

## Optimizing fluoride adsorption and removal using bone char in a lead-lag column configuration

A summary of the current state of research and development of a low-cost, field-deployable, and globally replicable fluoride and arsenic treatment system using functionalized biochars

Prepared by: Caminos de Agua  
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## ACKNOWLEDGEMENTS

Caminos de Agua would like to especially and sincerely thank the **Natural Health Research Foundation** and **Dr. Mercola** for their continued support of this important research and development, which makes a substantial difference in the lives of real people. Without this support, and the freedom to explore unique solutions and follow the research where it leads us, none of this work would be possible.

We would also like to thank **Engineers Without Borders UK** for continuing to partner with Caminos de Agua and provide expertise and on-ground support through long-term placements and fellows who perform the painstaking research necessary to make these treatment systems deployable. We would like to particularly thank Engineers Without Borders UK placement **Sarah Mitchell** who performed the research that has led to this current report. And we would like to also sincerely thank **Simona Dossi**, also an Engineers Without Borders UK placement, who has taken this research to the next level.

Many thanks to **Elena Diek** for providing most of the technical drawings, diagrams, and graphs, and for also performing numerous batch and column tests early on in this research.

Finally, we would like to thank **Dr. Joshua Kearns** of North Carolina State (NC State) University for providing unparalleled technical guidance, frequent on-ground support, and for sharing a world-view of providing safe and healthy drinking water – free from biological as well as organic and inorganic contaminants – through affordable and scientifically proven solutions.



## BACKGROUND

The Independence Aquifer in Central Mexico is in a permanent state of decline due to over-extraction of groundwater resources by commercial agriculture. This has led to concentrating dangerously high levels of naturally-occurring arsenic and fluoride – as much as 9 and 15 times the World Health Organization recommended limits, respectively. This toxic cocktail is known to cause dental fluorosis in children and crippling skeletal fluorosis, kidney disease, developmental disabilities, skin lesions, organ failure, and cancer among longer-term consumers.

Commercial options for arsenic and fluoride removal – such as activated alumina and reverse osmosis – are costly and beyond the reach of low-income communities. This is a locally acute, – but globally distributed – public health challenge, impacting other economically disadvantaged communities throughout Latin America, North Africa, Bangladesh, India, and China.

Caminos de Agua has been experimenting with biochar-based filtration media to remove these inorganic contaminants. We have focused on the development of biochar made from animal bones (bone char) and proven its effectiveness as a media with a high adsorption capacity for fluoride – the most widespread regional water quality concern to date. In contrast to physical adsorption used by the high-temperature wood-based biochar, bone char targets fluoride through a combination of ion-exchange and contact precipitation – chemical adsorption processes. For more information on our historical work to give better context for this report, take a look at our reports here: <http://caminosdeagua.org/biochar-water-treatment/>.

We have worked to prove these adsorption capabilities in real world conditions using water samples taken directly from contaminated community wells. This pioneering proof-of-principle work has been conducted with Engineers Without Borders UK Fellowship placements over the last three years, supervised by environmental engineers at NC State University, and supported by the Natural Health Research Foundation.

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## Current State of Research

In 2016, Caminos de Agua began working closely with Dr. Joshua Kearns of NC State University to streamline production of bone char filter media for fluoride adsorption, design and build full-scale prototypes for in-house column testing using real contaminated community water, and develop overall testing protocol and guidelines. Dr. Kearns has nearly a decade of experience designing and installing biochar treatment systems for the adsorption of synthetic organic chemical contaminants in Southeast Asia. These systems were heavily monitored and ultimately proven by Dr. Kearns as an effective and low-cost solution for organics. Read more about Dr. Kearns' work here: [aqueoussolutions.org](http://aqueoussolutions.org)

In addition to Dr. Kearns' support, Dr. Polizzotto and graduate student Maia Fitzstevens – both of NC State University – are also offering support in the the design of tests and trials as well as laboratory resources and university studies. Engineers Without Borders UK volunteer, Sarah Mitchell, has led most of the current research, and Simona Dossi, also from Engineers Without Borders UK, has taken the lead on research through the end of 2017. And all of this development is now being overseen by Caminos de Agua's Research and Technology Coordinator – Aaron Krupp.



*From left: Dr. Polizzotto, Dr. Kerans, and Maia Fitzstevens of NC State University work with Sarah Mitchell of Engineers Without Borders UK on the lead-lag adsorbers at the Caminos de Agua lab.*

Most recently we began expanding our work to develop and test iron-impregnated wood biochar, and other chemically treated wood biochars, as potential solutions for arsenic. Intern Martijn

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Eikelboom of Wageningen University is developing screening process and initial batch tests with the Caminos de Agua team through the summer of 2017.

## OPTIMIZING BONE CHAR MEDIA

### Production

Caminos de Agua has been working for two years to create a base bone char with a high fluoride adsorption capacity. The goal has been to produce and test various different bone chars, burned at different times and temperatures, test those bone chars for fluoride adsorption, and then design a low-tech gasifier and production method to meet the necessary time-temperature profile consistently, without needing much adjustment, and utilizing materials found easily anywhere in the world.

We began using a *top-lit-updraft* (TLUD) type gasifier based on Dr. Kearns' designs in 2016. This type of gasifier, referred to as the *TLUD-K*, does not limit the primary air intake as much as traditional TLUD gasifiers and, in doing so, allows more draft and significantly higher burn temperatures. One 55-gallon drum (the fuel chamber), with the bottom almost completely drilled out, is filled with wood scraps and raised off the ground – creating a significant primary air intake. A second drum – making up the combustion chamber – is placed upside-down on top of the fuel drum on rails (creating a small secondary air intake) with an attached chimney. The bottom fuel chamber burns downwards as the pyrolysis gases rise into the upper chamber and combust. A retort chamber filled with animal bones is placed inside the combustion chamber, or the upper portion of the gasifier, where where pyrolysis gases combust – becoming engulfed in the flames and creating secondary pyrolysis in the bone retort chamber. Thus, the bone char production is simply taking advantage of the excess energy created during the normal biochar process.

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## CAMINOS DE AGUA

After much testing, it became clear that the optimal bone char needs to reach temperatures between 400°C and 600°C – but not exceed 600°C – for at least 1.5 hours. To achieve these conditions regularly, a bone retort must go through two burns – one occurring immediately after the other. Utilizing the simple *TLUD-K* gasifier design, as the first fuel chamber begins to burn down to the bottom, a second fuel chamber – loaded with wood – is lit. The bone retort and combustion chamber are moved over together and placed on top of the second fuel drum (See *Image below*). Through this method, we are easily achieving the necessary time-temperature profile necessary to produce high-quality bone char. *Figure 1* illustrates the time-temperature profile of a typical bone char burn.

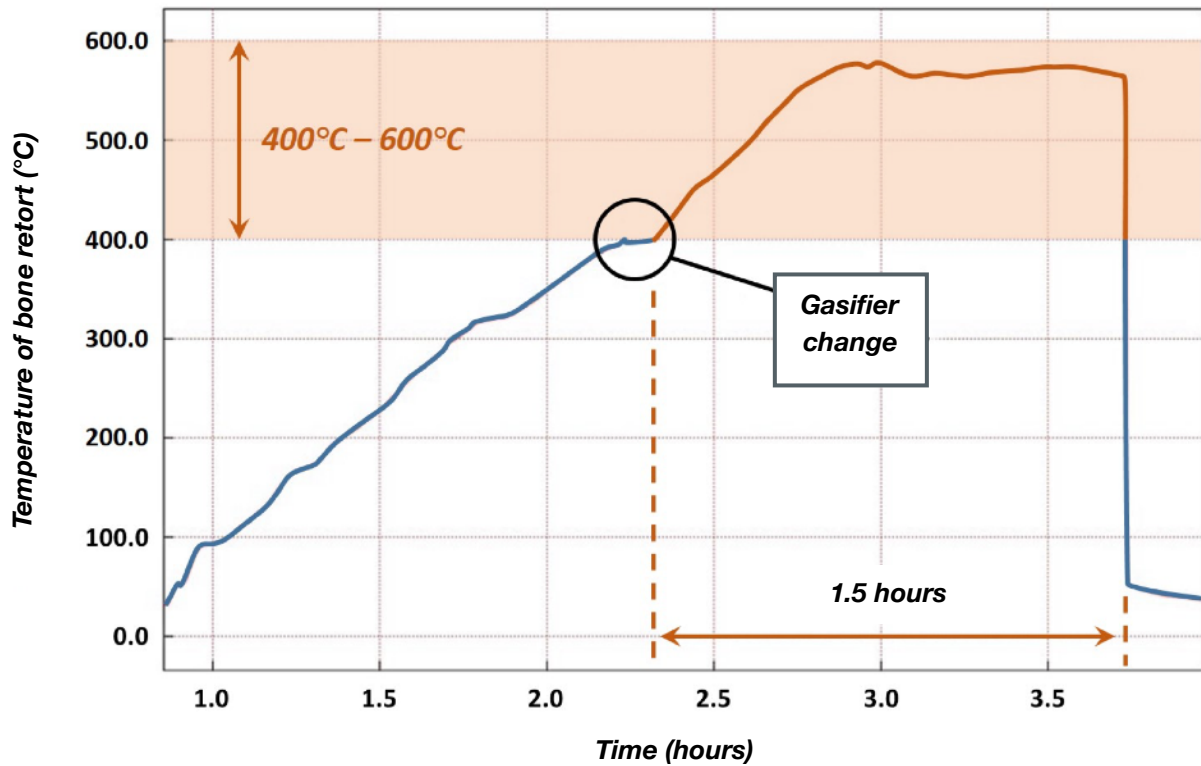
For more information on current bone char production processes, including gasifier designs, feedstock dryers, detailed explanations of the pyrolysis process, pre-burn preparation, etc, please



*Top left: Caminos staff cover the bone retort with the combustion chamber during a bone char burn; Top right: TLUD-K bone char gasifier ready to be moved over to the second fuel chamber/gasifier.*

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Figure 1



visit our website page dedicated to this research here: <http://caminosdeagua.org/biochar-water-treatment/>

## Processing

The raw bone char media is processed using an 8 x 30 sieve producing a particle size between 2.36mm (BCmax) and 0.6mm (BCmin) with an average particle size of 1.3mm. This particle size is small enough to create a large adsorption surface area and has shown to be a critical factor in achieving a high fluoride adsorption capacity specifically. However, the particles are still large enough as to not clog a point-of-use filtration system.

## Wood Biochar Byproduct

The high-temperature wood biochar created in the fuel chamber is a secondary product useful for physical adsorption for synthetic organic chemical contaminants or as a soil amendment for agricultural production. Caminos de Agua has built several biochar water treatment systems using this high-temperature wood biochar in rural communities throughout the region to deal specifically with chlorination and taste issues. However, in general, the application of these systems given our water quality concerns is limited in this region, and the focus of this byproduct will more likely be tied to soil conservation and amendment.

Additionally, we have begun impregnating this wood char with various chemicals, such as ferric chloride, to create functionalized biochar media specifically engineered for arsenic adsorption. If this line of investigation proves successful for arsenic, additional chemical treatments may be pursued to address other groundwater contaminants.



*Top left: Biochar workshop in a local community in northern Guanajuato, Mexico; Top right: Biochar treatment install in a local community elementary school.*

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## PROTOTYPE DESIGN

### Criteria

A study utilizing a double column bone char (BC) setup in lead-lag mode was designed in conjunction with Dr. Kearns and Caminos de Agua. The lead-lag design links one column to the next and should increase the use rate of the bone char filter media (explained in more detail later in this report). The criteria for the experimental set-up was as follows:

- Twenty bone char batches were produced under the aforementioned production protocol and mixed to create a representative bone char sample,
- Filter design should be based on a full-scale – or near to full-scale – prototype to receive data under real world conditions,
- Influent fluoride (F) concentration should be between 6 and 8 mg/L, which impacts the majority of the communities where Caminos de Agua works,
- Treatment objective is set at 1.5 mg/L of fluoride (WHO recommendations),
- Influent water must come from a real rural community well with regionally specific background water chemistry (i.e. not using distilled water spiked with fluoride),
- The system must produce a minimum of 25 L/day (175 L/week) for consumption,
- The absolute minimum fluoride adsorption capacity should be 0.4 mgF/gBC (*milligrams of fluoride per gram of bone char*).

### Filter Design

The bone char is processed using an 8 x 30 sieve (see “Processing” on page 7). The filters utilize easily accessible filter housings and replaceable internal columns. The internal columns, measuring roughly 6cm x 17cm, have a bed volume of 695 mL and a bed density of 0.67 g/cm<sup>3</sup>. This initial design is full-scale in size and can translate directly into a point-of-use (POU) household system. The up-flow lead-lag design works as follows (*Figure 2*):

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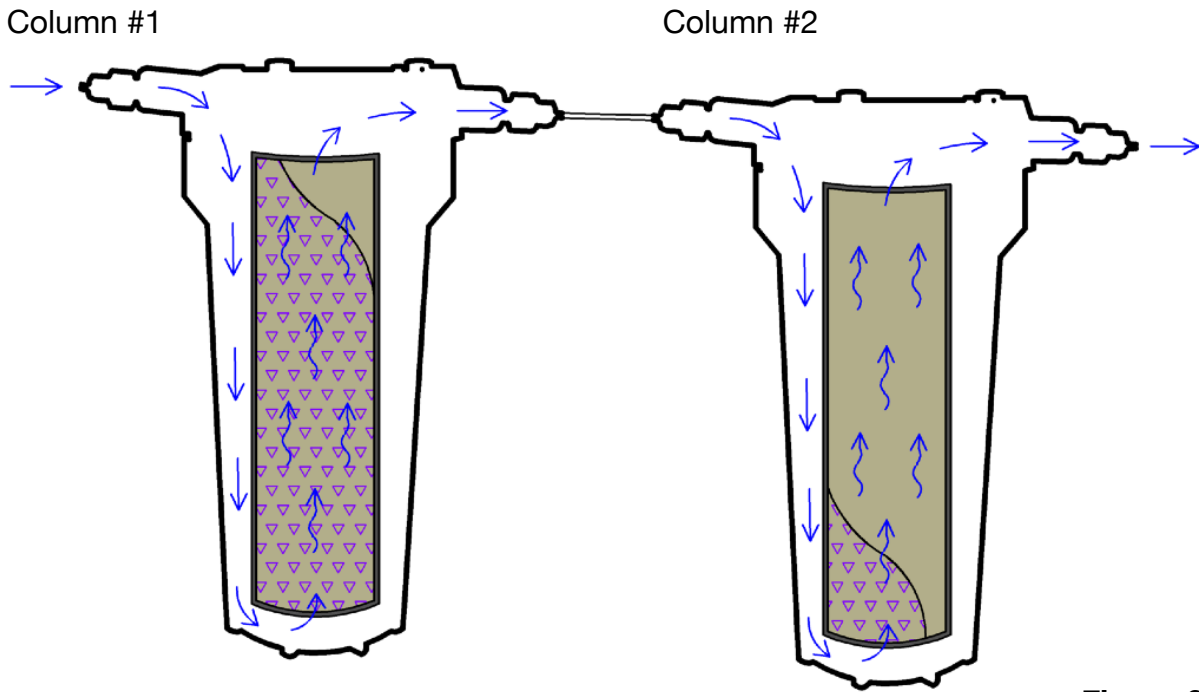


Figure 2

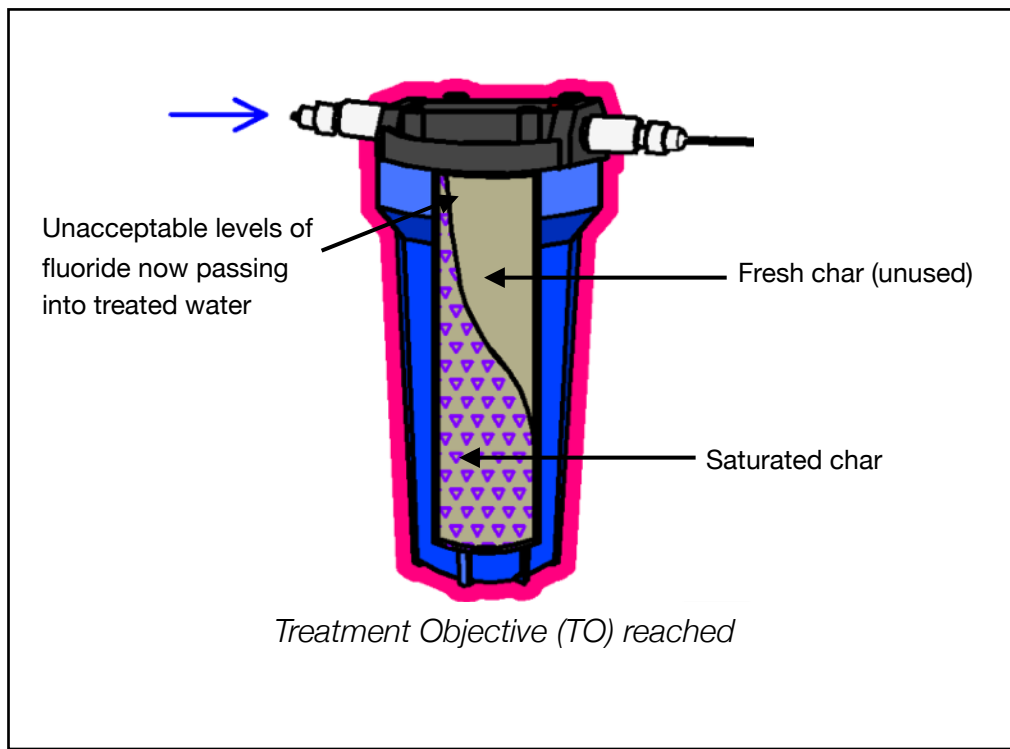
1. Contaminated groundwater enters column #1 and flows upwards through the first bone char bed,
2. The water then enters column #2 and flows upwards through the second bone char bed, and
3. Treated water flows out of column #2 for consumption or healthy water storage.

The purpose of using the double column lead-lag method is to increase the use rate of the bone char. In a single column system, fluoride is adsorbed through the column bed. Once the bed starts to become saturated, the fluoride will begin to pass through into the drinking water and the filter will need to be replaced. However, saturation does not occur uniformly as illustrated by *Figure 3*.

The example below (*Figure 3*) illustrates how a column could become saturated. In this scenario, the filter has reached its treatment objective (TO), and at least 1.5 mg/L fluoride is now passing through into the treated water. This means the column needs to be replaced with fresh bone char.

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**Figure 3: Saturation of a single column**



However, as illustrated, there is still plenty of unsaturated “fresh” bone char in the column. This relatively high percentage of char is simply going to be wasted in a single column scenario.

When an additional column is added, 100% of the bone char in both columns can be utilized through a lead-lag scenario. As column #1 becomes saturated and reaches its treatment objective, column #2 begins to adsorb fluoride until column #1 is completely saturated. At that time, column #2 is moved back into the column #1 – or *lead* – position and column #1 is recharged with fresh char and moved into the *lag* position (see Figure 6 for more detail).

## Full Scale Prototype Testing

The full-scale prototypes were being designed, built, and troubleshooted while 20 batches of bone char were being produced and mixed to achieve a representative sample. Roughly 2m<sup>3</sup> of contaminated groundwater were collected from the rural community of Exhacienda de Jesus,

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located roughly 1.5 hours from the Caminos de Agua lab. This community was selected due to its history of work with Caminos de Agua and its high levels of both fluoride and arsenic.

The Exhacienda de Jesus well has been tested by Northern Illinois University, Texas A&M University, Kansas State University, and University of Guanajuato in conjunction with Caminos de Agua numerous times since 2012. Fluoride has consistently tested at more than 10 times World Health Organization recommendations.

Exhacienda de Jesus Water Quality Monitoring 2012-2017	
Arsenic	Fluoride
46 - 80 $\mu\text{g/L}$	14.07 - 18.20 $\text{mg/L}$

\* WHO limits: Arsenic 10  $\mu\text{g/L}$ ; Fluoride: 1.5  $\text{mg/L}$

### Trial 1 - Worst Case Scenario & BC Fouling

The columns were packed with fresh bone char from the representative batch. The influent concentration of this first column study was not diluted. Thus, we were able to get a rough gauge on a worst-case-scenario situation where the influent fluoride concentration was much higher than we normally see (~14.2  $\text{mg/L}$ ). *Figure 4* illustrates the curves in both the *lead* and the *lag* columns. Given that this was a real world prototype, this initial study was run over the course of a couple of weeks. Unfortunately, we were not able to achieve full breakthrough curves for this study. Just when column #1 began to breakthrough, the flow rate of the system dropped to unmanageable levels. This was due to fouling of the bone char by background organic matter in the influent water, which essentially “clogged” the system. However, the initial adsorption looked very promising.

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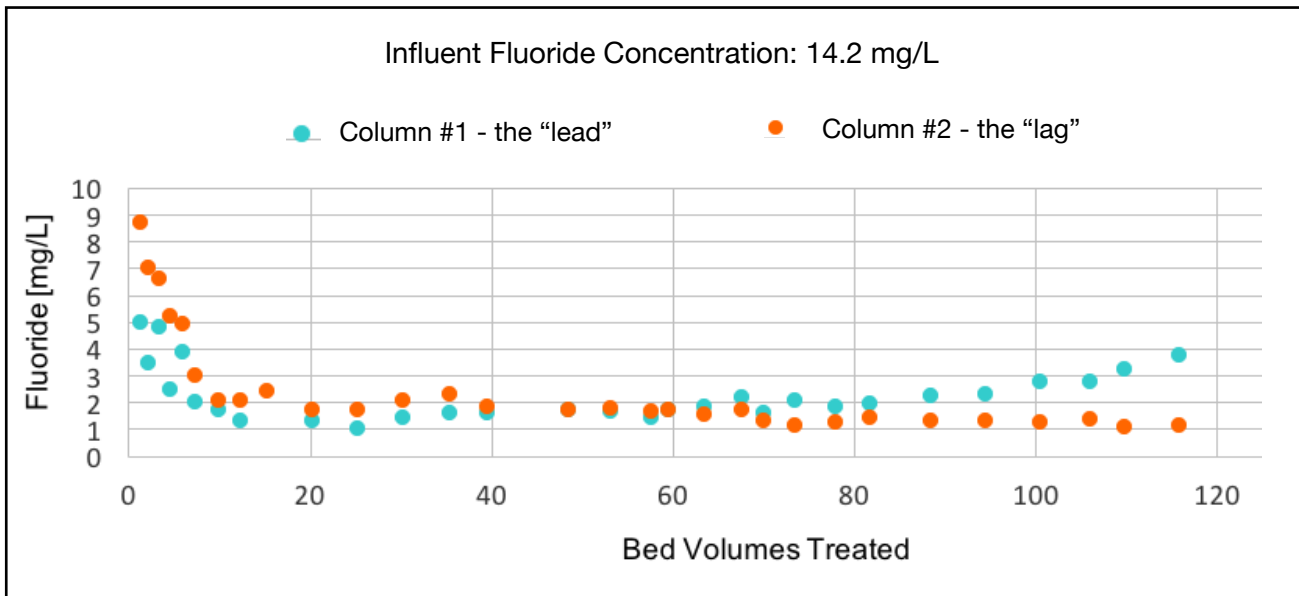


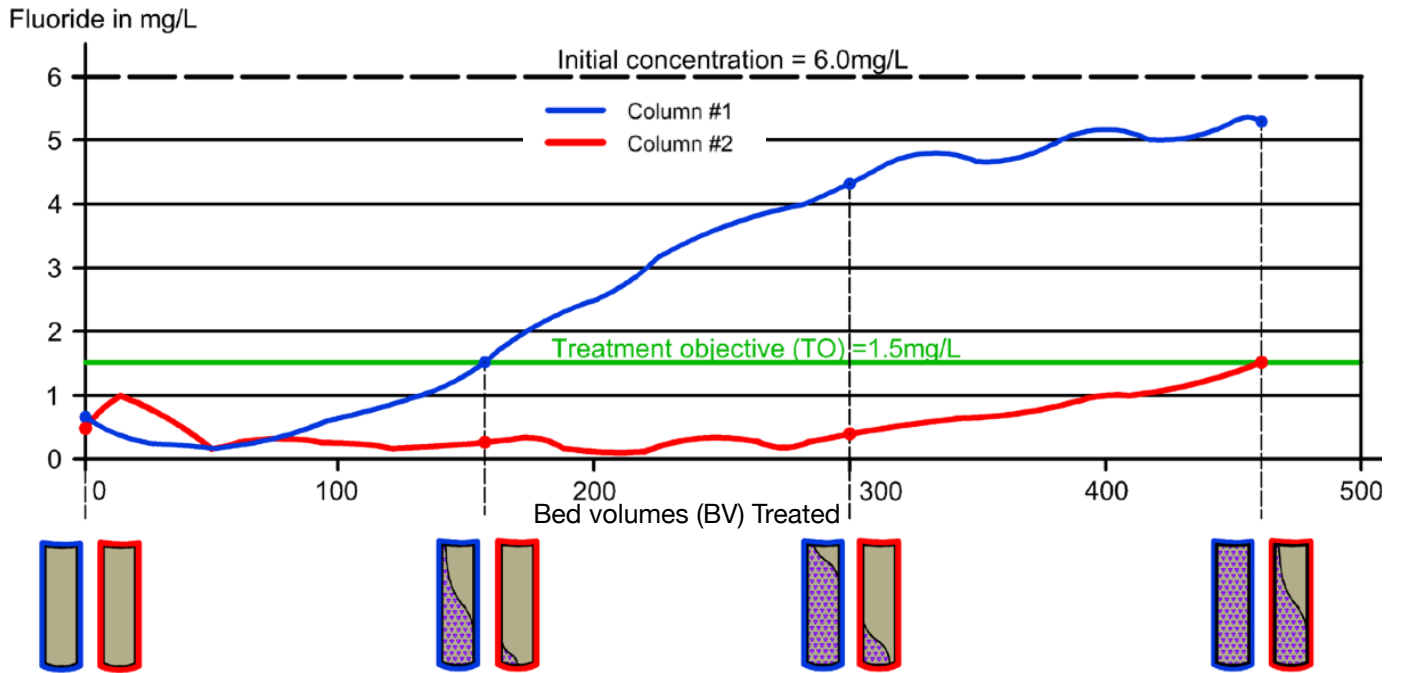
Figure 4: Worst Case Scenario

### Trial 2 - Proving the Lead-Lag Concept

For the second trial, the influent water was mixed with local water contaminated with far lower levels of arsenic and fluoride to achieve an end fluoride level of 6.0 mg/L, a more representative fluoride concentration that impacts roughly 95% of the communities where Caminos de Agua works. This time, prior to reaching the bone char adsorbers, the influent water was passed through Caminos de Agua’s ceramic water filters ([www.caminosdeagua.org/ceramic-water-filters](http://www.caminosdeagua.org/ceramic-water-filters)). This pre-filtration step proved crucial in preventing the bone char fouling seen in Trial 1 and improving the overall life of the bone char media.

As with the first trial, Trial 2 was performed under real world conditions. The influent water was run through the system consistently at roughly 17.5 (+/- 2) mL/min, and samples were taken roughly every 4 hours from column #1 and column #2 over the course of several weeks. Influent samples were taken sporadically throughout the trial. In total, the trial took roughly three weeks to complete.

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**Figure 5**

As *Figure 5* illustrates, column #1 began breaking through at the treatment objective at roughly 150 bed volumes (BV) of water treated. If there were no effect from the lead-lag model, then we would expect to see column #2 breakthrough at the treatment objective at roughly 300 BV. However, that was not the case. In this trial, column #2 did not hit the treatment objective until 450 BV. This increased use rate extends the life of the system and directly translates to changing out a filter every three weeks instead of every week.

Further, the fluoride adsorption capacity of this representative bone char sample was significantly higher than expected:

**Fluoride Adsorption Capacity: 2.34 - 4.39 mgF/gBC**

The reason an exact adsorption capacity cannot be calculated is due to fluctuations of the influent fluoride concentration. The influent water was mixed between two sources; however, mixing was not performed consistently. Consequently, the influent fluoride concentration varied from

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roughly 6 mg/L to 9 mg/L. Thus, we know there is a minimum adsorption capacity of 2.34 mgF/gBC; however, the actual adsorption capacity could be as high as 4 mgF/gBC or more. That stated, even the minimum adsorption capacity of 2.34 is nearly six times higher than our initial criteria.

### Illustrating the Lead-Lag Effect

Given the results of Trial 2, we can assume the columns in the lead-lag set-up need to be set back and replaced a maximum of every 3-weeks under normal use. After the initial first use, the lead-lag cycle will look as follows (Figure 6):

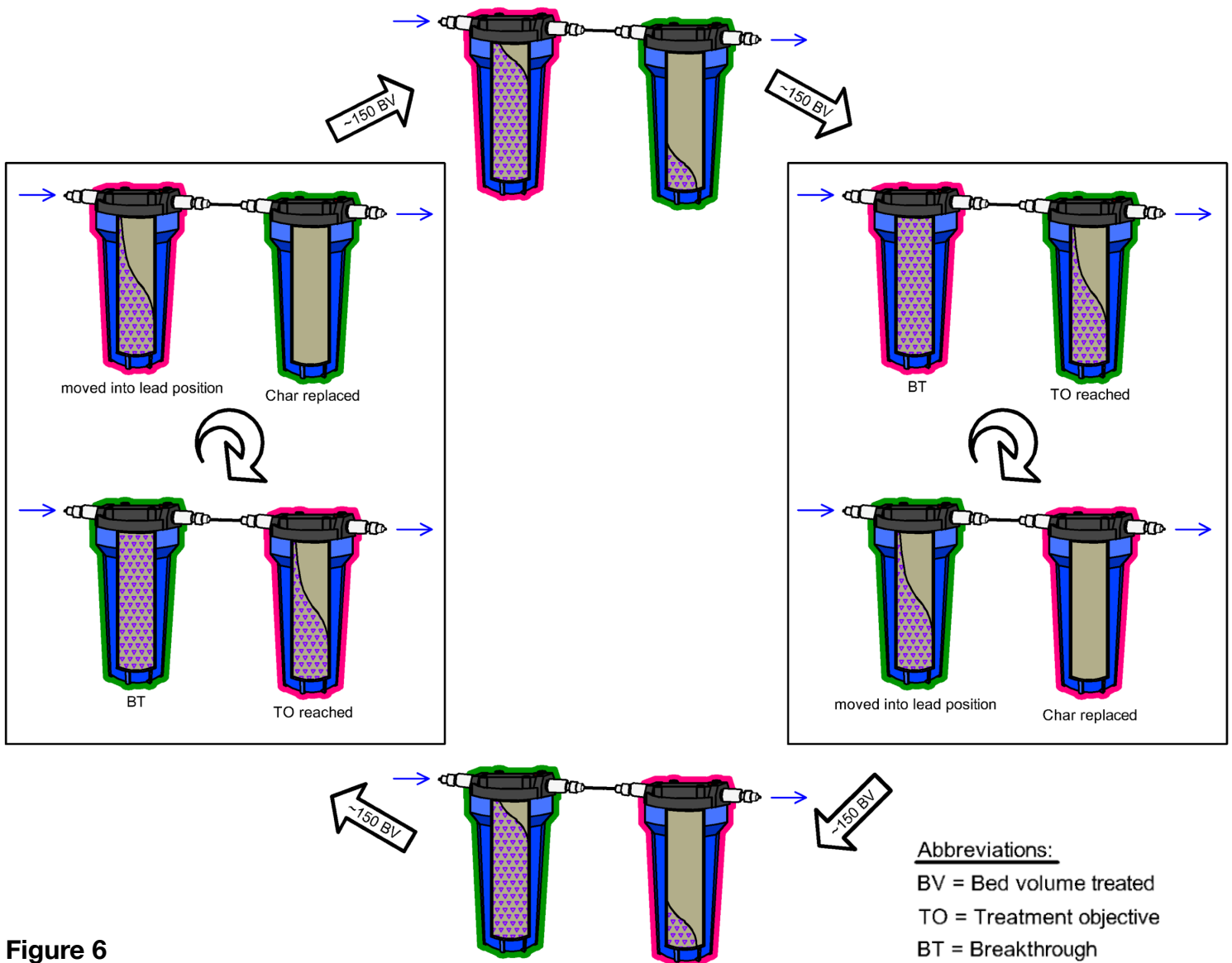


Figure 6

## Conclusions

The current state of bone char research is extremely promising. The fluoride adsorption of the current bone char is – at minimum – nearly 6-times higher than we had anticipated, meaning the filter media is extremely viable. The fact that this highly-effective bone char media can be produced consistently under low-tech conditions and utilizing materials found easily and inexpensively anywhere in the world further lends to the viability of this system through global deployment and wider impact. Further, the lead-lag model is proving an effective and extremely useful method of increasing the life of the bone char filter columns. By utilizing the lead-lag model, the bone char columns can last 3-times longer than a traditional single column before needing to be replaced.

## Next Steps

Camino de Agua has built a large-scale system with four (4) active prototypes connected to an influent source. This allows us to “plug-in” multiple bone chars and other filter medias and to run multiple real world trials on full-size prototypes simultaneously. Currently, we are working on



*Four prototype column set-up in lead-lag for testing fluoride and arsenic adsorption.*



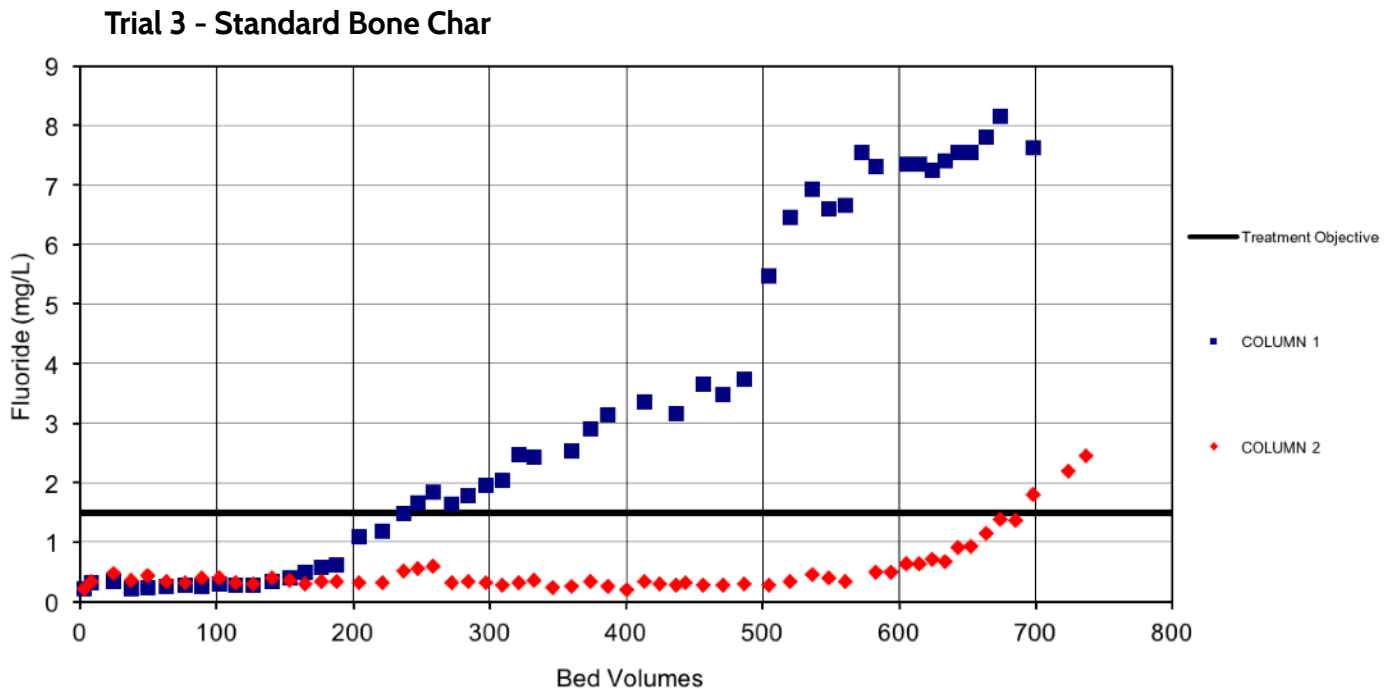
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## CAMINOS DE AGUA

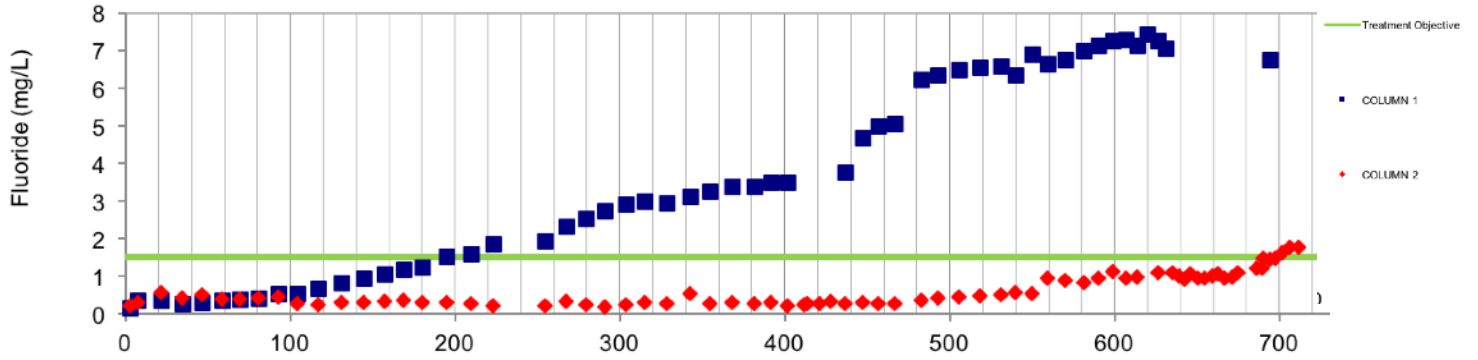
replicating the Trial 2 bone char several more times under various, and more consistent, influent conditions.

### Update – June 30, 2017

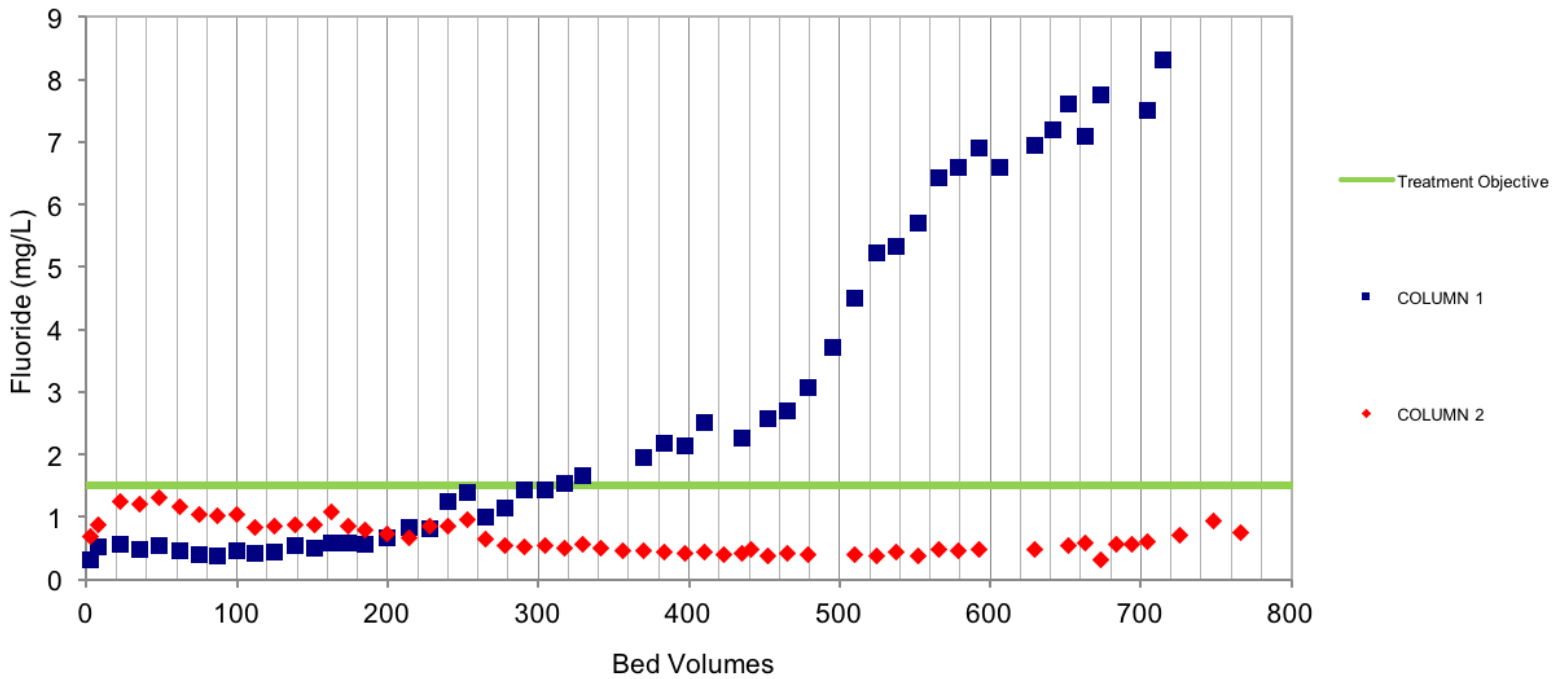
The Caminos de Agua research team just finished replicated the bone char fluoride adsorption media in three new trials. Trials 3 and 4 replicated the bone char Trial 2 testing (above). Trial 5 utilized the same bone char treated with acetic acid. Below are the results from the three trials, which illustrate an increase in adsorption in all three prototypes. Trail 3 and 4, which both utilized untreated bone char, reached overall breakthrough at column 2 at roughly 700 BV. Trial 5, utilizing the acetic acid-treated bone char, achieved breakthrough of column 2 at roughly 850 BV, an 18% increase in adsorption capacity. A more comprehensive update will be added soon.



**Trial 4 - Standard Bone Char**



**Trial 5 - Acetic acid-treated Bone Char**



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## CAMINOS DE AGUA

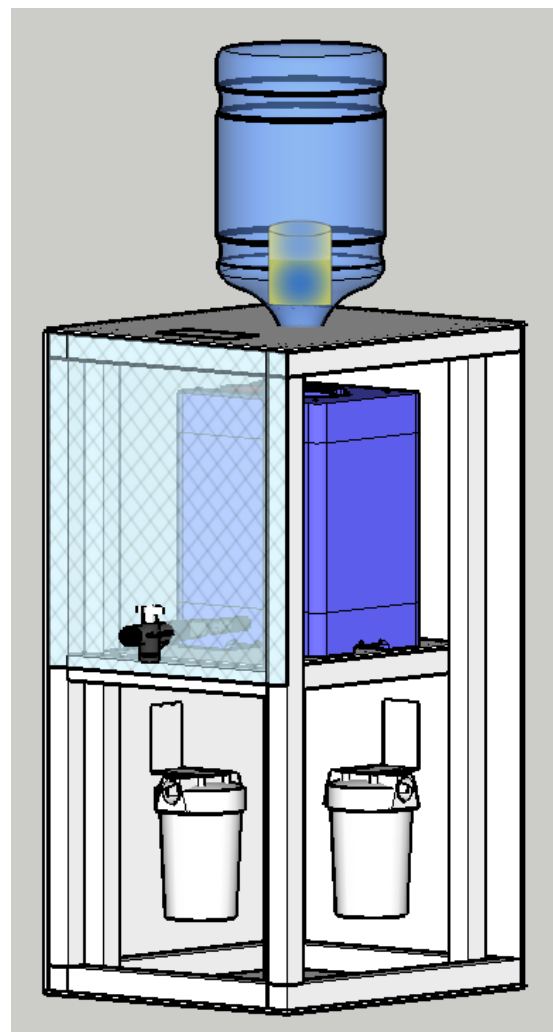
We are continuing bone char and other filter media trials for both increasing fluoride adsorption while also addressing arsenic concerns. Simultaneously, we have also begun to design and build initial prototypes of a fluoride filter (*Figure 7*). The initial point-of-use design incorporates the Caminos de Agua ceramic water filter for pre-filtration, a lead-lag column configuration of our current bone char for fluoride removal, and 10 L of safe and healthy water storage.

### Update – November 30, 2017

Currently, Simona Dossi of Engineers Without Borders UK is leading the final stages of fluoride adsorption studies, which are focused on rapid column filtration—to test the limits of the filtration media—as well as leaching studies. The purpose of the leaching studies is to assure that no unknown contaminants are leaching off the bone char media. The samples from these studies will be evaluated by a third-party laboratory to ensure independent evaluation, and are the final stage in implementing a field pilot.

Additionally, Dossi and the Caminos de Agua Tech Team are evaluating both arsenic field testing equipment and commercial arsenic adsorption medias in both batch and column set-ups to be included in the final prototype design.

A more comprehensive update on this work will be included soon.



**Figure 7:** Initial fluoride filter prototype utilizing ceramic pre-filtration and lead-lag bone char column configuration.