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Predicting trace organic compound breakthrough in granular activated carbon using fluorescence and UV absorbance as surrogates

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ABSTRACT

This study investigated the applicability of bulk organic parameters like dissolved organic carbon (DOC), UV absorbance at 254 nm (UV_{254}), and total fluorescence (TF) to act as surrogates in predicting trace organic compound (TOrC) removal by granular activated carbon in water reuse applications. Using rapid small-scale column testing, empirical linear correlations for thirteen TOrCs were determined with DOC, UV_{254}, and TF in four wastewater effluents. Linear correlations ($R^2 > 0.7$) were obtained for eight TOrCs in each water quality in the UV_{254} model, while ten TOrCs had $R^2 > 0.7$ in the TF model. Conversely, DOC was shown to be a poor surrogate for TOrC breakthrough prediction. When the data from all four water qualities was combined, good linear correlations were still obtained with TF having higher R^2 than UV_{254} especially for TOrCs with log $D_{ow} > 1$. Excellent linear relationship ($R^2 > 0.9$) between log D_{ow} and the removal of TOrC at 0% surrogate removal (y-intercept) were obtained for the five neutral TOrCs tested in this study. Positively charged TOrCs had enhanced removals due to electrostatic interactions with negatively charged GAC that caused them to deviate from removals that would be expected with their log D_{ow}. Application of the empirical linear correlation models to full-scale samples provided good results for six of seven TOrCs (except meprobamate) tested when comparing predicted TOrC removal by UV_{254} and TF with actual removals for GAC in all the five samples tested. Surrogate predictions using UV_{254} and TF provide valuable tools for rapid or on-line monitoring of GAC performance and can result in cost savings by extended GAC run times as compared to using DOC breakthrough to trigger regeneration or replacement.

Abbreviations: BOP, Bulk organic parameter; BV_{10}, Bed volume for 10% breakthrough; BT_{50}, Bed volume for 50% breakthrough; DEET, N,N-diethyl-meta-toluamide; DOC, Dissolved organic carbon; F-EEM, Fluorescence excitation emission matrix; GAC, Granular activated carbon; NOM, Natural organic matter; PFOA, Perfluorooctanoic acid; PFOS, Perfluorooctane sulfonate; TF, Total fluorescence; TOrC, Trace organic compound.

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1. Introduction

More than 65 million chemicals and chemical formulations are available commercially and approximately 15,000 new chemicals are given Chemical Abstract Service (CAS) numbers each day (Snyder, 2014). Thus, it is not surprising that an ever increasing number of synthetic chemicals are being detected in water. In recent years, a large number of studies have focused on pharmaceuticals, endocrine disrupting chemicals, and other trace organic compounds (TOrCs) which can be identified and quantified in nanogram per liter concentrations, or lower, in water using modern analytical techniques (Anumol et al., 2013; Wang and Gardinali, 2012). The ubiquitous nature of many TOrCs is well-known with several studies reporting that TOrCs are not completely eliminated by conventional wastewater or drinking water treatment processes (Carballa et al., 2004; Westerhoff et al., 2005, Benotti et al., 2009; Kosma et al., 2014). The adverse effects of certain steroid hormones and other endocrine disrupting compounds (EDCs) on the reproductive systems of aquatic wildlife have been demonstrated at environmentally relevant concentrations (Jobling and Sumpter, 1993; Bevans et al., 1995, vom Saal and Hughes, 2005; Kidd et al., 2007; Caldwell et al., 2008). However, the effects of the majority of TOrCs detected in water are largely unknown and often available data consider only one chemical and therefore do not address the reality of complex mixture exposures. Advanced treatment technologies, such as advanced oxidation processes (AOPs) and membrane desalination are capable of attenuating most of TOrCs, but with some drawbacks. For instance, AOPs produce transformation products of generally unknown toxicity (Merel et al., 2015; Pereira et al., 2011) and membrane processes generate concentrated brine streams (Roccaro et al., 2013). In contrast, adsorption processes like granular activated carbon (GAC) do not result in transformation products and are capable of removing a wide range of TOrCs (Snyder et al., 2006; Rakić et al., 2015). However, breakthrough dynamics vary considerably among substances depending on physical-chemical characteristics, operational parameters, water quality, and the type of carbon employed (Corwin and Summers, 2012; Dickenson and Drewes, 2010; Bjelopavlic et al., 1999).

Testing of a pilot or full scale GAC column is very laborious and time consuming. To counter this, rapid small-scale column testing (RSSCT) has been developed as a bench-scale tool to accurately predict GAC performance in a short period of time (Crittenden et al., 1991). The chief advantages of an RSSCT over full-scale testing are that it can be conducted in a small amount of time and with a fraction of the water required at full-scale (Crittenden et al., 1991). Isotherm data can also be used to predict GAC performance but is generally based on a steady state process and does not take into account the kinetics of adsorption (Corwin, 2010). Further, interactions between NOM and TOrCs are not well captured by isotherm data. Computer models can also be used to estimate GAC performance but these require experimental data to be corroborated. The RSSCT, on the other hand uses the principle of similitude to scale-down all the components of a GAC process. RSSCTs can also take into account the non-steady state interactions between NOM and the TOrCs to give representative results in a short time. While RSSCTs have certain limitations it is still the preferred choice of testing GAC performance.

The analysis of TOrCs at trace levels in water is laborious, time-consuming and expensive. Also, with the number of TOrCs introduced to the environment constantly increasing, it is impossible to monitor each one individually. The use of indicator compounds, while useful are still affected by similar problems while only slightly reducing the time and cost of analysis. Further, the selection of an indicator list varies depending on the location and goal of each study. Consequently, the use of bulk organic parameters (BOPs) of water has been proposed as surrogates to monitor TOrC removal during treatment processes.

The analysis of surrogates to monitor pathogen disinfection in water is widely adopted, and is becoming increasingly of interest for gaging chemical contaminant attenuation (Merel et al., 2015). Studies investigating the use of bulk water quality parameters such as color, total organic carbon, UV absorbance and fluorescence excitation/emission spectroscopy has shown good promise in predicting the removal of TOrCs in AOP treatments (Gerrity et al., 2012; Wert et al., 2009). The formation of disinfection by-products on chlorination has also been predicted by some of these parameters (Roccaro and Vagliasindi, 2010; Roccaro et al., 2011). Studies have also adopted fluorescence spectroscopy to distinguish reverse osmosis (RO) permeate quality and to predict membrane fouling in membrane bioreactors and RO treatments (Singh et al., 2009; Galinha et al., 2011). However, there is little information available to suggest if such relationships exist between these surrogates and TOrCs for adsorption processes like GAC. Recently, Zietzschmann and colleagues determined a relationship between UV_{254} absorbance and six TOrCs in a powdered activated carbon process for a specific TOrC removal (80%) (Zietzschmann et al., 2014). Further, no literature is available showing correlation between fluorescence and TOrC attenuation for an adsorption process.

The aims of the current research include correlating surrogate parameters DOC, UV_{254}, fluorescence – excitation emission matrix (F-EEM), and TF changes with adsorption of TOrCs by GAC processes. This study investigated 13 TOrCs across four different wastewater qualities using RSSCTs. Furthermore, a set of water samples from a full-scale plant operating with GAC columns was collected across two years to verify the model.

2. Experimental

2.1. Tested waters

Four secondary treated wastewater effluents from around the USA were used for bench-scale RSSCT testing. All waters were filtered using a 0.45 μm cartridge filter (GE Healthcare, USA) prior to testing. Water quality parameters after filtration, along with specific treatment trains are provided in the supplementary materials (Table S1 and S2).