

Meeting multiple water quality objectives through treatment using locally generated char: improving organoleptic properties and removing synthetic organic contaminants and disinfection by-products

Joshua P. Kearns, Kyle K. Shimabuku, Ryan B. Mahoney, Detlef R. U. Knappe and R. Scott Summers

ABSTRACT

A variety of natural and anthropogenic contaminants can compromise the safety and esthetics of surface water collected for drinking and disinfected using chlorine by households in developing communities. While household chlorination is effective against most microbial pathogens, many users find the taste and odor of chlorine unacceptable and revert to drinking untreated water. Moreover, reactions between chlorine and the dissolved organic matter form harmful disinfection by-products (DBPs) such as trihalomethanes (THMs). Char adsorbers have been used to treat drinking water for thousands of years and are still widely used today. Results obtained here demonstrate that locally produced biomass chars (biochars) exhibit removal capacities comparable to those of activated carbon for removal of THMs, synthetic organic chemicals (SOCs) such as warfarin (WFN) (anticoagulant pharmaceutical, rodenticide), and naturally occurring trace organics such as the taste-and-odor compound 2-methylisoborneol (cyanobacterial metabolite). Results show chars can be used effectively to remove objectionable tastes and odors related to chlorine and cyanobacteria, DBPs, and SOCs. The use of char may lead to microbial risk reduction through greater acceptance of chlorine-based disinfection due to improved water esthetics, as well as chemical risk reduction associated with DBP and SOC exposure.

Key words | adsorption, biochar, charcoal, chemical water contaminants, point-of-use water treatment

INTRODUCTION

While microbial pathogens typically represent the most immediate threat to health, a wide variety of natural (e.g., cyanotoxins) and synthetic organic chemicals (SOCs) can adversely impact the safety of surface and shallow ground waters collected for drinking in developing communities (Kearns *et al.* 2014a). Long-term chronic exposure to trace quantities (ppt to ppb levels) of SOCs such as pesticides, pharmaceutical residues, and fuel compounds, and halogenated disinfection by-products (DBPs) can lead to cancer, birth defects, reproductive disorders, endocrine disruption,

neurological dysfunctions, damage to internal organs, and other toxic effects (USEPA 2006; CDC 2009/2013). In addition, naturally occurring metabolites of cyanobacteria such as 2-methylisoborneol (MIB) and geosmin, and disinfectants such as chlorine, can impair the organoleptic properties of drinking water. While effective technologies for removal of SOCs and objectionable tastes/odors from drinking water such as adsorption by activated carbon (AC) are currently utilized in high-income regions, low-cost, simple and robust technologies for mitigating these

Joshua P. Kearns (corresponding author)

Kyle K. Shimabuku

Ryan B. Mahoney

R. Scott Summers

Department of Civil, Environmental, and Architectural Engineering,

University of Colorado-Boulder,

1111 Engineering Drive, ECOT 441, UCB 428, Boulder,

CO 80309,

USA

E-mail: joshua.kearns@colorado.edu

Detlef R. U. Knappe

Department of Civil, Construction, and Environmental Engineering,

North Carolina State University,

2501 Stinson Drive, Campus Box 7908,

Raleigh,

NC 27695,

USA

contaminants in developing communities have yet to be deployed. This study and others (Kearns *et al.* 2014a, 2014b) have demonstrated that, when prepared under appropriate conditions, biomass chars can be as effective as ACs for adsorption of trace organic contaminants. To achieve the goal of providing safe water for all, harmonization is needed between approaches to water treatment in developing communities and the philosophy and capabilities of affluent-world treatment works through establishing parity between chemical, microbiological, and esthetic concerns for water quality. Because char adsorbents can be produced at low cost from local biomass using simple, scalable technologies (Aqueous Solutions 2014; Kearns *et al.* 2014a), they offer an attainable and environmentally sustainable treatment option for households in rural and developing communities to achieve this harmonization with treatment trains in modern drinking water plants.

The objective of this study was to quantify uptake of (1) trihalomethanes (THMs, the compound class of DBPs typically formed at the highest concentrations); (2) the widely occurring trace level SOC WFN, an anticoagulant pharmaceutical and rodenticide; and (3) MIB, a naturally occurring odorant from surface water by wood-based chars produced under different conditions and in comparison with commercial ACs. To the best of our knowledge, no studies have yet been published describing the adsorption of any of these contaminants by (non-activated) biomass chars.

Chlorine taste and odor concerns and implications for water safety

There is ample evidence that correct and sustained usage of point-of-use (POU) chlorination improves water quality and reduces diarrheal incidence (Quick *et al.* 1996; Semenza *et al.* 1998; Sobsey *et al.* 2003; Chiller *et al.* 2006). However, surveys have demonstrated attenuation of health benefits within 6 months to 1 year from chlorine interventions (Arnold & Colford 2007; Sobsey *et al.* 2008; Hunter 2009). Chlorine residual tests performed in households show a high degrees of non-compliance, up to 73% (Quick *et al.* 1996; Mong *et al.* 2001; Olembo *et al.* 2004). Chlorination programs that do not employ continual advocacy by program staff in the form of regular visits, motivational

interviews, social marketing, and community mobilization often experience low uptake and/or substantial curtailing of use over time (Kirchhoff *et al.* 1985; Roberts *et al.* 2001; Reller *et al.* 2003; Chiller *et al.* 2006). Efforts to sustain consistent household chlorination practices are costly and resource-intensive for NGOs and public health agencies (Deb *et al.* 1986; Semenza *et al.* 1998; Sobsey *et al.* 2003). Water esthetics, especially undesirable taste and odor from chlorine, play a major role in the decline of household chlorination practices (Kirchhoff *et al.* 1985; Roberts *et al.* 2001; Chiller *et al.* 2006). Removal of residual chlorine while maintaining water safety could therefore potentially increase the consistency of POU disinfection practices for many populations. AC has long been used for dechlorination (Magee 1956) as it is capable of rapidly reducing free chlorine (HOCl , OCl^-) to chloride (Suidan *et al.* 1980). Column studies with AC have demonstrated reduction of up to 2.5–4 g of chlorine (as Cl_2) per gram of AC prior to exhaustion (Suidan & Snoeyink 1975; Suidan *et al.* 1980). In batch tests, Mahoney (2012) observed chlorine neutralization capacities by chars produced from a biomass cookstove to be 20–56% that of a commercial granular activated carbon (GAC).

DBP formation in household water treatment

Chlorine-based disinfectants, especially free chlorine, HOCl and OCl^- react with dissolved organic matter (DOM) and bromide, forming hundreds of DBPs known as possible mutagens and teratogens (Richardson *et al.* 2002). DBPs for which the USEPA has established regulatory limits include the sum of four trihalomethanes (total THMs), sum of five haloacetic acids (HAA5), bromate, and chlorite (USEPA 2006). The World Health Organization (WHO) has not established guidelines for DBPs other than THMs, considering THMs to be surrogate compounds for all DBPs in drinking water (WHO 2011). The four regulated THMs are chloroform (CHCl_3), bromoform (CHBr_3), bromodichloromethane (CHCl_2Br , BDCM), and chlorodibromomethane (CHClBr_2 , CDBM). Chloroform, bromoform, and BDCM are classified as probable human carcinogens, and CDBM is classified as a possible human carcinogen by USEPA (2014). WHO guideline values for THMs are 300 $\mu\text{g/L}$, 100 $\mu\text{g/L}$, 100 $\mu\text{g/L}$, and 60 $\mu\text{g/L}$ for chloroform, CDBM, bromoform, and DCBM,

respectively (WHO 2011). WHO also proposes an additive toxicity guideline (WHO 2011):

$$\frac{C_{\text{chloroform}}}{GV_{\text{chloroform}}} + \frac{C_{\text{BDCM}}}{GV_{\text{BDCM}}} + \frac{C_{\text{CDBM}}}{GV_{\text{CDBM}}} + \frac{C_{\text{bromoform}}}{GV_{\text{bromoform}}} \leq 1 \quad (1)$$

where C is concentration and GV is guideline value. The USEPA takes a more stringent approach, regulating the mass sum of the concentrations of the four individual THMs (total THMs, TTHMs) at a maximum contaminant level (MCL) of 80 $\mu\text{g/L}$ (USEPA 2006).

For household disinfection, WHO (2011) recommends free chlorine dose of ‘about 2 mg/L to clear water (<10 NTU) and twice that (4 mg/L) to turbid water (>10 NTU)’ while acknowledging that these doses are likely to lead to chlorine residuals that exceed recommended residuals at the point of delivery for water that is centrally treated (0.2–0.5 mg/L), and can lead to formation of elevated levels of DBPs. To our knowledge, only two studies have examined THM formation during household POU disinfection with chlorine in developing communities or emergency situations (Lantagne *et al.* 2008, 2010). Using sodium hypochlorite solution and local waters collected from rainwater catchment, groundwater, and surface sources (3–7 mg/L TOC) in western Kenya, Lantagne *et al.* (2008) found that 33% of samples taken 24 hours after chlorination with doses ranging from 1.9 to 3.8 mg/L and which resulted in residual free chlorine concentrations of 0.07–3.64 mg/L exceeded the USEPA MCL for TTHMs. No sample exceeded WHO guidelines for individual or additive THMs. In a follow-up study of hypochlorite and dichloroisocyanurate treated drinking waters collected from ground and surface sources (2–10 mg/L TOC) in Tanzania, Lantagne *et al.* (2010) again found that no sample exceeded WHO guidelines for individual or additive THMs for chlorine doses of 2–4 mg/L with 24 hours residuals of 0.2–2 mg/L. However, several samples of chlorinated surface waters approached or exceeded the USEPA MCL for TTHMs. In both of these studies, pretreatment of water by filtration using cloth, sand, or ceramic, or settling for 12 hours and decanting did not remove TTHM precursors.

The chlorine doses (2–4 mg/L) and contact times (1, 8, 24 hours) used by Lantagne *et al.* (2008) did not appear to

achieve full DBP formation potential for most of the Kenyan and Tanzanian surface waters. Household and community water treatment in the developing world is characterized by high degrees of variability in disinfectant dosing and contact times. For example, Lantagne (2008) reviewed recommendations by 18 nongovernmental and emergency agencies and identified variations in NaOCl dose from 0.2 to 28 mg/L. Chlorine overdosing, as well as highly variable contact times ranging from several minutes to several days, are therefore likely scenarios that can lead to increased DBP formation.

SOC occurrence in drinking water sources

Contamination of drinking water sources by SOC such as pharmaceutical residues, a wide variety of biocides, fuel compounds and industrial wastes is a major worldwide problem. A review in *Science* by Schwarzenbach *et al.* (2006) indicates that the >300 million tons of SOC produced annually constitute a major impairment to water quality on a global scale. The residues of human and livestock pharmaceuticals are emerging contaminants frequently detected in wastewater treatment plant effluent, landfill leachate, reclaimed wastewater used for irrigation, and runoff from livestock facilities, and are impacting surface and groundwater worldwide (Kolpin *et al.* 2002; Boxhall *et al.* 2003; Barnes *et al.* 2004, 2008; Sarmah *et al.* 2006; Ankley *et al.* 2007; Larsson *et al.* 2007; Foacchio *et al.* 2008; Carlsson *et al.* 2009; Zhao *et al.* 2010; Luo *et al.* 2011; Fenet *et al.* 2012). For example, as highlighted in *Nature* (Lubick 2009), ‘waste flowing out of a treatment plant near Hyderabad in India pollutes the region’s waters with some of the highest levels of pharmaceuticals ever detected in the environment.’

WFN is the most commonly used anticoagulant for the prevention and treatment of thromboembolic diseases (Ansell *et al.* 2008), and is widely prescribed in both the developed world and developing countries (e.g., in Thailand; Saokaew *et al.* 2012). WFN is also widely used as a rodenticide, with applications in the domestic, agricultural, municipal, and commercial sectors. It has been detected in aquifers and surface water bodies at ppt-to-low-ppb levels (Kinney *et al.* 2006; Godfrey *et al.* 2007). WFN is a polar molecule, and with a pK_a of 5.1, it occurs predominantly in anionic form in most natural waters and as a result is very

water-soluble. Prior research on the adsorption of trace level SOCs, including pesticides, pharmaceuticals, fuel and industrial compounds, by AC found that WFN is difficult to adsorb relative to most other SOCs (Kennedy *et al.* 2015). Thus, if a char adsorbent effectively removes WFN it will likely remove many other SOCs.

MIB is a naturally occurring cyanobacterial metabolite that does not constitute a human health risk. However, at levels as low as 7–10 ng/L (7–10 ppt), MIB imparts a musty flavor and odor to drinking water. In developed countries, AC has proven to be an effective means for controlling MIB-related tastes and odors in natural waters (Suffet *et al.* 1996). Up to 50% of water treatment plants in the US experience periodic taste and odor episodes associated with blooms of cyanobacteria and/or algae (Suffet *et al.* 1996); therefore periodic MIB outbreaks are expected to also occur in many developing community drinking water sources, especially considering that eutrophication management to reduce blooms is not as widely practiced. Like WFN, MIB is very water soluble and difficult to remove via adsorption relative to other SOCs (Kennedy *et al.* 2015). Because MIB is readily detectable by the human nose at very low levels and is more difficult to remove than most other SOCs, it can serve as an indicator for exhaustion of household POU char adsorber units prior to the breakthrough of toxic SOCs under some circumstances (discussed below).

SOC treatment by adsorption to char

Herein the nonspecific term ‘char’ is used for simplicity. Related terms include ‘biochar,’ which refers to the practice of applying biomass-derived char to agricultural soils in order to improve crop yields and sequester carbon, as well as ‘charcoal,’ which refers to biomass-derived char used as cooking fuel. Char is produced by pyrolysis – the thermal degradation of biomass in an oxygen-limited environment – using a range of reactor configurations including retorts, traditional kilns, and gasifiers (Antal & Gronli 2003).

Locally produced biomass chars have been employed in water treatment for thousands of years (Mason 1916). This traditional practice continues today, particularly in rural areas of the major charcoal producing countries such as Brazil, India, China, Thailand, and throughout SE Asia (UNSD

2011). Much recent research has shown that chars can possess appreciable capacity for sorption of a variety of SOCs including industrial compounds, pesticides, and pharmaceuticals. A list of published studies is presented in Table S1 (a)–(c) (available online at <http://www.iwaponline.com/washdev/005/172.pdf>). The potential for use of chars as adsorbents in water contaminant management and environmental remediation has recently been reviewed by Zhang *et al.* (2013a, 2013b), Ahmad *et al.* (2014), Mohan *et al.* (2014), and Nartey & Zhao (2014).

The majority of research to date indicates that SOC sorption, normalized to adsorbent mass, is highest in highly micro-porous chars with large internal surface areas generated at temperatures $\geq 800^\circ\text{C}$ (Chun *et al.* 2004; Chen *et al.* 2008; Uchimiya *et al.* 2010, 2012; Ahmad *et al.* 2012; Graber *et al.* 2012; Han *et al.* 2013; Wu *et al.* 2013; Zhang *et al.* 2013a, 2013b; Zheng *et al.* 2013). Studies with chars generated from traditional kilns and top-lit up-draft (TLUD) gasifier ovens have shown high-temperature chars to be very effective for adsorbing the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) (Kearns 2012; Kearns *et al.* 2014a, 2014b) and the sulfonamide antibiotic sulfamethoxazole (SMX) (Shimabuku *et al.* in preparation). In these batch studies conducted under equilibrium and non-equilibrium conditions, uptake of 2,4-D and SMX by high-temperature chars was equivalent to uptake by commercial AC.

METHODS

Batch mode equilibrium experiments were conducted to quantify uptake of THMs, WFN, and MIB from a representative simulated surface water by wood-based chars. Chars were produced at different temperatures from a retort and from gasifiers at two scales – a 3.8 L (1 gal) cookstove and a 200 L (55 gal) drum oven. Sorption by chars was compared with sorption by commercial powdered activated carbon (PAC) and GAC.

Char generation

Low and intermediate temperature retort (‘R___’) chars were produced from eucalyptus wood cut into slats (15 × 10 × 1 cm), placed in a metal bin, covered with sand to

exclude oxygen, and heated in a laboratory furnace to 350 °C over 96 hours ('R350') and 600 °C over 72 hours ('R600'). Previous research has established that laboratory chars produced in this manner are representative of chars collected from traditional charcoal 'beehive' kilns (Kearns 2012). A 3.8 L (1 gal) TLUD cookstove ('C___') gasifier operated in natural draft and forced draft modes was used to generate intermediate (625 °C, 'C625') and high (900 °C, 'C900') temperature chars from pelletized pine forestry waste (Kearns 2012). A 200 L (55 gal) TLUD gasifier drum oven ('D___'; Aqueous Solutions 2014) was used to produce char from chopped eucalyptus branches at around 900 °C ('D900'). Previous studies have established peak temperature and draft conditions within the pyrolysis reactor to be the dominant controlling variables in the adsorbent characteristics of the product, with biomass precursor identity exerting a negligible influence when comparing woody feedstocks (Antal & Gronli 2003; Downie *et al.* 2009; Kearns 2012; Kearns *et al.* 2014a, 2014b). Thus, chars made from either pine or eucalyptus woods under a given pyrolysis treatment can be considered to have equivalent sorption capacities. Furthermore, the R350 < C625 < C900 series of chars has been demonstrated to encompass the range of SOC sorption capacities – low, moderate, and high adsorption capacity – expected from chars produced from a variety of woody feedstocks using low cost, small-scale traditional kilns and drum ovens (Kearns 2012; Kearns *et al.* 2014a, 2014b).

All chars were ground by hand with a mortar and pestle to pass a US standard 200-mesh sieve (0.074 mm) and dried at least overnight at 105 °C prior to characterization and batch experiments. To measure ash content, around 1 g of each char was accurately weighed in a ceramic crucible and then combusted at 550 °C for 6 hours, cooled to room temperature in a desiccator, and re-weighed. Reported values are averages taken of triplicate measurements for each charcoal sample. Elemental (C, N, H) analyses of each charcoal sample were completed by the Analytical Services Laboratory at North Carolina State University using a CHN Elemental Analyzer (Perkin-Elmer model 2400) calibrated with an acetanilide standard. A reference coal (NIST, 1632c standard reference material trace elements in coal – bituminous) was included as a calibration standard. Oxygen content of each sample was estimated as the

remainder of mass after subtraction of C, N, H, and ash components. Brunauer, Emmett, and Teller (BET) surface areas were determined from N₂ gas adsorption (Autosorb MP-1, Quantachrome Instruments).

The GAC used for SOC uptake comparison with chars was bituminous-based Norit 1240, also ground by hand in a mortar and pestle to pass a US standard 200-mesh sieve. The PAC used for comparison was bituminous-based Calgon WPH, and used as received from the manufacturer (>90% passes US standard 325-mesh (45 µm) sieve).

Batch isotherm tests: THM, WFN, and MIB uptake

Batch sorption experiments were conducted with char doses ranging from 5 to 4,000 mg/L in simulated natural water at pH 7 (maintained throughout using 20 mM phosphate buffer: 1.6 g/L KH₂PO₄ and 1.1 g/L Na₂HPO₄) containing background DOM isolated from a surface water source near Big Elk Meadows, CO, USA. This watershed is non-impacted from a standpoint of wastewater discharges or agricultural runoff. A DOM concentration of 4 mg/L total organic carbon (TOC) was used and is representative of many surface waters. All suspensions were agitated for 2 weeks to reach adsorption equilibrium (contact time to equilibrium established previously, Kearns *et al.* 2014b), and then were filtered through pre-fired glass fiber membranes (1.2 µm Whatman GF/C) to remove the char, and the filtrate analyzed for target SOCs.

To determine WFN and MIB uptake at environmentally relevant levels, 100 ng/L each of ³H-labeled WFN and ¹⁴C-labeled MIB (American Radiolabeled Chemicals, Inc.) were introduced to the initial DOM solution matrix, and later quantified by liquid scintillation counting (method detection limit 5 ng/L for each compound). WFN uptake was determined in separate experiments that did not include chlorine, as it can be degraded by chlorine oxidation (Glassmeyer & Shoemaker 2005). MIB is stable in the presence of chlorine and so could be studied simultaneously with THM uptake. MIB uptake was also quantified in the absence of chlorine for direct comparison with WFN uptake in the presence of background DOM (4 mg/L TOC). Percent MIB and WFN uptake as a function of adsorbent dose was described with the ideal adsorbed solution theory (IAST) using a simplified equivalent background compound

(EBC) approach (Qi *et al.* 2007). Batch reactors were modeled as bi-solute systems containing either WFN or MIB and the EBC, which represents the competing fraction of the DOM. In this case, percent WFN or MIB removal can be expressed as a function of adsorbent dose as follows:

$$\frac{C}{C_0} = \frac{[n_{\text{EBC}}/nK]^n C_{0\text{EBC}}^{n-1}}{D_{\text{ad}}^n + [n_{\text{EBC}}/nK]^n C_{0\text{EBC}}^{n-1}} = \frac{A}{D_{\text{ad}}^n + A} \quad (2)$$

where C = the equilibrium concentration of the trace organic compound (μM); C_0 = the initial concentration of the trace organic compound (μM); $C_{0\text{EBC}}$ = the initial concentration of the EBC (μM); $1/n$ = the Freundlich isotherm exponent of the trace organic compound; $1/n_{\text{EBC}}$ = the Freundlich isotherm exponent of the EBC; K = the Freundlich isotherm capacity parameter of trace organic compound, $(\mu\text{mol}/\text{mg})/(\mu\text{M})^{1/n}$; and D_{ad} = the adsorbent dose (mg/L). In practice, since the numerator is a constant (denoted 'A' in Equation (2)) that also appears in the denominator, the logarithmic form of Equation (2) was used by inputting experimental data and applying the goal-seek function in MS Excel to search for A and $1/n$ such that the sum of squares of the error was minimized.

To determine THM uptake, batch tests were initiated after the DOM solution had been in contact with free chlorine at pH 7 for 7 days in dark, headspace-free amber bottles at 25 °C. Two residual free chlorine concentrations were targeted: (1) 5 mg/L (Standard Method 5710) and (2) 13 mg/L, by following the same method but with excess free chlorine, to represent a field-relevant scenario where over-chlorination occurred. Both chlorination conditions produced a concentration of stable TTHMs

of approximately 215 $\mu\text{g}/\text{L}$, a level that is roughly 2.7 times the USEPA regulatory level, simulating high but field-relevant DBP formation conditions. The solution conditions produced chloroform, DCBM and CDBM – in ratios of approximately 58%, 27%, and 15% of total THMs, respectively – but did not result in the production of bromoform. THMs were quantified using liquid-liquid extraction gas chromatography with electron-capture detection (USEPA Method 551.1). Residual free chlorine was evaluated by the USEPA DPD method (Standard Method 4500-Cl G).

As a preliminary assessment of trace contaminant desorption, the glass fiber membranes with the retained chars from batch uptake experiments were reintroduced to the same DOM background solution, absent WFN and MIB, and agitated for 4 weeks. The suspensions were then filtered and analyzed for desorbed WFN and MIB as described above.

RESULTS AND DISCUSSION

Char characterization

Surface area, ash content, and elemental analysis data are presented in Table 1. The trends of increasing surface area (Rutherford *et al.* 2005; Keiluweit *et al.* 2010), increasing C content and decreasing H:C and O:C ratios (Spokas 2010; Enders *et al.* 2012; Schimmelpfennig & Glaser 2012) with increasing pyrolysis temperature agree with other research. As pyrolysis temperature increased, the decrease in the H:C molar ratio suggests increased char aromaticity. The

Table 1 | Biochar and AC ash and elemental content, and surface area.

Adsorbent	HTT (°C)	%ash	%C	%H	%N	%O	H:C (mol %)	O:C (mol %)	N ₂ BET SA (m ² /g)
C900	900	3.1	94	0.54	0.12	2.5	0.068	0.020	491
D900	900	5.5	89	0.29	0.40	4.6	0.039	0.039	438
R600	600	1.7	93	0.79	0.16	4.5	0.102	0.037	349
C625	625	1.3	92	2.16	0.12	4.3	0.279	0.035	259
R350	350	1.7	72	3.00	0.32	23.4	0.499	0.245	69
GAC	–	5.5	94	0.71	0.53	2.1	0.090	0.017	902
PAC	–	6.3	88	0.12	0.56	5.4	0.017	0.046	697

HTT = highest treatment temperature; C = cookstove; R = retort; D = drum oven.

decrease in the O:C and N:C ratios suggests a reduction in the amount of polar functional groups. This is in agreement with spectroscopy studies that indicate significant presence of noncarbonized aliphatic organic moieties ('volatile matter') in low temperature chars that are mostly or completely absent in highly aromatized high-temperature chars (Chen *et al.* 2008; Keiluweit *et al.* 2010).

Chlorine removal

Chlorine reduction by char was evaluated in batch tests with solutions containing 5 or 13 mg/L as Cl_2 ; i.e., with the solutions resulting from the DBP formation experiments. Upon char addition (5–4,000 mg/L char), the free chlorine residual concentration was reduced to below detection limit (0.02 mg/L) in all batch tests, independent of the starting free chlorine concentration of 5 or 13 mg/L. This result illustrates that the chlorine reduction capacity exceeded 2.5 g Cl_2 /g char for the extreme case – a dose of 5 mg/L char and an initial chlorine concentration of 13 mg/L. Quantifying total chlorine reduction capacity was not an objective of this study. However, given the relatively large capacities for chlorine reduction exhibited by ACs (Suidan *et al.* 1980; Gillogly *et al.* 1998) and cookstove chars (Mahoney 2012), it is unlikely that the chlorine reduction capacity of biochars was reached under the experimental conditions used in the present study. Accordingly, char adsorbents

designed and operated for the control of SOCs, as discussed below, will likely achieve complete removal of free chlorine.

THM uptake

Figure S1 (available online at <http://www.iwaponline.com/washdev/005/172.pdf>) displays the total and individual THM concentrations remaining in solution at equilibrium after contact with chars and ACs for all adsorbents studied, as representatively illustrated for the C625 char in Figure 1(a). Horizontal dashed lines indicate initial concentrations of total and individual THMs (C_0), as well as the USEPA TTHM MCL of 80 $\mu\text{g/L}$. Relative removal (on a percentage basis compared with C_0) of total and individual THMs was approximately consistent for each adsorbent over a dose range corresponding to 10–90% uptake, although CDBM appeared to be slightly better removed by some adsorbents (Figure S2, available online at <http://www.iwaponline.com/washdev/005/172.pdf>). Because the USEPA MCL concerns only TTHMs, the following discussion will consider TTHMs. TTHM removal efficacy was observed in the order PAC > C900 \approx D900 > GAC \approx R600 > C625 > R350 (Figure 1(b)). For the chars, TTHM removal strongly correlated with pyrolysis temperature (R600 > C625 can be explained by a longer heating duration in the retort). This result is consistent with our prior work as well as that of many other researchers (Chun *et al.* 2004; Chen *et al.* 2008; Uchimiya *et al.* 2010, 2012;

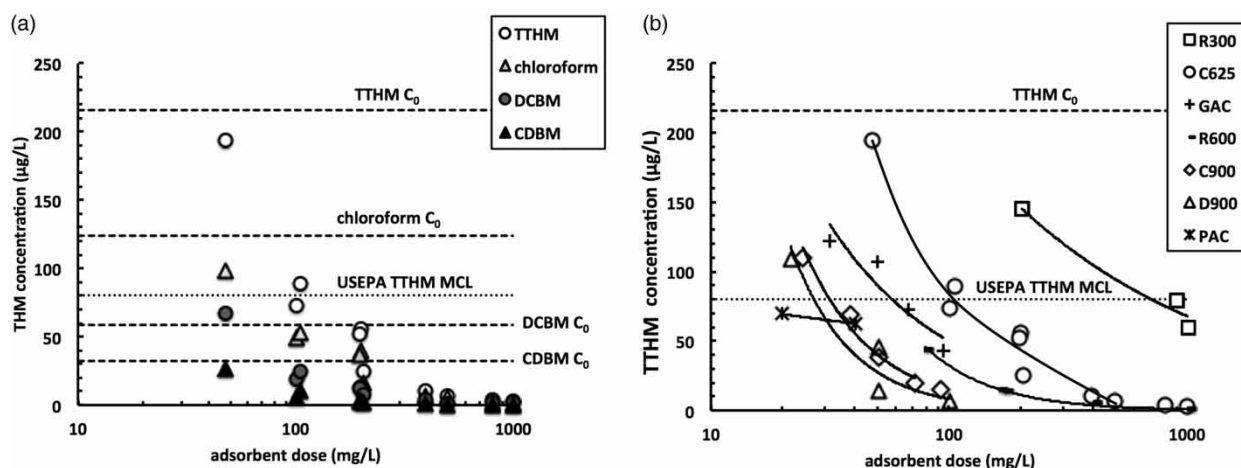


Figure 1 | Total and individual THM concentrations remaining in solution at equilibrium by C625 char (a), and TTHM remaining in solution at equilibrium after contact with chars and ACs (b). Horizontal dashed lines indicate starting concentrations of total and individual THMs (C_0), as well as the USEPA TTHM MCL of 80 $\mu\text{g/L}$. Lines connecting data points in (b) are drawn to guide the eye.

Ahmad *et al.* 2012; Graber *et al.* 2012; Han *et al.* 2013; Wu *et al.* 2013; Zhang *et al.* 2013a, 2013b; Zheng *et al.* 2013) who have observed OC sorption capacity to increase with pyrolysis temperature.

Considering the approximate adsorbent dose required to bring TTHM concentrations below the USEPA regulatory standard under the solutions conditions studied, the high-temperature (900 °C) gasifier chars removed TTHMs about three times as effectively as intermediate temperature (600–625 °C) chars, and about 25 times as effectively as low temperature (350 °C) char. Furthermore, TTHM removals by the high-temperature gasifier chars were comparable to AC. To meet the USEPA standard of <80 µg/L TTHMs under these solution conditions required doses of approximately 20 mg/L, 35 mg/L, and 65 mg/L of PAC, either of the C900 or D900chars, and GAC, respectively.

WFN and MIB uptake

WFN and MIB remaining in solution at equilibrium after contact with chars and PAC on a relative concentration basis (C/C_0 , expressed as a percentage) are shown in Figure 2. Prior research has shown that, when background DOM is present, adsorption of trace SOCs on a percentage basis is independent of initial concentration (Knappe *et al.* 1998). WFN was slightly better removed than MIB by all adsorbents, in accordance with expectations based on previous research with AC (Kennedy *et al.* 2015). Removal efficacy observed was PAC ≈ C900 > C625 > R350, where PAC and the C900 char exhibits about 10 times the sorption

capacity of the C625 char and 100 times the capacity of R350 char. This result is likewise in agreement with our prior work as well as that of many other researchers who have demonstrated sorption to increase with pyrolysis temperature (Kearns *et al.* 2014b).

Figure 3 illustrates the effect of initial free chlorine concentration and the presence of background DOM at a concentration of 4 mg/L TOC on MIB uptake by chars. The presence of DOM and chlorine exert a negative effect on MIB uptake by the intermediate and high-temperature chars. MIB adsorption by the C625 and the C900 chars is observed in the rank order: DI water > DOM in the absence of chlorine > DOM plus 5 mg/L chlorine > DOM plus 13 mg/L chlorine. Studies with ACs have shown background DOM to directly compete with trace SOCs for adsorption sites (Knappe *et al.* 1998; Graham *et al.* 2000; Corwin & Summers 2012). ACs are well graphitized, highly microporous adsorbents. As pyrolysis temperature increases, chars become more aromatic and condensed with less residual amorphous matter and more closely resemble AC physico-chemical properties such as highly developed microporosity (Antal & Gronli 2003; Chen *et al.* 2008; Keiluweit *et al.* 2010). Thus for intermediate to high-temperature chars a similar competitive effect from DOM likely occurs, as suggested in Figure 3.

The presence of chlorine can modify char capacity for MIB adsorption by either or both of two mechanisms: (1) directly, by oxidation of surface adsorption sites on the char, and (2) indirectly, by reaction with background DOM to produce low-molecular-weight compounds that

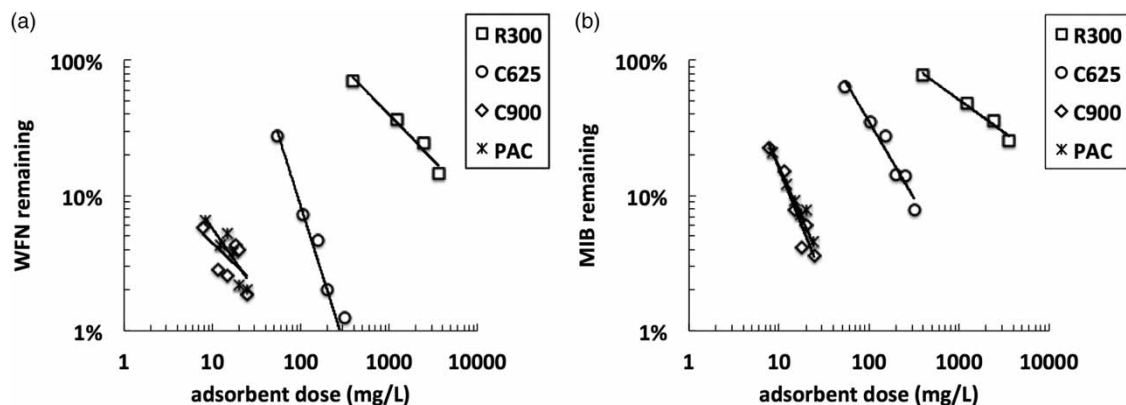


Figure 2 | WFN (a) and MIB (b) remaining in solution at equilibrium after contact with PAC and chars produced from wood at 350 °C (R350), 625 °C (C625), and 900 °C (C900). (The initial DOM concentration was 4 mg/L TOC and chlorine was absent.) Lines represent best fits of the simplified IAST (after Qi *et al.* 2007).

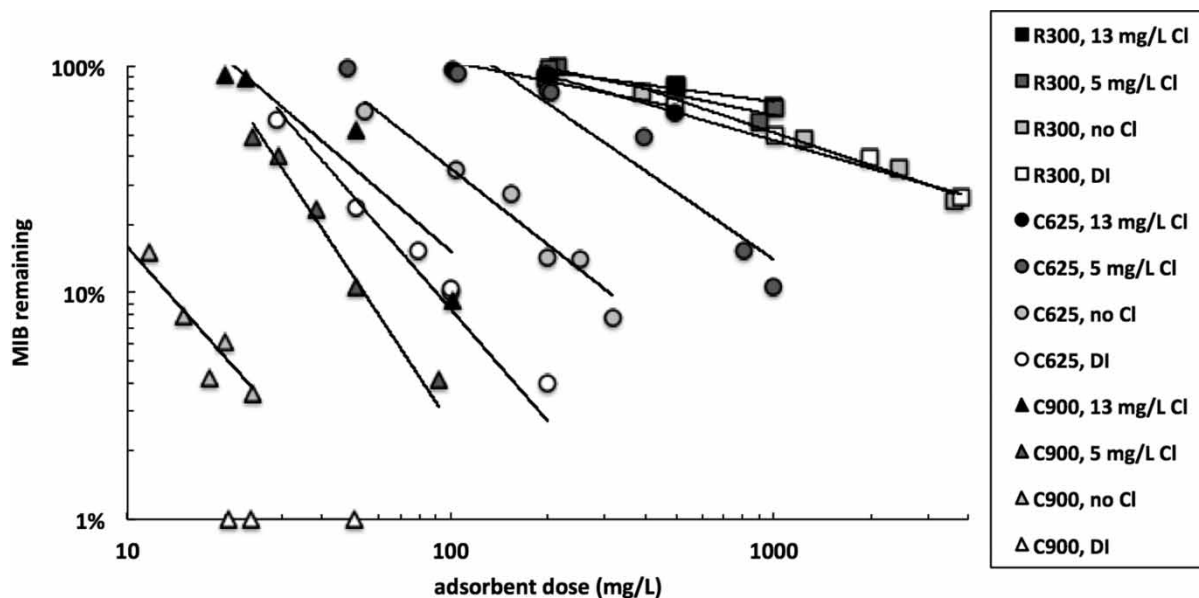


Figure 3 | Effect of initial free chlorine concentration (13, 5, and 0 mg/L as Cl_2) in the presence of background DOM (4 mg/L TOC), and compared with laboratory clean (DI) water, on MIB uptake by chars produced from wood at 350 °C (R350), 625 °C (C625), and 900 °C (C900). Lines represent best fits of the simplified IAST (after Qi *et al.* 2007).

compete with MIB for sorption sites. Gillogly *et al.* (1998) observed MIB uptake by PAC to decrease by about 50% in the presence of 3 mg/L chlorine, and to decrease further with increasing free chlorine concentration. The authors attributed this to the oxidation of MIB adsorption sites by chlorine. It can be hypothesized that oxidized surface sites attract water clusters through hydrogen bonding that physically block MIB access to surface adsorption sites and thereby reduce uptake, a phenomenon that has been observed in OC adsorption by ACs (Li *et al.* 2002). Cook *et al.* (2001) observed reduction in MIB uptake by PAC attributable to competitive adsorption by the increased concentration of low-molecular-weight compounds formed by DOM reaction with chlorine. Observations reported here do not permit discrimination between mechanisms for the decrease in MIB adsorption in the presence of chlorine – more research with biochar and various competing adsorbates is needed to investigate these phenomena.

Figure 3 indicates that MIB is sparingly taken up by R350 char, and uptake does not appear to be influenced by the presence of either chlorine or DOM under the solution conditions studied. It is possible that free chlorine reacts with the abundance of residual aliphatic ‘volatile matter’ in the char and is thereby quenched. OC uptake by low temperature chars is believed to occur mainly by

partitioning and complexation with oxygen-bearing functional groups rather than pore filling and surface adsorption mechanisms (Chun *et al.* 2004; Chen *et al.* 2008; Sun *et al.* 2011; Li *et al.* 2013). Since SOCs are known to partition into bulk organic matter, it is possible that MIB interacts with the amorphous aliphatic domains of low temperature char and adsorbed organic matter similarly. This could explain the observation that MIB uptake by R350 char is similar in DOM and DI water. Further study is needed to support these hypotheses, however.

In summary, an important result for the use of intermediate and high-temperature chars in household water treatment is that typical chlorination conditions reduce batch-mode adsorbent equilibrium capacity for SOCs – in the case of MIB, by about a factor of five. However, batch mode experiments likely overestimate the extent to which chlorine reduces SOC uptake by adsorption units operated in flow-through column mode – a probable configuration for household water treatment – since chlorine reacts rapidly within the top few centimeters of the adsorbent bed (Suidan & Snoeyink 1975; Suidan *et al.* 1980). The presence of background DOM also reduces adsorbent capacity for target SOCs. From a research/experimental perspective, this underscores the importance of quantifying SOC uptake from solutions that are representative of natural drinking

water sources, rather than from laboratory clean (DI) water which leads to overestimation of adsorbent capacity under real-world conditions.

WFN and MIB desorption

A concern regarding the use of char adsorbents is desorption (back-diffusion, or 'leaching') of contaminants out of the char. Recent research using AC has shown little leaching of adsorbed contaminants to occur (Corwin & Summers 2011). The preliminary assessment of trace contaminant desorption conducted in this study showed WFN and MIB below detection levels (5 ng/L) for all chars and AC after 4 weeks of agitation in simulated surface water (data not shown). These results are encouraging; however, the rate and extent of back-diffusion of SOCs adsorbed to chars needs to be better established by further research.

Application of results

Two important results from these studies relevant to application of the chars are: (1) C900 char removed all SOCs roughly equivalent to PAC, and removed TTHMs slightly better than GAC; and (2) that SOC removal by the three chars differs by about a factor of 10 each, in the order C900 > C625 > R30. For the chars, the trend of OC removal corresponds to the trends in increasing C content, decreasing H:C and O:C ratios, and increasing surface area (Table 1). It is interesting that C900 char exhibited similar OC uptake to GAC and PAC despite its significantly lower surface area (491 m²/g for C900 char compared to 697 m²/g and 902 m²/g for PAC and GAC, respectively).

To illustrate how the results of this study can be applied in household and community water treatment systems, Table 2 indicates the approximate adsorbent dose (mg/L) required to meet a given treatment objective for WFN, MIB, and TTHMs based on equilibrium contaminant uptake data. A separate study described a method for using adsorbent dose data collected in batch studies for design and operation of flow-through char adsorber units (Kearns *et al.* 2014a). The treatment objective of 90% removal was set for MIB because this corresponds to reducing MIB concentration to the approximate taste-and-odor threshold (~10 ng/L) given a relatively high initial MIB

Table 2 | Minimum adsorbent doses or use rates (mg/L) required to meet treatment objectives for WFN and MIB (C_0 100 ng/L), and TTHMs (C_0 215 µg/L) using activated carbon (PAC, GAC) and chars produced from wood at 350 °C (R350), 600 °C (R600), 625 °C (C625), and 900 °C (C900, D900)

Treatment objective	Adsorbent dose (mg/L) required to meet treatment objective			
	WFN, 90% removal	MIB, 90% removal	TTHMs, USEPA 80 µg/L	TTHMs, WHO additive method ≤ 1
Adsorbent				
AC	6* (PAC)	14 (PAC)	60 (GAC), <20 [#] (PAC)	35 (GAC), <20 [#] (PAC)
C900	3*	13	32	16*
D900	DNA	DNA	27	19*
R600	DNA	DNA	55*	27*
C625	92	304	105	69
R350	7725	29324	700	84

At these char doses all residual free chlorine was removed (data not shown). DNA, did not analyze.

concentration ($C_0 = 100$ ng/L). WFN is currently unregulated by USEPA and WHO, so its treatment objective was set equal to that for MIB, i.e., 90% removal. Two scenarios for TTHM removal were considered, corresponding to the USEPA MCL 80 µg/L and the WHO recommended additive guideline (Equation (1) and Figure S3, which is available online at <http://www.iwaponline.com/washdev/005/172.pdf>). Note that all residual free chlorine is removed using char doses that achieve WFN, MIB, and TTHM treatment objectives.

For the low and intermediate temperature R350 and C625 chars, MIB removal requires the greatest char dose and would thus govern char adsorber design and operation to meet MIB, WFN, and THM treatment objectives. This is fortuitous in climatic locations such as the tropics and in general during warm seasonal periods when MIB is likely to be present, since it can be readily detected by unaided human senses at low levels and does not pose a health concern. Detection of MIB taste/odor by users could therefore provide a convenient indicator for char replacement. With increasing char pyrolysis temperature, MIB and WFN removal efficiencies improved more dramatically than THM removal efficiency. As a result, char doses to meet the THM removal criterion were larger than those for MIB and WFN, and char adsorber design and operation would have to take this into account. Note, however, that

under the experimental conditions used here, the C900 char dose of 13 mg/L required for 90% MIB removal would be expected to achieve $\geq 50\%$ TTHM removal. This could be an acceptable treatment objective for waters with lower background DOM levels and/or under more moderate chlorination conditions that are likely to form fewer DBPs. The overall higher contaminant uptake capacity of high-temperature chars will reduce capital costs and adsorber unit maintenance frequency.

Starred values were derived by extrapolation beyond the range of data collected. Values for WFN and MIB were calculated using the simplified IAST (Qi et al. 2007).

Values for TTHMs were derived visually from Figures 1(b) and Figure S3 (available online at <http://www.iwaponline.com/washdev/005/172.pdf>).

The hatch denotes that for TTHM removal by PAC, the quantity of data points was insufficient to perform an extrapolation with confidence.

CONCLUSIONS

This paper has indicated that trace level organic contaminants and halogenated DBPs are a challenge to the provision of safe drinking water at the household level. Presented here is a viable low-cost treatment option for chemical and microbial risk reduction through (1) effective mitigation of chemical toxin exposure and (2) improvement of drinking water organoleptic properties that can reinforce safe water practices (i.e., disinfection using chlorine). This work has shown how traditional methods can be optimized for production of enhanced adsorbent chars. High-temperature ($\sim 900^\circ\text{C}$) wood chars produced from gasifier ovens were demonstrated to perform comparably with commercial ACs for equilibrium uptake of selected SOCs from representative surface water at environmentally and field-relevant concentrations. High-temperature gasifier chars have roughly 10 times the organic contaminant adsorption capacity of intermediate temperature ($\sim 600^\circ\text{C}$) chars and at least 100 times the capacity of low temperature ($\sim 350^\circ\text{C}$) retort chars. This work also revealed that chlorination and the presence of background DOM decrease the adsorption capacity for trace SOCs by biochars in a similar manner as has been observed here and elsewhere for ACs.

Adsorption using local biomass chars produced at high temperature is potentially a cost-effective, sustainable, and practical option for household and community water treatment. This work promotes harmonization between approaches to water treatment in developing communities and the philosophy and capabilities of affluent-world treatment works through advancing parity between chemical, microbiological, and esthetic concerns for water quality. Further efforts are needed to increase understanding of pollutant sorption mechanisms by a wider variety of chars under dynamic (non-equilibrium) conditions, as well as for long-term monitoring and validation of chlorination and char adsorber systems in the field at the household and small community scales in the context of sustained use, costs, and health outcomes.

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