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Activated carbons of varying pore structure eliminate the bioavailability of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin to a mammalian (mouse) model

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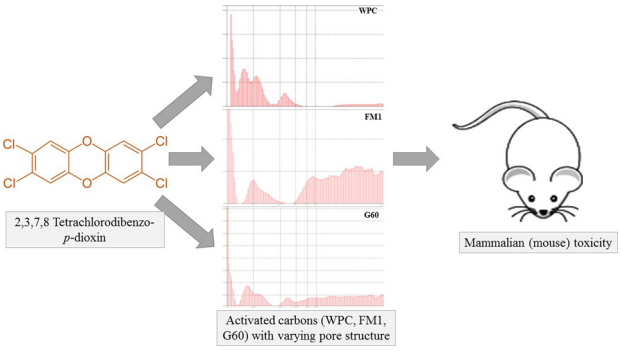
HIGHLIGHTS

- Sequestration of TCDD by ACs eliminated bioavailability to mammalian (mouse) model.
- Differing pore structures of three ACs had no effect on resultant bioavailability.
- Commercially available ACs appear suitable for in situ remediation of PCDD/Fs.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of activated carbon (AC) as an in situ sorbent amendment to sequester polychlorinated-dibenzo-*p*-dioxins and furans (PCDD/Fs) present in contaminated soils and sediments has recently gained attention as a novel remedial approach. This remedy could be implemented at much lower cost while minimizing habitat destruction as compared to traditional remediation technologies that rely on dredging/excavation and landfilling. Several prior studies have demonstrated the ability of AC amendments to reduce pore water concentrations and hence bioaccumulation of PCDD/Fs in invertebrate species. However, our recent study was the first to show that AC had the ability to sequester 2,3,7,8 tetrachlorodibenzo *p* dioxin (TCDD) in a form that eliminated bioavailability to a mammalian (mouse) model. Here we show that three commercially available ACs, representing a wide range of pore size distributions, were equally effective in eliminating the bioavailability of TCDD based upon two sensitive bioassays, hepatic induction of *cyp1A1* mRNA and immunoglobulin M antibody-forming cell response. These results provide direct evidence that a wide range of structurally diverse commercially available ACs may be suitable for use as in situ sorbent amendments to provide a cost-effective remedy for PCDD/F contaminated soils and sediments. Potentially, adaption of this technology would minimize habitat destruction and be protective of ecosystem and human health.

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1. Introduction

The ubiquitous occurrence of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) in the environment results from their formation as unintentional byproducts of chemical manufacturing, including pesticide production and the historic chlor-alkali process, and from both anthropogenic (incineration) and natural (forest fires and volcanic activities) combustion (Kulkarni et al., 2008; Alcock and Jones, 1996). The natural in situ formation of predioxins and octachlorodibenzo-*p*-dioxin may also occur on the surfaces of ball clays (Gu et al., 2008). In recent decades, significant technological and regulatory improvements have limited the anthropogenic release of these compounds to the environment. However, their widespread distribution and recalcitrance in soils and sediments, coupled with their high toxicity at low levels of exposure, contributes to their high priority for remediation throughout the world (Van Den Berg et al., 1998; USEPA, 2006).

Human exposure of PCDD/Fs is potentially associated with many adverse health effects including cardiovascular disease, diabetes, cancer, porphyria, endometriosis, altered hormone levels and reproductive health, skin, tooth, and nail abnormalities among others (USEPA, 2006; Mocarelli et al., 2008). Perhaps most alarming, exposure to PCDDs at levels only a single order of magnitude greater that current mean background levels for the general population (viz. 15 ppt serum lipid basis) manifests negative health outcomes (White and Birnbaum, 2009). Exposure to PCDD/Fs has been linked to prenatal mortality in a number of mammalian species including mice, rabbits and mink (Bursian et al., 2011). Interestingly, the proliferation of antibiotic resistance genes in the gut microbiota of mice has been associated with the immune response induced by TCDD exposure (Stedtfeld et al., 2017a).

Remediation of PCDD/F contaminated soils and sediments often involves removal by excavation or dredging and disposal in hazardous waste landfills, with varied degrees of effectiveness (Bridges and Gustavson, 2010; N.R. Council, 2003). This traditional remedy is associated with high cost and substantial habitat destruction, for example detrimental effects on benthic ecosystems, and can result in re-distribution of contaminated sediments (Akcil et al., 2015). Therefore, efforts have been made to develop new remediation technologies that are less expensive and destructive while being protective of ecosystem and human health. The use of activated carbon (AC) sorbent amendments has emerged as a particularly promising treatment alternative (Ghosh et al., 2011).

A select number of studies showing reductions in pore water concentrations of PCDDs and subsequent reductions in bioaccumulation among benthic organisms and soil invertebrates has provided the impetus for further scientific investigation of this technology (Ghosh et al., 2011; Josefsson et al., 2012; Cornelissen et al., 2012; Fagervold et al., 2010; Chai et al., 2012). However, from a public policy standpoint, mammalian exposure and bioavailability has been considered in order to make decisions protective of human health. In 2012, based on evidence that 16–28% of measured PCDD/Fs in Midland bulk soils were orally bioavailable to mammals, Dow Chemical (Midland, Michigan, USA) was granted a site-specific variance in soil remediation targets (from 90 to 250 ppt TEQ) by the Michigan Department of Environmental Quality (MDEQ) (Budinsky et al., 2008; MDEQ, 2012). The significance of the direct oral exposure pathway has been established through studies on the advertent and inadvertent ingestion of soil documented in humans, especially children, and wild animals (Beyer et al., 1994; Kreulen, 1985; Stanek et al., 2012).

We recently showed that a commercial AC has the ability to sequester PCDD/Fs in a form that eliminates mammalian bioavailability. When TCDD was sequestered by AC it failed to elicit a hallmark of TCDD exposure, i.e. suppression of immune system response; other sorbent materials including silica and smectite (e.g. montmorillonite) clays did not reduce TCDD bioavailability to the mammalian (mouse) model (Boyd et al., 2017; Boyd et al., 2011; Kaplan et al., 2011). In addition, TCDD sequestered by AC was shown to eliminate characteristic TCDD influences on the gut microbiome (Stedtfeld et al., 2017b). The beneficial effect of AC in reducing mammalian toxicant exposure in the gut has motivated its recommended use for livestock and humans following acute exposures (Bond, 2002; Cook and Wilson, 1971; Engebretson and Davison, 1971).

The efficacy of AC as a sorbent for organic contaminants is well established accounting for its use in many treatment processes including both water and gas flu treatment (Mohan and Pittman, 2007; Figueiredo et al., 1999). This is especially true in the case of planar hydrophobic compounds which are intrinsically suitable for hydrophobic pore-filling processes coupled with van der Waals attraction characteristic of contaminant sorption by AC (Lesage et al., 2010). The sorption capacity of ACs has been shown to be orders of magnitude greater than the primary native soil/sediment sorptive component for hydrophobic contaminants, namely amorphous organic matter (Johnston et al., 2012). Pore structure is known to play an important role in the sorption potential of all porous media across a variety of scales (Zachara et al., 2016). The pore structure of ACs is dependent on the source material as well as physical and chemical processes utilized in their formation. Because of this, the pore structure of ACs varies significantly among different commercially available products, likely affecting their suitability for specific applications (Panella et al., 2005).

Pore characteristics play a significant role in determining the irreversibility of contaminant sorption, or the kinetic release, by ACs. For example, a common assumption is that a pore size of 1.3–1.7 times the molecular (kinetic) diameter of a particular compound manifests the greatest sorption energy and preferential sorption (Bembnowska et al., 2003). This concept has been utilized in the pharmaceutical industry to help modulate drug delivery via a porous silica media (Coasne et al., 2013). Dynamic molecular simulations show that the energetics of sorption are most favorable with pores slightly larger than TCDD molecules (Gao et al., 2017). As the pore size increases, the mean potential energy of sorption for the TCDD molecule decreases. Molecular simulations also suggest that the water density within individual pores decrease as pore size decreases. The resulting sub-aqueous environment would plausibly be energetically favorable for hydrophobic compounds such as TCDD (Engebretson and Davison, 1971).

The goal of the current study was to investigate the effectiveness of AC materials representing a wide range of pore structure distributions, as well as specific surface areas, in reducing the bioavailability of TCDD using a mammalian (mouse) model. The mouse has been extensively characterized with respect to its biological and toxicologic responses to PCDD and dioxin-like compounds with induction of hepatic enzyme, cytochrome P-4501A1 (cyp1A1), and suppression of the primary IgM antibody response being among the most sensitive to PCDD/F exposure. For this reason the mouse and these specific responses were assayed when determining bioavailability of PCDDs. In addition to the WPC AC used in our previous study, two additional AC materials were selected for study (Table 1; FM1 and G60). The three ACs were loaded with TCDD via the incipient wetness method, and delivered to mice via oral gavage. Bioavailability in mice was determined through enumeration of the anti-sheep erythrocyte (sRBC) IgM antibody forming cells (AFC) and induction of *cyp1A1* mRNA, two hallmark responses of TCDD exposure in mammals.

2. Materials and methods

2.1. Selection of ACs

In a previous study, five activated carbons were characterized using nitrogen absorption to determine specific surface area and pore size distribution (Boyd et al., 2017). Of the five ACs, three were selected for use in the current study (Table 1). WPC, used in the previous feeding study,