

Synthetic organic water contaminants in developing communities: an overlooked challenge addressed by adsorption with locally generated char

Joshua P. Kearns, Detlef R. U. Knappe and R. Scott Summers

ABSTRACT

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, remote, and emergency/disaster relief/humanitarian crisis situations. Char filter-adsorbers have been used to treat drinking water for thousands of years and are still widely used today. Our studies show that some chars produced by traditional means from a range of feedstocks develop favorable sorption properties for uptake of 2,4-dichlorophenoxyacetic acid (2,4-D), a prevalent herbicide and water contaminant. However, more energy efficient, environmentally sustainable and scalable production of consistent highly sorptive chars can be accomplished with biomass gasification. Our laboratory studies demonstrate that locally produced char adsorbents derived from surplus agricultural and forestry biomass are effective for adsorbing 2,4-D. A year-long study of field-scale application of chars in Thailand is also presented. Based on these studies we present design recommendations for integrating char adsorbents into low-cost, multi-barrier treatment trains for on-site water provision.

Key words | biochar, charcoal, drinking water, herbicide, pesticide, Thailand

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INTRODUCTION AND BACKGROUND

The objectives of this paper are to demonstrate that synthetic organic compounds (SOCs) such as pesticides are a substantial, though often overlooked, impairment to drinking water safety in developing communities, and to present an overview of the development of local and sustainable treatment options using biomass char adsorbents. We utilize our experiences in Thailand to demonstrate the SOC occurrence problem, to illustrate traditional and improved char production, and to present a case study of char application for drinking water treatment. In the second section of this paper, results of batch-mode herbicide uptake studies are presented that quantify the adsorption capacity of chars produced with both traditional kiln and contemporary gasifier technologies from a variety of biomass precursors (feedstocks). Based on these studies, a conservative approach to the design and integration of char adsorber units in decentralized, locally managed water treatment trains is

presented, as are the results of more than one year of monitoring data for a multi-barrier treatment system serving a small Thai farm community.

Synthetic chemical contaminants

Contamination of drinking water sources by harmful SOC such as pesticides is a major worldwide problem. 'Pesticide pollution' appears 'twice' in the top ten of 'The World's Worst Toxic Pollution Problems Report 2011' by the Blacksmith Institute (Harris & McCartor 2011), and has been indicated in every year's report since initial publication in 2006. Pesticide exposure through drinking water has been linked to cancer, birth defects, reproductive disorders, endocrine disruption, neurological dysfunctions, and other deleterious human health effects (CDC 2009/2013). Effective, affordable and scalable 'green' treatment technologies for

SOC removal that are accessible to communities in remote regions of the developing world and in emergency/disaster relief/humanitarian crisis situations are, however, lacking.

A recent review in 'Science' (Schwarzenbach *et al.* 2006) indicates that the 300 million tonnes of SOCs produced annually, including 5 million tonnes of pesticides, constitute a major impairment to water quality on a global scale. The report highlights particular challenges in developing countries, including the overuse of pesticides, prevalent ignorance of relevant environmental and health hazards, and widespread unauthorized use of 'black market' chemicals. In South and South-East Asia, for example, around three-quarters of the pesticides used are banned or heavily restricted in the West due to deleterious ecological and human health effects (PANNA 1997). The 'Science' authors specify that 'small-scale, household-based removal techniques are often the only possible mitigation strategy due to the lack of a centralized infrastructure', and call for the development of 'reliable, affordable, and simple systems that local inhabitants could use with little training'.

Unfortunately, SOCs are not yet a priority in the water-sanitation-hygiene (WASH) sector of international development. The UN Millennium Development Goals, for example, are only concerned with mitigation of biological agents of waterborne disease (WHO & UNICEF 2010). Microbial pathogens present an acute threat to human health, and focus on these disease agents is therefore warranted. However, the chronic threat of bio-accumulating and acutely toxic chemicals such as pesticides should not be discounted. The immediacy and scale of this problem is illustrated by a survey of 'Hmong' tribe women living in Mae Sa Mai village in the Thailand–Burma border region that reported detection of DDT and its major metabolites in 100% of mothers' milk samples. A number of other biocides (e.g. hexachlorocyclohexane, hexachlorobenzene) were also frequently detected, and infants' exposure to DDT, heptachlor and heptachlor epoxide exceeded by up to 20 times the acceptable daily intakes as recommended by UN-FAO and WHO (Steutz *et al.* 2001).

Pesticide use and occurrence in Thailand

Panuwet *et al.* (2012) report that Thailand has experienced a fourfold increase in pesticide use over the last decade with

nearly 120,000 tonnes of active ingredients imported in 2010. Herbicides make up the largest proportion of pesticide imports at over 80,000 tonnes in 2010. The most commonly imported pesticides, constituting ~75% of the total imported herbicides, insecticides, and fungicides, are listed in Table 1 along with their potential human health effects.

Currently, over 20,000 unique pesticide formulations are sold in Thailand and there are over 26,000 retailers who are licensed to directly sell pesticides without restriction to any buyers or farmers as long as the products are legal to sell (Panuwet *et al.* 2012). However, many more unlicensed pesticide retailers exist. Because of the large number of unlicensed retailers there are widespread sales of unregistered and prohibited pesticides. At present, 98 pesticides are prohibited in Thailand; however, enforcement of restrictions is weak, and according to Panuwet *et al.* (2012) numerous reports have shown widespread use of banned chemicals throughout the country. Banned substances are illegally stocked by insufficiently policed vendors and continue to be smuggled into the country.

Panuwet *et al.* (2012) summarize several studies that report detection of organochlorine (OC), organophosphorus (OP), carbamate, and pyrethroid pesticides in water bodies throughout Thailand. According to Thapinta & Hudak (2000), pesticide residues, especially OC and OP compounds, have been found in soil, water, and agricultural products throughout the country. Between OC and OP compounds, OC insecticides are more commonly detected, although OP compounds tend to occur at higher levels. Potential human health effects of commonly detected pesticides are summarized in Table 1. OC insecticides, including aldrin, DDT, dieldrin, endrin, heptachlor, and lindane occurred frequently in environmental water samples (Thapinta & Hudak 2000). Many of these chemicals, notably DDT, dieldrin and lindane have been banned since the late 1980s. Endosulfan, methamidophos, monocrotophos, and methyl-parathion are still widely used though they have been banned since the early 2000s (Pliangbangchang *et al.* 2009; Panuwet *et al.* 2012).

Schreinemachers *et al.* (2011) surveyed 295 farmers across 12 villages in the highlands of northern Thailand and found that 97% of farms relied on synthetic pesticides for pest management. Over the period 1997–2010 the average quantity of active ingredients per hectare of farmland in the region increased at a rate of 11% per year, more

Table 1 | Potential human health effects and WHO Classifications (WHO 2009) of compounds identified by Panuwet *et al.* (2012), Pliangbangchang *et al.* (2009), and Thapinta & Hudak (2000) as frequently imported, applied, and detected in the environment in Thailand

Chemical name	Target	Chemical class	Toxicity	Developmental or reproductive toxin	Neurological agent	Endocrine disruptor	Carcinogen	Groundwater contaminant	WHO class.	Kearns survey
<i>Most imported compounds (Panuwet et al. 2012)</i>										
chlorpyrifos	insecticide	organophosphorus	moderate	?	yes	suspected	not likely	?	II,III	x
fenobucarb	insecticide	carbamate	moderate	?	yes	?	?	?	II	x
cartap hydrochloride	insecticide	nerve toxin	moderate	?	no	?	?	?	II	
cypermethrin	insecticide	pyrethroid	?	?	?	suspected	possible	?	Ib, II	x
methomyl	insecticide	carbamate	acute	?	yes	suspected	not likely	potential	Ib	x
glyphosate	herbicide	phosphonoglycine	slight	?	no	?	not likely	potential	III	x
paraquat dichloride	herbicide	bipyridium	acute	?	no	suspected	not likely	potential	II	x
2,4-D	herbicide	chlorophenoxy acid	moderate	?	no	suspected	possible	potential	II	x
ametryn	herbicide	triazine	slight	?	no	?	unclassifiable	potential	II	x
atrazine	herbicide	triazine	slight	?	no	suspected	known	known	III	x
mancozeb	fungicide	dithiocarbamate	not acute	yes	no	suspected	known	potential	U	x
carbendazim	fungicide	benzimidazole	slight	?	no	suspected	possible	?	U	x
propineb	fungicide	dithiocarbamate	not acute	yes	no	?	?	?	U	
captan	fungicide	thiophthalimide	acute	?	no	?	known	?	U	
<i>Frequently detected compounds (Thapinta and Hudak 2000, Pliangbangchang et al. 2009)</i>										
aldrin	insecticide	organochlorine	acute	?	no	suspected	known	?	O (RC, SC)	
DDT	insecticide	organochlorine	moderate	yes	no	suspected	known	?	II (RC, SC)	
dieldrin	insecticide	organochlorine	acute	?	no	suspected	known	?	O (RC, SC)	
endrin	insecticide	organochlorine	acute	yes	no	suspected	unclassifiable	?	O (SC)	
heptachlor	insecticide	organochlorine	acute	yes	no	suspected	known	?	O (RC, SC)	
lindane	insecticide	organochlorine	acute	?	no	suspected	known	?	II (RC, SC)	
methyl parathion	insecticide	organophosphorus	acute	?	yes	suspected	unclassifiable	potential	Ia (RC)	x
methamidophos	insecticide	organophosphorus	acute	?	yes	?	not likely	potential	Ib (RC)	x
mevinphos	insecticide	organophosphorus	acute	?	yes	suspected	not likely	potential	Ia	
monocrotophos	insecticide	organophosphorus	acute	?	yes	?	?	?	Ib (RC)	x
endosulfan	insecticide	organochlorine	acute	?	no	suspected	not likely	?	II	x

Health effects data extracted from pesticideinfo.org, the online database of the Pesticide Action Network, accessed April 2013. WHO Classification key: Ia = extremely hazardous; Ib = highly hazardous; II = moderately hazardous; III = slightly hazardous; U = unlikely to present acute hazard in normal use; O = considered obsolete as pesticide, thus not classified. Multiple classifications indicate different formulations of active ingredient. RC = International trade is regulated by the Rotterdam Convention on Prior Informed Consent. SC = Use and production is prohibited or severely restricted by the Stockholm convention on persistent organic pollutants.

than tripling over this period. Four groups of pesticides, OCs, OPs, carbamates, and benzimidazoles, accounted for 70% of the potential environmental impact. Farmers from this region tested positive for metabolites of OP insecticides and ethylene bisdithiocarbamates, as well as elevated concentrations of malathion, 2,4-dichlorophenoxyacetic acid (2,4-D), alachlor, and parathion (Panuwet *et al.* 2008). Researchers also detected OP insecticides, synthetic pyrethroid insecticides and herbicides in children's urine samples (Panuwet *et al.* 2009). The most frequently detected metabolites included breakdown products of malathion, chlorpyrifos, permethrin and other pyrethroids. The highest concentrations of pyrethroid insecticide metabolites were found in children of farmers.

Over the winters of 2006–2007 and 2007–2008, an informal survey of pesticide availability and use was conducted within a 10 km radius of a small farming village located in the same province as Mae Sa Mai village and the study carried out by Schreinemachers *et al.* (2011). Sixty pesticide products were found to be available and/or in use in the area, including several of the compounds listed in Table 1. Of these 60, 33 were identified as moderately to acutely toxic to humans, 15 as cholinesterase inhibitors (neurotoxins), 19 as suspected endocrine disruptors, 8 as reproductive or developmental toxins, 14 as possible carcinogens and 9 as known carcinogens, and 20 as known threats to groundwater contamination. It should be noted that these numbers add up to >60 because many compounds constitute a threat in multiple categories.

The case of Thailand can be related to the global picture of increasing land use intensity and agrichemical use. Schreinemachers & Tipraqsa (2012) demonstrated that, globally, a 1% increase in crop output per hectare is associated with a 1.8% increase in pesticide use per hectare. Thus, global pesticide use per hectare has increased more than proportionally with crop output per hectare. According to these authors, Thailand showed an increase in pesticide use per hectare of 9.1% per annum over the period 2000–2009, a similar trend to many low- and lower-middle income countries. They reviewed several studies indicating that pesticide use in developing countries has increased rapidly because these countries prioritize total food production over food safety and environmental concerns and thus only weakly regulate agrichemical usage. Their study

was also in accordance with other research demonstrating high pesticide application rates in developing countries. For instance, the average Thai farmer used 52 times as much active ingredient per ton of bell peppers as the average Dutch farmer and 21 times as much per ton of tomatoes. The result of this heavy use is increased human exposure. For example, average urinary pesticide metabolites in Thai children are roughly double those measured in US children (Panuwet *et al.* 2012).

For our laboratory research, 2,4-dichlorophenoxyacetic acid (2,4-D) was chosen as a target compound because of its environmental relevance as one of the most widely used herbicides worldwide and one of the most commonly detected pesticides in environmental waters (Gilliom *et al.* 2006; Parsons *et al.* 2008), as well as for its human health implications as a potential carcinogen, suspected endocrine disruptor, and toxicant to kidneys, liver, and reproductive and developmental systems (Gilliom *et al.* 2006; PAN 2013). 2,4-D occurs predominantly in anionic form at typical pH values, and thus is very water soluble. Research in our lab on the removal of dozens of organic micro-pollutants (pesticides, pharmaceuticals, fuel and industrial compounds, and their residues and breakdown products) by carbon adsorbents has consistently shown that 2,4-D is difficult to remove compared with other biocides (Corwin & Summers 2012). Thus, if a system effectively removes 2,4-D we can be confident it is also removing a host of other biocides.

Char production from kilns and gasifiers

Herein the non-specific 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 atmospheric carbon, as well as 'charcoal', which refers to biomass-derived char used as cooking fuel.

Chars can be produced using a range of pyrolysis systems including retorts, traditional kilns and gasifiers (Antal & Gronli 2003). Traditional kiln systems are used to produce charcoals from woody feedstocks, typically for use as cooking fuel (Foley 1986). We have monitored traditional charcoal production in 200 L steel drum/adobe kilns and brick-and-mud beehive kilns in collaboration with farmers

and villagers in northern Thailand and the Thai Royal Forestry Department Wood Energy Research Centre in Saraburi Province. Our laboratory experiments under pyrolysis conditions that simulate kiln production show that the manufacture conditions (e.g. peak temperature and duration of heating) exert a strong influence on char potential effectiveness for water treatment, as some but not all of these charcoals exhibit appreciable sorption capacity for SOCs (Kearns 2012, Kearns *et al.* 2013). Although these initial results are promising, traditional charcoal manufacture systems are energy inefficient and highly polluting, contributing substantially to greenhouse gas emissions, and often making use of unsustainably, and sometimes illegally, harvested feedstocks (Foley 1986; Smith *et al.* 1999; UNDP/UNEP 2009).

Energy efficient, environmentally sustainable and scalable production of consistent highly sorptive chars can be accomplished with biomass gasification. Biomass gasifier stoves are rapidly being disseminated for household cooking in developing communities as they provide energy efficient combustion with reduced emissions, (Grieshop *et al.* 2011; Johnson *et al.* 2011) and produce small batches of char from agricultural and forestry by-product fuels during normal daily use (Carter & Shackley 2011; Roth 2011). Intermediate and large-scale gasifier systems are also being deployed around the world for generation of 'biochar' as an agricultural soil amendment to increase crop yields and sequester carbon (Lehmann & Joseph 2009).

Gasifier char production is favorable from environmental and energy standpoints, when compared with traditional charcoal manufacture, since pyrolysis gases are combusted within the unit rather than emitted as pollutants (Grieshop *et al.* 2011; Roth 2011; Sparrevik *et al.* 2013), thereby providing the energy that drives pyrolysis and obviating the need for an external heat energy source. Also, biomass gasifiers permit the use of a wider range of biomass feedstocks including agricultural and forestry residuals, and can be readily coupled with other unit processes for bio-fuel collection and waste heat utilization (UNDP/UNEP 2009; Roth 2011; Herail 2012; Shackley *et al.* 2012a, 2012b). Moreover, gasifiers are easier and more pleasant to operate than labor-intensive and smoky traditional kilns (Sparrevik *et al.* 2013). Furthermore, gasifiers can be operated with small grained, chipped or pelletized biomass fuels. Gasifiers can readily be linked with other processes and applications

for capture and use of waste heat. Our research has shown both small scale (cookstove) and intermediate scale (200 L, 55-gallon drum) pyrolyzers to consistently achieve the high temperatures ($\geq 850^\circ\text{C}$) required for substantial development of surface area and porosity in the char product, concomitant with improved performance for herbicide uptake in batch experiments (Kearns *et al.* in press). Accordingly, gasifier chars are a promising appropriate, low-cost and environmentally sustainable technology for affordable decentralized water treatment in rural and developing communities and in emergency relief situations.

Sorption with char

Char filter-adsorbers have been used to treat drinking water for thousands of years (for example, the Sanskrit 'Ousruta Sanghita' written c. 2000 BCE states, 'It is good to keep water in copper vessels, to expose it to sunlight, and filter through charcoal'; Mason 1916) and are still widely used today – particularly in rural areas of major charcoal-producing countries such as Brazil, India, China, Thailand, and throughout South-East Asia (UNSD 2011). Locally managed treatment with char might represent the most effective barrier to SOC exposure available to households and communities in remote and impoverished regions of the world as well as in disaster situations, because char can exhibit properties similar to activated carbon; that is, a highly micro-porous structure with large internal surface area that provides a plenitude of adsorption sites (Chen *et al.* 2007). To date, however, few studies have quantified how effective chars can be for use in water treatment.

Granular activated carbon (GAC) is widely recognized as the best available technology for the control of many pesticides and synthetic organic chemicals in drinking water (EPA 2009). Implementation of char adsorber units in small scale decentralized water treatment systems is analogous to that of GAC adsorbers in advanced municipal water treatment facilities. Knappe (2006) and Summers *et al.* (2011) provide thorough reviews of the use of GAC in water treatment, and the scientific theory and engineering principles apply to char adsorbers as well. There are, however, a few important differences between locally generated charcoals/biochars and commercial activated carbon. First, local chars are (ideally) made from

agricultural and forestry residues and sustainably harvested renewable woody biomass. Most commercial activated carbons are made from (nonrenewable) subbituminous and lignite coal, although the availability of carbons prepared from wood and coconut shells is increasing. Both local chars and activated carbons undergo a carbonization/pyrolysis step where the feedstock is heated to several hundred degrees Celsius under an oxygen-restricted atmosphere. However, commercial carbons are subsequently 'activated' by physical and/or chemical processes to further develop the internal pore structure using steam and/or CO₂, or acids. Not only is this activation step expensive, it requires facilities, power, equipment and reagents that are not routinely accessible in developing communities or disaster/emergency scenarios. However, compared with activated carbon, local chars may contain substantial proportions of residual, incompletely carbonized tarry and oily compounds, particularly if the char is generated at lower temperature (i.e. below about 500 °C) as in cooking charcoal manufacture (Antal & Gronli 2003). Local chars may also contain a high proportion of ash if the feedstock consisted of high mineral content grasses or husks (e.g. rice hulls). Since local chars are not formally 'activated' they are not expected to exhibit the same water treatment capacity as commercial/industrial GACs. To compensate for this disparity, char adsorber systems are designed for higher carbon use rates; that is, the mass of carbon required to treat a given volume of water. The question of potential leaching of residual tars and oils is addressed in the next section.

Practical considerations in the use of char adsorbers

In char adsorbers, as in conventional granular media filters, a natural biofilm develops if no disinfectant residual is present in the effluent. The biofilm on the char surfaces is likely sparse (Herzberg *et al.* 2003) and may aid SOC removal. For example, some compounds typically classified as non-biodegradable were broken down in long-running bio-filters, including the herbicides 2,4-D and clofibric acid and the insecticides aldicarb and dimethoate (Zearley & Summers 2012).

An often-raised concern regarding char adsorbers is desorption (back-diffusion, or 'leaching') of contaminants out of the char, either during its lifetime in the adsorber bed or during the disposal phase. However, recent research

on GAC systems has shown little leaching of adsorbed contaminants to occur (Corwin & Summers 2011). Analogously, a study of over 50 diverse (non-activated) biochars found negligible leaching of native polycyclic aromatic hydrocarbons (PAHs) and dioxin compounds formed during char manufacture as these compounds are strongly bound within the char matrix (Hale *et al.* 2012). While results from prior studies suggest that the release of adsorbed SOC from GAC and native PAHs from char may not be a major concern, the rate and extent of back-diffusion of SOC from char needs to be established in future work. Such information is important for both the use phase of char in char adsorbers and the subsequent disposal phase. Spent chars may pose a problem and should be isolated from direct contact with surface and ground water. One isolation approach would be burial in a clay-lined pit above the local water table. While current research indicates slow desorption, further research is necessary to identify alternatives and develop best practices for spent char disposal.

UPTAKE CAPACITY OF CHARS FOR 2,4-D

The principal objective of the laboratory and field studies detailed here and below is to demonstrate the applicability of locally generated chars for small-scale decentralized water treatment. The goals of the bench-scale experiments described in this section were to: (1) compare the 2,4-D adsorption capacity between chars produced with both traditional kiln and contemporary gasifier technologies from a variety of biomass precursors (feedstocks); and (2) identify production conditions that yield char sorbents effective for SOC removal from drinking water sources.

Methods

A traditional 200 L steel drum/adobe kiln was used to generate chars from bamboo, split eucalyptus, longan (*Dimocarpus longan*), and pine logs. A lab pyrolyzer was developed at the University of Colorado-Boulder (UC-B) to produce chars under conditions that simulated the kiln method. Four feedstocks – bamboo, split eucalyptus, longan, and pine logs – were cut into slats of uniform size

(15 cm × 10 cm × 1 cm) and pyrolyzed under controlled temperatures (550 to 750 °C) and an oxygen-restricted atmosphere. A 1-gallon (3.8 L) top-lit up-draft (TLUD) cookstove gasifier was also developed at UC-B to generate chars from pine, sugarcane bagasse, *Jatropha curcas* seedcake waste pellets, bamboo chips, and rice husks under natural-draft ('ND') and forced-draft ('FD', with an electric fan) conditions. A 55-gallon (200 L) TLUD-ND gasifier was also developed and used to generate separate batches of char made from eucalyptus wood, chopped bamboo, and corn-cobs (Aqueous Solutions, 2012; Kearns 2012).

Batch sorption experiments were conducted with char doses of 5–5,000 mg/L and environmentally relevant initial 2,4-D concentrations. The USEPA maximum contaminant level (MCL) for 2,4-D in drinking water is 70 µg/L, while the WHO Guideline value is 30 µg/L. For brevity, only data from char doses of 100 mg/L and initial 2,4-D concentration 100 µg/L are presented here for making comparisons between chars. The complete dataset will be made available in forthcoming publications (Kearns *et al.* in prep.). Each char was ground by a mortar and pestle to pass a 200-mesh US Standard Sieve and introduced to solutions initially containing: (1) 100 µg/L ³H-labeled 2,4-D; and (2) background organic matter at a total organic carbon concentration of 4 mg/L (to simulate natural waters). Suspensions were agitated for two weeks to reach adsorption equilibrium, and

then were filtered through pre-fired glass fiber membranes (1.2 µm, Whatman GF/C) to remove the char, and the filtrate was analyzed for 2,4-D using liquid scintillation counting.

Results and discussion of laboratory 2,4-D sorption studies

A summary of the batch sorption results is shown in Figure 1. The traditional kiln data shown are average results from chars produced from the four feedstocks at temperatures ranging from 600 to 750 °C. The lab pyrolyzer data represent averages for chars made from the same four feedstocks at each of three separate, well-controlled pyrolysis temperatures. The cookstove gasifier char data are average results for chars made from pine, sugarcane bagasse, and jatropha seedcake pellets, and bamboo chips, each produced under ND and FD conditions which yielded peak temperatures of 625 and 900 °C, respectively. The 55-gallon (200 L) gasifier data reflect the average results from three batches of char made from chopped eucalyptus branches. Average data for multiple feedstocks charred under given conditions are presented because no substantial effect of the biomass precursor was observed for the feedstocks summarized in this study; peak temperature and draft conditions within the pyrolysis reactor were the predominant controlling variables in agreement with other research (Antal & Gronli 2003; Downie *et al.* 2009).

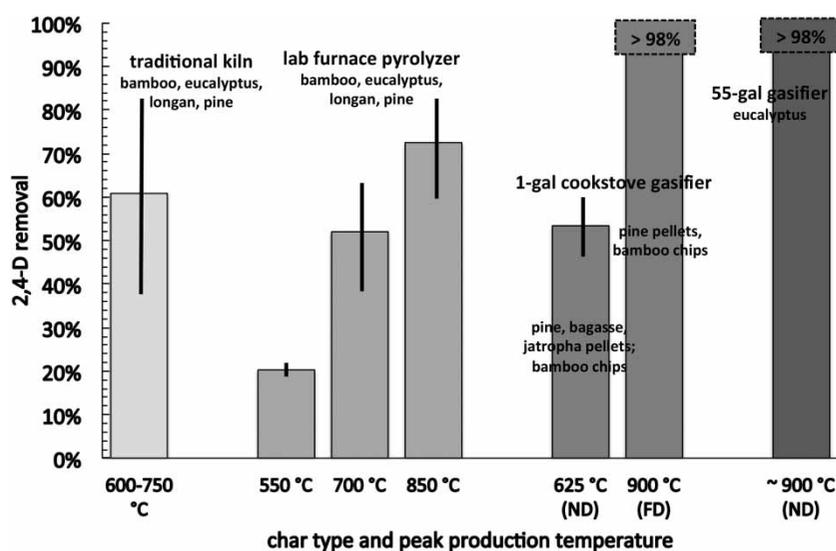


Figure 1 | Average percentage removal of 2,4-D from batch solutions by chars produced from a variety of feedstocks in different reactors and temperature regimes. Char dose: 100 mg/L, 2,4-D initial concentration 100 µg/L. Error bars represent one standard deviation.

The average results from the traditional kiln yielded ~60% removal of 2,4-D and these results were bracketed by the lab pyrolyzer results, 20 to 73% removal, at the three temperatures evaluated. The 2,4-D uptake data illustrate that chars produced under traditional kiln conditions developed for charcoal production can yield significant 2,4-D sorption. However, temperature regimes within traditional kilns vary widely within and between batches, and this temperature variability is one important reason for the large standard deviation associated with the traditional kiln char data shown in Figure 1.

Chars produced from a small cookstove gasifier operated under ND conditions yielded 2,4-D sorption capacities (54%) similar to those produced in kilns. However, utilization of a fan to create a forced draft increased the capacity such that 2,4-D was removed to below the detection limit (2 µg/L), yielding >98% removal. Results similar to those of the FD system were found with the 55-gallon (200 L) TLUD-ND gasifier (>98% removal). Furthermore, temperature regimes within the gasifiers were observed to be much more uniform within and consistent between batches compared with traditional kilns, which is reflected in the smaller standard deviation of the 1-gallon (3.8 L) cookstove ND data despite the diversity of feedstocks pyrolyzed. The summary results presented in Figure 1 illustrate: (1) the wide variability in herbicide uptake by chars obtained from different production methods; and (2) that some chars (i.e. those produced from high temperature gasifiers) exhibit substantial herbicide sorption capacity.

INTEGRATING CHAR INTO MULTI-BARRIER WATER TREATMENT SYSTEMS

The objectives of the field study were to illustrate the integration of a char adsorption unit into a multi-barrier treatment train, to estimate char bed life from bench-scale data, and to demonstrate the effectiveness of a char bed for organic matter removal. Based on the results presented in the previous section, a conservative approach to the design and integration of char adsorber units in decentralized, locally managed water treatment trains is presented here along with case study results comprising more than one year of monitoring data for a multi-barrier treatment system serving a small farm community in South-East Asia.

Treatment system designs

Our work with village and migrant communities in South-East Asia has produced designs that integrate chars into low-cost, multi-barrier treatment trains for decentralized and emergency drinking water provision. These 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 are used as illustrated 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

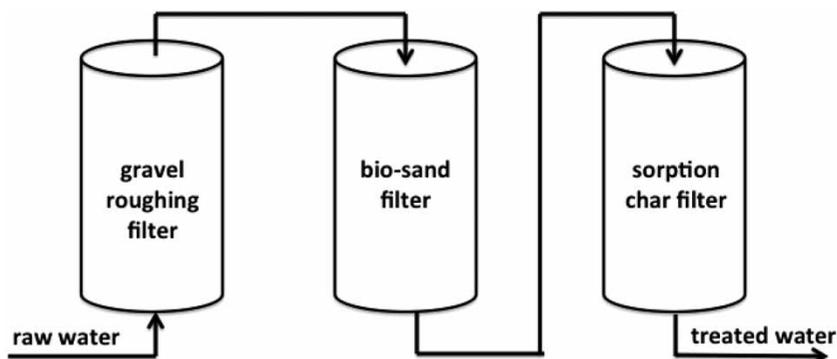


Figure 2 | Treatment flow diagram. Detailed schematics can be downloaded from Aqueous Solutions (www.aqsolutions.org).

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). A thorough rendition of effluent microbial quality assurance measures is beyond the scope of this document. Herein, we restrict our discussion to SOCs and recommend the reader to follow current best practices for microbiological monitoring and assessment (WHO 2006). Bio-sand filters can also remove some chemical compounds by biodegradation (Zearley & Summers 2012). The char adsorber, in addition to sorbing SOCs, also develops attached biomass, which can extend the treatment of biodegradable compounds.

Two throughput scales have been developed: 300 and 2,000 L/day. Their construction and operation are described in open-access handbooks (Aqueous Solutions, www.aqsolutions.org). The 300 L/day system is portable and thus suitable for emergency/disaster relief circumstances, and for households and communities in very remote areas. Containment is provided by four surplus 200 L HDPE (high density polyethylene) drums (note that HDPE does not contain bisphenol-A). Empty drums weigh less than 10 kg and can be readily transported (even carried into remote communities on foot), connected with a small number of PVC fittings, and installed using media generated on-site and acquired nearby. The system costs less than US\$125 to construct (local prices in South-East Asia), can be assembled with minimal hand tools and requires only periodic maintenance of the bio-sand filter ('filter harrowing') and char replacement once per year, as illustrated below. The nominal empty bed contact time (EBCT) for this system with a 70 L bed volume is 5.6 h at the design flow rate of 300 L/day.

The 2,000 L/day system is a more permanent installation meant to provide long-term service to established communities such as small farming villages, schools and children's homes with access to sufficient building materials for tank construction (e.g. concrete, or prefabricated plastic or metal tanks). The char bed volume is 800 L, which yields an EBCT of 9.6 h at the design flow rate. It costs around US\$500 to construct (at South-East Asia prices), and also requires periodic maintenance of the bio-sand filter along with char replacement every 2–3 years.

In the treatment system design presented here (Figure 2), the char adsorber functions analogously to a 'post-filter adsorber' employing GAC in advanced municipal water treatment facilities. The upstream unit processes – the gravel and bio-sand filters – remove a substantial portion of background dissolved organic matter (DOM) and biodegradable compounds from the source water before it encounters the char. These pretreatment steps facilitate optimal utilization of the char for adsorbing specific components of background organic matter (for example, compounds that cause undesirable tastes, odors, or appearance), and SOCs such as pesticides, pharmaceuticals and fuel hydrocarbons that are not well removed by the preceding unit processes.

Adsorber bed life estimation from batch adsorption data

The effective lifetime of the char adsorption media depends on the quality of the char, as well as the characteristics of the source water and efficacy of upstream treatment steps. In the rural developing community or disaster relief contexts, these factors are typified by high degrees of variability and uncertainty. Since char can be generated locally and inexpensively, a conservative approach is recommended, designing for a much larger carbon use rate than is employed in advanced GAC systems. The bed life of a char adsorber can be estimated from char doses used in batch sorption experiments (Figure 1) and the bed density of the char. Example calculations are shown in Box 1 based on the approach presented by Summers *et al.* (2011).

Thus, char adsorber lifetimes using gasifier char are 408 days (1.1 years) and 700 days (1.9 years) for the 300 and 2,000 L/day systems, respectively. Note, however, that these estimates should be taken as rough guidelines. For example, traditional kiln chars required a dose of 500 mg/L to achieve similar levels of 2,4-D removal (data not shown) – this translates to substantially shorter lifecycles of 82 and 140 days for the 300 and 2,000 L/day systems, respectively. Also, the presence of background organic matter is known to reduce the uptake capacity of adsorbents for SOCs and this impact is underestimated when using the batch sorption test (Summers *et al.* 2011). Our ongoing research is refining adsorber design specifications and recommended operation protocols. However, it is ultimately up to the discretion of

Box 1 | Estimating char adsorber bed life

For a char dose, i.e. char use rate, of 100 mg/L (0.1 g/L), gasifier char exhibited >98% 2,4-D removal (Figure 1). Char bed density is approximately 175 kg/m³ (g/L).

Total throughput to exhaustion (number of bed volumes[BV]) equals the bed density divided by the char dose:

$$\text{throughput} = \frac{175 \text{ g/L}}{0.1 \text{ g/L}} = 1,750 \text{ BV}$$

Time to exhaustion equals the number of BV multiplied by the volume of the char bed, divided by the flow rate. Char BV are 70 and 800 L for the 300 and 2,000 L/day systems, respectively.

For the 300 L/day system:

$$\text{time (days)} = \frac{1,750 \text{ BV} \times 70 \text{ L}}{300 \text{ L/day}} = 408 \text{ days}$$

For the 2,000 L/day system:

$$\text{time (days)} = \frac{1,750 \text{ BV} \times 800 \text{ L}}{2000 \text{ L/day}} = 700 \text{ days}$$

the community and water system operator(s) to consider factors such as variability in community water demands and seasonal source water quality concerns (e.g. turbidity and DOM increase during the rainy season, local agricultural cycles and pesticide application periods, nearby industrial development that may impact source water, etc.) in determining an appropriate char adsorber bed size and replacement frequency for each installation.

MULTI-BARRIER TREATMENT SYSTEM MONITORING STUDY

Study methods

A long-term study was initiated in November 2011 to monitor treatment efficacy by a multi-barrier system that has been in continuous use by a rural community in northern Thailand since February 2008. The system provides drinking

water as well as treated water for kitchen and restaurant uses for a population that varies between 10 and 100 people (annual average 40).

Column studies conducted in the laboratory using GAC have consistently shown that DOM, as measured by absorbance of UV light at 254 nm (UVA₂₅₄), breaks through well before 2,4-D and other more strongly adsorbing organic micro-pollutants (Corwin & Summers 2012). For example, in studies using commercial GAC, even when UVA₂₅₄ removal had declined to 30%, 2,4-D removal was still ≥90%. Monitoring UVA₂₅₄ 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.

Water samples were collected after each treatment step, filtered through pre-fired glass fiber membranes (1.2 μm, Whatman GF/C) to remove particulates, and analyzed using a field UVA₂₅₄ spectrophotometer (RealTech P200) with a 10 mm path length. Dissolved iron was

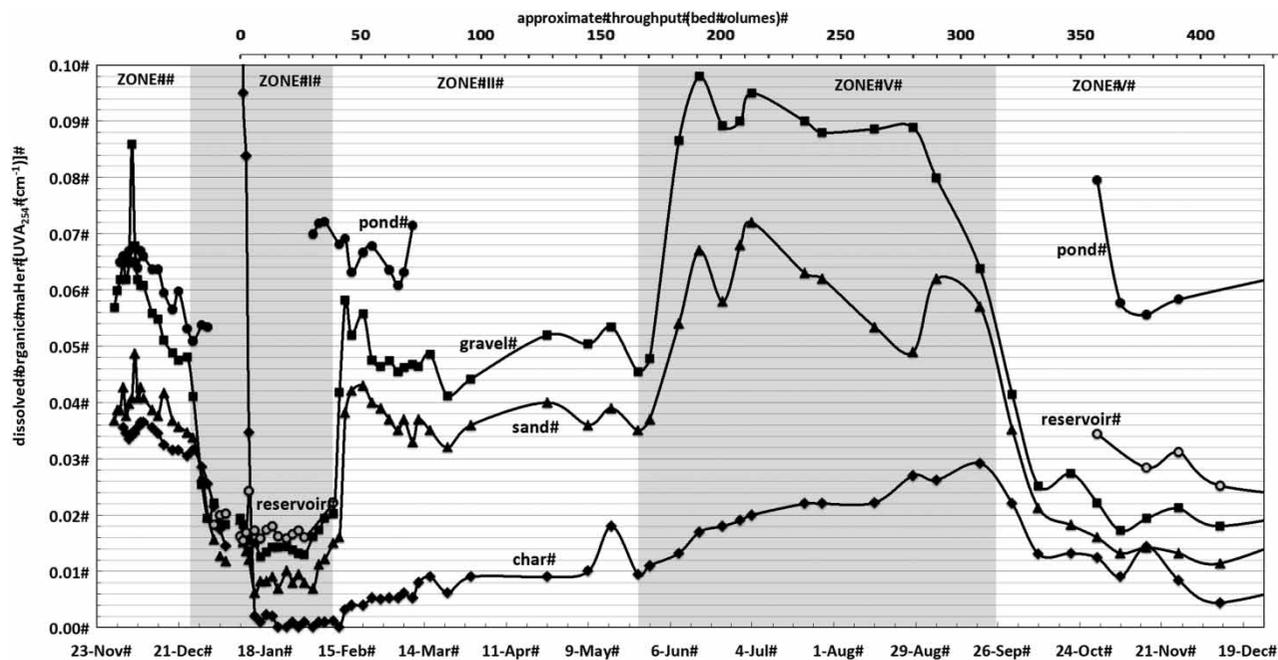


Figure 3 | Dissolved organic matter as measured by UVA_{254} of source waters (closed and open circles) and after subsequent treatment steps: gravel filter (squares), sand filter (triangles), and char adsorber (diamonds) November 2011–December 2012.

measured colorimetrically (Hach DR890 handheld colorimeter, ‘FerroVer’ method 10249) and used to estimate a UVA_{254} correction factor in accordance with Weishaar *et al.* (2003).

Results and discussion

Results of monitoring from November 2011 to December 2012 are presented in Figure 3. Operation time is expressed both as time and throughput in BV treated, where throughput is volume of water treated normalized to volume of char in the adsorption unit.

Zone I

The monitoring study was initiated in November 2011. The system had been in service since February 2008 with no prior maintenance performed on the char adsorber. Source water during this period was taken from a low-lying farm pond. Traditional kiln charcoal purchased in the local village was used by the community in the original installation. In Zone I the plot shows that treatment by the upflow gravel roughing filter

followed by filtration/biodegradation by the biological sand filter removed ~15% and ~30% of DOM, respectively (based on average raw water data). The char adsorber then removed another ~15% (relative to char adsorber influent) by sorption/biodegradation. The spike in gravel filter UVA_{254} was caused during maintenance when the filter was backwashed, the interior of the tank scrubbed, and then refilled.

Zone II

During the ‘Zone II’ period, source water with a lower DOM concentration was taken from a nearby reservoir. The gravel and bio-sand filters achieved ~25% and 35% DOM removal, respectively. The system was taken offline for a few days in early January for char replacement. In this case, 0.8 m³ (140 kg) of gasifier char produced from a 200 L TLUD unit was installed. Zone II shows a rapid decline in char adsorber UVA_{254} as ash and soluble compounds from the fresh char were washed out (this water was discarded and not consumed by the community). After the initial washout, the char adsorber removed essentially all DOM coming

from the bio-sand filter. Also in early January a flowmeter was installed on the system to monitor throughput; since this time average throughput has been 984 L/day (260 gallons/day), standard deviation 220 L/day (58 gallons/day). The throughput scale based on BV of the char adsorber in Figure 2 is an approximation based on an average EBCT of 9.6 h.

Zone III

Near the end of January 2012 the source water was changed back to the farm pond, resulting in increased DOM concentrations in the system influent. The gravel and bio-sand filters each achieved 20–25% removal. During this time DOM output from the char adsorber rose slowly, from nearly 100% removal to ~75% removal over a four-month period.

Zone IV

Late May/early June 2012 marked the onset of the monsoon season, greatly increasing the input and variability of dissolved and particulate matter to the water system. The source water was still taken from the farm pond, although raw water UVA₂₅₄ was not measured during this period. The char adsorber output of DOM continued to rise modestly over this period, from ~75% removal to ~50% removal during a four-month timespan.

Zone V

Near the end of the rainy season the community switched back to the lower DOM reservoir source. With the onset of the dry season and slowly declining DOM input to the system, the char adsorber output of DOM continued to rise modestly from ~50% removal to ~30% removal over a two-month period. As the 2012–13 dry season commenced, background DOM levels in the pond and reservoir source waters returned to approximately 2011–12 levels. At the end of the field monitoring data presented here, 425 BV of water had been treated by the char adsorber. We plan to continue monitoring for several more years in order to capture multiple cycles of char replacement and UVA₂₅₄ breakthrough. These data will be used to further refine

methods for scaling between laboratory SOC sorption studies and full-scale adsorber performance in the field.

SUMMARY, CONCLUSIONS, AND FUTURE DIRECTIONS

In this paper we have indicated that assaults to human health by synthetic chemical water contaminants, such as pesticides, are an inadequately addressed challenge in sustainable community development and emergency/disaster relief circumstances. We have presented a viable low-cost option to address this challenge that builds upon an ancient, traditional method of water treatment by establishing conservative parameters wherein char treatment can be effective for mitigating harms induced by the global proliferation of modern industrial toxins in the environment. We have advanced a low-cost contemporary variation on traditional char production that is less labor intensive, far less polluting, makes use of a wide array of sustainably derived agricultural and forestry by-products, and generates a more consistent and effective sorbent for decentralized water treatment applications. Results showed that the 2,4-D uptake capacity of char increased with increasing pyrolysis temperature, whereas the biomass feedstocks from which chars were prepared played a subordinate role. We have outlined a prototype multi-barrier drinking water system at two throughput scales and provided a robust field monitoring study encompassing annual seasonal variability in source water quality. The field study showed that after a period of one year (425 BV), the char adsorber was capable of removing approximately 30% of the influent UVA₂₅₄. For GAC adsorbers, >90% 2,4-D removal is achieved when UVA₂₅₄ removal is 30%. For the high but environmentally relevant initial 2,4-D concentration used in our laboratory sorption studies (100 µg/L), >90% removal corresponds to 2,4-D levels <10 µg/L, substantially below the USEPA MCL (70 µg/L) and the WHO Guideline value (30 µg/L). Our ongoing efforts will continue the field monitoring study over multiple annual cycles. We also are continuing to refine our understanding of pollutant sorption phenomena by charcoal and biochar materials 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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