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RESEARCH REVIEW

Potential of hemp (*Cannabis sativa* L.) for paired phytoremediation and bioenergy production

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Abstract

Hemp (*Cannabis sativa* L.) is a multi-use crop that has been investigated for its potential use in phytoremediation of heavy metals, radionuclides, and organic contaminants, and as a feedstock for bioenergy production. A review of research literature indicates that hemp is a suitable crop for phytoremediation, and a competitive option for bioenergy. Coupling phytoremediation and bioenergy production from a single hemp crop is a potential solution to overcoming the economic constraints of phytoremediation projects. The current challenge is ensuring that the extracted contaminants are not introduced into the consumer marketplace. After several decades of limited research on hemp in the United States, the purpose of this review is to identify the knowledge available for hemp applications in phytoremediation or in production of bioenergy, and if and how those two purposes have been combined. The literature shows that hemp growth has been demonstrated successfully at the field scale for phytoremediation and in several bioenergy conversion technologies. Little is known about the fate of contaminants during hemp growth or during post-harvest processing, especially the relationships between hemp genetics, metabolomics, and contaminant partitioning. Complicating the understanding is the expectation that contaminant fate will be dependent on the contaminant type, the concentration in the material, and the processing methods. Before hemp from phytoremediation applications can be used for bioenergy, the fractionation of heavy metals, radionuclides, and/or organic compounds during transesterification, anaerobic digestion, fermentation, and/or combustion of hemp must be evaluated.

KEYWORDS

biodiesel, bioethanol, biogas, combined heat and power, phytoextraction

1 | INTRODUCTION

The consistent rise in global population, and associated consumption of resources, has led to a steady decrease in the available arable land in developed countries (Evangelou et al., 2015; Kanianska, 2016). In addition to the decrease in arable land, there has been a simultaneous increase in greenhouse gases (GHG) from anthropogenic food production and industrial operations (Conesa et al., 2012; Evangelou et al., 2015; Lehmann, 2007). As a result of these events, there have been increased efforts to identify and improve sustainable practices through the use of alternative crops. Hemp has long been recognized internationally as a valuable fiber and grain crop, and has been reported as a candidate for more sustainable production systems. Legal restrictions have prevented hemp production in the United States for several decades. With the recent re-legalization of hemp production in the United States (Establishment of a Domestic Hemp Production Program, 2019), there has been a resurgence in research evaluating hemp's potential to alleviate issues involving agriculture and fuel production.

Two subjects of interest for mitigating the reduction of arable land and the GHG emissions from fossil fuels are phytoremediation and renewable energy production. Hemp (*Cannabis sativa* L.) has been proposed for use in both practices. The major issue with implementing phytoremediation projects arises when attempting to scale-up to field conditions; the majority of phytoremediation research has been performed with potted plants, often in controlled greenhouse settings. Successful phytoremediation field trials with hemp have been performed, as reported by Di Candilo et al. (2004), Linger et al. (2002), Mihoc et al. (2012), and Soudek et al. (2006). Also, while not cultivated by the researchers, data from Ahmad et al. (2016) came from hemp collected from a field site. This literature indicates that using hemp for phytoremediation in real-world scenarios is possible, however, there are still major gaps in understanding how to implement and manage phytoremediation projects, primarily the effectiveness of phytoremediation by hemp over multiple growing seasons.

Because of the controversial status of hemp in the past (particularly in the United States), there has been little work done to develop and improve hemp genetics and applications, including phytoremediation. The purpose of this study was to conduct a thorough review of what was previously known and what new information is available with regard to hemp for both phytoremediation and bioenergy production. Based on the results, a logical basis for combining the processes into implementable systems, that do not aggravate current environmental issues, can be established. Understanding the efficacy of hemp for various scenarios will facilitate the design of new field studies to address major knowledge gaps.

1.1 | Phytoremediation economics

Phytoremediation is the process of using plants and/or soil microbes to reduce the effects of environmental contaminants (Evangelou et al., 2015; Greipsson, 2011), and it has been of particular interest as a cost-effective and environmentally safe method for rehabilitation of contaminated soils. Major contaminants of concern include heavy metals, radionuclides, pesticides, explosives residues, and other organic compounds (Kumar et al., 2017; Marmiroli et al., 2007; Salt et al., 1998). Traditional methods for soil restoration include physical excavation of contaminated soil, chemical stabilization of contaminants, and simple non-biological processes, such as incineration, to sequester or volatilize contaminants from soil. While these methods are fast and effective, they are costly and environmentally invasive (Conesa et al., 2012; Gomes, 2012; Gong et al., 2018). Phytoremediation technologies, such as phytostabilization, phytodegradation, phytovolatilization, and phytoextraction, require longer periods of time to achieve the same levels of decontamination as traditional methods and cause less environmental disturbance; phytoremediation methods also allow for the concentration of toxins into smaller, more manageable volumes of material for disposal (Koźmińska et al., 2018; United States Environmental Protection Agency, 1999).

The major feasibility constraint of phytoremediation is the utilization of the contaminated biomass after harvest. Hyperaccumulators, plants that exceed an accumulation threshold of 1000 μg g^{-1} dry weight, are typically annual plants with minimal aboveground biomass growth and shallow root penetration depth (Brooks et al., 1977). This combination of limited aboveground biomass and root penetration depth poses a challenge for treatment of large soil volumes and for harvest. Many hyperaccumulators, such as *Thlaspi caerulescens* (Küpper et al., 1999) and *Arabidopsis helleri* (Küpper et al., 2000), have little to no economic value to provide a return on biomass harvest costs. One proposed solution to improve the economics of phytoremediation is the paired production of bioenergy. Hemp has been evaluated as a feedstock for liquid biofuel, biogas, bioethanol, and combustion (Finnan & Styles, 2013; Rice, 2008). Costs of growing hemp for bioethanol are similar to those of kenaf (*Hibiscus cannabinus*), and higher than those for switchgrass (*Panicum virgatum*) and sorghum (*Sorghum bicolor*). The revenue generated from hemp is estimated to be 3.64 times its growing cost, whereas the revenues generated from kenaf, switchgrass, and sorghum are only 1.25, 1.63, and 2.88 times their growing costs, respectively (Das et al., 2017).

Growing hemp for phytoremediation has the potential to alleviate many of the current challenges with hyperaccumulators: hemp has substantial aboveground biomass production, a deep root system, and options for value-added industrial products that do not introduce toxins into the consumer marketplace (Linger et al., 2002; Small, 2015; Small & Marcus, 2002). Bioenergy production from hemp has been proposed for utilizing the contaminated biomass, although the fate of contaminants after processing is not well understood. The major factors that impact the usability of phytoremediation hemp biomass for energy include the contaminant type and concentration in the biomass, the type of bioenergy production, and regulatory standards/guidelines on acceptable product quality.

1.2 | Hemp as a crop

Hemp is an herbaceous annual plant that has a 4- to 8-month life cycle, is naturally dioecious, and reproduces via seed propagation (Clarke & Watson, 2007; Ehrensing, 1998). The growth and reproductive cycle progression of hemp is photoperiod-sensitive. Hemp plants can grow to heights of up to 5 m and can develop a tap root penetrating up to 2 m into the soil (Chabbert et al., 2013; Clarke & Watson, 2007; Ehrensing, 1998). The majority of aboveground hemp biomass comes from the tall lignocellulosic plant stalk (Trey et al., 2019), which has been used for fiber for thousands of years (Li, 1973). The hemp stalk has two main fiber types: long bast fibers and short hurd fibers. The outer bast fibers surround the vascular tissue of the hemp stalk, whereas the hurd makes up the woody core (Trey et al., 2019). The different fiber types can be used to make a variety of textile and industrial products such as fabric, paper/pulp, insulation, composite boards, plastic, paint, sealant, and bioenergy (Small, 2015). The remainder of the aboveground biomass is leaves, seeds, and inflorescence. Hemp seeds are highly valued for their fatty acid-rich oil, which makes up approximately 25%–35% of the total seed mass. The remainder of the seed consists of 20%–35% protein, 20%–30% carbohydrates, and fiber (Leizer et al., 2000). This composition allows hemp seed to be used for products including, but not limited to, food and feed, nutraceuticals, personal care products, and fuel (Small, 2015). Hemp inflorescences are the primary location of C_{21} terpenophenolic compounds known as cannabinoids, which are unique to *Cannabis* plants (Mechoulam & Gaoni, 1967). The cannabinoids, primarily the cannabidiol (CBD) fraction, have recently gained significant interest among consumers for their benefits in nutraceuticals/pharmaceuticals and personal care products (Mark & Snell, 2019). Breeding and selection efforts have led to the development of *C. sativa* varieties specific to different end-uses: fiber hemp, seed/grain hemp, and CBD hemp.

Hemp production has only recently resurged in the United States and is primarily driven by CBD markets. The agricultural inputs (fertilizer, pesticide, equipment, etc.) for CBD hemp are much higher than inputs for grain or fiber hemp (Żuk-Gołaszewska & Gołaszewski, 2020). Countries in Europe and Asia have well-established production practices for seed and grain hemp, where agricultural input requirements are comparable to other major commodity crops (Van Der Werf, 2004). The legal definition of hemp is based on a maximum allowable concentration of the psychoactive cannabinoid, tetrahyrocannabinol (THC), which is primarily formed in the inflorescence. In the United States, the legal threshold is 0.3% total THC (Establishment of a Domestic Hemp Production Program, 2019), whereas the threshold is 0.2% in the European Union (EU Regulation 1307/2013). Not all varieties of *C. sativa* can be classified as hemp as THC content is a phenotypic expression.

2 | HEMP AS A PHYTOREMEDIATOR

Soil restorative properties attributed to hemp have been documented anecdotally throughout history and verified scientifically in the 20th century. One well-known case of using hemp as a phytoremediator is at the Chernobyl Exclusion Zone following the 1986 nuclear power plant meltdown (Charkowski, 1998), although the results have never been published in the peer-reviewed literature. A multitude of research has shown that hemp is capable of phytoextraction of heavy metals and radionuclides (Table 1), with the contaminants being distributed throughout the entire hemp plant in different concentrations. Phytoextraction involves the uptake of contaminants into harvestable materials (Sheoran et al., 2016). The phytoextraction potential of hemp is dependent on the contaminant's identity and concentration, soil characteristics, geographic location, and hemp variety.

A noteworthy body of literature for hemp phytoremediation focuses on polycyclic aromatic hydrocarbons (PAHs) and on cesium. Hemp grown in soil contaminated with PAHs (benzo[a]pyrene and chrysene), in concentrations from 25 to 75 $\mu g\ g^{-1}$, exhibited increased hemp growth rates from 140% to 314% by weight at each treatment level compared to controls. The highest growth rates for hemp exposed to benzo[a]pyrene or chrysene (227% and 314%, respectively) were achieved at soil concentrations of 50 $\mu g\ g^{-1}$ for each PAH. Degradation of benzo[a]pyrene and degradation of chrysene were noted in the soil at each concentration level. The largest decreases in PAH level (83 and 28 $\mu g\ g^{-1}$, respectively), occurring when hemp was planted in soil with at the highest concentration for each PAH (200 $\mu g\ g^{-1}$). The authors did note degradation of the main PAH contaminants in the control pots (no plants present) that were subjected to the same cultivation activities (i.e. fortification, watering). This observation suggests that degradation of PAHs takes place in soil regardless of plant presence, and that the presence of hemp plants increases that degradation over time. The authors did not determine whether the decrease in concentration of PAHs was a result of leaching or of chemical decomposition (Campbell et al., 2002). The PAH decomposition products could have been the drivers of the increased hemp growth, although it remains unclear if these degradation compounds accumulated within the plant or stimulated plant growth from the soil matrix. Hemp grown in soil contaminated with cesium exhibited decreased exchangeable cesium in the soil (11%–23% reduction; Vandenhove & Van Hees, 2005).

Although the roots cannot be readily harvested from mature hemp plants, the translocation of contaminants

TABLE 1 Literature describing the use of hemp for phytoremediation, grouped by contaminant

	Uptake by plant biomass fraction		
Compound	**Aboveground**	**Roots**	**Reference**
Arsenic	6.21–17,673 μg g^{-1} (leaf/stem; seedling)	34.6–2913 μg g^{-1} (seedling)	Petrová et al. (2012)
Cadmium	9.4–73.0 μg g^{-1} (leaf/stem)	109.2–1368.2 μg g^{-1}	Citterio et al. (2003)
	0.14–0.30 mg kg^{-1} (leaf/stem)	1.69–2.56 mg kg^{-1}	Di Candilo et al. (2004)
	0.8–3.5 ppm (leaf/stem/seed)		Linger et al. (2002)
	0–3 mg kg^{-1} (shoot only)		Meers et al. (2005)
	11.4–33.3 μg g^{-1} (shoot only)	217–481 μg g^{-1}	Shi et al. (2012)
	1.3–4 mg kg^{-1} (shoot only)		Mihoc et al. (2012)
	2.47–32,293 μg g^{-1} (leaf/stem; seedling)	547–33,457 μg g^{-1} (seedling)	Petrová et al. (2012)
	151 mg kg^{-1} (leaf only)		Ahmad et al. (2016)
Chromium	1.2–1.4 μg g^{-1} (leaf only)	6.2–9.0 μg g^{-1}	Citterio et al. (2003)
Copper	15–80 mg kg^{-1} (shoot only)		Meers et al. (2005)
	20.9–29,914 μg g^{-1} (leaf/stem)	1026–16,240 μg g^{-1}	Petrová et al. (2012)
	1530 mg kg^{-1} (leaf only)		Ahmad et al. (2016)
Lead	0.21–1.12 mg kg^{-1} (leaf/stem)	1.30–1.88 mg kg^{-1}	Di Candilo et al. (2004)
	1.8–22.4 ppm (leaf/stem/seed)		Linger et al. (2002)
	1–7 mg kg^{-1} (shoot only)		Meers et al. (2005)
	1.38–9627 μg g^{-1} (leaf/stem; seedling)	3738–66,280 μg g^{-1} (seedling)	Petrová et al. (2012)
Nickel	7.1–52.1 μg g^{-1} (leaf/stem)	35.8–321.8 μg g^{-1}	Citterio et al. (2003)
	6.9–63.6 ppm (leaf/stem/seed)		Linger et al. (2002)
	5–23 mg kg^{-1} (shoot only)		Meers et al. (2005)
	123 mg kg^{-1} (leaf only)		Ahmad et al. (2016)
Radium	0.28–0.52 Bq^{226}Ra g^{-1}		Soudek et al. (2006)
Selenium	<1400 mg kg^{-1} (seedling) <200 mg kg^{-1} (mature)	<800 mg kg^{-1} (seedling) <75 mg kg^{-1} (mature)	Stonehouse et al. (2020)
Strontium	0.0654–0.2697 mg g^{-1} (leaf/stem)	0.1902–0.3213 mg g^{-1}	Hoseini et al. (2012)
Thallium	3.46–12.90 mg kg^{-1} (leaf/stem)	2.87–4.07 mg kg^{-1}	Di Candilo et al. (2004)
Zinc	100–325 mg kg^{-1} (shoot only)		Meers et al. (2005)
	80.8–657.5 μg g^{-1} (shoot only)	220.0–5029.8 μg g^{-1}	Shi and Cai (2010)
	42–94 mg kg^{-1} (seed only)		Mihoc et al. (2012)
	39.2–37,440 μg g^{-1} (leaf/stem; seedling)	377–45,449 μg g^{-1} (seedling)	Petrová et al. (2012)

from the soil into the roots still allows contaminants to be temporarily fixed within the root zone to prevent further leaching into the soil (Di Candilo et al., 2004). The lack of plant-available forms of a contaminant in the soil, or limitations on contaminant soil mobility, can hinder hemp uptake of the compound from the soil. Amending the soil with chelating agents increases the availability and mobility of the heavy metals for phytoremediation (Gong et al., 2018; Lee, 2013; Malaviya & Singh, 2012). The most effective chelating agent depends on the target contaminant, for example, ethylenediaminetetraacetic acid (EDTA) is effective for Pb and ethyleneglycoltetraacetic acid is effective for Cd (Salt et al., 1998). Experimentation with EDTA and Pb has shown accumulation increases of more than 1000-fold compared to plants grown in unamended soil (Cunningham & Ow, 1996). Despite the benefit of large increases in phytoremediation accumulation, the use of chelating agents is generally outweighed by the potential for leaching of newly mobile, unaccumulated toxins (Conesa et al., 2012).

Hemp growth is generally not inhibited by low levels of some heavy metals in the soil. In the presence of trace elements Cd, Cu, Ni, Pb, and Zn at low levels of contamination (0.6–2.2, 0.1–0.3, 21–28.9, 82.9–272.8, and 149.7–550.3 mg kg^{-1}, respectively), hemp maintained significant aboveground biomass production with no significant negative impact on plant height (Nissim et al., 2018). Similarly, hemp grown in soils with moderate contamination of metal(loid)s As, Pb, V, and Zn (22.6, 115, 106.7, and 92.8 ppm, respectively) had yields and morphological traits comparable to plants grown in control soils. There were no statistically significant differences between the stem and inflorescence yields, the plant height, or the stem diameter of hemp cultivated in moderately contaminated soils when compared to cultivation in control soils (Pietrini et al., 2019). This indicates that low levels of contamination are not detrimental to the overall aboveground biomass yield of the crop, since the components of stem size/yield compose a large fraction of the total hemp plant mass.

Higher concentrations of contaminants in the soil generally result in higher concentrations accumulated in plant tissues; although high levels of accumulation are possible, there are thresholds at which plant productivity begins to suffer. For instance, hemp growth is unaffected by cadmium accumulation in roots up to 800 mg kg^{-1}; but leaf cadmium concentrations of 50–100 mg kg^{-1} can negatively impact photosynthesis. Hemp can be consistently grown for long-term remediation in soil with cadmium levels of up to 72 mg kg^{-1} without exceeding the detrimental root/tissue accumulation levels (Linger et al., 2005). The total metal uptake within individual plant parts, in relation to the mass of the entire plant, shows a wide range of relative concentrations: a high concentration of heavy metal found in seed biomass material (8%–10% total plant mass) is negligible compared to the total amount of metal in the other parts of the plant (Linger et al., 2002). While the low levels of contaminants on a whole plant basis may limit product use in consumer marketplaces, this does not eliminate their potential for use in industrial products or bioenergy production.

3 | HEMP AS A BIOENERGY FEEDSTOCK

3.1 | Biodiesel

Biodiesel is primarily produced from seed-oils that are rich in triglycerides by transesterification to fatty acid methyl esters (Vyas et al., 2010). Mechanical pressing is traditionally used to extract the oil; however, newer extraction techniques, such as supercritical carbon dioxide extraction, have also been used (Aladić et al., 2014). There are multiple transesterification reaction options including alkaline, acid, or enzyme-catalyzed reaction mechanisms (Čerče et al., 2005; Fukuda et al., 2001; Ma & Hanna, 1999). Impurities from contaminated raw oils can impact fuel properties, such as turbidity, cloud point, and color (Ma & Hanna, 1999). Methods to remove impurities before or after transesterification include wet washing to remove water-soluble compounds, dry washing with specific adsorbent materials, filtration, and ion-exchange (Banga & Varshney, 2010). Hemp seed is comprised of 25%–35% oil that is high in fatty acids (Leizer et al., 2000). The oil is traditionally used in foods (Farinon et al., 2020); however, the composition makes it promising for biodiesel. Investigations are ongoing into the optimum conditions for hemp-based biodiesel (Khan et al., 2019; Rashid et al., 2016), as well as its quality (Ahmad et al., 2011; Li et al., 2010) and usability for vehicle fuel or fuel blending (Afif & Biradar, 2019; Mohammed et al., 2020). The properties of hemp-derived biodiesel are comparable to those in fuel specifications ASTM D6751 (Afif & Biradar, 2019; Li et al., 2010; Rashid et al., 2016) and EN 14214 (Rashid et al., 2016; Table 2).

TABLE 2 ASTM D6751 and EN 14214 specifications compared with properties of *Cannabis sativa* oil biodiesel, data compiled from Afif and Biradar (2019), Gill et al. (2011), Li et al. (2010), and Rashid et al. (2016)

Fuel property	Hemp biodiesel	ASTM D6751	EN 14214
Cetane no.	55–63	>47	>51
Kinematic viscosity ($mm^2\ s^{-1}$; 40°C)	3.48–5.17	1.9–6.0	3.5–5.0
Cloud point (°C)	−5 to 3.7	[b]	[a]
Flash point (°C)	47–180	>93	>101
Sulfur content (wt. %)	0.00004–0.034	<0.05	<0.001
Acid value (mg KOH g^{-1})	0.25–0.45	<0.50	<0.50
Density (kg m^{-3}; 15°C)	810–890	[b]	860–900

[a]Not specified; EN 14314 uses time- and location-dependent values for the cold filter plugging point (CFPP) instead.

[b]Not specified; location and season dependent.

3.2 | Biogas

Biogas is the major product of biomass anaerobic digestion (AD) and is primarily composed of methane that can be used for fuel, and carbon dioxide. Minor compounds in biogas include hydrogen, oxygen, nitrogen, ammonia, hydrogen sulfide, and water (Alexopoulos, 2012). The major steps of AD are hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Achinas et al., 2017). Biogas can be produced from dry or ensiled hemp material (Prade et al., 2012). The raw biogas can either be combusted for combined heat and power (CHP), or refined to vehicle fuel quality. Typical methods for upgrading biogas to remove impurities and/or increase energy content include water scrubbing, cryogenic separation, physical and chemical adsorption, membrane technology, in-situ methane enrichment, hydrate formation, and/or biological methods (Sun et al., 2015). Steam pretreatment (Barta et al., 2013; Liu et al., 2017), harvest time (Kreuger, Prade, et al., 2011), and hemp variety (Adamovičs et al., 2014) are major influences on biogas yield/quality and methane content. At optimal harvest, green hemp can yield up to 296 GJ ha^{-1} $year^{-1}$

of energy from biogas (Prade et al., 2011). Biogas yields and quality from hemp crops from various experimental conditions are comparable to other biogas feedstocks (Adamovičs et al., 2014). Under growth conditions where green hemp yielded approximately 190 GJ ha^{-1} $year^{-1}$, other biogas crops grown under same conditions had comparable energy yields: 150 GJ ha^{-1} $year^{-1}$ for alfalfa (*Medicago sativa*), 170 GJ ha^{-1} $year^{-1}$ for clover-grass ley mix, 240 GJ ha^{-1} $year^{-1}$ for sugar beets (*Beta vulgaris* L.), and 210 GJ ha^{-1} $year^{-1}$ for maize (*Zea mays*; Prade et al., 2011).

3.3 | Bioethanol

Before undergoing fermentation, biomass feedstocks are often subjected to some kind of pretreatment, such as steam, to improve hydrolysis and bioethanol yield (Kreuger, Sipos, et al., 2011; Sipos et al., 2010). The main products of hydrolysis and fermentation are glucose and bioethanol, respectively (Kuglarz et al., 2014). Upon the completion of fermentation, the bioethanol is separated from the glucose and other minor byproducts, such as proteins, other alcohols, and secondary yeast metabolites, by distillation or vacuum stripping (Akbas & Stark, 2016). Dried or ensiled hemp biomass (primarily stalks) can be used as feedstock for bioethanol production (Sipos et al., 2010). The stalks, especially the hemp hurd fibers (Kreuger, Prade, et al., 2011; Kreuger, Sipos, et al., 2011), are rich in lignin, cellulose, and hemicellulose, which account for over 80 wt.% of the dry biomass (González-García et al., 2012; Zatta & Venturi, 2009). Harvest time is a major factor in hemp bioethanol yield because lignin and cellulose contents in hemp stalks increase with plant maturity (Kreuger, Prade, et al., 2011; Zatta & Venturi, 2009). The theoretical ethanol production from dry hemp stalk, harvested at different maturities, ranges from 2799 to 4503 L ha^{-1} (Zatta & Venturi, 2009). Hemp harvested at the optimum time has bioethanol yields comparable with other non-food lignocellulosic crops (Kreuger, Prade, et al., 2011; Zatta & Venturi, 2009).

3.4 | Solid biofuels

Solid biofuels can be any biomass material that has been dried, either in storage or in the field. These are most often combusted in CHP plants to generate heat and electricity, or utilized in small-scale boilers for heat generation (Kolarikova et al., 2014). Densified solid biomass is the most widely available biofuel (Zhou et al., 2016). Hemp solid biofuels are commercially available in niche markets (Prade et al., 2012). The amount of energy available from combusted biomass is influenced by harvest time, moisture content, particle size/shape, and composition of volatile components (Lu & Baxter, 2011; Prade et al., 2011). The composition of the feedstock impacts the amount of combustion emissions, such as carbon dioxide, carbon monoxide, nitrogen oxides, and unburnt hydrocarbons (Jasinskas et al., 2020), as well as the composition of the ash (Zajac et al., 2019). Hemp harvested under optimal conditions yields up to 246 GJ ha^{-1} $year^{-1}$. The hemp energy yield per hectare is similar to that of reed canary grass (*Phalaris arundinacea*) and 120% than that from wheat straw (*Triticum* sp.) grown under the same conditions (Prade et al., 2011).

4 | COUPLING PHYTOREMEDIATION AND BIOENERGY PRODUCTION

Using hemp for coupled phytoremediation and bioenergy production has been investigated to a small extent in the early 21st century, generally focused on biomass grown in soils contaminated with heavy metals (Linger et al., 2002; Meers et al., 2005; Van Ginneken et al., 2007). Recent work has established concepts for waste biorefineries (Alvarado-Morales et al., 2009) or co-production systems (Kreuger, Prade, et al., 2011; Kreuger, Sipos, et al., 2011) in which multiple bioenergy sources are produced from a single feedstock. These systems work to maximize yield and minimize waste volume. To incorporate contaminated biomass into bioenergy production, extra steps must be taken during processing to remove or sequester toxic compounds from/within the final product, depending on the contaminant identity, location, and concentration in the plant material, and the intended end-use.

Major pathways for bioenergy production from hemp have been developed: key process events are summarized in Figure 1 (Barta et al., 2013; Sathish Kumar et al., 2015) and are coupled to the production events associated with a phytoremediation crop (Van Ginneken et al., 2007). This design concept considers cultivation inputs; co-production of bioethanol, biogas, and CHP; separate production of biodiesel; potential solutions for sequestering contaminants; and contaminant waste stream destination. The primary barrier to the feasibility of implementing paired phytoremediation and bioenergy production is managing the safety and regulatory requirements associated with the fate of contaminants during processing. The actual fate of the contaminants will be specific to the process type and contaminant category. Modifications to standard bioenergy production methods can be made to incorporate contaminant removal: that is, using non-catalyzed supercritical methanol, rather than base-catalyzed reactions, for transesterification of seed oil enables simpler purification

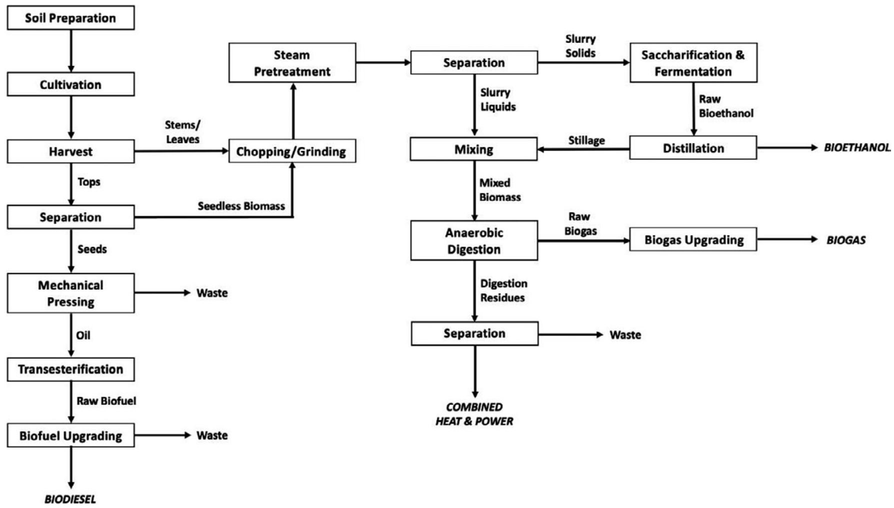

FIGURE 1 Flow chart for production of bioenergy from hemp, adapted from process diagrams described in Kreuger, Prade, et al. (2011) and Van Ginneken et al. (2007)

TABLE 3 Maximum ^{137}Cs soil contamination levels as a function of each plant component's end-use and the observed hemp transfer factors, adapted from Vandenhove and Van Hees (2005)

	Hemp transfer factor (TF)			Limit	Max ^{137}Cs soil contamination
	$\times 10^{-3}$ m^2 kg^{-1}	Use	Decontamination factor	Bq kg^{-1}	kBq m^{-2}
Stem fiber	1	Fiber	1	740[a]	740
Stem fiber	1	Building material	1	1850[a]	1850
Stem	0.7	Biofuel	1	740[a]	1057
Stem	0.7	Litter	1	1850[a]	2643
Seeds	3	Oil	10–50	185	610[c]
Seeds	3	Flour	1.3–2[b]	370	160[c]

[a]Szekely et al. (1994).

[b]International Atomic Energy Agency (1994); all other values were from GOPA (1994).

[c]Maximal ^{137}Cs soil contamination levels calculated using the lower value for the decontamination factor listed.

methods downstream (Van Ginneken et al., 2007). Two methods for sequestering contaminants involve the use of adsorbent materials and incineration. Adsorbent materials can be used to remove contaminants from both aqueous and gaseous waste streams (Angelidaki et al., 2018). For solid metals that are thermally stable, waste can be incinerated to concentrate contaminants in the ash (Nzihou & Stanmore, 2013). Disposing of a small volume of ash is much less impactful than disposing of large volumes of biomass (United States Environmental Protection Agency, 1999).

Evaluating soil-to-hemp transfer factors (TFs) for individual contaminants can help guide the best use of the hemp biomass following phytoremediation. TFs are the ratio of concentration in plants to concentration in soil for a particular species (Sakizadeh et al., 2016); these can vary for different parts of the plant (e.g., seeds vs. stems). Some work has used hemp TFs to estimate soil contamination limits that still allow for use of the harvested biomass. For example, stems from hemp cultivated on cesium-contaminated land can be used for bioenergy or certain fiber products when soil radioactivity levels are below 1057 and 740 kBq m^{-2}, respectively. Although contaminated hemp fiber cannot be utilized for consumer textiles (due to contact with skin), hemp fiber contaminated with heavy metals does retain its quality and is suitable for industrial products, such as combine material or for bioenergy production (Linger et al., 2002). TFs between cesium and hemp biomass are highest for hemp seeds (Table 3); as a result, hemp seed oil can only be used for bioenergy production when hemp is cultivated on land with radioactivity levels below 610 kBq m^{-2} (Vandenhove & Van Hees, 2005).

Since phytoremediation is influenced by cultivar selection and plant genetics (Adamovičs et al., 2014; Mihoc et al., 2012; Petrová et al., 2012; Shi et al., 2012), the legal limitation of hemp based on low THC content dramatically reduces the number of *C. sativa* varieties that can be investigated for combined phytoremediation and bioenergy production. Furthermore, research has indicated that cannabinoids are overexpressed as a result of heavy metal accumulation (Husain et al., 2019), which has the potential to exacerbate legality issues when hemp is used for phytoremediation. This area might be expanded with special policy exceptions, such as those granted to hemp breeders for variety development, to increase the allowable level of THC concentration in varieties used for research studies. Breeding programs can promote the selection of varieties that express genes involved in heavy metal tolerance to improve phytoremediation. For example, recent endeavors to understand the molecular mechanisms behind stress responses in plants have identified the important role of antioxidant enzymes, particularly glutathione and phospholipases, in plant stress signaling, gene expression, and cellular regulation (Wang, 2005; Yousuf et al., 2011). Two genes associated with these enzymes are *glutathione-disulfidereductase* (*GSR*) and *phospholipase D-α* (*PLDα*). They have been evaluated in numerous plants, such as *Brassica napus* (Russo et al., 2008), *Triticum aestivum* L. (Yannarelli et al., 2007), and *Gossypium* spp. hybrids (Meloni et al., 2003), for their activity in responses to various biotic and abiotic stresses. Researchers recently identified the presence of *GSR* and *PDLα* in hemp using reverse transcriptase-polymerase chain reaction methodology and by comparing sequences to those previously reported in other plants. High expression of both genes was observed in hemp material that exhibited increased levels of Cd, Pb, Cu, Ni, and Cr accumulation compared to surveyed literature, suggesting a positive correlation between heavy metal tolerance and expression of *GSR* and *PLDα* (Ahmad et al., 2016). This work indicates that these genes, or their metabolic pathways, are potential candidates for targeted genetic modification that could be used to enhance the phytoextraction potential of hemp.

Hemp has not responded well to attempts at genetic transformation (Salentijn et al., 2019). There has been only one successful attempt reported for genetic modification of hemp through *Agrobacterium* infection of root cell cultures (Wahby et al., 2013). The use of genetically modified hemp would likely be restricted to industrial/energy product development, since consumers are expected to perceive the resulting personal care or food products in a negative manner. Future work in genetics and genetic manipulation related to hemp tolerance and accumulation of contaminants would increase likelihood of hemp use in large-scale phytoremediation efforts.

5 | CONCLUSIONS

Hemp has been demonstrated as a phytoremediator of heavy metals, radionuclides, and PAHs, and as a bioenergy feedstock for biodiesel, bioethanol, biogas, and CHP. Based on hemp's substantial production of aboveground biomass, deep taproot depth, and commercial potential for bioenergy products, hemp is a strong candidate for generating profit from phytoremediation operations. Feasibility of hemp for this dual purpose must be analyzed on a case-by-case basis to choose the most appropriate hemp genetics for the contaminant in question. That choice must also consider the need for soil amendments to alter translocation of the contaminants, and the ultimate fate of the contaminants in the soil–plant–product system. Recent advances in biotechnology provide promising new avenues for improving the phytoremediation capabilities of hemp through better understanding of the genetic and phenotypic changes with breeding for successful phytoremediation practices. The establishment of longitudinal studies is needed for evaluating the long-term soil transfer effects from multiple cycles of crop production, and the fate of contaminants during processing.

A possible solution for mitigating the risk of contaminants dispersal, even at small volumes, is the implementation of a mostly closed system: contaminated material is disposed of on-site, while bioenergy is produced for on-site operations. Ideally, phytoremediation can result in other biomass-derived product(s) with a net profit. If profit cannot be achieved for the biomass, other strategies for disposing of the contaminated hemp, such as composting, compaction, incineration, ashing, and pyrolysis should be considered. Among those, incineration is currently the most feasible, cost-effective and environmentally friendly (Sas-Nowosielska et al., 2004). The ability of hemp to hyperaccumulate heavy metals suggests that there is a potential for the crop to bioaccumulate contaminants from soil with concentrations below detectable or harmful limits. There is, therefore, a need to test for contaminants in hemp destined for consumer products before and after processing.

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DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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