IBI White Paper

Implications and Risks of Potential Dioxin Presence in Biochar

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1. Introduction

The International Biochar Initiative (IBI) is a non-governmental organization (ngo) that promotes the development of biochar systems that follow Cradle-to-Cradle sustainability guidelines. As a new industry, it is important that systems for biochar production and use be analyzed and monitored for environmental impact and sustainability. Biochar systems analysis begins with complete characterization of biochar materials, and IBI has published *Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil*[1] (hereinafter referred to as *Biochar Standards and Testing Guidelines*) that provide a consistent framework for measuring and reporting essential biochar properties (physical and chemical), as well as determining whether any contaminants are present in a biochar material.

In most cases, contaminants such as heavy metals that may be present in biochar are introduced in the biomass feedstock source used to make the biochar (e.g., plants can take up heavy metals from soil). However, two particular classes of contaminants that are not strictly feedstock-dependent can be formed by the thermochemical processes used to make biochar. These compounds are Polycyclic Aromatic Hydrocarbons (PAH), and dioxins and furans (PCDD/F). This paper examines dioxins, and how IBI has addressed them in the context of the *Biochar Standards and Testing Guidelines*.

The term "dioxins" is used to refer to a family of compounds that includes polychlorinated dibenzo dioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs). The United Nations Environment Program (UNEP) lists dioxins as Persistent Organic Pollutants (POPs). Not all dioxin compounds are equally toxic. To

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reflect this range of toxicity, dioxins are reported using Toxic Equivalency Factors (TEFs) developed by the World Health Organization (WHO). Combined values in a material are reported as a Toxic Equivalency Quantity (TEQ), typically in units of micrograms per metric tonne, nanograms per kilogram, or picograms per gram of a reference compound [in the case of PAHs: benzo(a)pyrene and in the case of dioxins: 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)]. These units are all equivalent to parts per trillion (ppt).

This White Paper examines the potential for contamination of biochars with dioxins, and describes what is currently known about the implications for the environment and human health. This paper also explains the IBI approach to setting a dioxin reporting requirement and threshold in the *Biochar Standards and Testing Guidelines.*

2. History of Dioxins in the Environment

Dioxins in the environment are mostly the result of past and current industrial processes, but natural processes, such as volcanic eruptions and forest or grassland fires, also form dioxins. Industrial operations that can produce dioxins include smelting, chlorine bleaching of paper pulp, manufacture of some herbicides and pesticides, and waste incineration.[2]

Before the development of the chlorine industry in the late 19th century, human exposure to dioxins was limited. Starting in the 1920s, workers in the chlorine industry were observed to suffer liver damage and other ailments. Contamination from industrial accidents in the 1970s and 1980s led to public awareness of a dioxin problem. The US Environmental Protection Agency (EPA) issued a reassessment of dioxin in 1988 and began a study of dioxin sources.[3]

In 2001 the Stockholm Convention for Reduction of Persistent Organic Pollutants (POPs) was adopted and UNEP issued a Dioxin Toolkit in 2005[4] to provide a consistent framework for countries to construct national inventories of dioxin releases to the environment. The reason for this approach is explained in a 1999 UNEP report on chemicals:

> "Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) are environmental contaminants detectable in almost all compartments of the global ecosystem in trace amounts. PCDD/PCDF have never been produced intentionally and have never served any useful purpose unlike other POPs, e.g. polychlorinated biphenyls (PCB) or DDT. PCDD/PCDF are formed as unwanted by-products in many industrial and combustion processes. Consequently, it is impossible to eliminate dioxins and furans by prohibition of production and use. Indirect measures have to be taken to reduce the emissions of PCDD/PCDF into the environment and to minimize human exposure. Such work can be done successfully only if the sources of

PCDD and PCDF are identified and quantified. Only then can technologies and measures be put in place to minimize or eliminate these sources."[5]

Since the 1980s, the approach of monitoring dioxin sources and eliminating dioxin production through improved industrial process and emissions controls has been effective. In the United States, measurable air emissions of dioxins has declined by 90 percent since 1987, according to the US EPA, and today the largest remaining source of dioxin emissions is backyard burning of household trash.[6]

While the background level of dioxins in the environment before industrial development is not known, the establishment of dioxin inventories and emissions factors for naturally occurring and human caused forest fires and other forms of biomass burning allow estimates of the contribution of these sources to the current overall dioxin load in the environment. A recent evaluation of these emissions factors indicates they are quite low, on average 4 micrograms TEQ per metric tonne of biomass fuel (emissions to air) and on average 1.1 nanograms TEQ per kilogram of ash residual (emissions to land). These estimates indicate that the overall contribution of wild fires and agricultural biomass burning to the dioxin inventory is currently 24% to air and 16% to land.[7] As industrial sources of dioxins come under further control and reduction, these percentage contributions will increase, as the overall emissions of dioxins decrease.

3. Dioxin formation pathways and potential for dioxin formation in biochar

Washington State University conducted a literature review and analysis of dioxin and PAH formation during pyrolysis[8] that summarizes research on the various ways that dioxin formation can occur during thermal processes. Dioxins may be formed during combustion processes by two different thermochemical pathways, termed the "*precursor*" pathway and the "*de novo*" pathway. The *precursor* pathway starts with the synthesis of precursor chemicals from feedstocks containing chlorine at temperatures above 750 degrees C, but the dioxins themselves only form by condensation from the vapor phase at lower temperatures, with maximum formation taking place at around 300 degrees C. Formation is enhanced in the presence of metals, especially copper. The *de novo* pathway requires the presence of both oxygen and solid carbon and takes place between 200 and 400 degrees C in a catalytic reaction that occurs on particles of fly ash. Garcia-Perez (2008) noted that dioxin emissions are less dependent upon chlorine content than they are on processing parameters: "Systems ensuring high temperatures and long vapor residence times in the furnace as well as fast cooling of combustion products are likely to achieve low emissions of PCDD/F even while using feedstocks with large contents of chlorine."

Biochar feedstocks such as grasses, straws and food waste (which contains sodium chloride, i.e., salt) can be a source of chlorine (see Table 1, below). Other potential sources of chlorine in biochar feedstocks include biomass that has been exposed to salt (such as crops or trees grown near seashores), and the biomass fraction of

municipal solid waste (MSW) that may be contaminated with polyvinyl chloride (PVC) or other chlorine-containing plastics.

Given the fact that: 1) chlorine may be present in many types of biochar feedstocks; and 2) biochar can be produced at many different temperatures via many different thermochemical processes, we must conclude that dioxin formation is possible in at least some of the thermochemical processes used to make biochar. To date, there has been limited investigation of the range of biochar production processes and their potential for dioxin formation, though one recent study that tested multiple biochar samples[9] found the presence and amount of dioxins to be very low.

Several large-scale assessments of biochar have called attention to this information gap and have recommended further study.[10,11,12] In evaluating potential biochar risks, Verheijen et al. (2009) stated:

> "Contaminants (e.g. PAHs, heavy metals, dioxins) that may be present in biochar may have detrimental effects on soil properties and functions. The occurrence of such compounds in biochar is likely to derive from either contaminated feedstocks or the use of processing conditions that may favor their production. Evidence suggests that a tight control over the type of feedstock used and lower pyrolysis temperatures (<500 degrees C) may be sufficient to reduce the potential risk for soil contamination."

Verheijen et al. conclude: "Full and careful risk assessment for such contaminants is urgently required, in order to relate contaminant toxicity to biochar type, safe application rates and operating pyrolysis conditions."

While further study is needed, those biochar samples that have been tested have shown very low levels of dioxins, some of which were at or below the limits of detection. Granatstein (2009) tested biochars produced on a lab bench pyrolyzer and concluded: "the small content of furans and dioxins that could be present in the biochars produced in the project will not represent a hazard when this material is used as a soil amendment." Downie, et al. (2011)[13] also found that dioxins, although present in the three samples tested, were below levels of concern for application to soil.

Hale et al. (2012) measured both total and bioavailable concentrations of toxic PAHs and dioxins. Table 1, below, shows the results for the total toxic dioxin concentrations in 13 biochars. Bioavailable dioxins were also measured using passive samplers and were found to be below the limit of detection for all of the samples. The passive samplers measure the aqueous phase concentration of the toxicant. This is the concentration that is considered to be bioavailable. According to Hale et al., a "bioavailable" compound is one that is "freely available to cross an organism's cellular membrane from the medium at a given time."

Table 1. Toxic Dioxin Concentration in 13 Biochars - adapted from Table 2 in Hale et al. (2012)

Biochar (feedstock source and production temperature)	Toxic dioxin concentration (pg/g TEQ)	Chlorine content (percent)
Food Waste 400 C	0.15	
Food Waste 600 C	0.16	3.4
Digested Dairy Manure 600 C	0.13	
Pine Wood 900 C	0.15	
Lodgepole Pine	0.18	
Food Waste 300 C	1.20	2.9
Food Waste 500 C	0.008	
Laurel Oak 650 C	0.02	
Eastern Gamma Grass 650 C	0.02	
Pine Wood 800 C	0.005	
Switch Grass 800 C	0.008	0.44
Switch Grass 900 C	0.22	
Paper Mill Waste 600 C	0.06	

Hale et al. noted that the relatively higher concentration of dioxin in one of the food waste biochars is likely due to the high salt (sodium chloride) content of food waste. They analyzed the chlorine content of the some of the feedstocks and found that Food Waste 300 contained 2.9% chlorine, Food Waste 600 had 3.4% chlorine and Switch Grass 800 had .44% chlorine.

4. Analyzing the risk of dioxins in biochar

While it is encouraging for the prospects of biochar to see that dioxin concentrations in the samples reported to date are very low, it is important to recognize that only a few samples of biochar materials have been tested for these toxicants. Given the wide variety of feedstocks and production processes that can be used to make biochar, more samples must be tested and the results directly correlated with production processes in order to get an accurate picture of the overall impact of biochar production and use on dioxin formation and inventories.

Significant efforts have been undertaken globally to reduce the formation and threat of dioxins by controlling dioxin emission sources and identifying and cleaning up dioxin reservoirs in the environment. It is the responsibility of the emerging biochar industry and its proponents to do the investigative work necessary to assess biochar production processes for dioxin formation potential, and to apply this learning.

Risk assessment for biochar materials in the environment should also consider the final use of biochar as a soil amendment. The primary questions that should be addressed are:

1. How tightly bound are dioxins to the biochar carbon matrix and how easily can these toxicants leach out into the surrounding soil?
2. How do dioxins enter the food chain? Can plant roots take up dioxins in biochar or in the surrounding soil?
3. How long will dioxins remain in the biochar or the soil before breaking down into less toxic components?
4. Are there other pathways, such as direct ingestion of soil containing biochar, which could increase the body burden of dioxin in children or adults?

Currently, there are few definitive answers to these questions for biochar materials, but there is a large body of work on dioxins in soil and soil decontamination that can be drawn upon to create a basic framework for risk assessment. This work is summarized below in relation to the four questions posed above.

Question 1: *How tightly bound are dioxins to the biochar carbon matrix?*

Biochar materials share many characteristics with activated charcoal and a number of studies have shown that, similar to activated charcoal, biochar has a high sorption affinity for hydrophobic organic pollutants, such as herbicides and pesticides.[14] The US EPA *Technical Factsheet on Dioxin*[15] lists Granular Activated Charcoal as the "Best Available Technology" for treatment of dioxin contamination. A study comparing the effectiveness of different activated carbons (ACs) and biochar materials in sorbing dioxins found:

> "All sorbents (ACs and biochars) tested substantially reduced the availability of PCDD/Fs. To the extent that a biochar has high sorption properties, it can be expected to immobilize dioxins present in the biochar matrix."[16]

Hale et al. (2012) also found that leachable amounts of dioxin from each of the 13 biochar materials they tested were below the levels of detection.

Question 2: *How do dioxins enter the food chain? Can plant roots take up dioxins in biochar or in the surrounding soil?*

WHO (2010) estimates that greater than 90 percent of human exposure to dioxins is through the food chain. Dioxins are known to bind to organic matter in soil and in organisms:

> "Due to their high lipophilicity and low water solubility, PCDD/PCDF are primarily bound to particulate and organic matter in soil and sediment, and in biota, they are concentrated in fatty tissues."[17]

However, because dioxins are bound to soil particles (even in the absence of biochar), they are not readily taken up by plant roots. According to US EPA:

> "The transport [of dioxins] to plants may occur through the root system, but most occurs through air-to-plant transfer mechanisms."[18]

Such mechanisms begin with the deposition of dioxins from air emissions onto leaf surfaces that are consumed directly by humans or by cattle, and that become part of the human food chain. Fiedler (2003) describes two additional mechanisms other than plant uptake that can transfer dioxins from soil into the food chain: chickens ingest soil directly and dioxins can accumulate in their eggs; and sediments can transfer dioxin into the marine food chain where they can accumulate in fish.

Question 3: *How long will dioxins remain in the biochar or the soil before breaking down into less toxic components?*
Given the long half-lives for biochar materials, it is likely that any dioxins they contain may resist degradation for a very long time. Dioxins degrade within a few hours when exposed to sunlight, but are long-lived under the soil surface even in the absence of biochar. Fiedler (2003) states:

> "Soil is a typical accumulating matrix with a long memory; in other words, dioxin inputs received in the past will remain and, due to the very long half-lives of PCDD/PCDF in soils, there is hardly any clearance."

The implications of the tendency for dioxin to accumulate in soil are that attention must not only be paid to the concentration of dioxin in a biochar material, but also to the lifetime application of biochar to a particular field.

Question 4: *Are there other pathways, such as direct ingestion of soil containing biochar, which could increase the dioxin body burden of children or adults?*

As a limiting case, US EPA (2002) and other regulatory agencies have looked at the potential that young children (who are more sensitive to toxicants than adults and also more likely to put things in their mouths) living on a farm may directly ingest soil that contains dioxins. This scenario for dioxin exposure from soil ingestion has been used (along with other exposure factors) to establish safe threshold levels for soil dioxin content by US EPA, (2002) and Canadian[19] regulatory agencies.

While definitive answers to these four risk assessment questions have yet to be determined, it is important to keep in mind the history of biochar and black carbon in soils. Many soils worldwide contain large amounts of historically produced char

and other fire-derived organic matter that could potentially contain dioxins (even today a large proportion of dioxin emissions come from wildfires). Up to 40% of the total soil organic matter (SOM) in grasslands and boreal forests may be fire-derived.[20] Anthropogenic soils such as the Amazonian *Terra Preta* contain large amounts of pyrolyzed organic matter. Toxic effects from these soils have not been observed.

5. IBI Biochar Standards and Testing Guidelines *dioxin reporting requirement*

Dioxin testing and reporting is required by the *Biochar Standards and Testing Guidelines*. These *Guidelines* were developed to provide consistent information and market certainty about the attributes of biochars for use as a soil amendment. The *Biochar Standards and Testing Guidelines* are also intended to ensure that biochar materials are safe and will not compromise soil functions, including over time. Because biochar can be made from a wide range of feedstocks, using a variety of different production processes, it is necessary at this stage of industry development to test all biochar feedstock/production combinations for the presence of dioxins. All the information we currently possess indicates that in most cases, dioxins, if they can be detected at all, will be at very low levels and will not pose any threat to soils on any time scale. However, in the absence of definitive results confirming this supposition, biochar markets and regulators will demand assurance that specific biochar products are clean and safe to use, and the *Biochar Standards and Testing Guidelines* were developed to encompass this need.

The general approach that IBI used to determine threshold levels for potential contaminants (mostly heavy metals) in biochars was to adopt existing standards for other types of soil amendments such as composts and liming agents. In the case of dioxins, the most appropriate soil amendment standard is one for the application of wood ash as liming agent. In the context of regulation of dioxin in biochars, Hale et al. (2012) said, "use of wood ash as a fertiliser … could be analogous to using some biochars for agricultural improvement." A survey of the environmental impacts of wood ash as a fertilizer found low levels of dioxins in wood ash, similar to the results found for biochar samples, and found a further similarity to biochar in that "PCDD/Fs are not expected to leach out of wood ash, due to its absorbent nature, and are expected to be immobilised."[21]

Wood ash standards are in use in Finland, Sweden and Canada, among other countries, but only Canada's standard includes a threshold value for dioxins. IBI based the biochar dioxin threshold on the value given in *Standards and Guidelines for the Use of Wood Ash as a Liming Material for Agricultural Soils*, issued by Alberta Environment in 2002.[22] This standard provides guidance to generators of wood ash residues for assuring the safety of the residues. It requires annual testing of dioxin levels, and sets a threshold level of 27 ng/kg TEQ based on a lifetime (100 year) total maximum application amount of 45 tonnes per hectare.

In adapting the Canadian wood ash standard for use with biochar, an adjustment for land application rate was required. To provide conservative estimates and assumptions, it was assumed that a higher total application amount of 135 tonnes/hectare of biochar will be applied all at once or in smaller, incremental amounts over a 100-year period. This amount is based on biochar research literature[23] that has shown benefits at such high application rates, but in practice, this rate is rarely used; the benefits of applications of 10-30 tonnes/hectare are best supported in the research literature. Biochar is recalcitrant in soil and once the desired biochar concentration is reached, annual applications of large amounts will be unneccessary. Therefore, it can be assumed that most fields and garden beds will receive far less than 135 tonnes/hectare in 100 years.

Experts consulted supported the validity of a linear extrapolation of the application amount to produce an appropriate dioxin threshold for biochar materials. Assuming a total biochar application amount that is three times higher than the total wood ash application amount (135 tonnes/hectare vs. 45 tonnes/hectare), the threshold value of 27 ng/kg in the Canadian wood ash standard was divided by three, yielding a value of 9 ng/kg as a threshold value for allowable dioxin content in biochar. This is the threshold value used in the *Biochar Standards and Testing Guidelines*. Dioxin content is to be determined by US EPA method 8390A (1997).[24]

This level is very conservative based on the consideration of application rates. It is also conservative in terms of bioavailability. Studies cited previously show evidence that dioxins that may be present in biochar will be strongly bound and not easily bioavailable.

6. Conclusion

As the biochar industry develops and biochar material characteristics are linked more definitively to specific production processes and feedstocks, it should be possible to provide quality assurance of clean biochar materials by specifying and controlling production processes and feedstocks, thus avoiding the need to test all biochar materials for the potential presence of dioxins. However, given the current lack of knowledge, the testing of all biochar materials for potential toxicants will increase our knowledge base and provide requisite safety assurances for biochar producers, users, and regulators.

More information about dioxins can be found at these links:

WHO (World Health Organization) – Dioxins and dioxin-like substances
WHO – Dioxins and their effect on human health
Stockholm Convention on Persistent Organic Pollutants
US EPA (Environmental Protection Agency) – Technical factsheet on dioxin
US FDA (Food and Drug Adminstration) - Q&A about dioxins and food safety

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