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Trace organic contaminant removal from drinking water using local char

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Chemical contamination of drinking water sources is a worldwide problem. However, few locally managed, sustainable, and low-cost on-site treatment technologies are available in rural and remote situations. Char filter-adsorbers have been used to treat drinking water for thousands of years and are still widely used today. Our laboratory studies have shown that chars derived from surplus agricultural and forestry biomass using low-cost, low-emission gasifier cookstoves and drum-ovens develop favorable sorption properties for uptake of prevalent organic contaminants such as 2,4-D herbicide, environmentally persistent pharmaceuticals sulfamethoxazole and warfarin, algal metabolite 2-methylisoborneol, and trihalomethane by-products resulting from chlorine disinfection. Based on these studies we present design recommendations for integrating char adsorbers into low-cost multi-barrier treatment trains for on-site water provision. We also present field observations and monitoring data from application of char adsorbers in Thailand and eastern Burma.

Introduction

While microbial pathogens typically represent the most immediate threat to health, a variety of natural (e.g., microcystins) and anthropogenic (e.g. pesticides, pharmaceutical residues, fuel compounds, industrial waste chemicals) organic contaminants (OCs) impact the safety of surface waters collected for drinking in developing communities. A 2006 review in *Science* (Schwarzenbach et al., 2006) indicates that the 300 million tons of anthropogenic OCs produced annually, including 5 million tons of pesticides, constitute a major impairment to water quality on a global scale, and "pesticide pollution" appears twice in the top ten of *The World's Worst Toxic Pollution Problems Report 2011* by the Blacksmith Institute (Harris and McCartor, 2011). Long-term chronic exposure to trace quantities of OCs can lead to cancer, diseases of the endocrine and reproductive systems, and damage to the liver, kidneys, or central nervous system, and other toxic effects (CDC, 2009/2013). Additionally, naturally occurring algal metabolites (2-methylisoborneol, geosmin) and disinfectants (Chlorine) can adversely impact water aesthetics. Objectionable taste and odor has played a major role in the decline of household chlorination practices (Roberts, et al., 2001). Therefore, the development of effective, affordable and scalable "green" treatment technologies for OC removal and taste/odor control that are accessible to communities in remote regions of the developing world and in emergency/disaster relief/humanitarian crisis situations is warranted.

Char filter/adsorbers have been used to treat drinking water for thousands of years and are still widely used today – particularly in rural areas of major charcoal producing countries such as Brazil, India, China, Thailand, and throughout SE Asia (UNSD, 2011). Locally managed treatment with char might represent the most effective barrier to harmful OC exposure available to households and communities in remote and impoverished regions of the world, because char can exhibit properties similar to activated carbon (AC); i.e., a highly micro-porous structure with large internal surface area that provides a plenitude of adsorption sites (Chen et al., 2007). AC is the most widely employed sorbent medium in drinking water treatment plants in developed countries but is cost-prohibitive and inaccessible in rural, remote, and impoverished locations.

Our work with biomass chars generated from traditional charcoal kilns and low-emission up-draft gasifier cookstoves and drum-ovens have shown some of these materials to be very effective for sorbing the prevalent herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) (Kearns et al. in review; Kearns 2012), the environmentally persistent pharmaceuticals sulfamethoxazole (SMX; Shimabuku et al., in review) and warfarin (WFN; Kearns et al., in review), the algal metabolite 2-methylisoborneol (MIB; Kearns et al., in review), residual chlorine (Mahoney et al., in review), and trihalomethane disinfection by-products (Kearns et al., in review). Our findings are in agreement with those of other researchers indicating that contaminant sorption capacity, normalized to sorbent mass, is generally favored in highly micro-porous chars with large internal surface areas generated at high temperatures (≥750 °C) (Ahmad et al., 2012; Chen et al., 2008; Graber et al., 2012; Han et al., 2013; Uchimiya et al., 2012; Zhang et al., 2013, 2011; Zheng et al., 2013). Chars generated from high temperature biomass gasifiers such as 200-L drum-ovens and smaller cookstove units have demonstrated trace contaminant uptake equal to that by commercial AC (Kearns et al., in review; Mahoney et al., in review; Shimabuku et al., in review; Kearns 2012). Moreover, gasifier char production is favorable compared with traditional kiln char production because (1) it is more energy efficient and less polluting, (2) it can make use of a wider array of agricultural and forestry residues, (3) gasifier units can be more readily coupled with ancillary applications of emitted heat (e.g. cooking, heating water, drying crops, biofuel production), and (4) it generates a more consistent and high-performance adsorbent char for water treatment.

In this paper we stress that harmful trace level OCs are a substantial, though often overlooked, impairment to drinking water safety in developing communities, and present an overview of the development of local and sustainable treatment options using biomass char adsorbents. We summarize batch-mode laboratory studies that quantify the adsorption capacity of chars produced with both traditional kiln and contemporary gasifier technologies from a variety of biomass precursors (feedstocks) for 2,4-D, SMX, WFN, MIB, and total trihalomethanes (TTHMs) in comparison with commercial AC benchmark. Based on these studies and our field work with village and migrant communities in SE Asia, an approach to the design and integration of char adsorber units in decentralized locally managed water treatment trains at three throughput scales (30, 300, and 2000 L/day) is presented. If selected, our oral presentation will also discuss results from ongoing monitoring of multi-barrier treatment systems serving rural communities in Thailand and eastern Burma.

Laboratory study of trace OC uptake by chars

Materials and methods

Experimental chars were produced under low, intermediate, and high temperature regimes (350, 625, and 900 °C; "LT," "IT," "HT," respectively) from eucalyptus and pine wood using a laboratory retort pyrolyzer, and 1-gal and 55-gal top-lit up-draft (TLUD) gasifiers. Here, in agreement with other research (Downie et al., 2009; Antal and Gronli, 2003), peak temperature and draft conditions within the pyrolysis reactor were shown to be the predominant controlling variables in the development of char properties. Therefore, for brevity we do not make a distinction between wood chars made from pine or eucalyptus. LT char was produced from eucalyptus wood cut into slats, placed in a metal bin, covered with sand and heated in a laboratory furnace to 350 °C over 96 hours. Previous field observations and char characterization have shown this method to produce char representative of traditional charcoal kilning. A 1-gal TLUD gasifier cookstove operated in natural draft and forced draft mode was used to generate IT and HT chars, respectively, from pelletized pine forestry waste. A natural draft 55-gal TLUD gasifier drum oven was also used to produce HT char from chopped eucalyptus branches. Costs, construction and operation of these gasifiers are described in Kearns (2012) and at www.aqsolutions.org. Our studies have shown that these LT, IT, and HT chars encompass the range of sorption capacity expected from biochars produced from a variety of feedstocks using low cost, small scale traditional kilns, cookstoves and drum-ovens (Kearns et al., in review; Mahoney et al., in review; Shimabuku et al., in review). Sorption capacity comparisons were made using ACs (bituminous-based Norit 1240 GAC and Calgon WPH PAC) as benchmarks. All chars and the GAC were ground by hand in a mortar and pestle to pass a US standard 200-mesh sieve prior to batch tests, and 325-mesh prior to jar tests.

Batch tests were conducted using char doses ranging from 5-5000 mg/L in simulated natural water with neutral pH and a background dissolved organic matter matrix of 4 mg/L total organic carbon. This matrix was spiked with environmentally relevant initial OC concentrations: 2,4-D at 100 μg/L; and SMX, WFN, and MIB at 100 ng/L. For the disinfection by-products uptake tests, chlorination conditions were selected

(Standard Method 5710) to produce about 200 µg/L total THMs (sum of chloroform, bromoform, bromodichloromethane, and chlorodibromomethane) representative of typical household chlorination systems using surface water. Separate batch studies were used to quantify uptake of each OC (the four THMs were generated in mixture but quantified individually) to avoid solute competition effects and for ease of quantitation using liquid scintillation counting with ^{3}H and ^{14}C labelled reagents for 2,4-D, SMX, WFN, and MIB. SMX uptake was studied in rapid format using standard jar test procedure and 10, 30, and 60 minute contact times. 2,4-D, WFN, MIB, and TTHM uptake was quantified under pseudo-equilibrium conditions after 14 days' contact time under agitation.

Results

Full results of these studies will be made available in the referenced publications. For brevity, a summary dataset is presented here. Figure 1 indicates the sorption efficacy for 2,4-D, SMX, WFN, MIB, and TTHMs by LT, IT, an HT chars relative to commercial activated carbon benchmarks. Trace OC removal by the three chars differs by about a factor of 10, each, in the order HT > IT > LT. HT char removes these OCs with 50-100% the effectiveness of the commercial AC benchmark. Removal of residual chlorine is addressed by Mahoney et al. (in review) and will be omitted here, as conditions for trace OC removal already ensure complete residual chlorine removal.
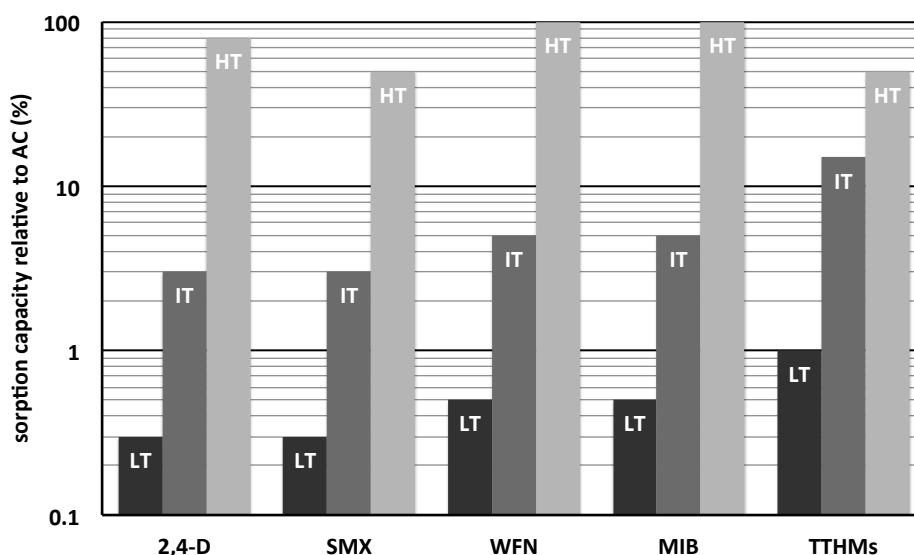

Figure 1. Trace contaminant adsorption capacity relative to commercial activated carbon (AC) as a function of pyrolysis temperature for LT, IT, and HT chars (350, 625, and 900 °C, respectively)

Integration of char adsorbers in multi-barrier treatment trains

System design

Our work with village and migrant communities in SE Asia has produced designs that integrate char adsorbers into low-cost, multi-barrier treatment trains for decentralized and emergency drinking water provision. Community systems at two throughput scales – 300 and 2000 L/day – have been developed and deployed, and a 30 L/day household system prototype is currently evaluated. System costs, design, construction and operation are described in detail at aqsolutions.org. The systems remove both biological and chemical contaminants, are implemented using common local materials and tools, and can be constructed to operate by gravity flow. A sequence of an up-flow gravel roughing filter followed by a down-flow biologically active sand filter and then a down-flow char adsorber is used as illustrated for the 2000L/day system in Figure 2. The roughing filter removes turbidity and some dissolved compounds that sorb to the particle and media surfaces. The biologically active sand filter removes microorganisms and particles by a variety of mechanisms (physical straining, adsorption, interception, sedimentation) and prevents the establishment of microbial pathogen colonies through competition and predation (Sobsey et al.,

2008). Bio-sand filters can also remove some chemical compounds by biodegradation (Zearley and Summers, 2012). The char adsorber, in addition to sorbing SOCs, also develops attached biomass, which can extend the treatment of biodegradable compounds.
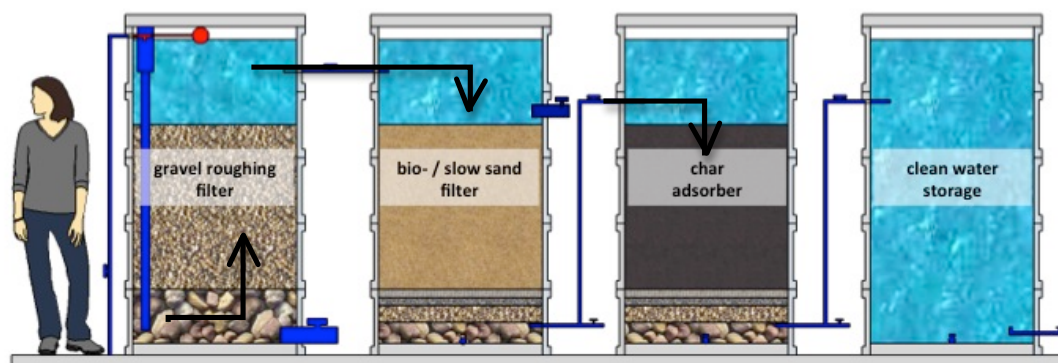

Figure 2. 2000 L/day gravity flow multi-barrier treatment system incorporating a char adsorber unit

Field monitoring methods

Monitoring individual trace level OCs in the field is typically problematic, impractical, and prohibitively expensive. Surrogate measures are therefore needed to assess char adsorber performance *in situ*. Column studies conducted in the laboratory using AC have consistently shown that background dissolved natural organic matter, as measured by absorbance of UV light at 254 nm (UVA_{254}), breaks through well before strongly adsorbing organic micro-pollutants (Corwin and Summers, 2012). For example, in studies using commercial GAC, even when UVA_{254} removal had declined to 30%, 2,4-D removal was still $\geq$90%. Monitoring UVA_{254} therefore provides a field-feasible and conservative approach to evaluating system performance for removal of pesticides and a means for estimating full-scale bed life of the char adsorber. For example, our ongoing field study has shown, in one particular installation, after one year of operation the char adsorber was capable of removing >30% of influent UVA_{254}. If we assume potential 2,4-D input to the system at high but environmentally relevant concentration (~100 μg/L), >30% UVA_{254} removal corresponds to 2,4-D removed to levels far below the USEPA MCL (70 μg/L) and the WHO Guideline value (30 μg/L).

Summary and conclusions

In this paper we stress that assaults to human health by trace level organic chemical water contaminants are an inadequately appreciated challenge in WASH development efforts. We present a viable low-cost option to address this challenge that builds upon traditional methods of water treatment using local biomass chars. We advance an optimized variation on traditional char production that exhibits vastly improved emissions, makes use of a wide array of sustainably derived agricultural and forestry by-products, and generates a consistent and effective sorbent for decentralized water treatment applications. In concert with other research, our results indicate that the trace OC uptake capacity of char increases with increasing pyrolysis temperature, and that high temperature gasifier chars can be 50-100% as effective as commercial AC. We have designed and deployed multi-barrier drinking water systems incorporating adsorption with char at different throughput scales, and developed an accompanying surrogate method for field monitoring. Our ongoing field efforts continue monitoring of extant water systems over multiple annual cycles, as we further refine our understanding of organic pollutant sorption phenomena by chars under laboratory conditions. This work will advance development agencies' goals to provide safe drinking water through the optimization of char adsorber units and their integration with real world decentralized water treatment system design and operation.

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