. All solid samples (raw form) and SPLP leachates (environmental form) from each sargassum category were analyzed for total arsenic and arsenic species. Due to logistical reasons, the fifth category (biogas) was collected as part of a separate sargassum harvesting operation. The raw form (substrate of the biogas system) and the environmental form (unfiltered biogas, filtered biogas, and digestate) of the biogas system were also analyzed for total arsenic and arsenic species. Sample collection and processing dates for each sample are listed in Table S-1 within the supplemental material.

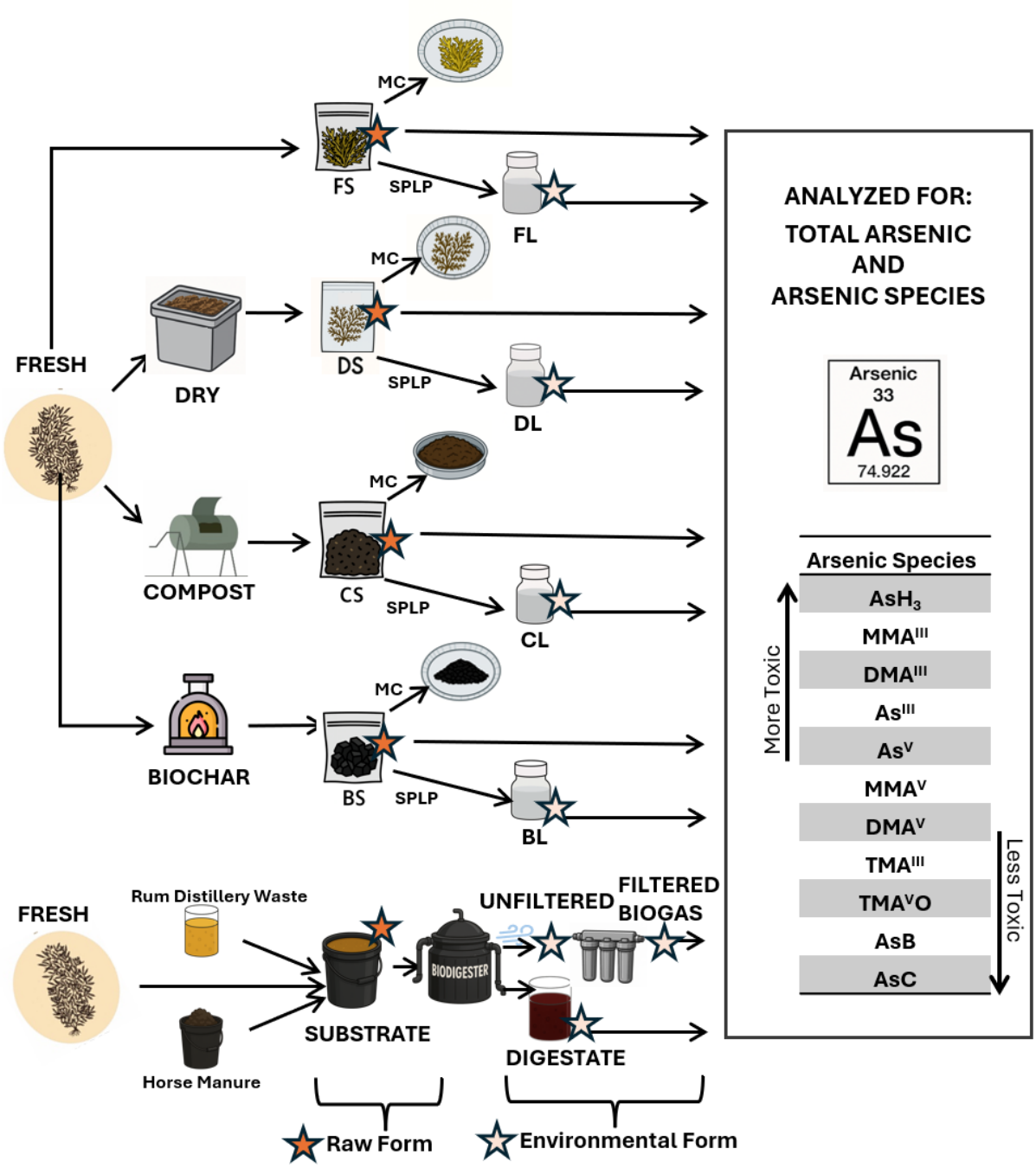


Figure II.1. Schematic of sample processing, splitting and analyses. Red stars emphasize sampling for the raw form and pink stars emphasize sampling for the environmental forms. All samples were analyzed for total arsenic and arsenic species.

II.2.1 Sargassum Beach Sample Collection and Splitting

Sargassum for the first four categories of analyses was collected at a local beach along the southeastern coast of Florida, Crandon Park Reserve, (GPS coordinates: 25.7083° N, 80.1583° W) using three large coolers lined with plastic. The sargassum was gathered along the shoreline and rinsed in knee deep water to remove sand before placement into the coolers. Upon returning to the laboratory, the contents of each cooler were homogenized and analyzed by X-ray fluorescence (XRF) to confirm the presence of arsenic (Abdool-Ghany et al. 2023b; Block et al., 2007). Of the 48 XRF measurements, 5 were positive for arsenic confirming the presence of arsenic. Additional details of the XRF measurements are provided in Table S-2 in the supplemental materials. Upon completion of the XRF measurements, the harvested sargassum was divided into four portions (fresh sargassum, dry sargassum, compost, and biochar). Once each of the four portions were prepared, they were split three ways, one for moisture content (MC) analysis by gravimetric methods (100 °C for 24 hours), one for arsenic analysis, and another for SPLP processing (Figure II.1). The aliquots for arsenic measurements were placed into pre-labeled zip top bags and stored at -20 °C. The aliquots for SPLP and moisture content were processed immediately.

The collection of sargassum from the shoreline was conducted on four different occasions, on March 13th 2024, July 2nd 2024, July 18th 2024 and July 30th 2024. The sample from the first date was used only for the preparation of compost. The samples from the following three dates were split to assess each of the four categories (fresh, dry, compost, biochar). Therefore, measurements were replicated three times for three categories of samples (fresh, dry, and biochar) and four times for compost.

For the biogas samples, sargassum used for the biodigester system was collected at approximately 7:00 am on May 12, 2025, from the northern coast of Barbados at Barclays Park Beach (GPS coordinates: 13.23645° N, 59.54297° W). Horse manure was collected from a private horse farm located in Belleplaine, St. Andrew, Barbados, and rum distillery wastewater was obtained locally within Barbados. The sargassum was then combined with horse manure, rum distillery wastewater, and rain/stagnant water and placed into an anaerobic bio-digestion system.

This combined feedstock solution is termed the “substrate” and was prepared using a volumetric ratio of 5% horse manure, 5% sargassum, 10% rum distillery wastewater, and 80% rain/stagnant water. The feedstock was placed into a 19 L bucket and mixed together for approximately 5 minutes using a handheld blender to produce the substrate for the biodigester. Samples from the anaerobic digester system were collected on a single occasion (May 15, 2025) in triplicate. Samples collected included substrate, digestate, and both unfiltered and filtered biogas.

II.2.2 Fresh Sargassum Preparation

Fresh sargassum (50 kg) used to assess the first four categories was re-homogenized and split four ways to assess fresh, dry, compost, and biochar. The split for the fresh sargassum analysis was cut using alcohol wiped scissors and then further split three ways as described above for moisture content, arsenic and arsenic speciation analysis, and for SPLP analysis followed by arsenic and arsenic speciation.

II.2.3 Dry Sargassum Preparation

Dry sargassum was prepared under controlled conditions using a mesocosm operated outdoors under natural light and rainfall for a period of two weeks. The mesocosm was located on the roof of a five-story building to eliminate impacts from street level contaminants. During the two weeks, the total rainfall was recorded using a standard rain gauge located immediately adjacent to the mesocosm. The rainfall during each of the three 2-week periods ranged from 1.25 to 4.88 cm (Table S-3). The mesocosm setup consisted

of placing 1 kg of sargassum on top of a 3 cm deep sand layer (harvested the same day as the sargassum from the supratidal zone of the beach). Underlying the sand layer was a reservoir which would allow for excess rainwater to infiltrate through the bottom of the sand layer and into the reservoir. Upon harvesting at the end of two weeks (0.5 kg after drying) the sample was then split the three ways.

II.2.4 Compost Preparation

Sargassum compost was processed using a small-scale tumbler system, adapted from methods outlined in Abdool-Ghany et al. (2023b). The tumbler (EJWOX® Dual Tumbler Composter) was constructed with plastic components to minimize metal contamination. The compost was turned biweekly to ensure aerobic conditions and facilitate decomposition). Samples were collected after 8 weeks, sealed in zip-top bags, and transported in a cooler to the laboratory for splitting.

II.2.5 Biochar Preparation

During each of the three sampling days, approximately 20 kg of sargassum was sent to a commercial biochar facility (Biochar Now) via overnight mail for processing. Biochar was produced by placing sargassum samples into a vented metal container, which was then positioned within a kiln. The kiln operated under a vacuum for up to 10 hours at 677 °C, allowing the sargassum to undergo co-pyrolysis.

II.2.6 Synthetic Precipitation Leaching Procedure (SPLP)

For each of the four categories of sargassum, 100 g of sample were processed for SPLP using standard protocols (FDEP, 2009). For the blank, 100 mL of Milli-Q water (17 MΩ) was used instead. In brief, samples were sifted through a 9.5 mm mesh size (No. 4 standard sieve size, 0.375 inches) sieve to remove large debris. The SPLP solution (2 L) was prepared by adding a 60:40 mixture of concentrated sulfuric and nitric acids to Milli-Q water until a pH of 4.2 was reached (20 µl of total concentrated acid). The sifted samples (100 g) were then added to the 2 L SPLP solution. Bottles were placed into a tumbler (Millipore Rotary Agitator) and left to rotate for 18 hours. After tumbling, the SPLP liquid leachate was filtered (0.7 µm glass fiber filter) and placed into pre-labeled sample bottles, while a separate aliquot was used to measure pH. (See Table S-4 in the supplement for the final pH values of the SPLP solutions).

II.2.7 Biogas Sample Collection

Gas samples were collected from a prototype 2500 L biodigester designed to generate biogas for small-scale cooking applications in a school kitchen located at 13.2472° N, 59.5630° W. The biodigester incorporated an internal gas-liquid separation unit. Samples were collected onto commercially available solid sorbent tubes packed with activated coconut shell charcoal (SKC Anasorb CSC) in a dual-bed configuration (100 mg front section / 50 mg back section), in accordance with NIOSH Method 6001 for arsenic monitoring (NIOSH, 1994). Gas samples were drawn by vacuum pump (SKC Pocket Pump) at a flow rate of 0.2 L/min. Pump flow-rate calibration was conducted prior to each sampling event (SKC Check-Mate Flowmeter, 375 Series). Sampling durations ranged from 25 to 30 minutes, yielding approximately 5 liters of biogas capture per sample. Following collection, each sorbent tube was immediately sealed with polyethylene caps and stored under ambient conditions for transport to the laboratory.

Two sets of three gas samples were collected. One set of three were drawn directly from the gas-liquid separation unit (called unfiltered biogas). A second set of three samples (called filtered biogas) was collected after integrating an external triple-filtration assembly into the biodigester exhaust line. This triple filtration system consisted of a charcoal filter, a bleach (sodium hypochlorite) filter, and a sodium bentonite/sodium bicarbonate filter (Arm and Hammer cat litter) designed to reduce arsenic and other airborne contaminants. In addition to the six biogas samples (three unfiltered and three filtered), field

blanks were collected in each sampling batch to assess background contamination during field handling, transport, and storage.

II.2.8 Arsenic Measurements on Solid, Liquid and Gaseous Samples

For all samples, total arsenic was analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Perkin Elmer NexION 2000) according to standard methods (Method 6020B, US EPA 1994a) and adhering to laboratory standard operating procedures (SOPs) modified after established protocols. The analysis included yttrium as an internal standard and certified reference materials (CRMs, Spex CertiPrep CLMS-2N for liquids and GBW10043 for solids), which were treated as samples and included in each analytical batch. Prior to analysis, samples underwent digestion following standard methods for processing liquids (Method 3010A, US EPA ,1992) and solids (Method 3050B, US EPA, 1996). Liquid samples (SPLP leachate and liquid biogas substrate and biogas digestate) were acidified with nitric acid (HNO_3) to a concentration of 2% HNO_3 (v/v) before analysis. For solid samples (fresh sargassum, dry sargassum, compost sargassum, biochar sargassum, and the unfiltered and filtered gas samples captured on charcoal), 0.5 g of ground material was weighed into digestion tubes, and 5 mL of concentrated HNO_3 was added. The tubes were heated on a hot block (Model 200, Environmental Express) for 1 h at 95 ± 5 °C, cooled to room temperature, and 1 mL of 30% H_2O_2 was then added slowly. Samples were reheated for 20 min at 95 ± 5 °C, left overnight for particulates to settle, and an aliquot of digestate was pipetted and diluted for analysis.

Arsenic species were measured by High Performance Liquid Chromatography (HPLC, Perkin Elmer Series 200) coupled with ICP-MS. The HPLC was fitted with a Waters Spherisorb C8 column (150 x 4.6 mm in dimension and 5 µm particle size) with the mobile phase consisting of 0.1% formic acid and acetonitrile in gradient mode at a flow rate of 1 mL/min. Liquid samples were preserved by the addition of 3 mL of pretested 6 M HCl per liter of sample, while solid samples (0.02 g of fresh sargassum, dry sargassum, sargassum compost, or sargassum biochar) were extracted using an ethanol-water (DI) solution (1:3 ratio) using a probe sonication method. The sonication method utilized a sonic dismembrator (Fisher Scientific Model 100) with triple pulses each for four seconds, while the centrifuge tube was dipped in an ice bath to prevent overheating. Following sonication, samples were centrifuged at 4000 RPM for 10 minutes (Thermo Scientific Sorvall ST 40 centrifuge). This sonication and centrifugation process was repeated two more times for each sample. The extracted samples were transferred into 10 mL centrifuge tubes after each round of sonication and centrifugation, and ethanol-water was added back into the 5 mL tubes containing the solids. All samples were filtered through a 0.45 µm pore size sterile nylon syringe filter (Whatman, USA) followed by the collection of the filtered extract into pre-labeled 1 mL vials for HPLC-ICP-MS analysis. Arsenic species detected using this method included As^{V}, MMA^{V}, DMA^{V}, As^{III}, MMA^{III}, DMA^{III}, $TMA^{V}O$, AsB, and AsC.

Arsenic species in the gaseous phase after collection on the carbon filters were measured using the following laboratory procedures modified after NIOSH Method 6001 and the literature (Thomas & Rhue, 1997; Khoury et al., 2008). An aliquot (~0.02 g) of the activated charcoal collecting the volatile inorganic and organic arsines was extracted by 2 mL of 0.1 M HNO_3/10% H_2O_2 to release and oxidize the arsines to their pentavalent oxyarsenicals, i.e., AsH_3 to As^{V}, CH_3AsH_2 to MMA^{V}, $(CH_3)_2AsH$ to DMA^{V}, and $(CH_3)_3As$ to $TMA^{V}O$, respectively, into the solution for HPLC-ICP-MS separation and detection as described above.

II.2.9 QA/QC for arsenic analysis

The recoveries from the CRM for liquids (Spex CertiPrep CLMS-2N) and for solids (GBW10043) were 90-108% and 83-103%, respectively, both within the acceptable ranges (85-115% and 70-130%,

respectively) specified in the laboratory SOPs. Since CRMs for speciation analysis of the As species involved in this study were not available, matrix spikes were used as QC samples, where As^{V}, MMA^{V}, DMA^{V}, As^{III}, $TMA^{V}O$, AsB, and AsC were spiked into the liquid or solid samples prior to extraction. For arsenic speciation in charcoal filters that were used to collect gaseous arsines, As^{V}, MMA^{V}, DMA^{V}, As^{III}, and $TMA^{V}O$ were spiked into the extracted samples, since the arsines were oxidized into respective pentavalent oxyarsenicals during extraction. The recoveries for matrix spikes were all within the acceptable range (70-130% for all As species). The relative percentage differences between CRM or matrix spike duplicates during an analytical batch were ≤ 24% for all As species, meeting the analytical requirement.

Concentrations were reported in µg/m³, µg/L, or mg/kg, for gaseous, liquid, and solid samples, respectively. Detection limits for total arsenic and arsenic species can be found in Table II.1. All blank samples (SPLP blank and biogas filter blanks) were below detection limits.

Table II.1. Detection limits for total arsenic and arsenic species

Sample Type	Detection Limit	
	Total Arsenic	Arsenic Species
Water Samples (µg/L)	0.05	0.2
Solid Samples (mg/kg dry weight)	0.02	0.1
Gaseous Samples (µg/m^3)	0.375	1.5

II.2.10 Statistical and Data Analysis

Assessment of the total arsenic data using the Shapiro Wilks test indicated that the data was not normal nor lognormally distributed. Therefore, differences in median total arsenic concentrations were compared across groups for both raw form and environmental form samples using the Kruskal–Wallis test. When significant or near-significant differences were observed, pairwise comparisons were performed using Dunn's test to identify specific group differences. Statistically significant differences were defined as $p < 0.05$, and marginal differences were defined as p-values between 0.05 and 0.10.

Arsenic species datasets were evaluated statistically for two characteristics, to determine the dominant species and to determine whether proportions of different species differed among sample types. For dominant species analyses, a Chi-square test of independence was used to determine whether the dominant species (the one with the highest proportion in each sample) differed across sample types. The Chi-square test is non-parametric and did not require log transformation or normality. To evaluate proportions of species among sample types, a univariate approach was used. Because species proportions are bounded between 0 and 1, species data were transformed using a logit transformation as follows in equation 1, converting the proportions into an unbounded scale suitable for ANOVA and Tukey HSD post-hoc tests.

$$\text{logit}(p) = \ln\left[\frac{p}{(1-p)}\right] \quad \text{equation 1}$$

where p is the proportion of the arsenic species of interest (expressed as a fraction between 0 and 1). For species with zero proportions, a small constant (0.001) was added to avoid undefined logarithms. After transformation, the ANOVA test was applied to evaluate differences in mean transformed proportions of each arsenic species across sample types. When the ANOVA test indicated significance ($\alpha = 0.05$), Tukey's Honestly Significant Difference (HSD) post-hoc tests were applied to identify pairwise differences between sample types. R software was used to conduct all statistical analysis for total arsenic and arsenic species.

We assessed the transfer of arsenic from raw form to environmental form for the fresh, dry, compost, and biochar sargassum using mass balance calculations. These calculations considered the mass of dry solids in the raw form (M_r) and the concentration of arsenic in the dry solids of the raw form (C_r). The product of M_r and Cr corresponds to the total arsenic originally within the raw form of the sample. This arsenic mass was then compared to the mass released into the environmental form. Which is the product of the concentration of arsenic in the environmental form (C_e) in the volume of liquid leached (L_e). Therefore, the percentage leached, *% Leached*, was defined as follows:

$$\%\ Leached = \frac{C_e \times L_e}{C_r \times M_r} \times 100\% \quad \text{equation 2}$$

II.3 Results

The results are presented first for raw samples and second for environmental forms of the samples. As a reminder, raw samples include the solid sargassum-derived materials (fresh sargassum, dry sargassum, compost, and biochar in units of mg/kg) and the input liquid associated with the biogas (substrate in units of µg/L). The environmental forms included the liquid SPLP leachates from fresh sargassum, dry sargassum, compost and biochar plus the biogas digestate (in units of µg/L) and the unfiltered and filtered gas (in units of µg/m³). The results for the unfiltered and filtered gas are presented separately because arsenic in these samples occurs in the gaseous phase and the speciation of the gas phase differed from that in the solid and liquid matrices. Accordingly, the results that follow first describe total arsenic concentrations and speciation in raw and environmental forms, followed by results for gaseous biogas samples.

II.3.1 Total Arsenic Evaluation in Raw and Environmental Samples

Among the raw samples (Figure II.2A), dry sargassum had the lowest median arsenic level at 13.2 mg/kg (10.9 to 75.4 mg/kg), followed by fresh sargassum at 19.8 mg/kg (15.2 to 19.9 mg/kg), and then compost at 21.7 mg/kg (12.1 to 45.5 mg/kg), with biochar's median of 104.8 mg/kg (17.2 to 141.8 mg/kg) at approximately five times higher than that of fresh sargassum. Substrate, the only liquid sample representing a raw form within the biogas system, exhibited comparatively low arsenic concentrations (2.6–3.6 µg/L).

The Kruskal–Wallis test indicated no significant differences ($p = 0.06$) in arsenic concentrations among the solid raw materials (fresh sargassum, dry sargassum, compost, and biochar). Dunn's pairwise comparisons found no significant differences among the four solid materials (all $p \geq 0.20$) (Table S-5A). Among the environmental samples (Figure II.2B), SPLP extracts derived from biochar had the lowest median arsenic level at 5.4 µg/L (5.2 to 8.6 µg/L), followed by compost at 38.0 µg/L (30.8 to 46.0 µg/L), dry sargassum at 38.7 µg/L (32.3 to 278.7 µg/L), and digestate at 97.3 µg/L (96.5 to 103.0 µg/L), with fresh sargassum's median of 120.7 µg/L (89.3 to 136.8 µg/L) as the highest.

The Kruskal–Wallis test indicated significant differences across environmental samples ($p = 0.02$). Dunn's pairwise comparisons showed that biochar released significantly less arsenic than fresh sargassum ($p = 0.002$) and digestate ($p = 0.02$), and marginally less than dry sargassum ($p = 0.07$); compost also released significantly less than fresh sargassum ($p = 0.04$). No other comparisons were significant (Table S-5B). Among the gas samples (Figure II.2B), median levels of filtered gas samples (0.38 µg/m³, range 0.37 to 1.85 µg/m³) were lower than median levels of unfiltered biogas (7.64 µg/m³, range from 6.38 to 8.57 µg/m³). The differences between these medians were not significant ($p = 0.10$).

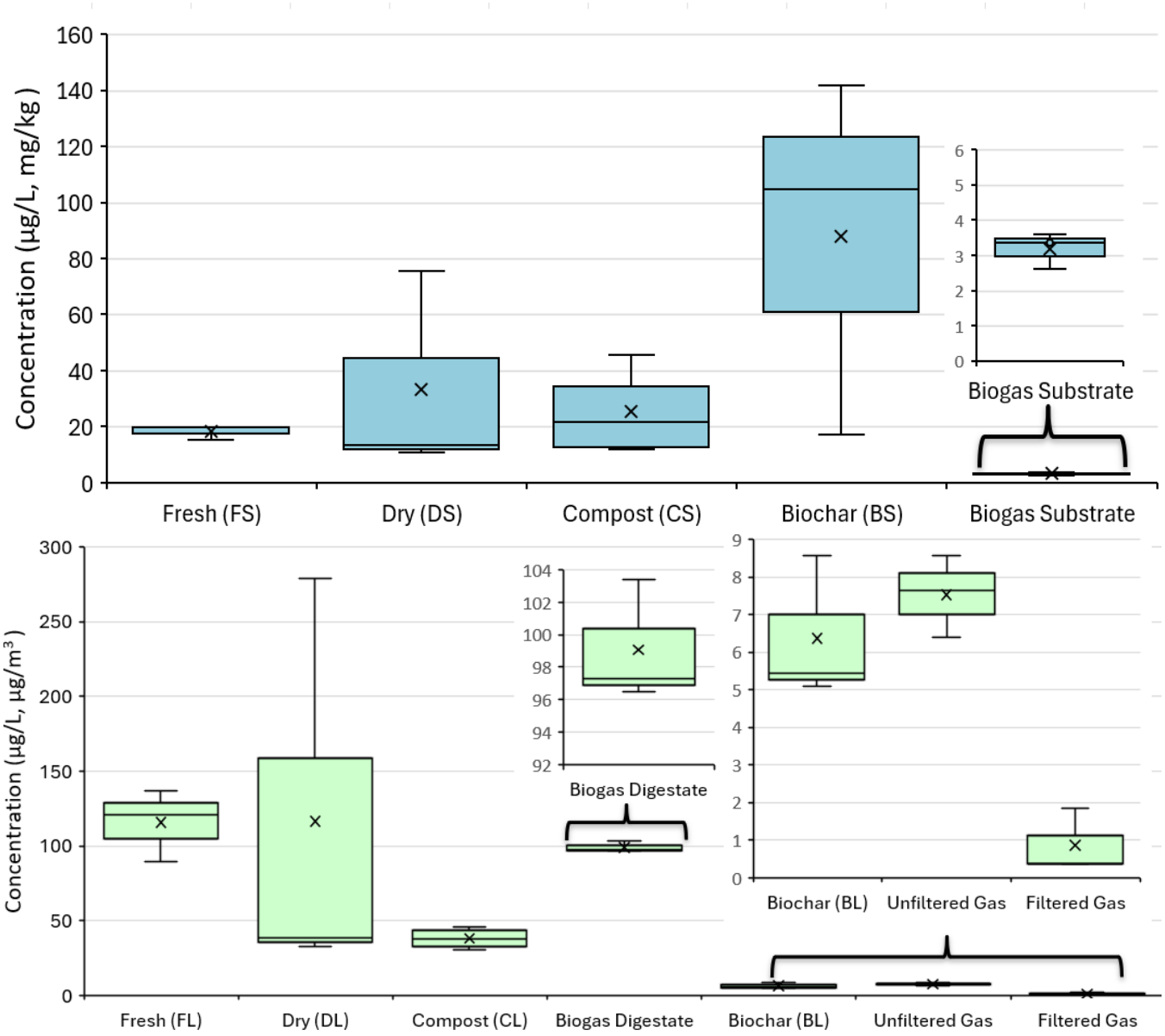


Figure II.2. Box-and-whisker plots illustrating total arsenic (As) concentrations across five sargassum-derived materials: fresh, dry, compost, biochar, and biogas (including substrate, digestate, unfiltered gas, and filtered gas). The upper and lower box edges represent the 25% and 75% quartiles. The line in the box represents the median. The× symbol represents the average. Panel A displays arsenic concentrations in the raw form of each material, representing the state in which sargassum is initially integrated or recycled. Panel B presents arsenic concentrations in the environmental form, reflecting the exposure pathways relevant to human health. Concentrations are reported in appropriate units: mg/kg for solids (fresh, dry, compost, biochar, and biogas substrate), µg/L for liquids (leachates from fresh, dry, compost, and biochar samples, plus biogas digestate), and µg/m³ for gases (unfiltered and filtered gas from biogas system).

II.3.2 Arsenic Species in Raw and Environmental Forms

Analysis of arsenic speciation in raw samples (Figure II.3), revealed distinct patterns in arsenic species (As^{V}, MMA^{V}, DMA^{V}, $TMA^{V}O$, As^{III}, MMA^{III}, DMA^{III}, AsC, and AsB), with As^{V} as the dominant species across most samples. The Chi-square test of homogeneity indicated no significant differences in species distributions among the raw sample types ($p = 0.99$). Across raw materials, As^{V} accounted for most of the arsenic.

Despite the overall dominance of As^{V}, species proportions differed significantly among sample types. Tukey HSD tests indicated that fresh sargassum had significantly higher As^{V} proportions than dry sargassum ($p = 0.023$) and substrate ($p = 0.001$), but did not differ significantly from biochar ($p = 0.64$) or compost ($p = 0.99$). Fresh sargassum, biochar, and compost therefore exhibited relatively high As^{V} proportions (77.0–81.9%), whereas dry sargassum (61.9%) and substrate (41.4%) were lower (Figure II.4).

MMA^{V} proportions were significantly higher in substrate (approximately 34–42%) than in fresh sargassum ($p < 0.009$) and all other sample types (all $p \leq 0.009$), while other pairwise comparisons were not significant ($p > 0.07$). Dry sargassum exhibited higher AsC proportions (approximately 9–27%) than fresh sargassum (approximately 2–4%; $p = 0.035$) and compost ($p = 0.033$). No significant differences were observed among sample types for DMA^{V}, As^{III}, or AsB ($p = 0.30$, 0.10, and 0.27, respectively), and MMA^{III}, DMA^{III}, and $TMA^{V}O$ were detected too infrequently for statistical analysis.

Overall, As^{V} remained the dominant species across raw samples, although its relative proportions varied among materials, with the highest values in biochar and lower proportions in dry sargassum and substrate. MMA^{V} and AsC also showed significant variability among sample types.

For environmental forms (Figure II.3B), the Chi-square test of homogeneity likewise indicated no significant differences in species distributions for all sample types ($p = 0.33$), except for biogas. As^{V} remained the dominant species across most samples, accounting for approximately 85–90% of arsenic in compost and 91.7% in fresh sargassum. Tukey HSD tests confirmed no significant pairwise differences among sample types (all $p > 0.05$), including compost–biochar ($p = 0.29$) and fresh sargassum–biochar ($p = 0.93$).

No significant differences were observed among sample types in the proportions (Figure II.S-2) for DMA^{V}, As^{III}, AsC, AsB, or $TMA^{V}O$ (all $p > 0.09$). MMA^{V} was the only species exhibiting statistically significant variation among environmental samples ($p < 0.001$) (Figure II.4). Digestate contained significantly higher MMA^{V} proportions (approximately 8–12%) than fresh sargassum ($p < 0.001$), dry sargassum ($p = 0.001$), and compost ($p = 0.005$). Biochar liquids also exhibited higher MMA^{V} proportions than fresh sargassum ($p = 0.001$), dry sargassum ($p = 0.003$), and compost ($p = 0.013$).

Overall, with the exception of biogas, As^{V} consistently dominated environmental samples, while MMA^{V} showed the greatest variability, particularly with elevated proportions in digestate.

II.3.3 Arsenic Species in Filtered and Unfiltered Biogas

Analysis of biogas samples revealed that volatile arsenic was present almost exclusively as arsine (AsH_3). In unfiltered biogas ($n = 3$), AsH_3 was the only arsenic species detected, with concentrations of 5.8–7.1 $\mu g/m^3$ (median 6.5 $\mu g/m^3$), while all other volatile arsenic species were below detection limits. Filtration removed most of the arsine (median of 0.4 $\mu g/m^3$ as the detection limit, range from the detection limit to 1.54 $\mu g/m^3$), indicating that a substantial fraction of the arsine in raw biogas was associated with the

airborne phase as either gas, suspended microparticles, or aerosols removable through the triple air filtration system.

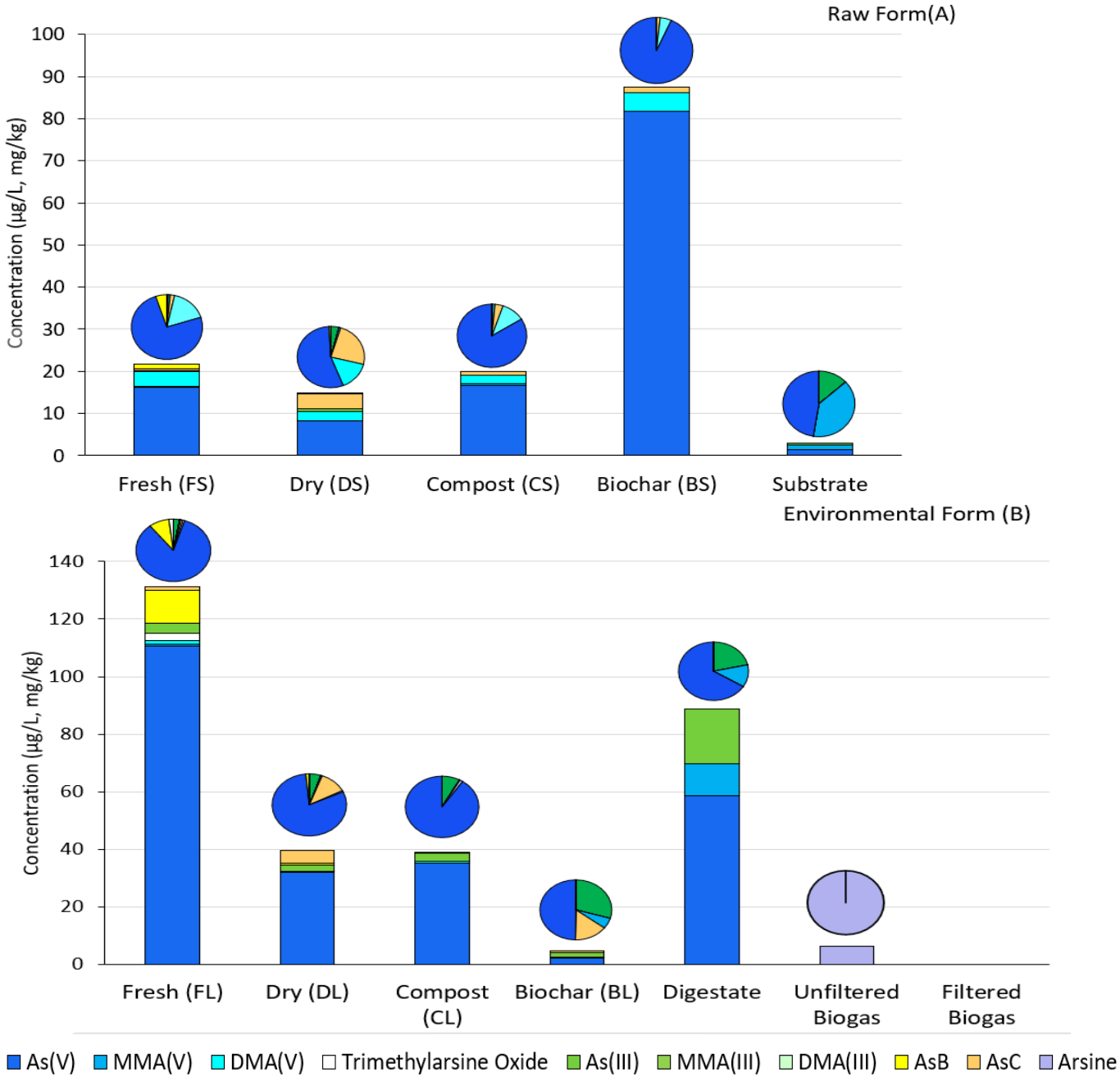


Figure II.3. Median arsenic species concentrations in raw form (Panel A) and environmental forms (Panel B). Raw samples include fresh and dry sargassum, compost, biochar, and biogas substrate. Environmental samples include SPLP extracts for fresh, dry, compost, and biochar plus for the biogas system, digestates and biogas (filtered and unfiltered). Pie charts show the relative distribution of arsenic species per sample. Concentrations are reported in appropriate units: mg/kg for solids (fresh, dry, compost, biochar and biogas substrate), µg/L for liquids (leachates from fresh, dry, compost, and biochar samples, and biogas digestate), and µg/m³ for gases (unfiltered and filtered gas from biogas system)

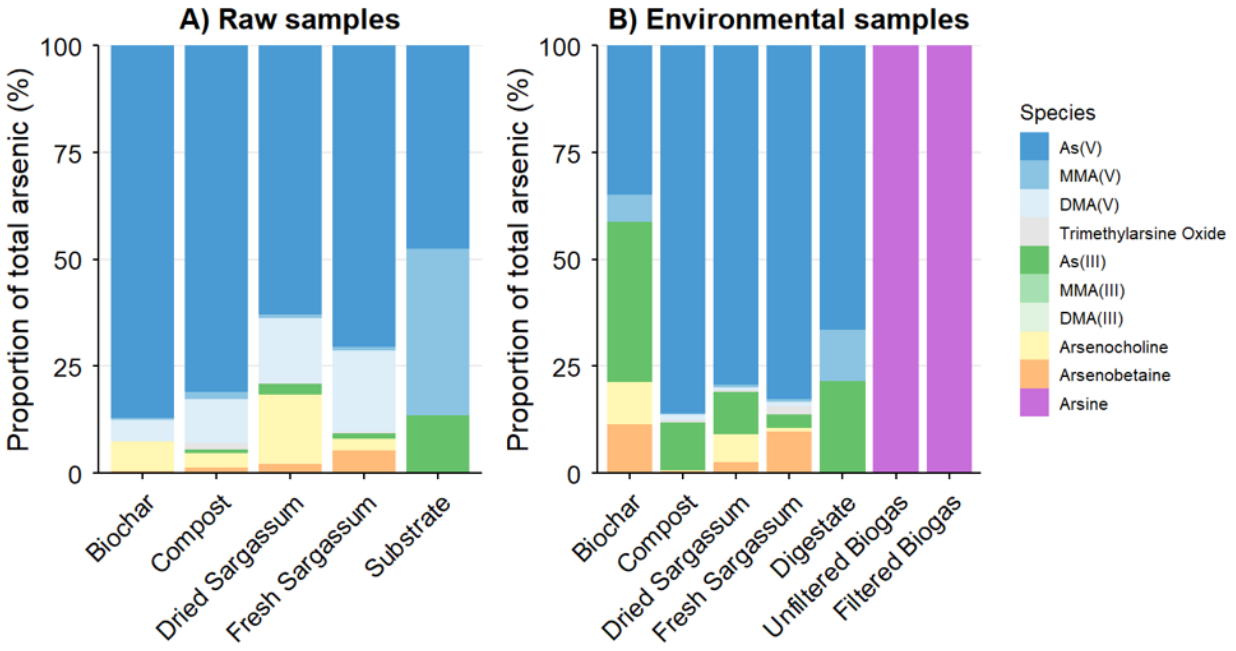


Figure II.4. Proportional distribution of arsenic species across (A) raw samples and (B) environmental samples derived from sargassum processing pathways. Arsenic speciation is presented as a percentage of total arsenic within each sample type.

II.3.4 Evaluation of Fraction of Arsenic Release Via SPLP Test

The leachability of arsenic, assessed through the SPLP test by measuring the percentage of arsenic leached from solid (raw products) into the liquid phase (environmental products), varied substantially among treatment types: fresh sargassum, dry sargassum, compost, and biochar (Figure II.5). Fresh sargassum samples exhibited the highest average arsenic leachability, at 55.4%. Replicates Fresh 1, Fresh 2, and Fresh 3 ranged between 50.9% and 59.2%, underscoring the considerable environmental mobility and leachability of arsenic in fresh biomass. The relatively low coefficient of variation (CV = 7.5%) indicates consistent leaching across replicates.

Dry sargassum treatments displayed a markedly reduced average arsenic leachability of 9.9%. Within this group, Dry 2 showed the highest mobility (15.5%), followed by Dry 1 (7.9%) and Dry 3 (6.5%). Despite the decrease in leachability compared to fresh biomass, the relatively high variability (CV = 48.3%) indicates that drying does not uniformly stabilize arsenic mobility, reflecting variability in arsenic release among dry sargassum samples.

Compost exhibited an average arsenic leachability of 7.1%, with values ranging from 3.2% (Compost 3) to 9.5% (Compost 2). This indicates moderate variability (CV = 47.2%), suggesting that composting can reduce arsenic release, although its effectiveness likely depends on compost composition and arsenic-binding properties.

Biochar treatments demonstrated arsenic stabilization via the SPLP assay, with an average leaching percentage of only 0.17%. Biochar 1 released 0.3%, while Biochar 2 and Biochar 3 each released 0.1%. Although the coefficient of variation was relatively high (CV = 69%), this reflects the extremely low absolute leaching values rather than substantial variability in arsenic release.

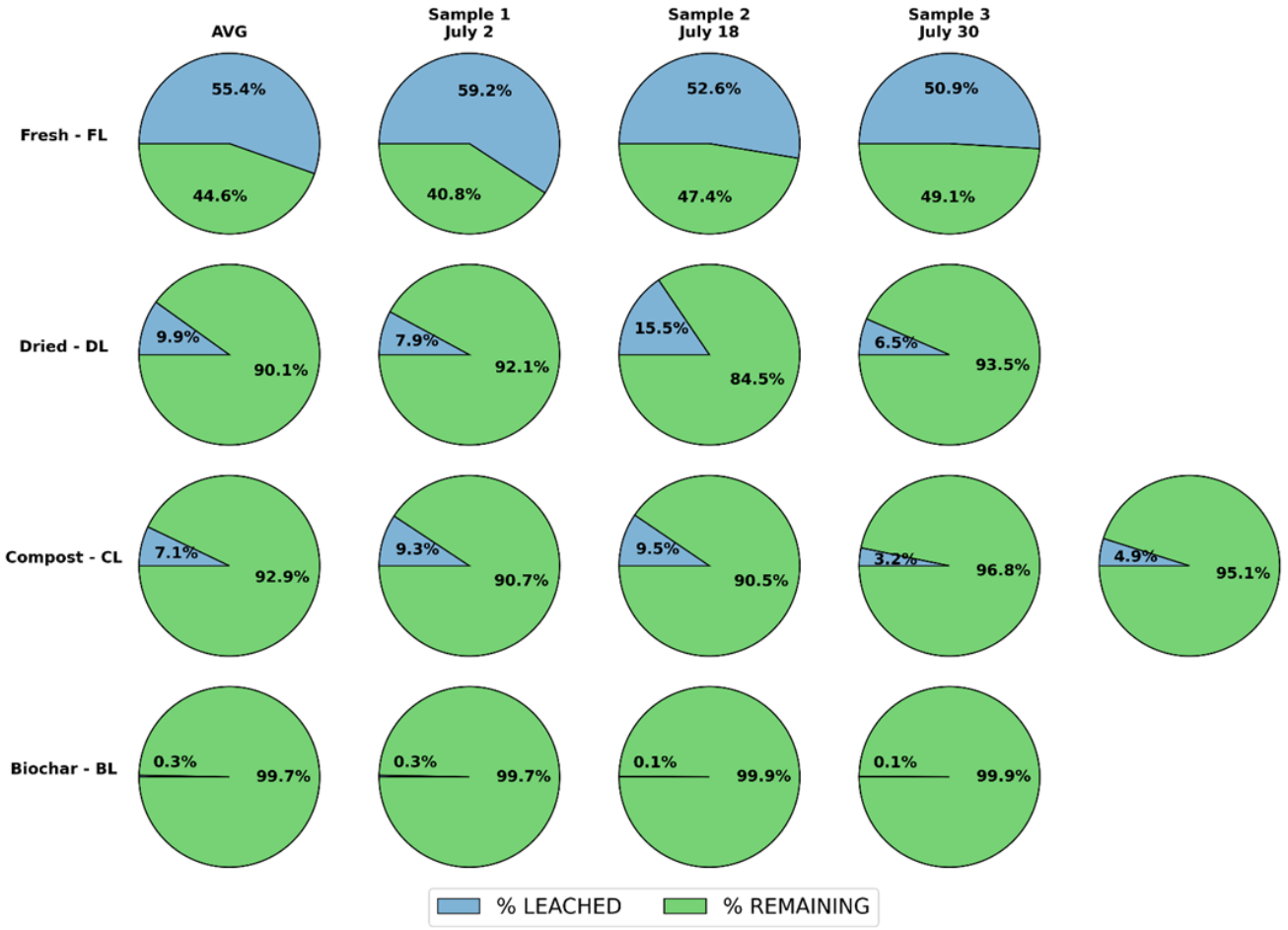


Figure II.5. Percent of total arsenic leached from solid samples of fresh sargassum, dry sargassum, compost, and biochar following the Synthetic Precipitation Leaching Procedure (SPLP). Each pie chart represents an individual sample, illustrating the proportion of arsenic leached into solution (% leached, blue) versus the proportion retained in the solid phase (% remaining, green).

II.4 Discussion

II.4.1 Arsenic Concentrations Compared to Regulatory Guidelines

All raw products exceeded both Florida's residential 2.1 mg/kg and commercial/industrial SCTL (12 mg/kg) (FDEP, 2005). Mean total arsenic was highest in biochar (88.0 mg/kg), followed by dried sargassum (33.2 mg/kg), compost (25.2 mg/kg), fresh sargassum (18.3). The concentration of arsenic in biogas substrate was low (3.2 mg/kg).

Comparing the SPLP leachates to the 10 µg/L drinking-water standard and the 5,000 µg/L RCRA toxicity-characteristic (TC) limit, only biochar leachate stayed below the drinking-water standard (mean 6.4 µg/L); compost (38.2 µg/L), digestate (99.1 µg/L), dried sargassum (116.6 µg/L), and fresh sargassum (234.7 µg/L) all exceeded it. Every leachate, however, remained far below the 5,000 µg/L TC limit, so none would qualify as hazardous waste.

II.4.2 Leachability of Arsenic from Recycled Sargassum Products

When total arsenic was evaluated in the environmental forms (SPLP leachates), clear differences emerged across treatments. Biochar had the lowest arsenic concentrations in the leachate and released less than 1% of total arsenic under simulated rainwater conditions, while fresh sargassum had the highest concentrations, with greater than 50% of total arsenic released into the aqueous phase. Compost and dry sargassum showed intermediate concentrations in the leachates. These results show that, although total arsenic levels in the raw materials were similar, the amount that becomes environmentally available differs significantly depending on the treatment.

The small proportion leached from biochar is consistent with its sorptive properties (Beesley et al., 2015; Mohan et al., 2007) driven by large surface area, microporosity, and oxygen-containing functional groups that promote arsenic complexation and immobilization (Beesley et al., 2011; Poo et al., 2018). In contrast, fresh sargassum showed the highest leachability, indicating a greater environmental risk from untreated biomass during decomposition or improper disposal, particularly under rainfall conditions, likely due to weak binding of water-soluble arsenic species such as arsenate in algal tissues. Compost and dry sargassum displayed intermediate leachability (~6% for compost), suggesting partial stabilization during processing, although mobility remained notable under precipitation events (Abdool-Ghany et al., 2023).

However, it is important to note that the SPLP uses synthetic rainwater as a relatively weak extractant, which may underestimate arsenic mobilization. Stronger extraction methods, such as acid or peroxide digestion, could result in greater arsenic release (Juhasz et al., 2009). In addition, other exposure conditions should be considered. For example, acidic conditions such as those in the stomach (pH ~2) may liberate arsenic from biochar if ingested, allowing it to become bioavailable (Smith et al., 2010). This highlights the need for future studies to evaluate arsenic stability under a wider range of environmental and biological conditions. Overall, these results highlight the high environmental mobility of sargassum in its naturally fresh and dry forms, underscoring the need for preprocessing (e.g., composting, pyrolysis to biochar) to mitigate risks, while biochar's stabilization potential positions it well for containment applications like remediation systems or concrete additives, despite elevated total As limiting direct soil use (Sirico et al., 2021; Barissov et al., 2021).

II.4.3 Arsenic Species and Toxicity

As^V dominated speciation, in both raw and environmental forms for all products evaluated except for the gaseous phase. This predominance is significant for risk assessment, as As^V is considered toxic. The dominance of As^V is consistent with its stability in oxidized settings (Cullen & Reimer, 1989).

Among the raw samples, biochar was overwhelmingly dominated by As^V, with minimal detection of organic forms, likely due to the oxidative stability imparted by pyrolysis (Soares et al., 2023). This contrasts with higher proportions of the organic species, AsB, AsC, and DMA^V within the raw natural fresh and dry sargassum forms. The presence of low fractions of AsB and AsC in natural sargassum forms aligns with the prior work of Devault et al. (2022) which showed the presence of these species in sargassum found in the field. The speciation of compost was intermediary between that observed by biochar, showing clear dominance of As^V, and showing the presence of AsC and DMA^V.

In environmental extracts, speciation was also dominated by As^V with a broader range of mobile arsenic compounds. Fresh and dry sargassum SPLP extracts contained significant As^V levels alongside organic species such as AsB, AsC, and very low but detectable TMA^VO. Similarly, biochar SPLP extracts also contained significant proportions of As^V (about half), with the balance of the extracts composed of As^{III}, AsC, and MMA^V. Among these species As^{III} is known for its mobility (Khan et al. 2006) and its significant proportions in biochar SPLP leachates indicates that the biochar matrix may not bind the As^{III} in the raw biochar sample. Similar to the pattern observed for the raw form, compost in the environmental form shows speciation intermediary between biochar and between fresh and dry sargassum. For compost, in addition to the As^V which dominates the SPLP leachates of all samples, some As^{III} is also observed but at a smaller proportion than for biochar.

II.4.4 Arsenic Species in Gaseous Form

For biogas emissions, unfiltered samples showed dominant arsine (AsH_3) under anaerobic conditions, with filtration trending toward lower levels ($p = 0.077$), aligning with effective volatile arsenic control (Salgado-Hernández et al., 2023). Microbial reduction of inorganic arsenic is the likely mechanism for the production of arsine during the anaerobic digestion of sargassum-derived materials (Zhu et al., 2017; Mestrot et al., 2009). Prior studies of anaerobic biogas digesters have shown that AsH_3 emerges as a key gaseous species from As^{III} and As^V (Mestrot et al., 2013).

Arsine's high toxicity, makes it a potent respiratory irritant capable of causing hemolysis and pulmonary edema at low concentrations (U.S. EPA, 1994; Mok et al., 2003; ATSDR, 2007), requiring treatment of the biogas. In this study, the unfiltered median arsine concentration (7.6 µg/m³) exceeded the NIOSH Recommended Exposure Limit (REL) of 2 µg/m³ (15-minute ceiling), suggesting potential risks for short-term occupational exposure (NIOSH, 2019). In contrast, the filtered median (assumed at the detection limit of 0.4 µg/m³) fell below this limit, indicating safer conditions after filtration. OSHA's Permissible Exposure Limit (PEL) of 200 µg/m³ (8-hour average) is not approached by either median (7.6 µg/m³ unfiltered, 0.4 µg/m³ filtered), suggesting compliance with this longer-term workplace standard (OSHA, 2023). The EPA's Reference Concentration (RfC) of 0.05 µg/m³ for chronic exposure is significantly exceeded by unfiltered (7.6 µg/m³) biogas. The RfC is also significantly below the detection limit and so it is unknown whether the filtered gas would comply with the RfC for chronic exposure (U.S. EPA, 1994). Results suggest that while filtration reduces arsine levels, more work is needed to quantify arsine concentrations after filtration, perhaps by increasing the air sample collection volume. The elevated levels in unfiltered biogas underscore the need for enhanced control measures in biogas production.

II.4.5 Environmental Implications

Given the seasonal influx of sargassum and the increasing frequency of large-scale strandings, the identification of safe, scalable treatment options is paramount, especially in human exposure zones where people including children can come in contact with excessive amounts of sargassum (Mc Intyre et al., 2026). The health risks associated with arsenic are influenced not only by total arsenic concentrations but also by chemical speciation, as certain arsenic metabolites have been shown to exhibit greater toxicity

than inorganic arsenic and may play a role in arsenic carcinogenesis (Stýblo et al., 2002).

While biochar showed lowest leaching levels, we need to consider that the levels of total arsenic in the raw product exceeded the Florida residential and industrial SCTLs and may be limited to recycled products that immobilize the arsenic instead of its use in agriculture or soil applications. Composting, while beneficial in terms of organic matter recycling, requires optimization to further reduce arsenic mobility. Additional measures such as co-composting with adsorptive amendments (e.g., iron oxides or activated carbon) may enhance arsenic retention and can promote volatilization or conversion of arsenic to a less toxic form, which should be explored in future studies. Fresh sargassum's higher leachability (54%) poses risks of groundwater contamination, as arsenic can cycle into aquatic systems under rainfall conditions (Oremland & Stolz, 2003). Biochar and biogas production from sargassum, may be used as recycling options but require careful management, particularly in the case of biochar due to the accumulation of arsenic in high concentrations and in the case of biogas due to the production of arsine gas.

These environmental risks extend to human health, particularly through pathways such as dietary exposure, contaminated water sources, and through inhalation in confined spaces. For instance, if sargassum-derived compost or leachate from untreated biomass enters agricultural soils, it could contribute to arsenic release and uptake in food crops, leading to chronic exposure via the food chain. Research has shown that dietary arsenic, often from contaminated water used in irrigation or from soil amendments, is a primary exposure route for many populations, with inorganic arsenic species posing carcinogenic risks even at low levels (Nachman et al., 2017a). The potential for bioaccumulation in agricultural systems is also a concern, as arsenic can enter the food chain through crops and animal feed, increasing long-term human exposure and cancer risk (Nachman et al., 2013; Nachman et al., 2017b). Additionally, while gas filtration may reduce inhalation risks associated with arsenic-containing biogas emissions, residual arsenic in digestate applied to soils could still contribute to dietary exposure through crop uptake and livestock production. These implications underscore the need for risk mitigation strategies to prevent arsenic from entering human exposure pathways and exacerbating public health burdens in coastal communities reliant on local agriculture.

Finally, the differential speciation profiles highlight the need for regulatory frameworks to consider not just total arsenic, but also the form in which it exists, given the vast differences in toxicity and mobility. Effective sargassum management requires integrative solutions that balance recycling with the potential toxicity of different arsenic compounds within recycled products.

II.4.6 Study Limitations and Future Work

This study faces several limitations that affect the interpretation of results and recommendations for reuse. The total arsenic levels in biochar and compost exceed regulatory guideline levels, such as Florida's Soil Cleanup Target Levels (SCTLs) of 2.1 mg/kg for residential and 12 mg/kg for industrial use. Although biochar demonstrates low leachability in the Synthetic Precipitation Leaching Procedure (SPLP), which uses a less potent acid to simulate rainfall, this test underestimates bioavailability through ingestion, where stronger gastric acids may enhance arsenic release (Juhasz et al., 2006). This discrepancy suggests that SPLP results may not fully reflect human exposure risks, particularly for children in residential scenarios, necessitating a reevaluation of biochar and compost for safe recycling.

Future studies should increase sample sizes to improve statistical power, incorporate acid digestion models to better assess bioavailable arsenic, and explore preprocessing techniques to mitigate regulatory exceedances (Abdool-Ghany et al., 2023a). Further investigation into arsenic speciation and leachate fate under varied environmental conditions is also recommended to enhance risk assessment accuracy.

Given the production of arsine gas from the biogas system, more work is needed to refine biogas sample collection by increasing air sample volumes so that detection limits can be further lowered.

II.5 Conclusion

Arsenic mobility and speciation vary among recycled sargassum materials. Biogas samples showed the potential release of highly toxic arsine (AsH_3) suggesting that careful emission controls are necessary to ensure biogas safety. Among the remaining recycling options evaluated including fresh and dry sargassum, the dominant form of arsenic was As^V, which is also toxic. Among the recycling options evaluated, biochar was the most effective in retaining arsenic, with minimal leaching observed, however the raw recycling product contained high levels of arsenic that exceed both residential and industrial SCTLs. Biochar may be more suited for recycled products that further immobilize arsenic. Compost showed moderate arsenic release, indicating a need for improved stabilization practices. Fresh and dry sargassum exhibited high levels of arsenic leachability and should not be used without further treatment. To further assess the impacts of arsenic from the products evaluated, risk assessments should be conducted to identify which option poses acceptable health risks. The results from this current study can serve as a starting point for risk assessment.

Overall, in conclusion the results of this study emphasize that arsenic is released from sargassum in varying amounts depending upon the form of the sargassum (fresh, dry, compost, biochar), with most of the arsenic released in primarily the known toxic As^V form. Biogas releases arsenic in the highly toxic arsine gas form. More research is needed to evaluate ways that sargassum can be transformed into a valuable resource that aligns with the principles of circular economy and environmental stewardship, while minimizing the impacts associated with the arsenic it bioaccumulates.

Chapter III

Evaluation of Sargassum Recycling Options through Risk-Based Approaches

Chapter III

Evaluation of Sargassum Recycling Options through Risk-Based Approaches

III.1 Introduction

The rapid proliferation of pelagic sargassum spp. (collectively *Sargassum natans* and *Sargassum fluitans*) across the Atlantic Ocean, Caribbean Sea, and Gulf of Mexico has emerged as one of the most significant coastal management challenges of the past decade (Smetacek & Zingone, 2013; Wang et al., 2019). Once regarded as a critical ecological asset providing habitat, refuge, and nutrient cycling for marine biodiversity in the open ocean, massive and recurrent beach strandings now impose severe environmental, social, and economic burdens on coastal communities (Rodríguez-Martínez et al., 2020; Chávez et al., 2020). Decomposing biomass releases hydrogen sulfide and attracts pests, while removal and disposal strain municipal budgets and landfill capacity (Robledoet al., 2021).

In response, regional governments, researchers, and industry stakeholders have explored beneficial reuse pathways including composting, biochar production, anaerobic digestion, and substrate formulation as circular-economy strategies to transform this liability into a resource (Thompson et al., 2021; Desrochers et al., 2022). These approaches aim to recover nutrients, enhance soil health, and generate bioenergy while reducing disposal pressures. However, growing evidence of elevated trace metal and metalloid concentrations, particularly arsenic (As) in stranded sargassum biomass has raised critical concerns about the safety of such recycling practices (Devault et al., 2021;).

Arsenic, a highly toxic metalloid, is of particular concern due to its persistence, complex speciation, and well-documented human health effects (Agency for Toxic Substances and Disease Registry, 2007; World Health Organization, 2022). Inorganic arsenic species (iAs), including arsenite [As(III)] and arsenate [As(V)], are classified as Group 1 carcinogens by the International Agency for Research on Cancer (IARC, 2012), with chronic exposure linked to skin lesions, cardiovascular disease, diabetes, and multiple cancers (Naujokas et al., 2013). Marine macroalgae, including sargassum, are known to bioaccumulate arsenic from seawater, often at levels orders of magnitude above ambient concentrations (Devault et al., 2021; Rodríguez-Martínez et al., 2020). When stranded biomass is processed into soil amendments or biogas digestate, arsenic may persist, transform, or become more bioavailable depending on pH, redox conditions, and thermal or microbial processing (Milledge et al., 2021).

To date, few studies have quantitatively assessed the human health risks associated with arsenic in sargassum-derived recycled products. This gap is critical, as land application of compost, biochar, or digestate in agricultural or landscaping contexts introduces new exposure pathways via incidental ingestion, dermal contact, or inhalation of particulates for workers, farmers, and the general public (U.S.EPA, 2009, 2011; Black et al., 2016). Moreover, total arsenic concentrations in some recycled materials have been reported to exceed regulatory soil screening levels, including Florida's Soil Cleanup Target Levels (SCTLs; Florida Department of Environmental Protection, 2005), necessitating a formal risk evaluation.

This study applies the National Research Council's (1983) risk assessment framework comprising hazard identification, exposure assessment, dose-response evaluation, and risk characterization (Altomare et al., 2021 & NRC, 1983) to quantify potential non-cancer and cancer risks from total arsenic in sargassum-

derived materials. Using empirical concentration data and probabilistic Monte Carlo modeling, we evaluated arsenic transfer and exposure among adults in recreational and occupational settings. The recreational scenario was based upon an updated assessment of exposure by children during beach play, and the occupational exposure scenarios were based upon handling and application of sargassum based recycled products. One study (Mc Intyre et al. 2026) evaluated children's risks to exposure to sargassum and found mean lifetime cancer risks on the order of 10^{-5} (up to 10^{-4} at the upper bound), driven primarily by dermal exposure, with non-cancer hazard quotients below one. However, this study did not evaluate the impacts of arsenic speciation on potential health risks. No studies we are aware of have evaluated the occupational exposure to arsenic associated with sargassum recycling activities. The objective of this study was to address this data gap by evaluating health risks associated with stranded sargassum using a unified approach that evaluates both recreational and occupational exposures. This work represents one of the first comprehensive human health risk assessments of arsenic in sargassum recycling streams. By integrating field-derived data with standardized risk modeling, it provides actionable insights for policymakers, waste managers, and agronomists seeking to balance circular-economy benefits with public health protection. Ultimately, this study supports the development of evidence-based guidelines for safe sargassum use, ensuring that resource recovery does not compromise human or environmental health.

III.2 Methods

III.2.1 Hazard Identification

In this paper, the hazard identified, arsenic, has become a major concern due to its known bioaccumulation in sargassum (Devault et al., 2021; Rodríguez-Martínez et al., 2020) and in sargassum derived recycled materials and products (Abdool-Ghany et al. 2023b). Arsenic exists in many species which greatly impact its toxicity. Arsenic occurs in a range of chemical forms whose toxicity differs by orders of magnitude, so the health significance of a given total concentration depends heavily on which species are present (Stýblo et al., 2002). The element is found in inorganic, methylated, and complex organic forms spanning several oxidation states. Among the inorganic forms, arsenite generally drives greater toxicity and environmental mobility than arsenate (Khan et al., 2006), and inorganic arsenic as a class is recognized as a Group 1 human carcinogen (IARC, 2012). Methylated pentavalent compounds such as MMA(V) and DMA(V) tend to be less hazardous than their inorganic counterparts, while organoarsenicals typical of marine biota, including arsenobetaine and arsenocholine, are largely benign products of biological detoxification (Di et al., 2019). Because regulatory thresholds are written for total arsenic while toxicity tracks speciation, resolving the species distribution is essential to a meaningful risk evaluation of sargassum-derived materials.

Total arsenic and arsenic species concentrations (Table III.1) in recycled materials were determined from measurements in sample types conducted as part of a related study on arsenic speciation in sargassum recycling products. To provide a basis for comparison, concentrations in sargassum and recycled products were compared to regulatory guidelines. However, except for gaseous exposures, regulatory guidelines were based solely upon arsenic concentration, without a separation of guidelines by arsenic species.

For sediment, the total arsenic concentrations in several recycled materials exceeded the Florida Soil Clean Up Target Levels (SCTLs) established for arsenic in residential applications (2.1 mg/kg; FDEP., 2005). Some were within the industrial guideline level (12 mg/kg; FDEP, 2005). The arsenic levels observed in certain samples, such as compost and digestate, exceeded both residential and industrial SCTLs. The maximum levels of arsenic observed in some materials approached the US Environmental Protection Agency's guideline level for land application of biosolids (75 mg/kg). The established Florida SCTLs was specifically designed to assess potential health risks associated with soil contaminant concentrations, with

the industrial SCTL intended for assessing arsenic exposure by adults in occupational environments (FDEP, 2005). Given that arsenic levels in these recycled materials exceed the established SCTLs coupled with their proximity to the biosolids standard, a risk assessment specific to handling and application scenarios was warranted.

For aerosol and gaseous exposures, guidelines exist for both particulate inorganic arsenic, for which OSHA sets an 8-hour permissible exposure limit of 10 $\mu g/m^3$, and arsine gas (AsH_3), for which OSHA sets a permissible exposure limit of 0.05 ppm (0.2 mg/m^3) (OSHA, 2024) and NIOSH recommends a 15-minute ceiling of 0.002 mg/m^3 and an immediately dangerous to life or health (IDLH) concentration of 3 ppm (NIOSH, 2007).

III.2.2 Exposure Scenarios

The assessment of health risks associated with exposure to sargassum, and sargassum-derived materials was based on a series of exposure scenarios representing both recreational and occupational contexts (Table III.2). These scenarios encompassed exposures across multiple life stages, and incorporated age-specific exposure factors along with their corresponding probability distributions (Ferguson et al., 2019; U.S. Environmental Protection Agency [U.S. EPA], 2011). The recreational scenario represents a child at the beach and assumes exposure beginning in infancy through beach visits, followed by continued contact during childhood play and adolescent recreational activities in coastal environments, and extending into adulthood through incidental contact in the same setting. Consideration was given to two sets of children, children with and without pica behavior. Pica behavior is the recurrent ingestion of nonnutritive, nonfood substances, such as sand or soil, persisting for at least one month (Al Nasser et al., 2023) most prevalent among those aged 3 to 6 years, which constitutes a critical pathway for elevated incidental ingestion and associated risk (U.S. EPA, 2011).

The occupational scenarios begin at the age of 16 and continue through lifetime exposure. Four occupationally relevant exposure scenarios were evaluated to capture higher-intensity and task-specific exposures across the sargassum management and reuse value chain. The first three occupational scenarios represent exposures to unprocessed sargassum through beach cleanup and removal workers, exposures to compost through agricultural applications, and exposures to biochar through occupational settings, reflecting repeated incidental ingestion, dermal and inhalation exposure during manual handling and transport of materials. The fourth occupational scenario evaluates exposure within biogas production systems, including inhalation of gases and contact with process inputs and outputs, particularly substrate and digestate, in agricultural or industrial environments.

Across all scenarios, exposure factors and their associated probability distributions were parameterized using established EPA guidance, with scenario-specific assumptions applied for exposure frequency, duration, and pathways (Tables III.3). Collectively, the scenarios provide a structured representation of both recreational and occupational exposure pathways, ranging from baseline public exposure to higher-risk, process-specific interactions across the sargassum utilization continuum.

Table III.1. Minimum, mean, and maximum concentrations of total arsenic and arsenic species in sargassum and sargassum recycling products, measured for total arsenic in mg/kg, µg/L, and µg/m³ for solid, liquid, and gas samples respectively, as documented in McIntyre et al. 2026 (in review). ND, not detected.

Sample	Minimum	Mean	Maximum
Sargassum[a] (mg/kg)			
Total arsenic	10.91	25.74	75.38
As(V)	6.62	16.72	41.81
DMA(V)	0.36	4.83	15.06
As(III)	0.10	0.37	0.68
Compost (mg/kg)			
Total arsenic	12.06	25.24	45.48
As(V)	8.95	20.30	38.86
DMA(V)	1.00	2.41	4.26
As(III)	0.00	0.41	1.63
Biochar (mg/kg)			
Total arsenic	17.20	87.95	141.84
As(V)	12.11	64.15	98.66
DMA(V)	0.75	3.65	5.76
As(III)	ND	ND	ND
Biogas Substrate (mg/kg)			
Total arsenic	2.61	3.19	3.60
As(V)	1.35	1.39	1.44
DMA(V)	ND	ND	ND
As(III)	0.38	0.39	0.41
Biogas Digestate (µg/L)			
Total arsenic	96.53	99.08	103.42
As(V)	54.54	58.26	61.60
DMA(V)	ND	ND	ND
As(III)	17.09	18.78	20.21
Unfiltered Biogas (µg/m³)			
Total arsenic	6.38	7.53	8.57
AsH_3 (arsine)	5.76	6.44	7.12
Filtered Biogas (µg/m³)			
Total arsenic	0.37	0.87	1.85
AsH_3 (arsine)	ND	ND	1.54

[a] Includes results from fresh and dried sargassum

III.2.3 Exposure Parameters

Exposure represents the quantity of a contaminant that reaches the human contact boundary, such as the mouth, skin, or lungs. Accordingly, this assessment considered exposures through oral ingestion (subscript o), dermal contact (subscript d), and inhalation (subscript i) pathways.

Dose represents the uptake of the contaminant into the human body following exposure. To assess exposure and dose to arsenic, standardized equations were employed consistent with U.S. EPA human health risk assessment guidance (U.S. EPA, 2011). The complete set of equations used for calculating exposure and dose through oral (D_o), dermal (D_d), and inhalation (D_i) pathways are presented below. Ingestion and dermal exposure were assumed to occur through contact with solid material matrices, while inhalation exposure was based on measured contaminant concentrations associated with aerosolized

solids, or biogas capable of generating airborne gases.
The general equations for ingestion, dermal, and inhalation dose are:

$$D_o = \frac{C \times IR \times RBA \times EF \times CF}{BW} (1)$$

$$D_d = \frac{C \times SA \times AF \times ABS \times EF \times CF}{BW} (2)$$

$$D_i = \frac{C \times (1/PEF) \times IR_a \times RBA_i \times EF \times CF}{BW} (3)$$

Oral Exposure Route

For oral exposure (Equation 1), *C* represents the concentration of total arsenic in the material (mg/kg for sargassum and mg/L for liquid digestate for the biogas recycling scenario) as described in Table III.1.

IR represents the ingestion rate. For sargassum in recreational settings, was taken from the U.S. EPA Exposure Factors Handbook, using soil ingestion rates as surrogates for incidental ingestion of raw sargassum (U.S. EPA, 2011). Age-specific ingestion rates were applied, including elevated ingestion assumptions for children aged 3 to 6 years exhibiting pica behavior (U.S. EPA, 2011).

For occupational recycled-material scenarios, ingestion rates of sargassum and recycled materials were estimated from the Exposure Dose Guidance for Soil and Sediment Ingestion (ATSDR, 2018). The central tendency exposure (CTE) was used as the mean and the reasonable maximum exposure (RME) as the maximum. Since minimum values were not available, the minimum was assumed to be two-thirds of the mean. For liquid forms which applied to biogas digestate only, ingestion rates were expressed in milliliters per day using EPA-derived incidental ingestion assumptions and values reported in environmental exposure studies (U.S. EPA, 2011).

The relative bioavailability factor (*RBA*) for arsenic was estimated at 0.33 for solids consistent with values used to estimate the Florida SCTL (Florida Department of Environmental Protection [FDEP], 2005). This value applies to the ingestion of solid matrices. The only liquid ingestion pathway considered, as mentioned earlier, was incidental ingestion of the liquid digestate in the biogas production scenario, for which a relative bioavailability of 1 was assumed, consistent with the use of fully soluble arsenic (sodium arsenate) as the reference compound that defines unit relative bioavailability in swine bioassays (U.S. EPA, 2003) and reflecting the greater bio accessibility of arsenic dissolved in the aqueous phase relative to arsenic bound within solid materials.

The exposure factor (*EF*) was defined as:

$$EF = \frac{F \times ED}{AT} (4)$$

where F is exposure frequency (days/year), ED is exposure duration (years), and AT is averaging time (days) (U.S. EPA, 2011). For recreational scenarios, these parameters were based on reported beach visitation patterns (Ferguson et al., 2019). For occupational scenarios, exposure duration was based on a standard 40-hour work week (8 hours/day, 5 days/week), corresponding to approximately 2,000 hours per year of potential contact (Occupational Safety and Health Administration [OSHA], 2023; U.S. EPA, 2011).

Conversion factors (*CF*) were applied as needed so that the final dose units corresponded to milligrams of arsenic per kilogram body weight per day. Body weights (*BW*) were obtained from National Center for Health Statistics anthropometric reference data using age-specific minimum, mean, and maximum values (National Center for Health Statistics [NCHS], 2018). For adult occupational scenarios, the adult body-weight distribution was applied (U.S. EPA, 2008; Ferguson et al., 2021).

Dermal Exposure Route

Dermal exposure was calculated using Equation 2, where *SA* represents exposed skin surface area, *AF* represents the adherence factor, and *ABS* represents the dermal absorption fraction. Skin surface area values were obtained from the U.S. EPA Exposure Factors Handbook (U.S. EPA, 2011). Adherence factors were derived from Elmir et al. (2007, 2009) and Ferguson et al. (2021). Because decomposed sargassum becomes integrated into sediments and exhibits similar surface contact characteristics, adherence factors for sand were applied to sargassum materials.

For liquid matrices, in which arsenic is present in solution rather than adhered as a solid, dermal uptake was estimated using a species-specific permeability-coefficient approach following Ouypornkochagorn and Feldmann (2010). That work demonstrated that percutaneous absorption of arsenic depends strongly on its chemical speciation, with trivalent and methylated species penetrating human skin substantially faster than arsenate. The absorbed mass of arsenic (M, in μg) was calculated as shown in equation 2a as:

$$M = C \times A \times K_p \times t \quad (2a)$$

where C is the arsenic concentration in the contacting medium (mg/L), A is the exposed skin surface area (cm^2), K_p is the species-specific dermal permeability coefficient (cm/hr), and t is the contact (sorption) time (hr). The product $K_p \times t$ represents the depth of skin penetration, and $A \times K_p \times t$ the penetrated skin volume; because a concentration of 1 mg/L is numerically equivalent to 1 $\mu g/cm^3$ (assuming a medium density of approximately 1 g/mL), the product of concentration and penetrated volume yields absorbed mass directly in μg. For finite-source exposures, such as application of a fixed amount of material, absorbed mass was capped at the available applied arsenic mass (source concentration × amount applied); for immersion exposures, such as showering, the source was treated as effectively unlimited and no cap was applied.

Table III.2. Risk assessment scenarios for each waste recycled material from Sargassum.

Contaminant / Material	**Exposure Scenario**	**Exposure Routes**
Sargassum	Recreational Beach Exposure from childhood through adult. Two child exposure scenarios were considered, one for a child with pica and one for a child without.	Ingestion (hand-to-mouth contact with sargassum), dermal contact (direct contact with sargassum), inhalation (aerosol particulate emissions from decomposing sargassum). Excludes consideration of contact from secondary sources such as contaminated sand and water. Also does not include volatile gas emissions from sargassum.
Sargassum	Occupational (Sargassum Removal and Handling Operations)	Ingestion (hand-to-mouth contact during handling), dermal contact (direct contact with sargassum), inhalation (aerosol particulate emissions during handling)
Compost	Occupational (Compost Handling and Application)	Ingestion (hand-to-mouth contact with compost), dermal contact (direct contact with compost), inhalation (aerosol particulate emissions during handling and application)
Biochar	Occupational (Biochar Handling and Application)	Ingestion (hand-to-mouth contact with biochar), Dermal contact (direct contact with biochar), Inhalation (aerosol particulate emissions during handling and application)
Biogas System (Gas, Digestate, Substrate)	Occupational (Biogas Production System Exposure)	Inhalation (biogas volatile gas emissions and aerosol particulates), ingestion (hand-to-mouth contact with substrate and digestate), dermal contact (direct contact with substrate and digestate)

Table III.3. Assumptions for exposure parameters that vary across different age groups (16-20 years and 20 years over) for oral, dermal, and soil inhalation exposure routes. The mean, maximum and minimums for each of the parameters were estimated based on existing literature. All parameters were assumed to have a triangular distribution, determined at a 95% confidence level (alpha = 0.05).

Parameter		16 to 20 (Occupational)	20 and over	Reference
Frequency, *F* (days/year)	Min	1	1	(OSHA, 2016)
	Mean	260	260	
	Max	365	365	
Skin Surface Area, *SA* (cm^2)	Min	2800	2800	(US EPA, 2011)
	Mean	3300	3300	
	Max	3300	3300	
Body Weight. *BW* (kg)	Min	47.7	46.4	(NCHS,2018)
	Mean	72.2	84.1	
	Max	112.1	127.6	
Inhalation Rate, IR_a (m^3/day)	Min	15.2	6.24	(USEPA,2011)
	Mean	16.3	14.3	
	Max	24.6	24.04	
Ingestion Rate, IR_s *and* IR_g (mg/day)	Min	20.0	20.0	(USEPA,2011)
	Mean	30.0	30.0	
	Max	100	100	
Adherence Factor, *AF* (mg/cm^2)	Min	0.01	0.01	(USEPA,2011)
	Mean	0.02	0.02	
	Max	0.20	0.20	

A species-specific dermal absorption factor was then defined as the ratio of absorbed mass to available applied mass; this factor is undefined for immersion scenarios, in which no finite dose is applied. The permeability coefficients applied were 9.2×10^{-5} cm/hr for arsenate (As^{V}) and 5.4×10^{-2} cm/hr for dimethylarsinic acid (DMA^{V}), taken from Table 1a of Ouypornkochagorn and Feldmann (2010); coefficients for arsenite (As^{III}) and monomethylarsonic acid (MMA^{V}) will be incorporated as those values are finalized. Because arsenic in sargassum and its recycled products is dominated by As^{V} (Mc Intyre et al., 2026, in preparation), with smaller contributions from more readily absorbed species, this approach allows the dermal pathway to be resolved by arsenic species rather than a single default absorption fraction based upon total arsenic.

Inhalation Exposure Route

Inhalation exposure was estimated for inhalation of aerosol particulates (all scenarios) and for inhalation of gases (for biogas scenario only). Inhalation dose of aerosol particulates was calculated using Equation 3, where *IRa* represents inhalation. Age-specific inhalation rates were obtained from the U.S. EPA Exposure Factors Handbook (U.S. EPA, 2011). The *PEF* represents a factor that takes into account wind speeds and land cover in the generation of particulate aerosols.

Inhalation dose for biogas was obtained from gaseous arsenic measurements. For biogas samples (unfiltered and filtered), exposure was assumed to occur primarily through inhalation in an occupational setting. This assessment followed EPA methodologies for evaluating inhalation risks from airborne contaminants (U.S. EPA, 2011; U.S. EPA inhalation risk assessment guidance). Because no specific reference concentration (RfC) is available for inorganic arsenic via inhalation, non-cancer risks were evaluated using the inhalation unit risk (IUR) for inorganic arsenic (Integrated Risk Information System [IRIS], 1995).

Two occupational inhalation scenarios were considered: routine exposure to unfiltered biogas and exposure to filtered biogas. Air concentrations of arsenic (C_{air}) were measured in the breathing zone during biogas handling operations. The exposure-adjusted air concentration (EC) was calculated by incorporating time-activity and exposure duration factors:

$$EC = C_{air} \times (ET/24) \times (F \times ED / AT)$$

Where ET represents the exposure time in hours and is divided by 24 to convert to fraction of a day. Inhalation cancer risk was estimated using the exposure concentration approach recommended by U.S. EPA RAGS Part F, where exposure-adjusted air concentration was multiplied by the inhalation unit risk for inorganic arsenic (U.S. Environmental Protection Agency, 2009). Cancer risk was calculated as:

$$Cancer\ Risk = EC \times IUR$$

Table III.4. Exposure parameters used for gaseous inhalation exposure assessment in occupational biogas handling scenarios

Parameter	Value	Description	Reference
Exposure time (*ET*)	8 hours/day	Hours per day exposed to biogas in occupational setting	OSHA (2023); U.S. EPA (2011)
Exposure frequency (*F*)	250 days/year	Days per year exposed, based on full-time work schedule	OSHA (2023); U.S. EPA (2011)
Exposure duration (*ED*)	25 years	Years of exposure in occupational setting	U.S. EPA (2011)
Averaging time (*AT*)	9125 days for non cancer, 28,470 days for cancer	Averaging time for non-cancer effects (*ED* × 365 days). For cancer effects the *IUR* method is used where *AT* (the expected lifetime of 28,470 days) is embedded in the exposure fraction (see next row).	U.S. EPA (2011)
Exposure fraction	Calculated	Calculated as (ET/24) × (EF/365) × (ED/AT)	Calculated
Inhalation rate (*IRa*)	1.3 m^3/hour	Occupational default inhalation rate for adults	U.S. EPA (2009)

Table III.5. Dose-response values and reference values used for inhalation risk assessment

Parameter	Value	Description	Reference
Reference concentration (*RfC*)	0.00003 mg/m^3	Conservative reference value applied for non-cancer risk	OEHHA (2008)
Inhalation unit risk (*IUR*)	4.3×10^{-3} $(\mu g/m^3)^{-1}$	Cancer risk per unit concentration in air (continuous lifetime exposure)	U.S. EPA (1995)
Relative bioavailability (RBA_i)	1.0 (assumed for inhalation)	Assumed 100% bioavailability for inhaled arsenic	U.S. EPA (2011)

The inhalation unit risk for inorganic arsenic was obtained from the U.S. EPA Integrated Risk Information System (IRIS) database (U.S.EPA, 2023). These calculations assumed conservative occupational exposure conditions, including approximately 250 exposure days per year, consistent with full-time work schedules (OSHA, 2023. Cancer Risks were evaluated for routine handling scenarios in biogas production facilities. Parameters for inhalation equations are defined in Tables III.4 and III.5.

III.2.4 Cancer Risk

Cancer risk was estimated separately for oral, dermal, and inhalation exposure pathways and subsequently combined to obtain total lifetime cancer risk for each scenario. Oral and dermal cancer risks were calculated by multiplying pathway-specific dose estimates by the corresponding cancer slope factors.

$$Risk = Dose \times Slope\ factor$$

Inhalation cancer risk was estimated using the exposure concentration approach recommended by U.S. Environmental Protection Agency Risk Assessment Guidance for Superfund (RAGS) Part F, where exposure-adjusted air concentration was multiplied by the inhalation unit risk for inorganic arsenic (U.S. Environmental Protection Agency, 2009). The inhalation unit risk was obtained from the U.S. Environmental Protection Agency Integrated Risk Information System (IRIS) database (U.S. Environmental Protection Agency, 2023). Total lifetime cancer risk was calculated as the sum of pathway-specific risks for each exposure scenario.

III.2.5 Non-Cancer Risk

Non-cancer risk was characterized using the hazard quotient (HQ), defined as the ratio of the estimated exposure dose to the corresponding chronic reference value (US EPA 2001). An HQ ≤ 1 indicates that exposure is unlikely to result in adverse non-cancer effects, whereas an HQ > 1 indicates a potential hazard. Exposure doses were estimated for each recycling product (total Sargassum, dried Sargassum, compost, biochar, substrate, and digestate) using the route-specific intake equations described above. A chronic exposure factor (EF = F/365) was applied to represent daily exposure averaged over one year (Ferguson et al. 2018, Black et al. 2016), and doses were evaluated for occupational exposure scenarios considering two age categories (16–20 and ≥20 years).

For the oral route, the Agency for Toxic Substances and Disease Registry (ATSDR 2018) chronic minimal risk level (MRL) for inorganic arsenic, 3×10^{-4} mg/kg-day, was used as the reference value. Arsenic MRLs are not established for the dermal or inhalation routes. For the dermal route, a reference dose was derived from the oral value following EPA's Supplemental Guidance for Dermal Risk Assessment (US EPA 2004; RAGS Part E), in which the oral reference value is adjusted by the gastrointestinal absorption fraction (GIABS): RfDdermal = RfDoral × GIABS. Because inorganic arsenic is efficiently absorbed from the gastrointestinal tract (GIABS = 1), the derived dermal reference dose equals the oral value (3×10^{-4} mg/kg-day), and the dermal HQ was computed using the absorbed dermal dose.

III.2.6 Statistical Analysis

Uncertainty and inter-individual variability were evaluated using Monte Carlo simulation in Oracle Crystal Ball. For each material and pathway, input parameters were represented by probability distributions defined by literature-based minimum, mean, and maximum values (US EPA 2001). Pathway-specific doses and risks were calculated for each simulation trial ,with 10,000 trials run per scenario. Total risk for each material was obtained by summing risks across oral, dermal, and inhalation pathways within each trial. Output statistics included minimum, mean, median, maximum, base case, and selected percentiles.

III.3 Results

III.3.1 Dermal Exposure in Beach Settings vs Occupational Setting

In the beach setting, median total arsenic dermal risk ranged from 9.66×10^{-7} (0–3 years) to 1.09×10^{-5} (20+ years), with corresponding mean values of 1.20×10^{-6} and 2.47×10^{-5}. The 90th percentile total arsenic risk ranged from 2.36×10^{-6} (0–3 years) to 5.04×10^{-5} (20+ years) (Table III.7).

In the occupational setting, median total arsenic dermal risk for sargassum was 1.98×10^{-7} for the 16–20 age group and 2.04×10^{-6} for the 20+ age group. Across compost and biochar, median total arsenic risk values for the 16–20 age group were 1.51×10^{-7} (compost) and 4.41×10^{-7} (biochar); for the 20+ age group, corresponding values were 1.61×10^{-6} (compost) and 4.68×10^{-6} (biochar) (Table III.8).

III.3.2 Dermal Risk by Arsenic Species Compared to Total Arsenic

As(V) dermal risk values were lower than corresponding total arsenic risk values across all percentiles, age groups, and sample types evaluated. In the beach setting, median As(V) risk ranged from 3.47×10^{-7} (0–3 years) to 6.97×10^{-6} (20+ years), compared to median total arsenic risk of 9.66×10^{-7} and 1.91×10^{-5} for the same age groups, respectively. In the occupational setting, median As(V) risk values ranged

from 7.15×10^{-8} (sargassum, 16–20 years) to 2.04×10^{-6} (biochar, 20+ years).

DMA(V) dermal risk values were higher than corresponding total arsenic risk values across all percentiles, age groups, and sample types evaluated. In the beach setting, median DMA(V) risk ranged from 4.39×10^{-6} (0–3 years) to 8.55×10^{-5} (20+ years), compared to median total arsenic risk of 9.66×10^{-7} and 1.91×10^{-5} for the same age groups, respectively. In the occupational setting, median DMA(V) risk values for the 16–20 age group were 8.82×10^{-7} (sargassum), 3.54×10^{-7} (compost), and 4.62×10^{-7} (biochar); for the 20+ age group, values were 9.18×10^{-6} (sargassum), 3.77×10^{-6} (compost), and 4.87×10^{-6} (biochar). This pattern was consistent across the base case, mean, and all reported percentiles.

III.3.3 Total Lifetime Cancer Risk Across Exposure Scenarios

Monte Carlo simulation results demonstrated substantial variation in lifetime cancer risk across exposure scenarios, with mean total risks spanning more than an order of magnitude. Scenario-specific mean risks ranged from 9.07×10^{-7} for biogas system exposure to 5.23×10^{-5} for children exposed to sargassum-contaminated beach environments with pica behavior (Table III.9). ***Across all scenarios, the highest mean lifetime cancer risks were associated with children in beach environments, followed by occupational exposure to recycled sargassum-derived materials***, while biogas system exposures consistently produced the lowest risks.

III.3.4 Recreational Exposure: Children at Contaminated Beaches

Children exposed to sargassum-contaminated beaches exhibited the highest lifetime cancer risks among all scenarios evaluated (Table III.9). The mean total risk for the non-pica scenario was 4.33×10^{-5}, increasing to 4.78×10^{-5} under pica behavior. These values exceed all occupational scenarios by approximately a factor of three to six. Despite the inclusion of pica behavior, the increase in mean risk was relatively modest, approximately nine percent, indicating that baseline exposure pathways dominate total risk even in the absence of pica. Maximum values reached 2.71×10^{-4} and 2.79×10^{-4} for non-pica and pica scenarios, respectively, demonstrating substantial variability in exposure outcomes and indicating that upper-bound risks extend into the 10^{-4} range.

III.3.5 Occupational Exposure: Sargassum Handling and Reuse Materials

Among the compost and biochar occupational scenarios, mean lifetime cancer risks ranged from 6.17×10^{-6} to 1.84×10^{-5}, with a clear ranking observed across exposure contexts (Table III.9). Exposure to biochar-derived materials produced the highest occupational risk, with a mean of 1.84×10^{-5}, approximately 2.2 times greater than sargassum removal and handling operations, which had a mean risk of 8.39×10^{-6}, and approximately three times greater than compost handling and application, which had a mean risk of 6.17×10^{-6}. These differences indicate that processing and reuse of sargassum into biochar substantially increases exposure potential relative to raw biomass handling. Maximum values for occupational scenarios ranged from 2.52×10^{-5} for compost to 6.95×10^{-5} for biochar, indicating that upper-bound risks for biochar approach those observed in recreational exposure scenarios.

III.3.6 Biogas System Exposure

Biogas system exposure scenarios produced the lowest lifetime cancer risks among all scenarios evaluated (Table III.9). Mean risks for filtered and unfiltered biogas system exposure were 9.09×10^{-7} and 9.07×10^{-7}, respectively, differing by less than 0.3%. The near-identical mean values and overlapping distributions indicate that gas filtration has a negligible effect on total lifetime cancer risk. Maximum values for both scenarios remained below 2.5×10^{-6}, further confirming the relatively low magnitude of risk associated with this exposure context.

III.3.7 Comparative Risk Patterns and Distribution Characteristics

Comparison of mean lifetime cancer risks across all scenarios reveals a consistent hierarchy, with children exposed in beach environments representing the highest-risk group, followed by workers handling biochar, workers engaged in sargassum removal, and workers handling compost, while biogas system exposures represent the lowest-risk scenarios. ***This pattern demonstrates that recreational exposure pathways for children can exceed occupational exposures in magnitude, even under high-intensity worker scenarios.***

Across all scenarios, risk distributions were positively skewed, with mean values consistently exceeding median values. For example, in the worker sargassum scenario, the mean risk of 8.39×10^{-6} exceeded the median of 7.48×10^{-6}, while in the children pica scenario, the mean of 5.23×10^{-5} exceeded the median of 4.78×10^{-5}. Maximum values were typically one order of magnitude higher than minimum values, reflecting substantial variability in exposure conditions. Deterministic base-case estimates consistently underestimated mean risk values, with base cases ranging from approximately 30% to 60% lower than corresponding means across multiple scenarios. These findings demonstrate that incorporation of variability through probabilistic methods substantially alters risk characterization and provides a more complete representation of potential exposure outcomes.

III.3.8 Non-Cancer Risk

For the oral and dermal routes, hazard quotients fell below 1 for every recycling product in both exposure-duration scenarios. Oral HQs ranged from 8.4×10^{-5} for digestate to 2.9×10^{-2} for biochar, and dermal HQs from 7.2×10^{-6} (digestate) to 7.5×10^{-3} (biochar). Biochar gave the highest values on both routes, in line with its higher arsenic content, and digestate the lowest. The ≥20-year and 16–20-year scenarios gave similar results, differing only in body weight and intake rate.

With the oral reference dose applied, inhalation HQs also fell below 1. Particulate inhalation from handling the solid products was very low, on the order of 10^{-6} to 10^{-5} for all products. Biogas gave higher values: unfiltered biogas reached 0.060 in the ≥20-year scenario and 0.012 in the 16–20-year scenario, and filtration lowered these by roughly eightfold, to 0.0071 and 0.0014. Filtering the biogas therefore cut inhalation exposure by close to an order of magnitude.

III.4 Discussion

III.4.1 Inhalation Unit Risk, Arsenic Speciation, and Model Assumptions

Cancer risk estimates in this study were derived using the inhalation unit risk (*IUR*) for inorganic arsenic, consistent with established risk assessment frameworks (U.S. EPA, 2009; U.S. EPA, 2023). The *IUR* represents the excess lifetime cancer risk associated with continuous inhalation exposure to a unit concentration of a contaminant in air and is based primarily on epidemiological evidence linking arsenic exposure to lung cancer in human populations.

A critical consideration in the application of this parameter is the chemical speciation of arsenic. Arsenic occurs in multiple forms, including inorganic species such as arsenite [As(III)] and arsenate [As(V)], organic species such as arsenobetaine, and as arsine gas, which differ significantly in toxicity. Arsine gas is the most toxic of the species. Inorganic arsenic species are also toxic and carcinogenic, more so than most organic forms and form the basis of regulatory risk values (Hughes, 2002; Francesconi & Kuehnelt, 2004; U.S. EPA, 2023).

In the context of sargassum-derived materials and emissions, the specific distribution of arsenic is variable, but is known to release arsine gas and concentrate As (V) (See Chapter II). Previous studies have

demonstrated that pelagic sargassum can accumulate elevated concentrations of arsenic, with variability in both total concentration and speciation depending on environmental conditions (Rodríguez-Martínez et al., 2020; Devault et al., 2021). Given this uncertainty, the application of the inorganic arsenic *IUR* represents a conservative approach that likely overestimates risk where less toxic organic species dominate but ensures that potential risks are not underestimated, consistent with EPA guidance on health-protective defaults (U.S. EPA, 1989).

III.4.2 Dermal Absorption and Material-Specific Exposure Considerations

Dermal exposure was incorporated using standard assumptions for contaminant adherence and absorption, consistent with U.S. EPA guidance (U.S. EPA, 2004). The dermal absorption factor (*ABS*) represents the fraction of a contaminant that penetrates the skin and becomes systemically available and is typically derived from experimental data or surrogate values where compound-specific information is limited.

In the absence of material-specific dermal absorption data for arsenic associated with sargassum and its derivatives, literature-based default values were applied. Experimental studies indicate that dermal absorption of arsenic from soil and particulate matrices is generally low but can vary depending on physicochemical properties and exposure conditions (Wester et al., 2004). Material characteristics such as particle size, surface area, and moisture content may influence dermal exposure potential. For example, fine particulate materials such as biochar may enhance adherence to the skin surface and increase exposure potential relative to coarser materials (Beesley et al., 2011). These assumptions introduce uncertainty but are consistent with screening-level risk assessment practices. To partially address the limitation that a single default absorption factor cannot distinguish among arsenic species, dermal uptake from liquid and environmental matrices was additionally evaluated using a species-specific permeability-coefficient model (Ouypornkochagorn & Feldmann, 2010), which recognizes that more permeable species such as arsenite and methylated arsenicals can cross the skin substantially faster than arsenate. ***The partitioning of arsenic towards DMA(V) in sargassum promotes the dermal uptake of arsenic through skin exposure routes.*** This observation merits further exploration through controlled studies using sargassum in skin permeability experiments.

III.4.3 Influence of Material Form on Arsenic Exposure Risk

The results of this study are consistent with and extend findings reported in the literature on arsenic exposure and sargassum management. Elevated arsenic concentrations in pelagic *Sargassum* have been widely documented, with potential implications for human exposure through both environmental contact and reuse pathways (Rodríguez-Martínez et al., 2020; Devault et al., 2021).

The observed dominance of oral exposure pathways in total risk estimates aligns with established understanding that ingestion is a primary pathway for arsenic exposure in environmental contexts (Smith et al., 2002). Similarly, the relatively minor contribution of inhalation to total risk is consistent with evidence that airborne arsenic exposures are generally limited outside high-intensity industrial or combustion settings (International Agency for Research on Cancer [IARC], 2012).

The elevated risks associated with biochar handling observed in this study are supported by findings that fine particulate materials can increase exposure potential due to dust generation and increased surface area (Beesley et al., 2011). These results suggest that transformation of sargassum into secondary materials may alter exposure dynamics and should be carefully evaluated in reuse strategies.

Finally, the comparatively low risks associated with biogas system exposure are consistent with expectations that gas-phase arsenic concentrations are typically low relative to solid-phase materials, and

that exposure in such systems is more strongly influenced by contact with process inputs and outputs rather than inhalation of the gas itself. This observation, however, should be more fully explored given the limited information about the inhalation cancer risks associated with different arsenic species.

III.4.4 Implications for Sargassum Management and Risk Mitigation

The findings of this study have direct implications for sargassum management strategies. Children exposed in beach environments exhibited the highest lifetime cancer risks, exceeding occupational scenarios even in the absence of pica behavior, indicating that environmental exposure pathways alone can drive elevated risk (Figure III.1). This highlights the need for targeted public health interventions in areas affected by sargassum accumulation.

Among occupational scenarios, exposure to biochar-derived materials resulted in the highest cancer risks, suggesting that processing and reuse of sargassum may increase exposure potential relative to raw biomass. In contrast, biogas system exposure produced the lowest cancer risks, with negligible differences observed between filtered and unfiltered scenarios, indicating that gas-phase exposure is not the dominant contributor to risk. More work is needed to assess non-cancer risks for the biogas processing scenario given the production of highly toxic arsine gas.

Overall, these findings suggest that cancer risk mitigation efforts should prioritize reduction of direct contact with contaminated materials, particularly in recreational settings and during handling of processed sargassum products. Implementation of engineering controls, safe handling practices, and public awareness measures will be critical in minimizing exposure and supporting sustainable sargassum management.

III.5 Conclusion

This study provides a probabilistic assessment of lifetime cancer risks associated with arsenic exposure across recreational and occupational sargassum-related scenarios. The results demonstrate that exposure context is a critical determinant of risk magnitude, with children in beach environments representing the highest-risk population, exceeding occupational exposure scenarios even under conservative assumptions. Among reuse pathways, biochar handling exhibited the greatest exposure potential, while biogas systems consistently produced the lowest risks.

Across all scenarios, oral exposure was the dominant contributor to total cancer risk, followed by dermal exposure, with inhalation representing a minor pathway. Among the dermal exposure scenarios, absorption of arsenic through direct contact with sargassum merits further research given the high sorption rates of DMA(V) relative to other inorganic arsenic forms. Moreover, the application of Monte Carlo simulation revealed substantial variability in exposure outcomes and demonstrated that deterministic approaches may underestimate risk, particularly under upper-bound conditions.

The findings from this study highlight the need for targeted risk mitigation strategies that prioritize reduction of direct human contact with contaminated sargassum, particularly in recreational settings and during handling of processed materials. Implementation of appropriate occupational controls, including dust management and protective measures, will be essential for minimizing exposure during reuse applications.

Future research should focus on improving characterization of arsenic speciation across sargassum-derived materials and refining pathway-specific exposure parameters to reduce uncertainty in risk estimates.

Table III.6. Interpretation of computed risk values.

Value	Risk Level
10^{-1}	"Very High" increased risk
10^{-2}	"High" increased risk
10^{-3}	"Moderate" increased risk
10^{-4}	"Low" increased risk
10^{-5}	"Very Low" increased risk
10^{-6}	"Extremely Low" increased risk

Table III.7. Dermal risk estimates for total arsenic, As(V), and DMA(V) in the recreational beach setting, by age group. Results based upon stochastic computations (Monte Carlo, n = 10,000).

Age Group (years)	Species	Base Case	Min	P10	P25	Median (P50)	Mean	P75	P90	Max
0–3	Total As	5.22×10^{-7}	1.71×10^{-8}	3.51×10^{-7}	5.77×10^{-7}	9.66×10^{-7}	1.20×10^{-6}	1.56×10^{-6}	2.36×10^{-6}	8.39×10^{-6}
0–3	As(V)	2.09×10^{-7}	9.49×10^{-9}	1.28×10^{-7}	2.13×10^{-7}	3.47×10^{-7}	4.27×10^{-7}	5.54×10^{-7}	8.27×10^{-7}	3.42×10^{-6}
0–3	DMA(V)	2.51×10^{-6}	5.87×10^{-8}	1.37×10^{-6}	2.43×10^{-6}	4.39×10^{-6}	5.57×10^{-6}	7.26×10^{-6}	1.14×10^{-5}	3.94×10^{-5}
3–6	Total As	2.83×10^{-6}	1.15×10^{-7}	1.67×10^{-6}	2.91×10^{-6}	5.17×10^{-6}	6.59×10^{-6}	8.67×10^{-6}	1.34×10^{-5}	5.57×10^{-5}
3–6	As(V)	1.13×10^{-6}	3.41×10^{-8}	6.04×10^{-7}	1.07×10^{-6}	1.86×10^{-6}	2.38×10^{-6}	3.12×10^{-6}	4.85×10^{-6}	1.68×10^{-5}
3–6	DMA(V)	1.36×10^{-5}	3.54×10^{-7}	6.48×10^{-6}	1.22×10^{-5}	2.28×10^{-5}	3.02×10^{-5}	4.03×10^{-5}	6.29×10^{-5}	2.54×10^{-4}
6–11	Total As	2.91×10^{-6}	1.33×10^{-7}	1.62×10^{-6}	2.86×10^{-6}	5.23×10^{-6}	6.90×10^{-6}	9.14×10^{-6}	1.42×10^{-5}	6.00×10^{-5}
6–11	As(V)	1.16×10^{-6}	3.35×10^{-8}	5.98×10^{-7}	1.04×10^{-6}	1.92×10^{-6}	2.50×10^{-6}	3.31×10^{-6}	5.15×10^{-6}	1.84×10^{-5}
6–11	DMA(V)	1.40×10^{-5}	5.62×10^{-7}	6.34×10^{-6}	1.21×10^{-5}	2.35×10^{-5}	3.23×10^{-5}	4.24×10^{-5}	7.02×10^{-5}	2.85×10^{-4}
11–16	Total As	1.87×10^{-6}	9.16×10^{-8}	1.09×10^{-6}	1.94×10^{-6}	3.52×10^{-6}	4.64×10^{-6}	6.12×10^{-6}	9.67×10^{-6}	4.78×10^{-5}
11–16	As(V)	7.48×10^{-7}	4.09×10^{-8}	3.93×10^{-7}	7.12×10^{-7}	1.28×10^{-6}	1.66×10^{-6}	2.17×10^{-6}	3.35×10^{-6}	1.36×10^{-5}
11–16	DMA(V)	9.01×10^{-6}	1.10×10^{-7}	4.22×10^{-6}	8.13×10^{-6}	1.58×10^{-5}	2.16×10^{-5}	2.89×10^{-5}	4.66×10^{-5}	2.13×10^{-4}
16–20	Total As	1.06×10^{-6}	5.50×10^{-8}	6.51×10^{-7}	1.18×10^{-6}	2.11×10^{-6}	2.67×10^{-6}	3.49×10^{-6}	5.38×10^{-6}	2.50×10^{-5}
16–20	As(V)	4.22×10^{-7}	2.50×10^{-8}	2.49×10^{-7}	4.38×10^{-7}	7.71×10^{-7}	9.62×10^{-7}	1.28×10^{-6}	1.92×10^{-6}	6.65×10^{-6}
16–20	DMA(V)	5.08×10^{-6}	1.64×10^{-7}	2.66×10^{-6}	4.96×10^{-6}	9.44×10^{-6}	1.25×10^{-5}	1.67×10^{-5}	2.63×10^{-5}	1.01×10^{-4}
20+	Total As	9.10×10^{-6}	2.42×10^{-7}	6.02×10^{-6}	1.09×10^{-5}	1.91×10^{-5}	2.47×10^{-5}	3.31×10^{-5}	5.04×10^{-5}	1.95×10^{-4}
20+	As(V)	3.64×10^{-6}	9.49×10^{-8}	2.21×10^{-6}	3.97×10^{-6}	6.97×10^{-6}	8.88×10^{-6}	1.18×10^{-5}	1.78×10^{-5}	7.95×10^{-5}
20+	DMA(V)	4.38×10^{-5}	5.87×10^{-7}	2.41×10^{-5}	4.47×10^{-5}	8.55×10^{-5}	1.16×10^{-4}	1.53×10^{-4}	2.45×10^{-4}	1.09×10^{-3}

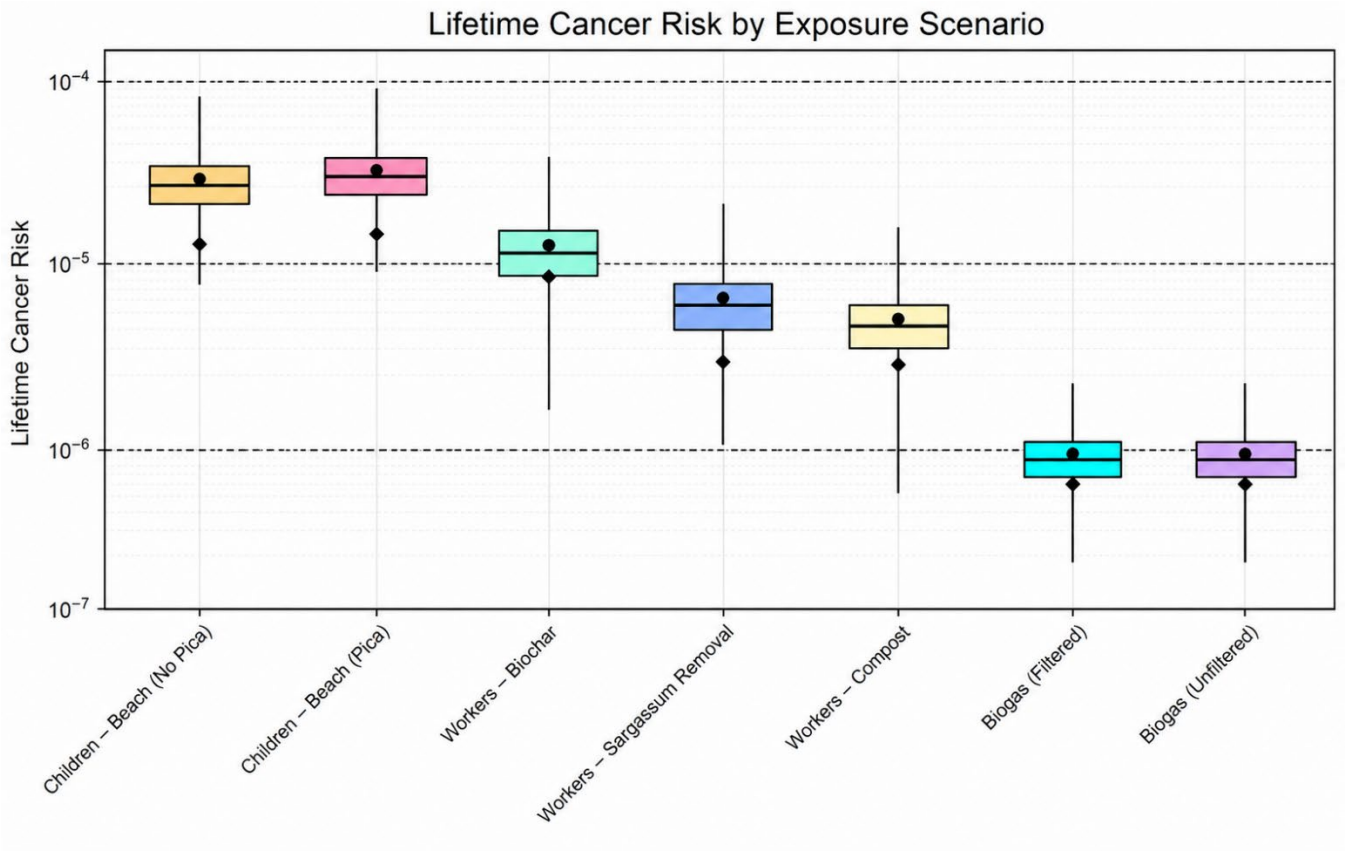
Table III.8. Dermal risk estimates for total arsenic, As(V), and DMA(V) in the occupational (Sargassum recycling) setting, by age group and sample type. Results based upon stochastic computations (Monte Carlo, n = 10,000).

Age Group (years)	Sample Type	Species	Base Case	Min	P10	P25	Median (P50)	Mean	P75	P90	Max
16–20	Sargassum	Total As	6.62×10^{-8}	1.20×10^{-9}	5.36×10^{-8}	9.84×10^{-8}	1.98×10^{-7}	2.68×10^{-7}	3.59×10^{-7}	5.72×10^{-7}	2.06×10^{-6}
16–20	Sargassum	As(V)	2.64×10^{-8}	3.28×10^{-10}	1.99×10^{-8}	3.73×10^{-8}	7.15×10^{-8}	9.61×10^{-8}	1.31×10^{-7}	2.05×10^{-7}	7.93×10^{-7}
16–20	Sargassum	DMA(V)	3.18×10^{-7}	9.93×10^{-9}	2.17×10^{-7}	4.30×10^{-7}	8.82×10^{-7}	1.24×10^{-6}	1.68×10^{-6}	2.73×10^{-6}	1.08×10^{-5}
16–20	Compost	Total As	6.49×10^{-8}	1.06×10^{-9}	4.49×10^{-8}	7.86×10^{-8}	1.51×10^{-7}	1.98×10^{-7}	2.73×10^{-7}	4.18×10^{-7}	1.48×10^{-6}
16–20	Compost	As(V)	3.21×10^{-8}	6.40×10^{-10}	2.21×10^{-8}	4.01×10^{-8}	7.61×10^{-8}	9.99×10^{-8}	1.37×10^{-7}	2.09×10^{-7}	6.61×10^{-7}
16–20	Compost	DMA(V)	1.59×10^{-7}	2.70×10^{-9}	1.05×10^{-7}	1.85×10^{-7}	3.54×10^{-7}	4.69×10^{-7}	6.46×10^{-7}	9.89×10^{-7}	3.00×10^{-6}
16–20	Biochar	Total As	2.26×10^{-7}	3.36×10^{-9}	1.26×10^{-7}	2.28×10^{-7}	4.41×10^{-7}	5.91×10^{-7}	8.10×10^{-7}	1.26×10^{-6}	4.47×10^{-6}
16–20	Biochar	As(V)	1.01×10^{-7}	1.48×10^{-9}	5.40×10^{-8}	9.96×10^{-8}	1.93×10^{-7}	2.58×10^{-7}	3.54×10^{-7}	5.50×10^{-7}	1.51×10^{-6}
16–20	Biochar	DMA(V)	2.41×10^{-7}	2.72×10^{-9}	1.30×10^{-7}	2.39×10^{-7}	4.62×10^{-7}	6.19×10^{-7}	8.59×10^{-7}	1.31×10^{-6}	4.44×10^{-6}
20+	Sargassum	Total As	6.59×10^{-7}	2.94×10^{-8}	5.56×10^{-7}	1.05×10^{-6}	2.06×10^{-6}	2.83×10^{-6}	3.79×10^{-6}	6.09×10^{-6}	2.22×10^{-5}
20+	Sargassum	As(V)	2.63×10^{-7}	5.78×10^{-9}	2.05×10^{-7}	3.86×10^{-7}	7.52×10^{-7}	1.00×10^{-6}	1.36×10^{-6}	2.14×10^{-6}	9.02×10^{-6}
20+	Sargassum	DMA(V)	3.17×10^{-6}	6.43×10^{-8}	2.21×10^{-6}	4.39×10^{-6}	9.18×10^{-6}	1.30×10^{-5}	1.74×10^{-5}	2.88×10^{-5}	1.13×10^{-4}
20+	Compost	Total As	6.46×10^{-7}	1.61×10^{-8}	4.53×10^{-7}	8.30×10^{-7}	1.61×10^{-6}	2.07×10^{-6}	2.81×10^{-6}	4.36×10^{-6}	1.32×10^{-5}
20+	Compost	As(V)	3.20×10^{-7}	8.31×10^{-9}	2.29×10^{-7}	4.21×10^{-7}	8.01×10^{-7}	1.04×10^{-6}	1.42×10^{-6}	2.19×10^{-6}	7.03×10^{-6}
20+	Compost	DMA(V)	1.58×10^{-6}	5.39×10^{-8}	1.08×10^{-6}	1.98×10^{-6}	3.77×10^{-6}	4.92×10^{-6}	6.82×10^{-6}	1.03×10^{-5}	3.70×10^{-5}
20+	Biochar	Total As	2.25×10^{-6}	5.01×10^{-8}	1.31×10^{-6}	2.43×10^{-6}	4.68×10^{-6}	6.20×10^{-6}	8.38×10^{-6}	1.33×10^{-5}	4.51×10^{-5}
20+	Biochar	As(V)	1.01×10^{-6}	3.27×10^{-8}	5.45×10^{-7}	1.04×10^{-6}	2.04×10^{-6}	2.68×10^{-6}	3.65×10^{-6}	5.68×10^{-6}	2.06×10^{-5}
20+	Biochar	DMA(V)	2.40×10^{-6}	4.44×10^{-8}	1.34×10^{-6}	2.52×10^{-6}	4.87×10^{-6}	6.50×10^{-6}	8.91×10^{-6}	1.39×10^{-5}	4.92×10^{-5}

Table III.9. Distribution Metrics for Total Lifetime Cancer Risk

Scenario	Min	P10	P25	Median (P50)	Mean	P75	P90	Max	Base Case
Workers: Sargassum Removal and Handling Operations	1.07×10^{-6}	3.81×10^{-6}	5.27×10^{-6}	7.48×10^{-6}	8.39×10^{-6}	1.00×10^{-5}	1.41×10^{-5}	3.16×10^{-5}	3.40×10^{-6}
Workers: Compost Handling and Application	5.44×10^{-7}	3.04×10^{-6}	4.10×10^{-6}	5.72×10^{-6}	6.17×10^{-6}	7.74×10^{-6}	9.96×10^{-6}	2.52×10^{-5}	3.33×10^{-6}
Workers: Biochar Handling and Application	1.79×10^{-6}	8.53×10^{-6}	1.17×10^{-5}	1.66×10^{-5}	1.84×10^{-5}	2.34×10^{-5}	3.06×10^{-5}	6.95×10^{-5}	1.16×10^{-5}
Biogas System Exposure (Filtered)	2.49×10^{-7}	5.63×10^{-7}	6.89×10^{-7}	8.65×10^{-7}	9.09×10^{-7}	1.09×10^{-6}	1.32×10^{-6}	2.44×10^{-6}	6.43×10^{-7}
Biogas System Exposure (Unfiltered)	2.46×10^{-7}	5.60×10^{-7}	6.87×10^{-7}	8.63×10^{-7}	9.07×10^{-7}	1.09×10^{-6}	1.31×10^{-6}	2.43×10^{-6}	6.40×10^{-7}
Children: Beach Recreational Exposure (No Pica)	9.86×10^{-6}	2.54×10^{-5}	3.25×10^{-5}	4.33×10^{-5}	4.78×10^{-5}	5.81×10^{-5}	7.55×10^{-5}	2.71×10^{-4}	1.84×10^{-5}
Children: Beach Recreational Exposure (Pica Behavior)	1.19×10^{-5}	2.93×10^{-5}	3.70×10^{-5}	4.78×10^{-5}	5.23×10^{-5}	6.31×10^{-5}	8.06×10^{-5}	2.79×10^{-4}	2.11×10^{-5}

Figure III.1. Total Lifetime Risk Across all Exposure Pathways for Each Scenario.



CHAPTER IV

SUMMARY, CONCLUSIONS, & RECOMMENDATIONS

CHAPTER IV

SUMMARY, CONCLUSIONS, & RECOMMENDATIONS

IV.1 Summary and Conclusions

This report evaluated the arsenic implications of recycling sargassum through two linked studies. The first measured total arsenic and arsenic speciation across recycled products and natural sargassum. It found that arsenic mobility and form vary substantially by pathway: biochar held the most arsenic but released almost none by leaching, fresh sargassum released more than half of its arsenic into solution, and biogas processing produced arsine, a highly toxic gaseous form. Arsenate was generally the dominant species, with smaller and variable fractions of methylated and organic forms.

The second study translated these concentrations into human-health risk. Non-cancer risks stayed below thresholds across recreational and occupational, although more research is needed to further evaluate biogas given the release of highly toxic arsine gas. Lifetime cancer risk was highest for children recreating on sargassum-covered beaches, on the order of 10^{-5}, exceeding the occupational scenarios, with oral exposure as the dominant route. More research is recommended to evaluate the dermal pathway given the partition of arsenic in sargassum towards DMA(V) which studies using liquids demonstrate high sorption through skin. Taken together, the two studies show that both the recycling pathway and the exposure context determine the magnitude and route of arsenic risk, with recreational risk settings illustrating potentially higher lifetime cancer risks relative to occupational settings focused on recycling of sargassum.

IV.2 Recommendations

The results suggest several directions worth considering. Reducing direct contact with stranded sargassum in recreational settings, particularly for children, appears to be the most direct way to lower the highest risks observed. For processing operations, biogas systems may warrant gas-phase controls given the formation of arsine, while the biochar and compost pathways showed comparatively low leaching. Further work would help confirm these patterns, including speciation and risk data from additional product batches, and evaluation of how underlying soils and end-use conditions affect arsenic transfer to crops in tropical and subtropical settings. Additionally, research is recommended to further evaluate the non-cancer risks associated with arsine gas produced during recycling as biogas. Studies are also needed to further evaluate potential dermal arsenic sorption directly from sargassum by considering differing arsenic species.

IV.3 Practical Benefits for End Users

The Florida Department of Environmental Protection (FDEP) is developing waste-management guidance specific to sargassum and seaweed strandings. Currently the FDEP is considering whether to classify sargassum as yard waste. The arsenic content of the material may require stricter waste management strategies. Because this project characterizes both the total arsenic and the specific arsenic forms that leach or volatilize from each recycling pathway, its results give FDEP and solid-waste managers a basis for rule-making on how sargassum and its recycled products can be handled, composted, and reused.

The recycling-products study shows that reuse pathways differ substantially in how they hold or release arsenic. Biochar retained the highest total arsenic but released very little through leaching (under one percent by SPLP), whereas fresh sargassum released more than half of its arsenic into solution. Biogas production converted much of the arsenic into arsine gas, a highly toxic form. For an end user choosing a reuse route, this points toward biochar and compost as lower-leaching options and flags biogas as a

pathway that requires gas-phase controls.

The risk assessment translates these concentrations into human-health terms across recreational and occupational settings. Non-cancer risks remained below thresholds for every scenario, although more work is needed to evaluate biogas as non-cancer inhalation of arsine should be further characterized. The highest cancer risk among the scenarios evaluated were children recreating on sargassum-covered beaches, on the order of 10^{-5}. Oral exposure was the dominant contributor. For managers and operators, this supports reducing direct contact with sargassum in recreational settings and applying appropriate handling controls when processing sargassum into products.

From a broader perspective, many subtropical and tropical regions including South Florida and the Caribbean islands sit on karst limestone soils that are poor in organic matter, and sargassum-derived compost may be one of the few locally available soil amendments for growing food crops. By clarifying which recycled forms carry higher or lower arsenic risk, this work can be used by the FDEP to assess management strategies for sargassum and also helps additional partners such as the Caribbean Agricultural Research and Development Institute (CARDI) evaluate the conditions under which sargassum-based inputs can be used safely for agriculture.

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Appendix A

Supplemental Material for Chapter II

Appendix A

Supplemental Material for Chapter II

Table S-1. List of Samples and Sample Collection, Processing, and Analysis Dates for Each Sample

Solid Samples					
ID	**Description**	**Date Sargassum Collected**	**Date Sifted**	**Date dropped off at lab**	**Date Analyzed for Total As and Species**
BS-240313	Biochar Solid	3/13/2024	7/2/2024	8/13/2024	8/29/2024 – 9/9/2024
BS-240723	Biochar Solid	7/2/2024	7/23/2024	8/13/2024	8/29/2024 – 9/9/2024
BS-240806	Biochar Solid	7/23/2024	8/6/2024	8/13/2024	8/29/2024 – 9/9/2024
CS-240313	Compost Solid	3/13/2024	7/2/2024	8/13/2024	8/29/2024 – 9/9/2024
CS-240718	Compost Solid	3/13/2024	7/18/2024	8/13/2024	8/29/2024 – 9/9/2024
CS-240930	Compost Solid	7/2/2024	9/30/2024	11/6/2024	11/6/2024 – 12/3/2024
CS-241016	Compost Solid	7/30/2024	10/16/2024	11/6/2024	11/6/2024 – 12/4/2024
DS- 240723	Dried Sargassum Solid	7/2/2024	7/23/2024	8/13/2024	8/29/2024 – 9/9/2024
DS-240806	Dried Sargassum Solid	7/23/2024	8/6/2024	8/13/2024	8/29/2024 – 9/9/2024
DS-240827	Dried Sargassum Solid	7/30/2024	8/27/2024	11/6/2024	11/6/2024 – 12/3/2024
GS- 240702	Sargassum Solid	7/2/2024	7/2/2024	8/13/2024	8/29/2024 – 9/9/2024
GS-240718	Sargassum Solid	7/18/2024	7/18/2024	8/13/2024	8/29/2024 – 9/9/2024
GS-240730	Sargassum Solid	7/30/2024	7/30/2024	8/13/2024	8/29/2024 – 9/9/2024

Table S-1. Continued

Liquid Samples					
ID	**Description**	**Date Sargassum Collected**	**Date SPLP Performed**	**Date dropped off at lab**	**Date Analyzed for Total As and Species**
BL-240313	Biochar Liquid	7/2/2024	7/2/2024	8/13/2024	8/29/2024 – 9/9/2024
BL-240723	Biochar Liquid	7/2/2024	7/23/2024	8/13/2024	8/29/2024 – 9/9/2024
BL-240806	Biochar Liquid	7/23/2024	8/6/2024	8/13/2024	8/29/2024 – 9/9/2024
CL-240313	Compost Liquid	3/13/2024	7/2/2024	8/13/2024	8/29/2024 – 9/9/2024
CL-240718	Compost Liquid	3/13/2024	7/18/2024	8/13/2024	8/29/2024 – 9/9/2024
CL-240930	Compost Liquid	7/2/2024	9/30/2024	11/6/2024	11/6/2024 – 12/3/2024
CL-241016	Compost Liquid	7/30/2024	10/16/2024	11/6/2024	11/6/2024 – 12/3/2024
DL-240723	Dried Sargassum Liquid	7/2/2024	7/23/2024	8/13/2024	8/29/2024 – 9/9/2024
DL-240806	Dried Sargassum Liquid	7/23/2024	8/6/2024	8/13/2024	8/29/2024 – 9/9/2024
DL-240827	Dried Sargassum Liquid	7/30/2024	8/27/2024	11/6/2024	11/6/2024 – 12/3/2024
GL-240702	Sargassum Liquid	7/2/2024	7/2/2024	8/13/2024	8/29/2024 – 9/9/2024
GL-240718	Sargassum Liquid	7/18/2024	7/18/2024	8/13/2024	8/29/2024 – 9/9/2024
GL-240730	Sargassum Liquid	7/30/2024	7/30/2024	8/13/2024	8/29/2024 – 9/9/2024
Z-240702	Blank Liquid	–	7/2/2024	8/13/2024	8/29/2024 – 9/9/2024

Table S-1. Continued

Gaseous Samples					
ID	**State**	**Sample Description**	**Date Collected**	**Date Dropped Off**	**Date Analyzed for Total As and Species**
F-01	Solid (Charcoal)	Gas 1 - Filtered	5/15/2025	5/16/2025	6/3/2025
F-02	Solid (Charcoal)	Gas 2 - Filtered	5/15/2025	5/16/2025	6/3/2025
F-03	Solid (Charcoal)	Gas 3 - Filtered	5/15/2025	5/16/2025	6/3/2025
UF-01	Solid (Charcoal)	Gas 1 – Un-Filtered	5/15/2025	5/16/2025	6/3/2025
UF-02	Solid (Charcoal)	Gas 2 -Un Filtered	5/15/2025	5/16/2025	6/3/2025
UF-03	Solid (Charcoal)	Gas 3 – Un - Filtered	5/15/2025	5/16/2025	6/3/2025
Blank1	Solid (Charcoal)	Gas Filtered Blank	5/15/2025	5/16/2025	6/3/2025
Blank2	Solid (Charcoal)	Gas Unfiltered Blank	5/15/2025	5/16/2025	6/3/2025
DIS-01	Liquid	Digestate 1	5/15/2025	5/16/2025	6/3/2025
DIS-02	Liquid	Digestate 2	5/15/2025	5/16/2025	6/3/2025
DIS-03	Liquid	Digestate 3	5/15/2025	5/16/2025	6/3/2025
SUB-01	Solid(Slurry)	Substrate – 1	5/15/2025	5/16/2025	6/3/2025
SUB-02	Solid (Slurry)	Substrate -2	5/15/2025	5/16/2025	6/3/2025
SUB-03	Solid (Slurry)	Substrate - 3	5/15/2025	5/16/2025	6/3/2025

Table S-2. XRF Measurements for sample days 1 2 and 3 (July 2nd, July18th and July 30th, 2025).

Sample 1 Metals	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Fe	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Rb	24	21	28	26	30	24	-	17	21	33	24	25	25	19	30	24
Sr	318	202	324	273	230	295	216	420	354	290	290	259	274	239	230	295
Zr	34	30	27	32	49	57	-	43	48	36	55	49	37	48	49	57
Mo	51	42	58	41	65	83	70	50	32	67	62	68	53	61	65	83
As	-	-	-	-	-	-	-	-	-	-	-	30	32	-	-	-
Ti	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sb	-	-	-	-	756	-	-	-	-	-	-	-	-	756	-	-
Zn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Pb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sample 2 Metals	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Zn	22	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Rb	26	22	27	19	27	39	28	21	28	30	24	29	44	22	29	-
Sr	306	306	337	261	381	311	307	321	250	337	239	273	365	356	276	337
Zr	43	53	62	55	56	80	65	56	46	51	47	69	73	46	45	41
Mo	60	53	54	80	78	117	84	82	78	56	65	117	120	62	75	66
Ti	-	-	16614	-	-	-	-	-	-	-	-	-	-	-	-	-
As	-	-		27	-	-	-	-	-	-	-	-	-	-	19	-
Pb	-	-	-	-	-	-	-	24	-	-	-	-	-	-	-	-
Sample 3 Metals	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Zn	16	-	-	-	-	-	-	-	-	-	-	28	-	-	-	-
Pb	13	-	-	-	-	-	-	-	19	-	-	-	-	-	-	-
Rb	30	33	38	37	33	21	38	32	29	40	27	18	23	22	34	40
Sr	327	335	319	313	387	378	330	320	251	296	302	452	254	305	322	316
Zr	46	61	56	62	65	59	53	79	65	67	59	69	57	63	74	54
Mo	73	86	88	64	122	92	101	121	104	122	99	100	88	113	103	92
As	33	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Sb	-	-	-	-	-	-	-	-	235	-	-	-	-	-	-	-

Table S-3. Rainfall during the preparation of dry sargassum samples

Sample Set up	Date	Rainfall Gauge (cm)	Total Rainfall (during 2 weeks)
DS-1	7/2/24	0.00 (set up)	1.25
	7/7/24	0.98	
	7/16/24	0.27	
DS-2	7/23/24	0.27 (set up)	4.87
	7/30/24	1.76	
	8/2/24	0.03	
DS-3	8/6/24	2.81 (set up)	
	8/13/24	0.99	4.88
	8/20/24	2.05	
	8/27/24	1.84	

Table S-4. Synthetic Precipitation Leaching Procedure (SPLP) pH measurements for leachate samples where, BL represents biochar leachate, CL compost leachate, DL dried sargassum leachate, GL fresh sargassum leachate, and ZL a blank sample.

Sample ID	pH before tumbling	pH after 18 hours of tumbling
BL-240313	4.25	7.32
BL-240723	4.35	12.14
BL-240806	4.16	13.41
CL-240313	4.27	8.62
CL-240718	4.36	8.75
CL-240930	4.19	8.42
CL-241016	4.24	8.56
DL- 240723	4.28	6.89
DL-240806	4.26	6.77
DL-240827	4.32	6.93
GL- 240702	4.31	7.56
GL-240718	4.13	7.62
GL-240730	4.17	7.29
BL-240313	4.18	4.36

Table S-5. Dunn's post hoc test results for pairwise comparisons of total arsenic concentrations among sargassum-derived materials. (A) Raw sample pairwise comparisons (B) Environmental sample pairwise comparisons.

***(A) Raw samples** — Kruskal–Wallis p = 0.06*

	Fresh Sargassum	**Dry Sargassum**	**Compost**	**Biochar**	**Substrate**
Fresh Sargassum	—	0.732	0.855	0.346	**0.049**
Dry Sargassum		—	0.855	0.198	0.103
Compost			—	0.233	0.054
Biochar				—	**0.004**
Substrate					—

(B) Environmental samples — Kruskal–Wallis p = 0.02

	Fresh Sargassum	**Dry Sargassum**	**Compost**	**Biochar**	**Digestate**
Fresh Sargassum	—	0.170	**0.037**	**0.002**	0.391
Dry Sargassum		—	0.536	0.072	0.607
Compost			—	0.192	0.242
Biochar				—	**0.021**
Digestate					—

***Biogas (gas form):** Filtered vs. Unfiltered, Wilcoxon rank-sum p = 0.10.*

*Note: Values are two-sided, unadjusted Dunn's test p-values (FSA::dunnTest, method = "none") following a significant or marginal Kruskal–Wallis result. **Bold** = $p < 0.05$; italic = marginal ($0.05 \leq p < 0.10$). Diagonal (—) and lower-triangle cells are not applicable*

Figure S-1. Tukey HSD Comparisons – Raw Samples

Figure S-2. Tukey HSD Comparisons – Environmental Samples

Table S-6 (A) Arsenic species and total arsenic concentrations for raw samples.

Sample Type	Sample ID	As (III)	MMA(III)	DMA(III)	MMA(V)	AsC	DMA(V)	As(V)	AsB	TMAO(V)	Total As
Biochar (mg/kg)	BS-240313	ND[a]	ND	ND	ND	1.413	0.747	12.112	ND	ND	17.20
Biochar (mg/kg)	BS-240723	ND	ND	ND	0.801	1.268	5.759	81.694	1.23	ND	104.82
Biochar (mg/kg)	BS-240806	ND	ND	ND	ND	11.000	4.444	98.656	ND	ND	141.84
Compost (mg/kg)	CS-240313	ND	ND	ND	0.414	0.337	1.622	9.161	ND	ND	12.87
Compost (mg/kg)	CS-240718	ND	ND	ND	0.162	0.387	1.004	8.951	ND	ND	12.06
Compost (mg/kg)	CS-240930	1.63	ND	ND	ND	1.377	4.259	38.858	2.39	2.53	45.48
Compost (mg/kg)	CS-241016	ND	ND	ND	0.597	1.110	2.740	24.229	ND	ND	30.53
Dry Sargassum (mg/kg)	DS-240723	0.58	ND	ND	0.985	7.742	15.062	41.807	3.59	0.35	75.38
Dry Sargassum (mg/kg)	DS-240806	0.12	ND	ND	ND	3.571	0.361	8.189	0.13	ND	13.24
Dry Sargassum (mg/kg)	DS-240827	0.62	ND	ND	0.131	0.958	2.248	6.624	ND	ND	10.91
Fresh Sargassum (mg/kg)	GS-240702	0.10	ND	ND	0.203	0.425	3.610	16.886	1.11	0.16	19.93
Fresh Sargassum (mg/kg)	GS-240718	0.68	ND	ND	0.207	0.864	3.368	16.244	1.11	ND	19.82
Fresh Sargassum (mg/kg)	GS-240730	0.13	ND	ND	0.144	0.367	4.334	10.588	1.00	ND	15.15
Substrate (µg/L)	SUB-01	0.38	ND	ND	1.115	ND	ND	1.353	ND	ND	2.61
Substrate (µg/L)	SUB-02	0.41	ND	ND	1.184	ND	ND	1.436	ND	ND	3.60
Substrate (µg/L)	SUB-03	0.39	ND	ND	1.144	ND	ND	1.387	ND	ND	3.36

[a]ND=Not detected. See Table 1 in main text for detection limits.

Table S-6(B) Arsenic species and total arsenic concentrations for environmental form (from SPLP test plus biogas digestate)

Sample Type	Sample ID	As (III)	MMA(III)	DMA(III)	MMA (V)	AsC	DMA(V)	As(V)	AsB	TMAO(V)	Total As
Biochar (μg/L)	BL-240313	3.90	ND	ND	0.274	ND	ND	ND	ND	ND	5.08
Biochar (μg/L)	BL-240723	0.59	ND	ND	0.000	0.707	ND	2.373	1.72	ND	5.43
Biochar (μg/L)	BL-240806	1.41	ND	ND	1.050	1.230	ND	4.557	ND	ND	8.57
Compost (μg/L)	CL-240313	8.94	ND	ND	ND	ND	ND	18.041	ND	ND	30.77
Compost (μg/L)	CL-240718	ND	ND	ND	ND	0.190	0.932	33.343	ND	ND	33.24
Compost (μg/L)	CL-240930	0.93	ND	ND	ND	ND	0.170	37.901	0.713	0.806	42.8
Compost (μg/L)	CL-241016	5.19	ND	ND	0.451	0.288	0.888	37.047	ND	ND	46.0
Dry Sargassum (μg/L)	DL-240723	47.62	ND	ND	3.114	14.126	2.250	149.604	14.90	3.48	278.70
Dry Sargassum (μg/L)	DL-240806	1.43	ND	ND	0.235	4.686	0.000	31.949	0.60	ND	38.70
Dry Sargassum (μg/L)	DL-240827	2.01	ND	ND	0.000	0.277	0.276	25.872	ND	ND	32.3
Fresh Sargassum (μg/L)	GL-240702	5.95	ND	ND	0.86	0.19	1.71	129.05	15.15	0.42	136.78
Fresh Sargassum (μg/L)	GL-240718	1.86	ND	ND	0.64	1.56	1.12	110.69	11.49	3.12	120.70
Fresh Sargassum (μg/L)	GL-240730-1	17.78	ND	ND	3.16	5.43	4.61	322.94	44.60	12.56	446.69
Digestate (μg/L)	DIS-01	19.03	ND	ND	10.964	ND	ND	58.638	ND	ND	96.5
Digestate (μg/L)	DIS-02	17.09	ND	ND	11.975	ND	ND	54.536	ND	ND	97.3
Digestate (μg/L)	DIS-03	20.21	ND	ND	8.477	ND	ND	61.600	ND	ND	103.4

Table S-6 (C) Arsenic species and total arsenic concentrations for gas samples (from biogas system)

Sample Type	Sample ID	As (III)	MMA(III)	DMA(III)	MMA (V)	AsC	DMA(V)	As(V)	AsB	TMAO(V)	AsH_3	Total As
Unfiltered Biogas ($\mu g/m^3$)	UF-01	ND	ND	ND	ND	ND	ND	ND	ND	ND	6.452	7.64
Unfiltered Biogas ($\mu g/m^3$)	UF-02	ND	ND	ND	ND	ND	ND	ND	ND	ND	7.115	8.57
Unfiltered Biogas ($\mu g/m^3$)	UF-03	ND	ND	ND	ND	ND	ND	ND	ND	ND	5.765	6.38
Filtered Biogas ($\mu g/m^3$)	F-01	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.539	1.85
Filtered Biogas ($\mu g/m^3$)	F-02	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Filtered Biogas ($\mu g/m^3$)	F-03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Appendix B

Project Administration

Appendix B

Project Administration

Project title: Evaluation of Sargassum Recycling Options through Risk-Based Approaches
Principal Investigator: Dr. Helena Solo-Gabriele, University of Miami, Department of Chemical, Environmental, and Materials Engineering (hmsolo@miami.edu, 305-284-3467)
Lead Doctoral Student: Brittany Mc Intyre, PhD Student, University of Miami (bzm4@miami.edu)
Project website: https://eel.miami.edu/projects/index.html
Project duration: August 1, 2024 to July 31, 2026
Funding: Hinkley Center for Solid and Hazardous Waste Management.
Abstract: Sargassum's high arsenic concentrations have raised concerns about health impacts when repurposed for potential beneficial uses. Potential health impacts depend upon the speciation or specific chemical form of the arsenic, with inorganic forms more toxic than organic forms. The goal of this study is to assess the risk of arsenic from Sargassum in different recycling scenarios. Specifically, the objectives of this study are to 1) evaluate arsenic levels (total and speciation) in products made from recycled Sargassum (compost, biochar, biogas), and to use this information 2) to determine risks to humans from environmental exposures. Baseline risks will be assessed when Sargassum is not managed by leaving it on the beach. These baseline risks will be compared to health risks associated with its reuse as either compost, biochar or biogas. Through this study we will produce dried Sargassum to simulate beach conditions and compost. We will collaborate with commercial vendors to provide biochar (BiocharNow Inc.) and biogas digestate (Rum & Sargassum Inc.). Samples will be analyzed for total arsenic and arsenic species (arsenite, arsenate, monomethylarsonic acid, dimethylarsinic acid, arsenobetaine, and others). Results from the arsenic analysis will be combined with exposure assessments to compute risk. The results of this study can be used to identify beneficial re-use options that are acceptable from a human health perspective.
Key words: Sargassum, seaweed, recycling, beach, arsenic, arsenic species, risk assessment

Metrics Reporting

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1. Research publications from this Hinkley Center project.

Journal Articles

- Mc Intyre, B., Cai, Y., Liu, G., Henry, L., Abdool-Ghany, A. A., Li, J., & Solo-Gabriele, H. M. (2026). Evaluation of Total and Species Distributions of Arsenic in Sargassum Recycling Products. *Waste Management* (Under Review).
- Mc Intyre, B., Cerna, M., Puente, I., Li, J., & Solo-Gabriele, H. M. (2026). Evaluation of Sargassum Recycling Options through Risk-Based Approaches. (In Preparation).
- Mc Intyre, B., Cerna, M., Abdool-Ghany, A. A., Liu, G., Cai, Y., Ferguson, A., … & Solo-Gabriele, H. (2026). Does Sargassum on Beaches Pose Health Risks to Children Through Arsenic Exposure During Recreational Play? *Exposure and Health*, 18(2), 24.

Abstracts

- **2026 Solid Waste Association of North America (SWANA) Conference** (poster)
  - **Title:** Evaluation of Total and Species Distributions of Arsenic in Sargassum Recycling Products

- **Abstract:** The recycling potential of sargassum has been questioned due to its elevated arsenic (As) levels and its potential toxicity which depends upon As species. This study evaluated total arsenic concentrations and speciation in products derived from recycled sargassum, including compost, biochar, and biogas, to provide data for assessing arsenic risks from these materials. Additionally, the study evaluated two additional categories of sargassum, fresh and dry, as baseline references of sargassum under natural beach conditions. All sample types were analyzed for arsenic in their "raw" form (as a solid except for the substrate for biogas) and in their "environmental" form. Environmental forms, which represent possible arsenic releases from the recycled products, were assessed through the Synthetic Precipitation Leaching Procedure (SPLP) for all evaluated categories except for biogas for which the liquid digestate and gas samples were analyzed instead. Results revealed that biochar retained the highest total arsenic concentrations in the solid phase, with arsenate (As^V) as the dominant species, yet exhibited minimal arsenic leaching (<1%) by SPLP. Compost and dry sargassum showed moderate leachability and a broader distribution of arsenic species, including small fractions of lower toxicity organoarsenicals such as dimethylarsinic acid (DMA^V) and arsenobetaine. Fresh sargassum exhibited the highest leachability, with over 50% of total arsenic mobilized into solution, primarily as As^V. Arsine gas, a highly toxic form of arsenic, was the predominant form of arsenic in biogas. These findings demonstrated that arsenic mobility and toxicity vary significantly across recycled waste management scenarios.

- **2025 Society for Risk Analysis Annual Meeting** (poster)
  - **Title:** Does Sargassum on Beaches Pose Health Risks to Children Through Arsenic Exposure During Recreational Play?
  - **Abstract:** Sargassum seaweed (Sargassum fluitans and Sargassum natans) bioaccumulates arsenic, an element that is toxic at low concentrations. With increasing sargassum strandings attributed to warmer oceans and climate-driven shifts in winds/currents, and increased nutrient availability, concerns now arise regarding potential health impacts on vulnerable populations, especially children. The objective of this study was to employ the risk assessment framework (hazard identification, exposure analysis, dose-response evaluation, and risk characterization) to assess non-cancer and cancer health risks from arsenic for children across different age groups who play at beaches impacted by sargassum. Risk simulations using a Monte Carlo approach were based upon ranges of arsenic levels measured in sargassum at beaches in southeast Florida (9.9 to 64.3 mg/kg in sargassum). Exposure analysis considered oral, dermal, and inhalation routes, accounting for potential contacts with beach water, sand, and sargassum that contain arsenic. Given the limited data on the release of arsenic from sargassum, samples of fresh and dried sargassum were analysed in this study using the Simulated Precipitation Leachate Protocol (SPLP). Results showed that non-cancer risks across all exposure routes were negligible with hazard quotients less than one. For cancer, low increased risks (10^{-4}) were driven by dermal exposures. Exposure through particulate inhalation was considered negligible and exposure through non-dietary ingestion contributed towards low increased cancer risks (10^{-4}) for children who engaged in pica activity (a condition associated with the intentional consumption of non-food items). Results from SPLP tests showed that between 7 and 59% of the arsenic is released from fresh and dried sargassum, supporting that the arsenic may be in an accessible form for exposure. Overall results underscore the cumulative nature of risks across exposure routes and age groups, necessitating a comprehensive understanding of beachgoers' behaviors, fate of arsenic during sargassum decay, and confirmation of dermal uptake

rates of arsenic through environmental media. The findings advocate for enhanced beach hygiene practices, public health awareness, and potential sargassum removal to reduce arsenic exposures.

2. Research presentations resulting from this Hinkley Center project.

- "Evaluation of Total and Species Distributions of Arsenic in Sargassum Recycling Products." 2026 Solid Waste Association of North America (SWANA) Conference. (Poster presentation by Brittany Mc Intyre).
- "Does Sargassum on Beaches Pose Health Risks to Children Through Arsenic Exposure During Recreational Play?" 2025 Society for Risk Analysis Annual Meeting. (Poster presentation by Brittany Mc Intyre).
- Sargassum Use in Caribbean Farming, Caribbean Agricultural Research and Development 2025 (Oral Presentation) 2025

3. List who has referenced or cited your publications from this project (data from Scopus).

- Gutierrez- Girl MK, Baez López DL, Carballo GA, Ordóñez Murillo MDC (2026) Review of studies on *Sargassum* spp. (Sargassaceae) in Cuba (2011-2026). Environ Sci Ecol: Curr Res 7: 10128

4. How have the research results from this Hinkley Center project been leveraged to secure additional research funding?

- A proposal was submitted to the Conservation, Food & Health Foundation to assess the use of Sargassum in Caribbean farming. This proposal was funded, with an award of $60,000 USD.
- Dr Beneti (Black soldier fly larvae), Seagrant proposal.

5. What new collaborations were initiated based on this Hinkley Center project?

- Collaboration with BiocharNow, led by James Gaspard, focused on creating biochar from Sargassum collected by the University of Miami research team. James Gaspard provided expertise and support in the pyrolysis process, transforming the Sargassum into biochar to assess its potential benefits for environmental management and soil improvement.
- Legena Henry – UWI and Rum&Sargassum. In this collaboration, the research team will be supplied with biodigestate and biogas samples from a rum distillery, which were tested for arsenic levels. This initiative aims to understand the safety and potential applications of byproducts from the rum production process in environmental and agricultural contexts.
- Caribbean Agricultural Research and Development Institute (CARDI). CARDI's extensive farmer network facilitated the collection of crop and soil samples to evaluate the use of Sargassum-derived products, such as fertilizer and compost. Additionally, CARDI offers opportunities to collaborate on future training programs for farmers in the Caribbean, enhancing their knowledge of sustainable practices involving sargassum-based agricultural inputs.

6. How have the results from this Hinkley Center funded project been used by the FDEP or other stakeholders?

- Members of the FDEP have participated in our TAG meetings.Dr. Solo-Gabriele has also met with the FDEP TAG members one-on-one to discuss arsenic and sargassum issues as the FDEP team assesses rule-making for the management of disposed sargassum.

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TAG Meeting Participants

Note: Participation in the TAG meetings does not imply an endorsement of the research.

Meeting 1 (Online), June 21, 2024

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Elizabeth Kelly	Martin County
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Meeting 1 (Online), June 21, 2024 (continued)

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Meeting 2 (Online), March 26, 2025

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Meeting 3 (Online), February 20, 2026

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Meeting 3 (Online), February 20, 2026 (continued)

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