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PII: S0048-9697(21)07704-4

DOI: <https://doi.org/10.1016/j.scitotenv.2021.152626>

Reference: STOTEN 152626

To appear in: *Science of the Total Environment*

Received date: 13 September 2021

Revised date: 29 November 2021

Accepted date: 19 December 2021

Please cite this article as: S. Cosgrove, B. Jefferson and P. Jarvis, Application of activated carbon fabric for the removal of a recalcitrant pesticide from agricultural run-off, *Science of the Total Environment* (2022), <https://doi.org/10.1016/j.scitotenv.2021.152626>

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Application of activated carbon fabric for the removal of a recalcitrant pesticide from agricultural run-off

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Abstract

Removal of pesticides from agricultural run-off close to the point of application has the potential to prevent or reduce the pollution of water sources used for drinking. This research considered the novel application of activated carbon (AC) fabric as a sorbent material for removal of pesticides from field run-off. AC fabric was tested for the removal of the molluscicide pesticide metaldehyde under a range of flow rates at both laboratory and pilot scale. Metaldehyde at an initial concentration of 10 µg/L was removed effectively from deionised (DI) water and real source water by the AC cloth under all conditions tested, reaching removal of 1375 and 876 µg/g (equivalent to 169 and 264 mg/m²), respectively. The adsorption followed pseudo-second order kinetics (k_2 of 29.9 and 34.8 g/µg min for the AC fabric and GAC), providing rapid removal of metaldehyde within the first 5 minutes of contact. In single pass and flow through conditions, stabilised removal of 46% metaldehyde was achieved by the AC fabric bundle for treatment of 700 L of real water in a pilot scale flume. This equated to removal of 454 µg/m², although significantly more removal would be expected over longer duration testing given the stabilised removal and the equilibrium capacity of the fabric seen during the batch isotherm testing. The work provides evidence to show that AC fabric could be used in the catchment to reduce peak loads of pesticides in sources used for drinking water.

Keywords: pesticides, metaldehyde, water quality, adsorption, activated carbon cloth, drinking water

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1. Introduction

The use of pesticides is necessary in intensive agriculture to ensure the robust and resilient supply of food for a growing global population (Morsi et al., 2020). This, however, can present significant treatment challenges for water utility companies when residual micropollutants reach water sources used for drinking. This research considers how the use of novel engineered systems for the removal of pesticides close to the point of application can be used to reduce micropollutant loadings into drinking water sources and hence extend the armoury of tools available for catchment management.

Pesticides remain an important pollutant of the environment, being found in soil and surface waters in most countries of the world. These chemicals have been associated with pollution events, loss of biodiversity, contamination of food resources and direct and indirect health impacts (Bilal et al., 2019). Pesticides found in many source waters used for drinking can be particularly problematic, requiring treatment processes to effectively remove them (Morsi et al., 2020). Across Europe, most pesticides must be controlled to concentrations below 0.1 µg/L in drinking water (Drinking Water Inspectorate, 2017). The concentration of pesticides in source water can be significantly higher than these permitted levels and so require specific processes to remove them at water treatment works (WTWs). Certain pesticides have proven to be particularly recalcitrant to treatment and when present at high concentrations can cause breaches of the regulations (Giribaldi, 2013; Tao and Fletcher, 2013; Salvestrini, *et al.*, 2017). The molluscicide metaldehyde is one such example of a problem pesticide in the UK, occurring in many drinking water sources. For example, a study of the river Thames catchment found metaldehyde peaks of up to 0.9 µg/L in surface waters (Kay and Grayson, 2014). Agricultural run-off typically

has higher pesticide concentrations than receiving surface waters, with reported peaks as high as 10 $\mu\text{g/L}$ (Rolph et al., 2020). An assessment of six different pesticides in a headwater stream in an agricultural catchment saw pesticide spikes typically occurring during storm events following application of the chemicals (Ramos et al, 2017; Ramos et al, 2019). For example, metaldehyde reached 9 $\mu\text{g/L}$ in the stream, conditions which were coincidental with intense rainfall and increased flow discharge.

Removing pesticides close to the source of application has a number of potential benefits: 1) the high concentration of pesticides in run-off increases the chemical driving force for removal processes such as adsorption; 2) much lower flow volumes require treatment than would be required at full scale drinking water systems; and 3) treatment need only be applied only during high-risk periods, such as directly after pesticide application and following high intensity rainfall (Cosgrove et al., 2019). Such *in situ* treatment may therefore reduce both the overall load and the range of pesticides that may reach water treatment plants. However, the removal of pesticides from agricultural run-off is challenging for a number of reasons. Maximum pesticide peaks are typically observed following the application of the pesticide and during high intensity rainfall events (Rolph et al., 2020). Run-off events therefore have high flows, typically discharges of 10 L/s or above (Maillard *et al.*, 2011; Xu, *et al.*, 2015), and the water will contain a range of other dissolved substances as well as particulate debris. At present, constructed (or stormwater) wetlands, buffer strips and vegetated ditches are the most commonly used means of slowing flows and treating run-off from agricultural environments. It has been noted in a comprehensive review that pesticide removal across these processes is highly variable (Vymazal and Březinová, 2015). In order to perform effective pesticide removal, comparatively

high hydraulic residence times in the region of hours to days are needed (Sherrard, 2004; Maillard et al., 2011; Vallée et al., 2015; Ramos et al., 2019). Methods that can achieve faster rates of removal and be applied for use only when needed would therefore offer significant benefits. Temporary devices that have been used previously in the catchment include filtration socks that are designed for use on agricultural land. These use filtration materials such as compost, straw or wood bark contained within a mesh sock (Auckland Council, 2018). Filtration socks are generally used to catch and retain sediment rather than to filter out pollutants such as pesticides, although some have been tested with special additives to improve the removal of pollutants such as phosphorus, metals and hydrocarbons (Faucette et al., 2009). However, Shipitalo et al. (2010) found low reductions in concentration of glyphosate (5%) and alachlor (18%) when filter socks were used. These reductions were not sufficient to reduce pesticide concentrations to acceptable levels. The study also noted that the filter socks used in the study significantly increased the release of nutrients into the water (Shipitalo et al., 2010). Additionally, the build-up of sediment behind filter socks has been acknowledged to be a significant source of headloss (Keener et al., 2007).

In order to achieve improved removal of micropollutants, adsorption media such as granular activated carbon (GAC) is a more feasible option given their proven affinity for various micropollutants (Sanchez-Lopez et al., 2021). However, this requires large media volumes for the run-off water to filter through in order to provide the appropriate contact times required for effective removal. In addition, significant headloss would be generated very quickly, due to the small grain size of the GAC media, which is typically 1-2 mm (Golea et al., 2020), and through accumulation of solid debris at the filter surface. The concept of using sorbent media in forms that

have much greater hydraulic conductivity is therefore of great potential benefit. This research presents a novel use of AC fabric to develop highly porous filter structures that enable rapid passage of water through the media, while also providing adequate surface area and contact for adsorption to occur. This is particularly important for pesticides such as metaldehyde, where adsorption onto activated carbon is thermodynamically favourable but relatively weak, with a low negative delta Gibbs free energy (Larasati et al., 2022). To the authors' knowledge there has been no other research that has used AC fabric for this application, which has mainly been used for wound dressing, air filtration and for protective clothing for hazardous environments (Subranet et al., 2005). There has been some limited research on using pieces of AC fabric in batch laboratory studies for removal of micropollutants from water (Ayranci and Hoda, 2004; Ayranci and Hoda, 2005; Fontecha-Camara et al., 2006; Duman et al., 2010; To et al., 2021) and in risers of tile drainage depressions (Gonzalez et al., 2020). The present paper therefore aimed to determine the effectiveness of activated carbon fabric for the removal of the pesticide metaldehyde from raw water, examining adsorption parameters in batch tests, culminating in testing of a single-pass flow through system at pilot scale.

2. Materials and methods

AC fabric was obtained from Calgon Carbon (Tyne and Wear, UK). The fabric was composed of individual fibres of AC of approximately 10 to 15 μm in diameter. These fibres were twisted together to form strands of 0.5 mm diameter which in turn were woven into a highly permeable mesh, between 1-2 mm thick (Figure 1). The voids between the woven strands accounted for 17% of the total fabric area. The media had a specific surface area of 1,200 m^2/g . Initial testing compared the kinetics and equilibrium adsorption characteristics of pesticide onto the AC fabric with equivalent masses of conventional Filtrasorb 400 (F400) GAC, obtained from Calgon Carbon. F400 had a median particle size of 589 μm and specific surface area of 993 m^2/g . Metaldehyde was used as the target model pesticide for investigation in this research as it has been a problematic pesticide in the UK for numerous water companies due to its low adsorption partition coefficient (K_d) of 0.23 and low soil organic carbon/water partitioning coefficient (K_{oc}) of 240. The pesticide is relatively polar with a moderate/low octanol water coefficient ($\log K_{ow}$) of 0.12. Metaldehyde is a cyclo-octane with chemical formula of $\text{C}_8\text{H}_{16}\text{O}_4$ and a MW of 176.21, with a solubility of 188 mg/L.

2.1 Batch adsorption experiments

Isotherm and kinetics modelling was carried out in order to understand the capacity and dynamics of the adsorption process, determine which factors were dominant in the adsorption process and to compare the mechanisms of adsorption for the media. The fabric sheets were cut up into 2 x 2.5 cm squares and dosed into water at equivalent masses as used for the granular media. During batch adsorption tests, 100 mg of media was added to 100 mL of water in conical flasks giving a media concentration of 1 g/L. Each experimental condition was run in triplicate. The media

was pre-wetted in DI water overnight to remove any dust and particulates, and to saturate the medium with water. The excess water was then removed by sieving and air drying prior to experiments. For both kinetics and isotherm experiments, tests were initially run using pesticides spiked into deionised (DI) water to provide control data for comparison. Isotherm experiments were then carried out in real surface water to understand the impact of the background matrix on adsorption capacity. 100 mL of DI water spiked with individual pesticides to a concentration of 10 µg/L was then added to the flask. Kinetic tests were carried out to inform on the time needed for adsorption to reach equilibrium and to determine the respective rate of adsorption for the different media. The test solution was mixed on an orbital shaker (Stuart SSL1) for 1, 5, 10, 20, 30, 60, 120 and 480 min. For isotherm experiments, solutions using pesticide concentrations of 1, 10, 100, 500, 800, 1000, 2000, 3000, 4000, 5000 and 7000 µg/L for metaldehyde were prepared. Adsorbents were added to conical flasks at a concentration of 1 g/L. The conical flasks were then placed on an orbital shaker at 150 rpm for 24 h. Flasks were removed from the shaker and filtered into glass vials using 0.25 µm syringe filters and frozen at -4°C prior to analysis. The surface water tested had a pH of 7.5, a turbidity of 38.2 NTU, total organic carbon (TOC) of 13.8 mg/L and dissolved organic carbon (DOC) of 9.3 mg/L. This source water received run-off from both arable agricultural and urban run-off, containing significant background organic matter (both soluble and particulate) to be a reasonable proxy for water that might be treated in rural arable agricultural drainage systems. Importantly, this water contained organic matter that would act as a competitor for adsorption of micropollutants.

Established models appropriate for metaldehyde uptake onto carbon adsorbents were used for both equilibrium (Freundlich) and kinetics (2nd order) to quantify the

impacts of different media and other components in the raw waters (Sanchez Lopez et al., 2021). Adsorption rates and capacities were determined for the kinetic and batch studies using Equation 1 to give the adsorbate mass removed normalised to the mass of adsorbent, q_e ($\mu\text{g/g}$):

$$q_e = (C_0 - C_e) \frac{V}{m} \quad \text{Equation 1}$$

C_0 is the initial pesticide concentration ($\mu\text{g/L}$), C_e is the equilibrium concentration of pesticide ($\mu\text{g/L}$), V is volume of solution (L) and m is the mass of media used in grams (Jusoh et al., 2011).

The kinetics of adsorption was modelled using the linearised pseudo-second order (Equation 2) expressions following protocols used by others (Nethaji et al., 2013; Saucier et al., 2015; Sanchez Lopez et al, 2021).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{Equation 2}$$

k is the rate constant ($k_2 \text{ g } \mu\text{g}^{-1} \text{ min}^{-1}$; $k_i \mu\text{g g}^{-1} \text{ min}^{1/2}$) and t is time in minutes.

The adsorption data was fitted to the Freundlich model (Equation 3) which describes multilayer adsorption (Boudesocque et al., 2008).

$$q_e = K C^{(1/n)} \quad \text{Equation 3}$$

q_e is equilibrium adsorption capacity ($\mu\text{g/g}$), C is the chemical concentration in solution ($\mu\text{g/L}$). K_f is an empirical constant indicating the capacity of the adsorbent for the adsorbate at equilibrium ($\mu\text{g/g})(\mu\text{g/L})^{1/n}$, and $1/n$ is unitless and is also an empirical constant that indicates the intensity of adsorption (Crittenden et al., 2012; Njoku et al., 2015).

2.2 Activated carbon cloth cross flow testing

Initial cross flow tests were carried out using a Sterlitech membrane distillation cell (Washington, USA) (Figure 1), with flow rates between 0.5 to 2 L/min using a Watson Marlow 520S peristaltic pump (Falmouth, UK). These tests were carried out by circulating 1 L batches of water with a starting concentration of 10 $\mu\text{g/L}$. The active membrane area was 140 cm^2 (Sterlitech, 2016). A shim spacer was used in the setup to give a cross sectional area of 141 mm^2 , such that the cross-flow velocity was varied between 0.06 and 0.24 m/s. The permeate outlet was blocked off so that all outlet flow from the cell was from the retentate flow across the fabric. Aliquot samples of 1 mL were taken from the batch at timed intervals. Tests were carried out in recirculated batches for raw water and DI water to show the impact of background matrix on removal across the AC fabric. The batch concentration was renewed to the 10 $\mu\text{g/L}$ starting concentration after each 100 minutes run time (equivalent to 3.5 minute contact time with the AC fabric). Raw water was collected from a nearby brook and used for the laboratory scale testing. The raw water had a TOC 7.1 mg/L, DOC 4.6 mg/L, UV_{254} 0.14 ± 0.003 1/cm and pH 7.7. Prior to spiking, the water was analysed for metaldehyde, however no traces were found.

2.3 Pilot testing of carbon cloth filter

Pilot scale trials were conducted in a 30 L open channel flume with dimensions of 2.5 m length, 0.1 m wide and 0.12 m water depth controlled by a weir (Figure 2). Strips

of 0.1 m x 1 m AC fabric were cut and collected into 2 m² or 8 m² bundles and fixed into the flume to filter the flow of water (see Supporting Information Figure S1 for photographs of set-up). 5 mm plastic beads were used as spacers between fabric sheets in order to maintain an even distribution of fabric across the width of the flume. Bundles were held in place using carabiner clips attached to chains that ran the length of the flume. The flume was operated in single-pass mode at flow rates of 2 L/min and 10 L/min equivalent to a velocity of 0.003 and 0.014 m/s at a water level of 120 mm. The velocity range was selected to ensure full submergence of the media. This meant that operation was at a lower velocity range than previously considered in the cross flow cell. Raw water was spiked with metaldehyde to ensure a 10 µg/L concentration. The solutions were made up as 1000 L batches which were used as a single pass through the flume for each run. After each run, solution from the outlet intermediate bulk container (IBC) was pumped back into the inlet IBC and the pesticide concentration in the inlet was topped back up to 10 µg/L. The pilot testing was carried out at a different time to the lab membrane tests, here the feed water characteristics were: DOC 6.0 ± 0.5 mg/L, UV₂₅₄ 0.083 ± 0.003 1/cm, pH 9.3, turbidity 5.27 NTU. Aliquots of 1 mL were taken and filtered in preparation for analysis at timed intervals.

2.4 Analysis

Pesticide standards for metaldehyde were acquired from Sigma-aldrich (Darmstadt, Germany) and made into 1 g/L stock solutions with DI water (conductivity = 0.05 mS cm⁻¹) and then diluted down to the required test concentration, again using DI water. Pesticide analysis was undertaken using a direct injection method on an LC-MS/MS. 1 mL samples were filtered using 0.25 µm filters into glass vials immediately after

being taken. Metaldehyde calibration standards for LC-MS/MS methods were carried out within a range of 0.1-10 µg/L. Quality controls of 5 µg/L were used throughout the analysis alongside blank standards. All water sources were characterised by pH (Hanna Instruments, UK), UV₂₅₄ (Spectroquant Pharo 300, Germany), turbidity (2100N Turbidimeter HACH, USA), DOC and TOC (TOC-V CSH total organic carbon analyzer, Shimadzu, UK). Samples were filtered through a 0.45 µm filter (cellulose nitrate, Whatman, Germany) for DOC and UV₂₅₄ measurements.

3. Results

3.1 Adsorption kinetics and isotherms

Batch adsorption experiments comparing the AC fabric with a commercial GAC (F400) highlighted some important differences between the sorbent materials. For equivalent adsorption exposure times, the AC fabric adsorbed more metaldehyde than the GAC from DI water (Figure 3(a)), with 8.5 $\mu\text{g/g}$ removed after 5 minutes (61%) and 12.4 $\mu\text{g/g}$ removal after 30 minutes (92%) for the fabric. For the F400 GAC, equivalent results were 4.7 $\mu\text{g/g}$ removed after 5 minutes (44%) and 10.1 $\mu\text{g/g}$ removal after 30 minutes (89%). Respective uptake rates during the initial 30 minutes of exposure were 0.41 and 0.34 $\mu\text{g/g min}$. The data for metaldehyde adsorption was best fitted to the pseudo-second order model using the linear form of the equation (Equation 2) on a plot of $\frac{t}{q_t}$ vs t , with R^2 values >0.99 resulting in k_2 of 29.9 and 34.8 $\text{g}/\mu\text{g min}$ for the AC fabric and GAC, respectively (Figure 3(b)). With respect to overall adsorption capacity, in DI water there was little difference between the media at high C_e of $>10 \mu\text{g/L}$, however the GAC achieved greater removal at C_e values $<1 \mu\text{g/L}$ (Figure 4). In raw water, the removal capacity for metaldehyde reduced by an order of magnitude for equivalent C_e values. There was also less distinction between the two AC media, particularly for $C_e >1 \mu\text{g/L}$. The good fit of the data to the Freundlich model agrees with results seen for metaldehyde adsorption in previous studies (Tao and Fletcher, 2013; Salvestrini *et al.*, 2017), indicating multi-layered adsorption occurred for the pesticide on to both of the AC media (Crittenden *et al.*, 2012). The differences in the K_f for DI and raw water confirm how the background organic matter reduces the capacity for pesticide adsorption for all media (Table 1). To demonstrate, for GAC the equilibrium capacity constants K_f

decreased by 93% from 1189 to 81 $(\mu\text{g/g})(\mu\text{g/L})^{1/n}$, while this was 584 to 150 $(\mu\text{g/g})(\mu\text{g/L})^{1/n}$ for the AC fabric. The impact of background organic matter on adsorption was therefore significant. Background natural organic matter (NOM) has been shown to hinder removal of micropollutants onto AC through competition for adsorption sites and blockage of pores. These processes result in a reduction in both external transfer of pollutants to the sorbent and intraparticle diffusion within the media (To et al., 2008; Fallou et al., 2021). As NOM matrices are complex, and variable both temporally and spatially, it is important to understand the influence of organic matter characteristics on micropollutant adsorption at locations where these sorption systems might be implemented.

At the equilibrium concentration of pesticide investigated in the raw water for the subsequent flow through experiments (10 $\mu\text{g/L}$), the adsorption capacity of the AC cloth was 1374 and 886 $\mu\text{g/g}$ for the pesticide in DI and raw water, respectively. The results demonstrated the potential for AC fabric to be used as an effective adsorbent, enabling faster uptake but reduced overall capacity compared to traditional ACs. The fabric was therefore taken forward for testing in a membrane cell to determine how the material would remove a micropollutant in flow through mode.

3.2 Flow-through testing of AC fabric

The metaldehyde concentration continually decreased across all cross-flow trials, reaching final values of 0.1 $\mu\text{g/L}$ for the 1 L/min and 2 L/min runs and between 0.17 and 0.26 $\mu\text{g/L}$ for the 0.5 L/min runs (Figure 5). The time required to reach the final levels varied with flow rate such that it was achieved after 3.5, 14 and 56 minutes for the 2, 1 and 0.5 L/min runs, respectively. Accordingly, the 0.014 m^2 of adsorbent

fabric treated a total of 7, 14 and 28 L of water before removal of nearly all the available metaldehyde from the batch solution. The equivalent mass removal rates were 0.08, 0.26 and 1.01 $\mu\text{g/g min}$ (15.4, 51.9 and 202.5 $\mu\text{g/m}^2 \text{ min}$), indicating that the system was mass loading limited given that the rate of removal increased as the flow rate was increased. The total uptake during the current trial using the AC fabric was 3.8 $\mu\text{g/g}$, representing 0.32% of the previously measured equilibrium capacity.

The above runs indicated that the metaldehyde uptake rate onto the AC fabric was underutilised, implying it could treat substantially more volume. To test this, a single piece of fabric was repeatedly used to treat multiple batches of water containing 10 $\mu\text{g/L}$ metaldehyde solution (Figure 6). Each cycle consisted of 60 circulations through the membrane and was run at 2 L/min to give a contact time of 3.5 minutes per cycle. Metaldehyde removal continued throughout the six batches tested during the DI water trial, with only a small decrease in uptake such that the overall residual in the batch was 0.49 $\mu\text{g/L}$ higher at the end of the sixth cycle as compared to the first cycle, increasing from 0.08 $\mu\text{g/L}$ to 0.57 $\mu\text{g/L}$, demonstrating that the fabric was still effectively removing metaldehyde and had the potential to remove more of the pesticide. Across the six cycles, the 0.014 m^2 fabric membrane had a normalised removal of 4136 $\mu\text{g/m}^2$. The residual concentration was best fitted to a linear regression line (R^2 of 0.99) with the expression:

$$\text{Residual metaldehyde concentration } (\mu\text{g/L}) = 0.0265(\text{contact time (minutes)}) + 0.0127$$

The equivalent trials in raw water reduced the uptake of metaldehyde during each cycle more significantly than was observed in the case of DI water, alongside a decrease in the adsorbed capacity (Figure 6). To illustrate, the residual metaldehyde

concentration in the batch after each set of 200 circulations was 2.2, 4.0, 4.8, 5.9, 6.2 and 6.9 $\mu\text{g/L}$ for cycles 1 to 6. This equated to a total removal of metaldehyde of 30.1 μg as compared to 57.9 μg during the equivalent six cycles treated in DI water, giving a removal of 2150 $\mu\text{g/m}^2$. This 52% reduction was explained by competition for adsorption sites from background organic matter and other compounds present in the water (Rolph *et al.*, 2018). This, compared with the 74.3% reduction seen during equilibrium batch studies, reflected the impact that kinetics had on the overall affinity of adsorption for the metaldehyde pesticide. The residual metaldehyde concentration after each cycle followed a logarithmic expression with an R^2 of 0.99, and indicated that while removal was reducing, there was further capacity in the cloth for additional removal.

$$\text{Residual metaldehyde concentration } (\mu\text{g/L}) = 2.516 \ln(\text{contact time}(\text{min})) - 0.9121$$

A previously reported batch test experiment using an AC fabric for pesticide removal showed a tenfold reduction in the concentration of 2,4-D, metribuzin, bromacil and atrazine after 125 minutes using approximately 0.75 cm^2 of AC cloth (Ayranci and Hoda, 2004). This equates to a capacity of 128.4 g/m^2 with the concentrations reducing from 10.4 to 1 mg/L for 2,4-D, 12.2 to 1.2 mg/L for bromacil, 10.1 to 1 mg/L for metribuzin and 10.1 to 1 for atrazine (Ayranci and Hoda, 2004). These results are two orders of magnitude greater than those seen here, partly explained by the longer contact time and higher starting concentrations of the pesticides, but also due to the higher affinity of these compounds for adsorption than is seen for metaldehyde, which is known to be weakly sorbed onto AC (Rolph *et al.*, 2018).

3.3 Pilot scale testing of AC fabric

Larger scale pilot tests were carried out with 2 m² AC fabric at 2 and 10 L/min flow rates, equivalent to cross flow velocities of 0.003 and 0.014 m/s and contact time with the water of approximately 60 and 12 seconds (Figure 7). Metaldehyde was removed throughout treatment of 540 L of water, with the concentration initially dropping to a minimum before increasing up to a stabilised value slightly below that of the feed (Figure 7). For example, in the case of the first of the 2 L/min trials, the metaldehyde concentration decreased from an initial level of 11.29 µg/L to a minimum value of 6.44 µg/L after a cumulative flow of 10 L had been treated before increasing up to a stabilised level of 10.6-10.9 µg/L after 80 L of water was treated. Increasing the flow rate had no appreciable impact on the removal of metaldehyde with the minimum occurring at the same volume of 10 L, reaching concentrations of 6.7 and 7.4 µg/L during the repeat trials. The stabilised levels were also similar, representing an uptake of between 0.7 and 1.8 µg/L for all flow rates (Figure 7). This demonstrates a resilience of uptake to changing flowrates which is likely to be important in field applications. The initial reduction reflects the volume required to fill the channel representing a surrogate of the initial flow that would pass through the filter following a heavy rainfall event, again showing the resilience of the fabric to the rate of flow. In total, across the trial, this represents total uptake of 884 µg of metaldehyde, equivalent to a capacity of 442 µg/m² (2.21 µg/g).

Increasing the area of the fabric in the channel to 8 m² had a substantial impact on the profile of the residual metaldehyde concentration, resulting in significantly lower levels when compared to the tests using 2 m² of fabric (t-test at p<0.05). In this case, the metaldehyde concentration reached a minimum value of 2.8 µg/L after treating 30 L before inclining to a stabilised value of between 5.1 and 6.1 µg/L. Across the trial, this represented an average removal of 4.5 µg/L (46% removal from the starting

concentration). The total amount of metaldehyde removed using 8 m² of fabric was 3632 µg. The corresponding capacity was 454 µg/m² (2.27 µg/g), a value consistent with that seen for the reduced AC surface area test. Accordingly, the improved performance reflects an increase in the total contact time between the water and the fabric to 48 seconds showing how the level of removal for in situ application can be modulated by increasing available surface area.

4. Discussion

At present, constructed or stormwater wetlands, buffer strips and vegetated ditches are the most commonly used means of preventing or treating run-off from agricultural lands. Pesticide removal across these systems has been shown to be highly variable (Vymazal and Březinová, 2015) with comparatively high hydraulic residence times in the region of hours to days are needed (Sherrard, 2004; Maillard et al., 2011; Vallée et al., 2015). This is because these systems typically rely on biochemical processes for removal of pesticides. These are processes that can be slowed under colder water conditions, often coinciding with periods when many molluscicides such as metaldehyde are applied (Asfaw et al., 2018). This is in comparison to the fabric filter described in this research, which needed contact times of <1 minute to be effective. The filter devices could be applied temporarily into agricultural drainage channels during high-risk periods when pollutants are present in run-off, before the removal and regeneration of the temporary filters before re-use.

The AC fabric filters were able to remove pesticides under a range of flow rates, had faster adsorption kinetics uptake and was least impacted by treatment of real water when compared to granular media. Previous mechanistic investigations have shown

that, as a relatively small molecule, metaldehyde is more effectively removed when there is an abundance of accessible meso- and micro-pores (Li et al, 2019). The pore size distribution of the AC materials used were not measured here, but the increased removal was attributed to the easy access of surface sorption sites on the AC fabric fibres when compared to the GAC, an effect analogous to that seen when comparing adsorption kinetics for powdered activated carbon with the granular form (Li et al., 2019; Golea et al., 2020). AC fabric has also been reported to have a much higher proportion of micropores when compared to granular media (Martín-Gullón and Font, 2001). Given the small diameter of the fibres in the fabric, these micropores are accessible close to the media fibres, allowing a relatively small molecule like metaldehyde rapid access and hence quick uptake. In comparison, GAC has a network of interconnected macro, meso and micropores, through which it takes a much longer time for molecules to pass through.

When compared to the performance seen using filter socks (5 and 18% removal for glyphosate and alachlor), the ~50% removal achieved by the 8 m² AC fabric filters for a hard to remove pesticide compared favourably (Shipitalo et al., 2010). These observations were explained by differences in adsorbent properties and the affinity between adsorbate and adsorbent. Filter socks are typically filled with soil, compost or straw and hence the available surface area is much lower than that seen for activated carbon materials. Hence, while glyphosate is relatively well sorbed onto carbon materials, including soils, the available surface area is much less than for the AC fabric system (Mamy and Barriuso, 2005). One way by which filter sock performance could be improved would be to consider filling them with granular activated carbon media and using activated carbon fabric to make the 'sock'.

However, the filter socks are also not designed for being fully submerged in water channels and have a much lower capacity with respect to the flow that can be treated before being overwhelmed due to their much lower hydraulic capacity.

While the AC fabric filters did not reduce the pesticide to below regulatory limits for drinking water, the ability to substantively decrease the pesticide load entering receiving surface water rivers and streams offers significant benefits. In turn, this would reduce the spikes of pesticide that enter a WTWs or receiving reservoir. Under some circumstances the combined effects of pesticide peak-logging and dilution might negate the need for introducing expensive treatment options or reduce the treatment costs for system already in place. A full cost-benefit analysis is required to appraise the potential usefulness of using the AC fabric in agricultural catchments. This would need to account for the potential reduction in water treatment costs against those required to manufacture and maintain the fabric systems, crucially determining the true capacity and regeneration requirements of the fabric following use.

For such systems to be successful, farmers would need to be engaged and informed on where and when to apply the AC fabric filters and for how long, considering the timing and period of pesticide application, prevailing rainfall duration and intensity conditions and preceding conditions, factors all known to impact on the extent of pesticide concentrations in field run-off (Cosgrove et al., 2019). For example, >10 mL of rainfall in the preceding 24 hours is known to increase the concentrations of pesticide in run-off (Cosgrove et al., 2019). Additional in situ testing of scaled up AC fabric filters is needed to test their mechanical strength under real storm flow

conditions. Further, it is important to establish that the adsorption profile seen for the surface water investigated here can be extrapolated to agricultural run-off water from a range of different sources. In addition determination of the AC surface area required to treat a range of storm events is needed to determine whether the pesticide capacity of $454 \mu\text{g}/\text{m}^2$ seen at pilot scale holds for more extensive storm flows. However, the potential to use the fabric as a temporary load reducing tool within catchments provides a novel opportunity to respond to micropollutant contamination of water sources used for drinking. The approach could be targeted towards a range of contaminants that adsorb onto activated carbon, including a multitude of pesticides, hormones and pharmaceuticals that are found in polluted catchments.

5. Conclusions

These experiments demonstrated the efficacy of using AC carbon fabric as a means of reducing peak loads of a difficult to remove pesticide. The solution proposed considered using the AC fabric in parallel sheets that allowed for high water conductivity and effective contact between adsorbent and adsorbate. The system was resilient to variable flow rates and offered a meaningful level of metaldehyde removal which should assist in reducing pesticide loads at drinking water production sites. In the present case, nearly 50% removal of metaldehyde was maintained for treatment of more than 700 L of water, using 8 m^2 of AC fabric. Reducing pesticide load in agricultural run-off that eventually ends up in receiving surface waters would have significant benefit on water treatment, potentially reducing treatment costs and the need for investing in expensive and energy intensive new process technology. When combined with other catchment management initiatives for pesticide control

(for example, intelligent pesticide application, using alternative products and control measures, and the use of buffer strips, swales and retention ponds), further water quality improvements will be seen.

The work provides initial evidence for the suitability of temporary catchment interventions as part of a complete catchment management strategy that enables rapid response and deployment potential to reduce peak load risks. The research highlighted that such systems were mass load limited, associated with predominately surface uptake as opposed to intraparticle diffusion, a feature commonly observed for granular carbons. The implication is that operation will remain resilient over the typical peak load periods encountered. The pathway for implementation of such systems requires further testing and optimisation of highly permeable reactor configurations in the field to determine their robustness and performance under stormflow conditions, while maintaining available surface area for adsorption. Future design developments should focus on enriching the understanding of area and packing density on the achievable total uptake. Additional further work is required to assess the impact of a mix of pesticides and differential raw water characteristics to establish the influence of competition on uptake to ensure robust design for field testing.

Acknowledgements

This research is gratefully supported by the Natural Environment Research Council (NERC) through their funding of the PhD (NE/L009218/1) and from the project sponsor Severn Trent.

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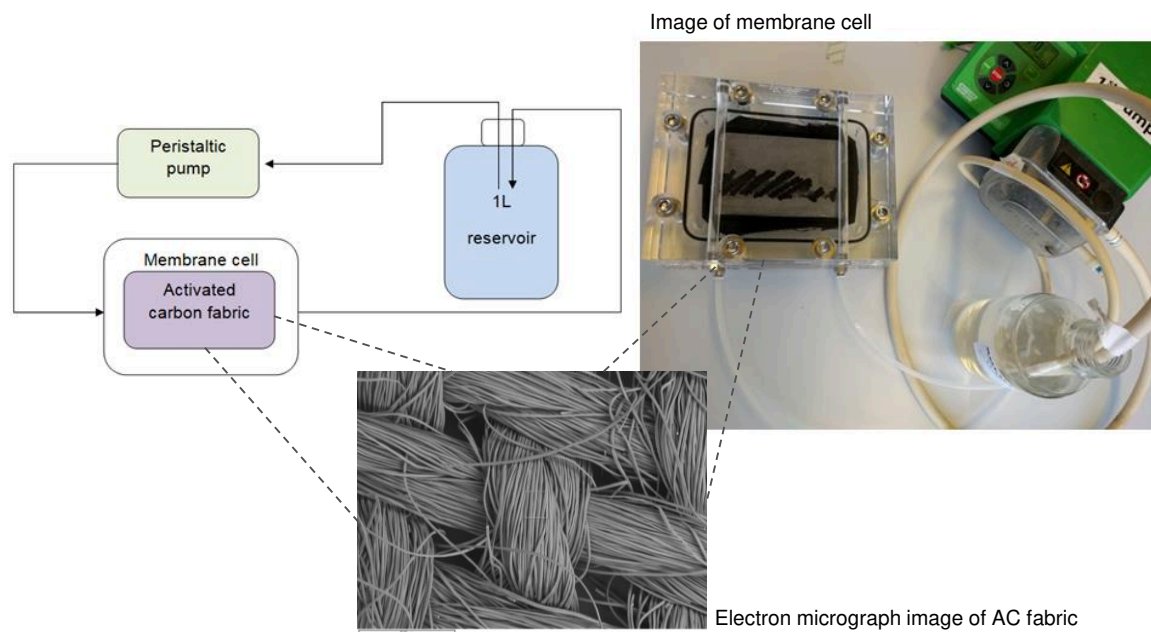


Figure 1. Activated carbon fabric membrane cell setup schematic and photograph.

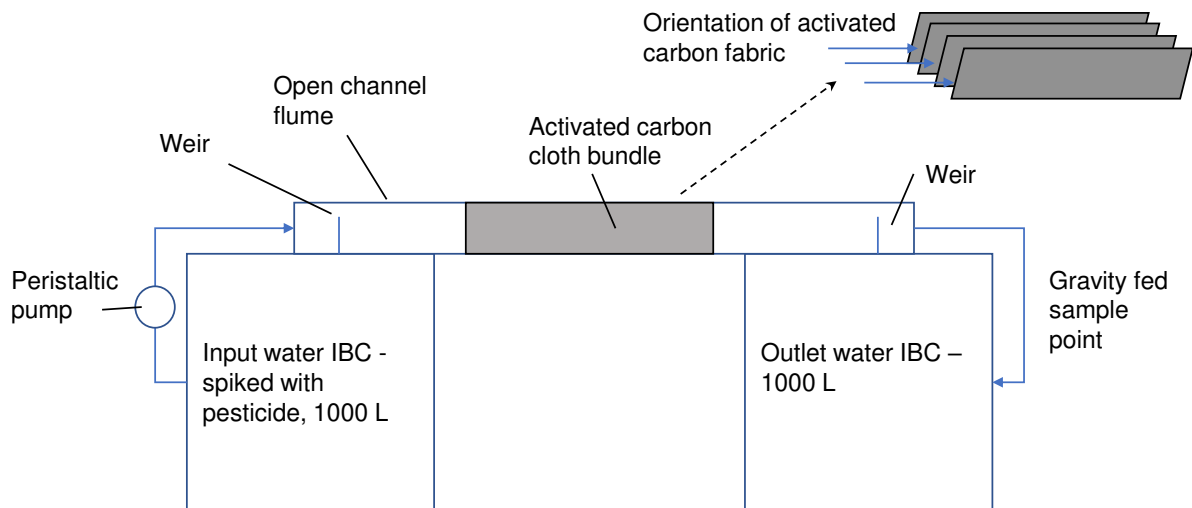
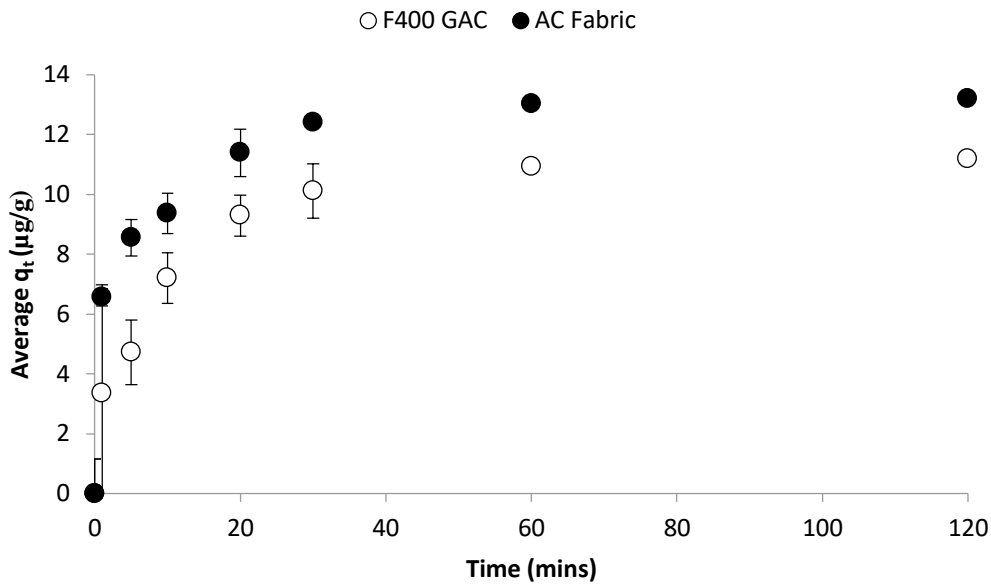
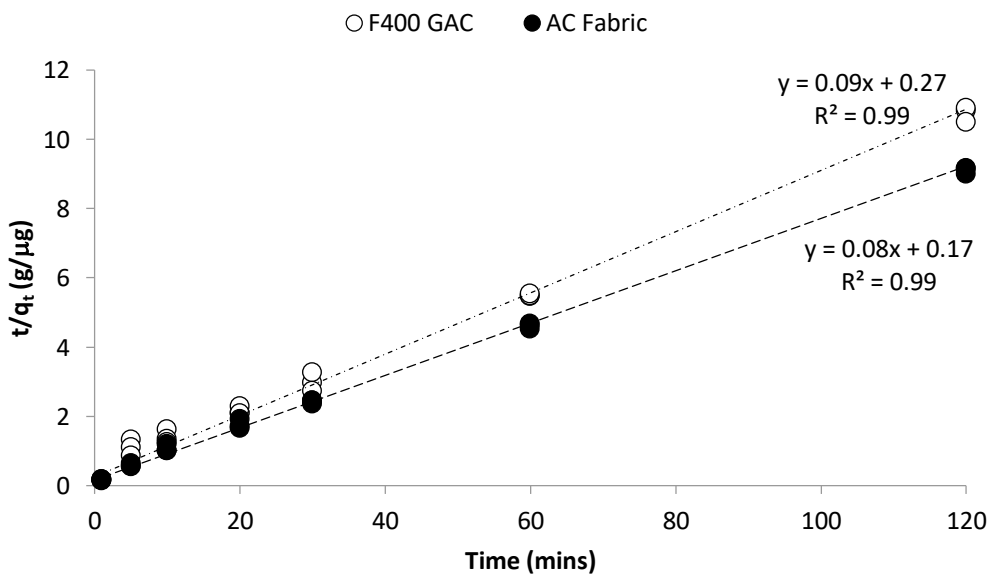


Figure 2. Side view schematic of pilot channel and fabric bundle in flume channel.



(a) Adsorption with time



(b) Pseudo second order model

Figure 3. Metaldehyde removal from DI water over 120 minutes for the different AC media (a) and fitted to the linearised pseudo-second order rate model (b).

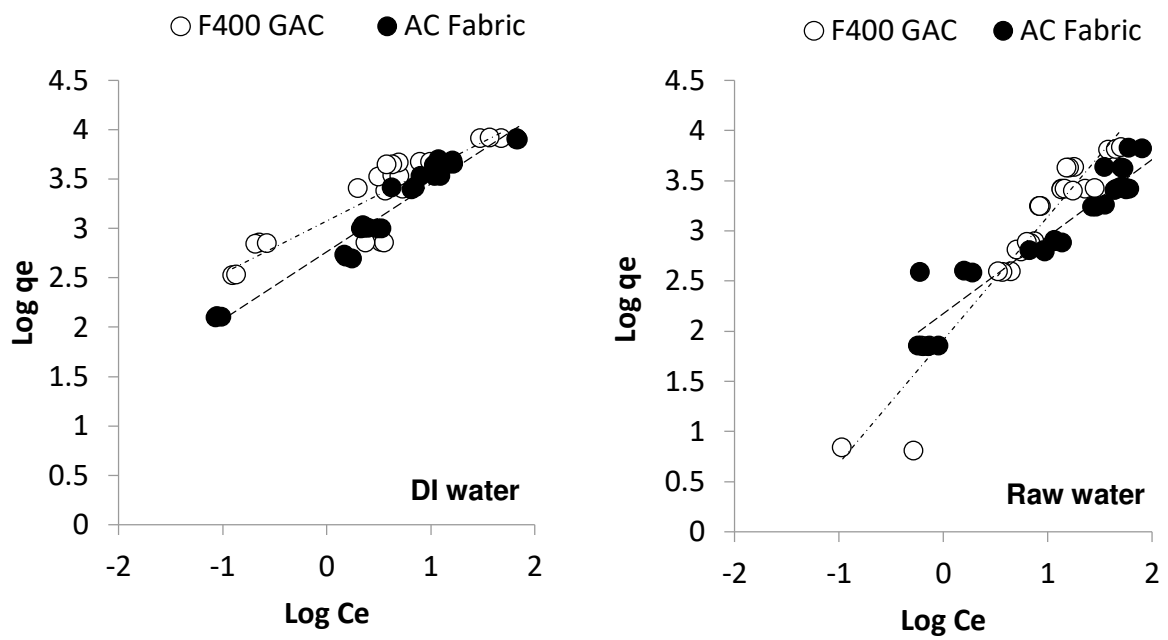


Figure 4. Freundlich adsorption isotherms for removal of metaldehyde onto activated carbon in DI water and in raw water.

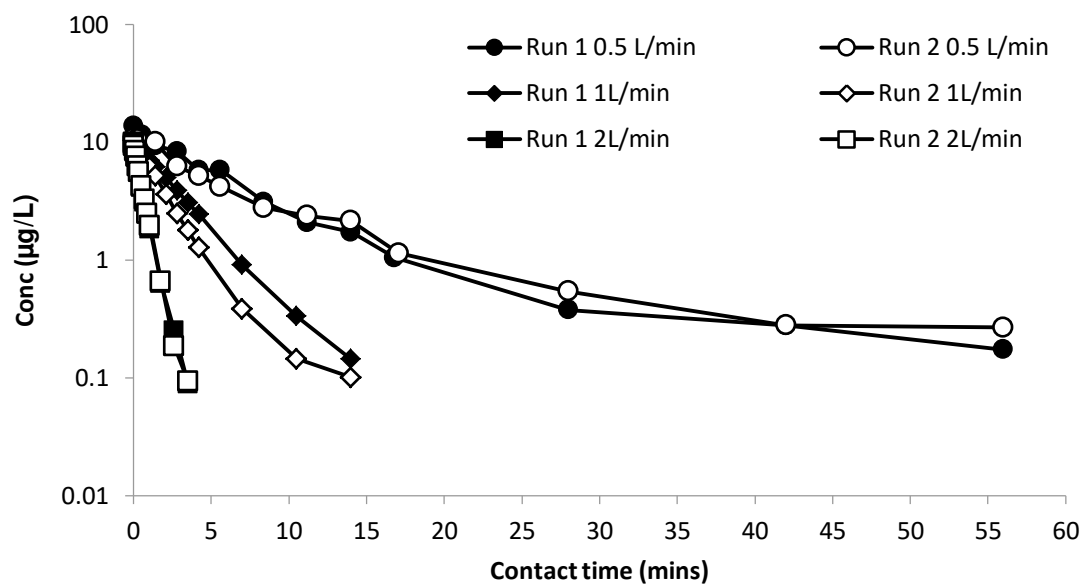


Figure 5. Removal of metaldehyde from raw water using the membrane flow cell containing AC fabric at different flow rates.

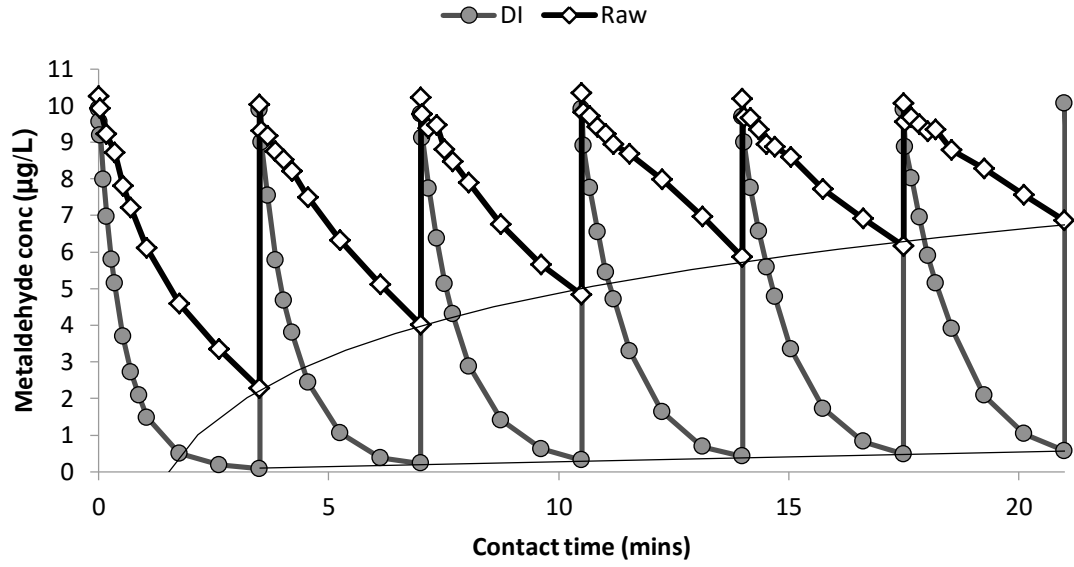


Figure 6. Metaldehyde removal from DI and raw water per cycle with a projection of diminishing removal of metaldehyde per subsequent cycles.

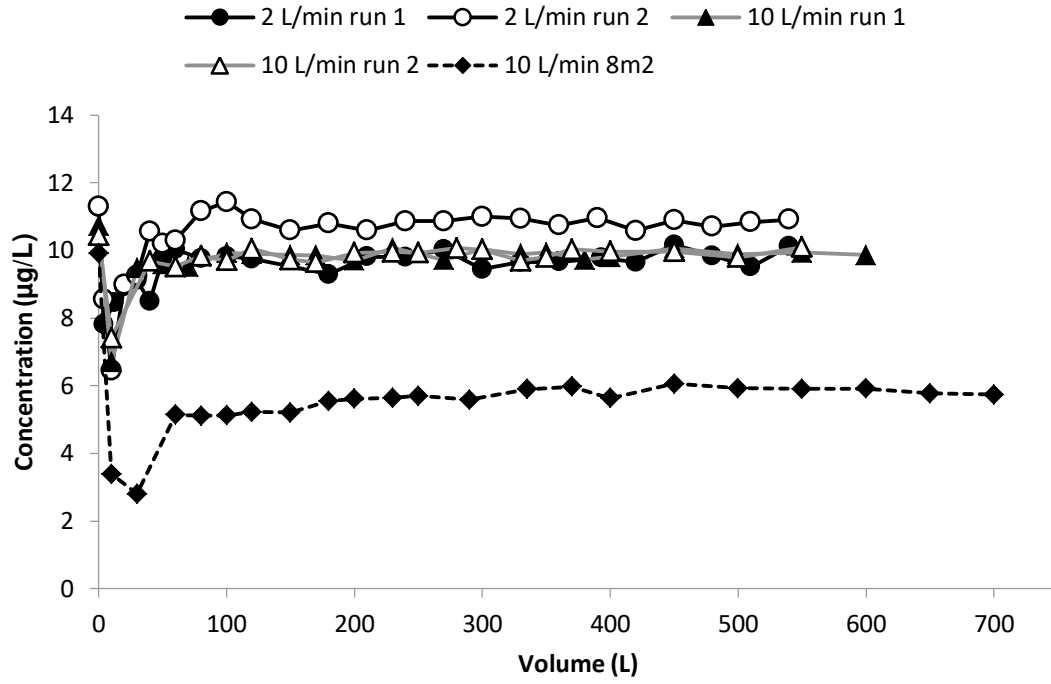


Figure 7. Metaldehyde removal at flow rates of 2 and 10 L/min with 2 m² AC fabric and 10 L/min with 8 m² of AC fabric

Table 1. Freundlich isotherm data for metaldehyde removal from DI and raw water.

Medium	DI water			Raw water			Difference K_f $(\mu\text{g/g})(\mu\text{g/L})^{1/n}$
	1/n	K_f $(\mu\text{g/g})(\mu\text{g/L})^{1/n}$	R^2	1/n	K_f $(\mu\text{g/g})(\mu\text{g/L})^{1/n}$	R^2	
F400 GAC	0.53	1189.1	0.77	1.23	81.3	0.94	1107.7
AC Fabric	0.69	584.0	0.95	0.77	150.2	0.89	433.8

Author credit statement

Stephanie Cosgrove: Data curation; Formal analysis, Investigation; Methodology; Writing - original draft. Bruce Jefferson: Conceptualization; Supervision Writing - review & editing. Peter Jarvis: Funding acquisition; Conceptualization; Supervision; Writing - review & editing.

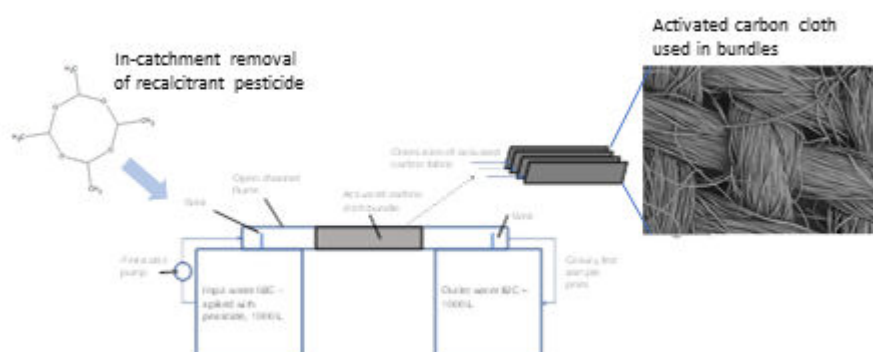
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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Graphical abstract:



Highlights

- Activated carbon fabric used for novel in-catchment removal of pesticides
- Flow through testing of media could reduce pesticides by 50% from real water
- System was resilient to changing water flow rates
- Novel catchment management strategy presented for control of pesticides