Using absolute and relative UVA_{254} to estimate biochar bed lifecycle

This supplement describes how absorbance of light at 254 nm (UVA_{254}) can be measured in the field to provide a conservative surrogate for removal of organic micropollutants in biochar water treatment systems.

Background

Biochar adsorbent can be produced in low-resource settings using local materials and simple pyrolysis technology, and has shown promise for uptake of micropollutants such as pesticides, pharmaceuticals, industrial compounds, and chemicals that are released from the breakdown of wastes. They are termed "micropollutants" (MPs) because they typically occur in natural and anthropogenic water at ng/L-μg/L (i.e., parts-per-trillion to parts-per-billion) levels. Even at such low concentrations MPs can be harmful to human health, for example by disrupting the endocrine system, impairing the immune system, or causing cancer. Quantifying the variety of MPs that could be in a water sample requires expensive and sophisticated laboratory analyses, and so is cost-prohibitive for low-resource settings and is not feasible for measurement in the field. Therefore, identification of surrogate parameters(s) for adsorbent bed-life that can be measured inexpensively and in the field is a high priority.

All water sources contain background dissolved organic matter (DOM) at concentrations ranging from less than 1 mg/L to more than 100 mg/L (i.e., ~1 to >100 parts-per-million) total dissolved organic carbon. DOM, which is a complex mixture of organic compounds of different sizes and with different chemical properties, can be relatively inexpensive to measure using portable field instruments. Like MPs, DOM also adsorbs to biochars. When DOM adsorbs to biochar, it limits the biochar's ability to remove MPs, which is called "fouling". Fouling happens when DOM directly competes with target MPs for adsorption sites or when DOM limits MP adsorption by constricting and blocking MP access to adsorbent pores that contain adsorption sites. DOM therefore affects the length of time a biochar water treatment unit can be in service while maintaining confidence that high levels of MP removal (e.g., ≥90%) are achieved.

Aromatic compounds have delocalized electrons in double and triple bonds that absorb ultraviolet light at a wavelength of 254 nm (UVA_{254}). A portion of DOM is aromatic in character, and so absorbs UV light in this wavelength range. Many UV-absorbing DOM

components are strongly adsorbed by biochar and are responsible for adsorbent fouling compared with DOM components that do not absorb UV light. Therefore, tracking the progress of biochar fouling by monitoring and comparing UVA_{254} of the filter influent and effluent can provide an indirect estimate of MP removal. Furthermore, most MPs of concern are more strongly adsorbed by biochar than UV_{254}-absorbing DOM. Thus, the UVA_{254}-absorbing DOM usually breaks through (i.e., is detected in filter effluent) before most MPs of concern (Figure 1). Since UVA_{254} breaks through first, it can provide a conservative indicator of a biochar adsorber's remaining capacity for removing MPs.

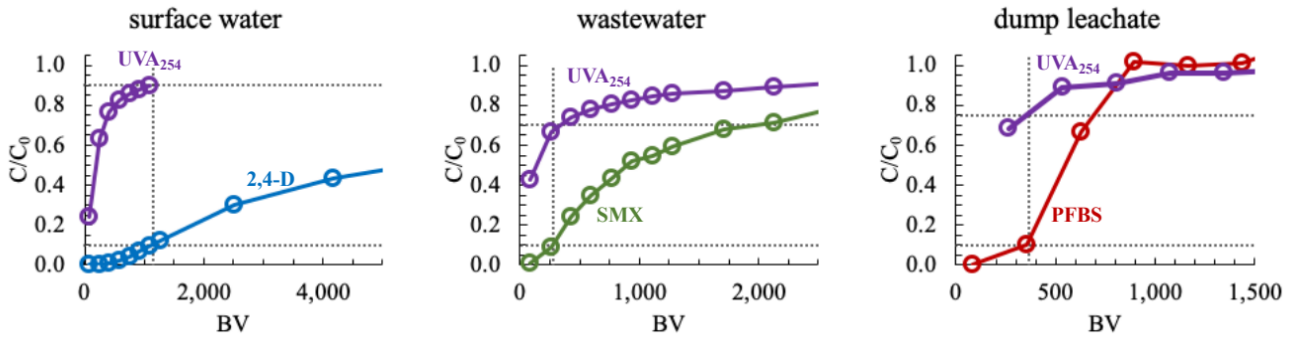

Figure 1. Results from laboratory biochar column experiments showing UVA_{254} and MP breakthrough curves for surface water, wastewater, and dump leachate. The amount of water treated is expressed as volume of water treated per volume of the empty adsorbent bed ("bed volumes," or BV). The total volume of water treated can be calculated by multiplying BVs by the volume of the adsorbent bed. Filter run time can be determined by dividing the total volume of water treated by the flow rate. The herbicide 2,4-dichlorophenoxyacetic acid (2,4-D), and the antibiotic sulfamethoxazole (SMX) were the first MPs to break through in surface water and wastewater experiments, respectively. The fluorochemical perfluorobutanesulfonate (PFBS) broke through just after two short chain perfluorocarboxylic acids in leachate experiments – however, early breakthrough was not well resolved for those compounds so PFBS is shown here. 90% removal of MPs (i.e., 10% breakthrough) corresponded with relative UVA_{254} values of 0.9 for 2,4-D in surface water, 0.7 for SMX in wastewater, and 0.75 for PFBS in leachate. Overall, relative UVA_{254} values of 0.6-0.9 corresponded to ≥90% MP removal for the MP-water combinations included in our study.

Besides DOM, other background substances in water can absorb UV_{254} light. One commonly occurring example is dissolved iron. In some water sources, iron can occur at high enough concentrations to have a significant contribution to the overall UVA_{254} of a water sample. Compared with DOM, however, iron does not have a significant impact on biochar fouling for MP removal. Therefore, it is a good practice to measure dissolved iron in a water sample, and correct the sample's overall UVA_{254} measurement to reflect just the DOM component.

This supplement describes the process and equipment needed to measure dissolved iron and UVA_{254} in biochar water treatment system influent and effluents, and how to use these measurements to estimate when biochar should be regenerated or replaced. This can be accomplished by nearly anyone, with a little training, regardless of level of formal or technical schooling. The equipment needed is inexpensive compared with sophisticated lab-based analytical methods. However, it is not so inexpensive as to be easily accessible to households and villages in very low-resource settings. It is probably within the budget of many small water and health NGOs, local municipalities, and small water treatment and supply businesses, for example. The field kit described below includes a portable UV spectrometer (~ $2,150 USD) and a handheld visible light colorimeter (~$350 USD). Testing supplies come to about $1.50 USD per test.

Water sampling and pre-treatment

Figure 2 shows a common biochar water treatment system design[1] with water sampling points indicated at the inlet (C_0) and outlet (C) of the biochar adsorber. In order to plot a UVA_{254} breakthrough curve like those shown in Figure 1, we need to measure the absolute influent (C_0) and effluent (C) UVA_{254} values, and obtain the relative fraction of UVA_{254} (i.e., C/C_0) in the effluent.

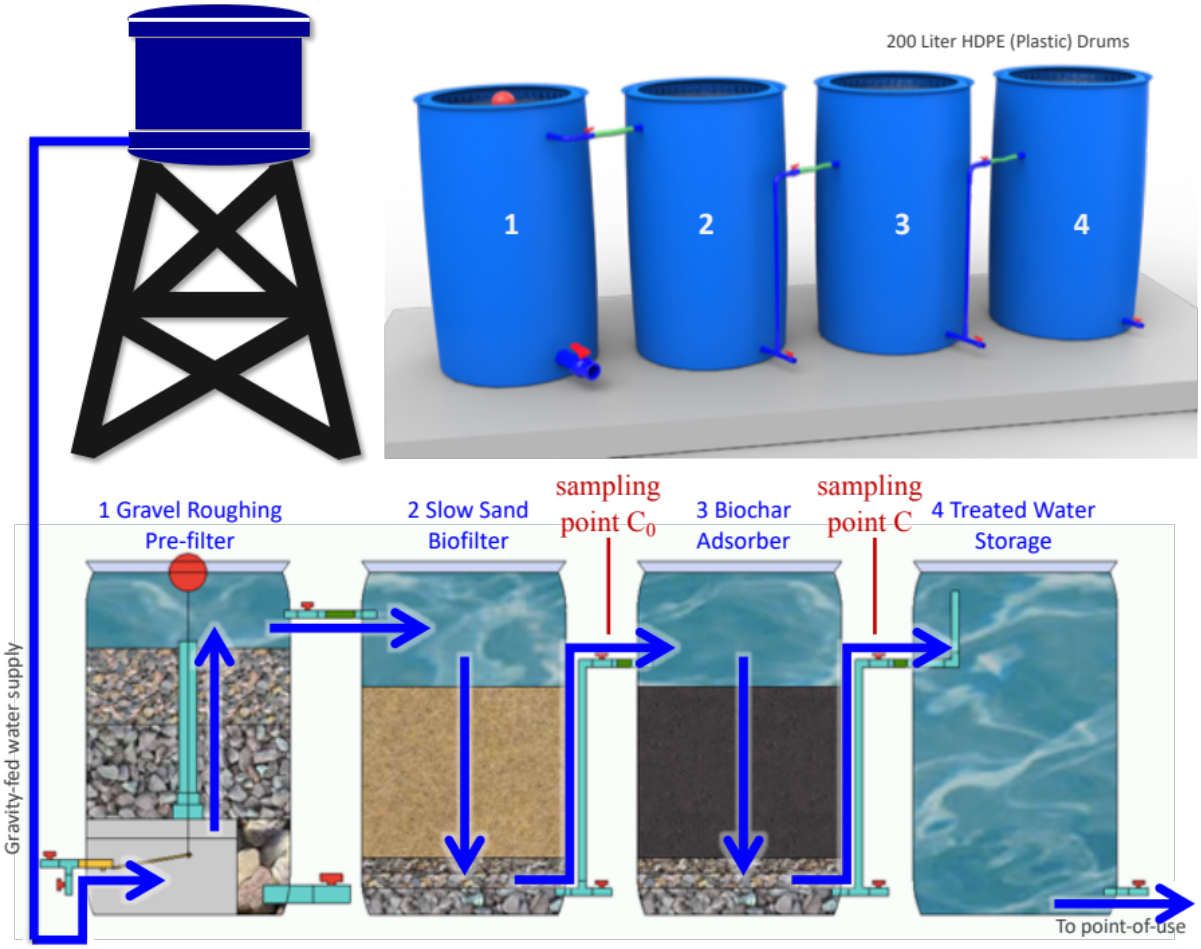

Figure 2. Common biochar water treatment system design made from surplus 200 L (55 gal) HDPE drums capable of producing 300 L of treated water per day.

Particles that may be present in water samples can interfere with measurement of iron and UVA_{254}. Since we are concerned with DOM and dissolved iron, it is necessary to pre-filter water samples prior to analysis to remove particles. The most convenient way to do this (though perhaps not the most environmentally friendly) is by using disposable syringe filters. Glass fiber syringe filters with 1.0 ฀m pore size can be obtained *filters with 1.0 µm pore size can be obtained for less than $1 USD per unit.*. 10 mL syringes (without needles) can be obtained *filters with 1.0 µm pore size can be obtained for less than $1 USD per unit.*. (NOTE – The proper technique for using syringe filters is to withdraw 10 mL of water sample directly into the syringe. Then attach a syringe filter and push the water sample through the membrane to remove particles. Use the first 10 mL to wet the filter membrane with sample, discarding the filtrate. Remove the filter withdraw a second 10 mL of water sample, then reattach the filter.

This 10 mL of filtered sample water can be dispensed directly into a spectrometer sample cell or cuvette for analysis.)

Also – it is necessary to obtain a supply of distilled ("DI") water for cleaning hardware and to provide a blank UVA_{254} reference point to zero the instrument. In low-resource settings, bottled DI water can often be obtained from local mechanic shops, since it is used to refill motorbike and farm equipment batteries.

Determining the contribution of dissolved iron to total UVA_{254} in a water sample

The overall UVA_{254} of a water sample is sensitive to dissolved iron at levels relevant to many water sources. Therefore, it is important to accurately determine this parameter. Inexpensive disposable test strips sold online might not provide the necessary precision and detection limits. We recommend the FerroVer® colorimetric method developed by Hach for measuring dissolved iron. The low-range (up to 3 mg/L dissolved iron) should work for most waters, in particular if a slow-sand biofilter is used upstream of the biochar contactor. The reagent packets cost less than $0.30 USD per test. A visible light spectrometer (colorimeter) is required. We have used Hach DR/890 handheld portable colorimeters for dissolved iron quantitation. Hach does not make this model anymore. It's replacement, the DR900, costs ~$1,500 USD. However, as of this writing, used DR890 units can still be found online (e.g., E-Bay) for $300-400 USD. Step-by-step instructions for using the FerroVer® method with a DR890 colorimeter are available online. Instructions with our own notations added are as follows:

1. Turn on Hach colorimeter (Button that says "Exit" and has this symbol: ⊘).
2. Press button "PRGM 7" and enter "3 3" for Fe measurement in mg/L.
3. Rinse the glass sample cell very well with DI water.
4. Suck up 10 mL of sample water and eject this 10 mL through the syringe filter into the waste jug to wet the filter disk with sample water.
5. Remove the syringe filter, suck up 10 mL of sample water, reattach the syringe filter, and eject the sample water through the syringe filter assembly into the glass sample cell.
6. Place the sample cell into the colorimeter slot and cover with lid. Press button "ZERO 0" to record the blank value.
7. Add the contents of one packet of "FerroVer® Iron Reagent" to the sample cell, cap, and shake well for about 5 seconds to dissolve powder. Place in colorimeter slot and cover with lid.
8. Press button 'TIMER CE" – 3:00 will appear. Press button "ENTER" to start the countdown.

9. After the 3:00 countdown, the instrument will beep 5 times. Press button "READ" and record value. NOTE – after the 3:00 expires, "0.00 mg/L" may appear on the screen. This is NOT the measurement. You must push "READ" to get the measurement.
10. When you have measured all the water samples, clean the glass sample cell very well with DI water.

Dissolved iron measurements in units of mg/L then need to be converted into equivalent UVA_{254} in units of cm^{-1} (denoted $^{Fe}UVA_{254}$). This is accomplished using Equation 1, obtained from Poulin et al., 2014[2]:

$$^{Fe}UVA_{254}\ (cm^{-1}) = 0.0653 \times \text{iron (mg/L)} \qquad (1)$$

Measuring UVA_{254} of DOM in a water sample

A variety of manufactures such as StellarNet, Ocean Optics, Photonic Measurements, and RealTech offer portable UV spectrometers. We have used RealTech RealUV254 P200 portable spectrometers with 10 mm pathlength, purchased for around $1,700 without or $1,950 with a rechargeable battery pack. Note that quartz glass cuvettes must be used for UV spectroscopy. Regular glass and plastic are opaque to UV light and therefore will not work. Quartz glass cuvettes can be obtained for $30-80 per unit They are quite delicate so it is a good idea to carry spares. Step-by-step instructions for using the RealTech portable spectrometer are as follows:

1. Turn on UV spectrometer to warm up and stabilize lamp for at least 10 minutes.
2. Rinse a 10 mL syringe and syringe filter with DI water.
3. Rinse quartz glass cuvette with DI water 2-3 times and fill. Never touch the clear sides of the cuvette – only touch the frosted sides.
4. Press "calibrate" and insert cuvette with DI water. Instrument should set to 0.000.
5. Suck up 10 mL of sample water with the syringe. Eject this 10 mL through the syringe filter into the waste jug to wet the filter disk with sample water.
6. Remove the syringe filter and suck up 10 mL of sample water. Reattach syringe filter assembly.
7. Remove cuvette with DI water and press "calculate." Reinsert cuvette and make sure that the instrument reads 0.000. Always check the instrument returns to 0.000 before and after every sample measurement. If the readings with DI water drift away from 0.000, then rinse the cuvette very well with DI water and check for air bubbles, smudges, or debris on cuvette. If the instrument does not go to zero, the recalibrate according to step #4.
8. Fill the cuvette with sample water (through the syringe filter assembly) and dump this into waste jug to rinse the cuvette with sample. Then fill the cuvette, press "calculate," and record value. Then immediately rinse the cuvette with DI water, fill it with DI water and "calculate" the UV absorbance – make sure it goes back to 0.000.

9. When you have measured all water samples, rinse the cuvette very well with DI water, empty it and shake any drops off, place it in the instrument and turn the instrument off.

Once the overall UVA_{254} ($^{total}UVA_{254}$) value for a water sample has been determined, the contribution from dissolved iron should be subtracted to obtain a value for the proportion of $^{total}UVA_{254}$ attributable to DOM ($^{DOM}UVA_{254}$) (Equation 2). Relative $^{DOM}UVA_{254}$ values (denoted C/C_0) are obtained by dividing effluent $^{DOM}UVA_{254}$ values (C) by the influent $^{DOM}UVA_{254}$ value (C_0) (Equation 3).

$$^{DOM}UVA_{254} = {}^{total}UVA_{254} - {}^{Fe}UVA_{254} \qquad (2)$$

$$\text{relative } {}^{DOM}UVA_{254} = C/C_0 = \text{effluent } {}^{DOM}UVA_{254} \div \text{influent } {}^{DOM}UVA_{254} \qquad (3)$$

Selecting a relative UVA_{254} indicator value for biochar regeneration/replacement

Our study quantified the relationships between adsorption of DOM-UVA_{254} and 20 different weakly- and moderately- adsorbing MPs in three different waters by biochar columns. Specifically, we collected breakthrough curve data for two herbicides (2,4-D and simazine) and one antibiotic (SMX) from surface water; 2,4-D and simazine, the flame-retardant tris(2-chloroethyl) phosphate (TCEP), SMX and nine other pharmaceuticals and personal care products from wastewater; and seven short- and medium-chain perfluoroalkyl substances (PFAS) from dump leachate.

To establish a monitoring criterion to indicate the end of a biochar bed lifecycle, we focused on weakly adsorbing (i.e., first to break through) sentinel MPs in a relevant background water and their corresponding relative $^{DOM}UVA_{254}$ breakthrough (C/C_0) values. These compounds were selected because if they are removed by the biochar, it is likely that other compounds that adsorb more strongly than sentinel compounds will also be removed to a high degree. $^{DOM}UVA_{254}$ C/C_0 values of approximately 0.6, 0.7, and 0.9 corresponded to 90% removal of short-chain PFAS in leachate, SMX in wastewater, and 2,4-D in surface water, respectively. At these $^{DOM}UVA_{254}$ C/C_0 values it is expected that moderately and strongly adsorbing MPs will be removed to levels >90%.

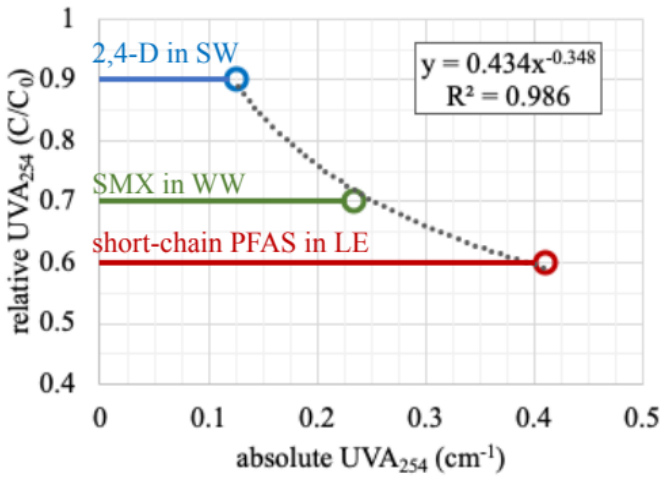

Figure 3. Relationship between absolute $^{DOM}UVA_{254}$ values of surface water (SW), wastewater (WW), and dump leachate (LE) and relative $^{DOM}UVA_{254}$ breakthrough values that indicate a likelihood of high levels of MP removal in biochar fixed-bed adsorbers.

The absolute $^{DOM}UVA_{254}$ value of a water reflects both the total DOM concentration and its spectrochemical character (e.g., aromaticity), parameters that simultaneously influence adsorbent fouling. Thus, the absolute $^{DOM}UVA_{254}$ value of a water is expected to be proportional to the DOM "fouling strength" of the water. For example, biochar adsorbers treating waters with high absolute $^{DOM}UVA_{254}$ values are expected to foul sooner than adsorbers treating waters with low absolute $^{DOM}UVA_{254}$ values. Thus, a water's absolute $^{DOM}UVA_{254}$ value can be used as a guide to select a relative $^{DOM}UVA_{254}$ C/C_0 value to indicate the end of a biochar bed lifecycle.

Because $^{DOM}UVA_{254}$ breakthrough curves flatten with service time (e.g., due to biodegradation of some UV absorbing DOM constituents in the adsorbent bed), $^{DOM}UVA_{254}$ C/C_0 bed-life indicator values >90% should be avoided. Also, because many UV absorbing DOM constituents break through early in the adsorbent bed lifecycle, selecting $^{DOM}UVA_{254}$ C/C_0 indicator values less than 60% would probably be impractical as it would lead to very short service times (e.g., 100-200 BV under our study conditions). The absolute influent $^{DOM}UVA_{254}$ values for the surface water with 2,4-D, wastewater with SMX, and leachate with PFAS used in our study were 0.128, 0.234, and 0.411 cm^{-1}, respectively. A plot of absolute $^{DOM}UVA_{254}$ values versus respective relative breakthrough values indicating high levels of MP control is shown in Figure 3, and fitted with the power law shown in Equation 4.

$$\text{relative } {}^{DOM}UVA_{254}\ (C/C_0) = 0.434 \times (\text{absolute } {}^{DOM}UVA_{254})^{-0.348} \quad (4)$$

For example, if the absolute ${}^{DOM}UVA_{254}$ of an influent water was found to be 0.205 cm^{-1}, then the corresponding relative ${}^{DOM}UVA_{254}$ C/C_0 value of ~0.75 would likely indicate that, up to that point, high levels of MP removal were achieved by the adsorber. In other words, when ${}^{DOM}UVA_{254}$ C/C_0 reaches ~0.75, it is probably time to replace the biochar.

Note that this method is based on experiments with only three waters. One objective of our ongoing research is to provide further method validation. Operator caution, periodic MP monitoring for validation, and appropriate safety factor(s) should be always applied.

Acknowledgements

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