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Field assessment of coconut-based activated carbon systems for the treatment of herbicide contamination

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Abstract

Once released into the environment, herbicides can move through soil or surface water to streams and groundwater. Filters containing adsorbent media placed in fields may be an effective solution to herbicide loss in the environment. However, to date, no study has investigated the use of adsorbent materials in intervention systems at field-scale, nor has any study investigated their optimal configuration. Therefore, the aim of this paper was to examine the efficacy of low-cost, coconut-based activated carbon (CAC) intervention systems, placed in streams and tributaries, for herbicide removal. Two configurations of interventions were investigated in two agricultural catchments and one urban area in Ireland: (1) filter bags and (2) filter bags fitted into polyethylene pipes. Herbicide sampling was conducted using Chemcatcher® passive sampling devices in order to identify trends in herbicide exceedances at the sites, and to quantifiably assess, compare, and contrast the efficiency of the two intervention configurations. While the Chemcatcher® passive sampling devices are capable of analysing eighteen different acid herbicides, only six different acid herbicides (2,4-D, clopyralid, fluroxypyr, MCPA, mecoprop and triclopyr) were ever detected within the three catchment areas, which were also the only acid herbicides used therein. The CAC was capable of complete herbicide removal, when the water flow was slow ($0.5 – 1$ $m^3.s^{-1}$), and the interventions spanned the width and depth of the waterway. Overall, the reduction in herbicide concentrations was better for the filter pipes than for the filter bags, with a 48% reduction in detections and a 37% reduction in exceedances across all the sampling sites for the filter pipe interventions compared to a 13% reduction in the number of detections and a 24% reduction in exceedances across all sampling sites for the filter bag interventions ($p < 0.05$). This study demonstrates, for the first time, that CAC may be an effective *in situ* remediation strategy to manage herbicide exceedances close to the source, thereby reducing the impact on environmental and public health.

Keywords:

Herbicides, Chemcatchers®, Monitoring, Interventions, Water quality, Remediation

1. Introduction

Herbicides are substances used to control undesired plants, also known as weeds (de Souza et al., 2020; Mojiri et al., 2020; Ighalo et al., 2021). However, extensive and inefficient use of herbicides has led to the contamination of soils and waterways (Khalid et al., 2020; Shahid et al., 2021; Zeshan et al, 2022). Once released into the environment, herbicides can move through soil or surface water to streams and groundwater, where they can accumulate in aquatic organisms as well as causing loss of ecosystem biodiversity (Aksoy et al., 2017; Ramakrishnan et al., 2021; Wenzel et al., 2022). In the European Union (EU), the Council Directive 2020/2184 (EU, 2020) on the quality of water intended for human consumption sets the maximum allowable concentration (MAC) for herbicides, either individually or in total, as 100 ng.l^{-1} or 500 ng.l^{-1} , respectively. However, these values are frequently exceeded (Postigo et al., 2021; EPA, 2022; McGinley et al., 2023). Such exceedances are particularly problematic as conventional water treatment methods are ineffective for the removal of herbicides (Larasati et al., 2021; Intisar et al., 2022; Taylor et al., 2022). While some water treatment facilities incorporate powdered or granulated activated carbon (GAC) filters to remove herbicides (EPA & HSE, 2019; de Souza et al., 2020), this is not common practice in many countries due to prohibitive costs. An alternative approach may involve treatment at the source, i.e., in the field, rather than in a treatment plant. This early intervention for removal of pollutants would positively impact both human and environmental health by reducing herbicide exposure.

Many low-cost media, based on either raw or pyrolysed waste materials coming from an agricultural or industrial origin, have been used as adsorbents for herbicides (Franco et al., 2021; Jatoi et al., 2021; Taylor et al., 2022). An adsorbent that is often used for herbicide removal is GAC, due to its large surface area (300–2500 m^2.g^{-1}) and highly microporous structure (Chen et al., 2020; McGinley et al., 2022). In recent years, novel activated carbons, derived from renewable, readily available, low-cost agricultural materials, including canola stalk, orange peel, and coconut husk, have been widely researched in batch adsorption studies (Pandiarajan et al., 2018; Herath et al., 2019; Amiri et al., 2020). Kodali et al. (2021) reported that coconut-based activated carbon (CAC) was a promising adsorbent as it had an adsorption capacity of 103.9 $mg.g^{-1}$ for the organophosphorus pesticide monocrotophos mainly due to its relatively large surface area of 79.4 $m^2.g^{-1}$. However, there is a dearth of field/pilot studies using activated carbon, including CAC, as adsorbents for herbicides. Instead, research work has mainly comprised batch adsorption studies of herbicides using source water, environmentally-relevant aqueous solutions, or spiked samples, which are not representative of realistic field remediation conditions (Carra et al., 2020; Kodali et al., 2021; Singh et al., 2021; Sanz-Santos et al., 2022). Such field/pilot studies would be informative in providing information of the configuration of potential intervention devices and their implementation in waterways.

Therefore, the aims of this study were to evaluate the extent of exceedances in two agricultural catchments and one urban catchment in Ireland, and using those data to design, install and assess the efficacy of two low cost, CAC-based *in situ* remediation systems capable of herbicide removal close to the source of contamination. Based on these assessments, the questions of whether there is a difference in the configuration of the intervention in herbicide retention and whether the stream flow could impact performance can be addressed.

2. Methodology

2.1 *Study areas*

This study examined herbicide exceedances and the efficiency of remediation measures in two agricultural catchments, within the Agricultural Catchments Programme, and one urban catchment in Ireland (Fig. 1). The Corduff catchment (53° 57’ 40’’ N, 6° 45’ 22’’W) is located northwest of Carrickmacross in Co. Monaghan. The site is 578 ha in area, 89% of which is grassland (mainly beef production, with some dairying and sheep), and the remainder used for non-agricultural purposes. The topography of the Corduff catchment ranges from alluvial flatlands to shaped drumlins, with fairly steep slopes and intervening U-shaped valleys. Acid brown earths dominate the hill tops, with stagnic luvisols and gleys on the hill slopes and valley bottoms, and the underlying rock is mainly sandstone. The average daily temperature is 10.1 °C while the average precipitation is 2.6 mm per day. The Dunleer catchment (53° 50’ 6’’ N, 6° 23’ 46’’ W) is situated west of Dunleer in Co. Louth. It is 948 ha in area, with 50% in grass (mainly for dairy and beef production), 33% in tillage (mainly winter wheat, but also winter barley, spring barley and potatoes), and the remainder in woodland and non-agricultural uses. The Dunleer catchment is dominated by an undulating landscape, with many slopes. The dominant soils in this catchment are typical and stagnic luvisols, underlain with greywacke, mudstone and limestone geology. The average daily temperature is 10.6 °C while the average precipitation is 2.2 mm per day. The urban site is a drain running through a golf course located in the north west of Ireland. The golf course is a parkland course, which is 46.5 ha in area. The average daily temperature is 11.1 °C while the average precipitation is 3.4 mm per day. Due to a confidentiality agreement, further details on its location are not disclosed. The water network within each of the agricultural catchments (Corduff and Dunleer) confluences and exits the catchment through a single outlet. Each site was instrumented with a weather station, from which the total daily rainfall (mm) was obtained.

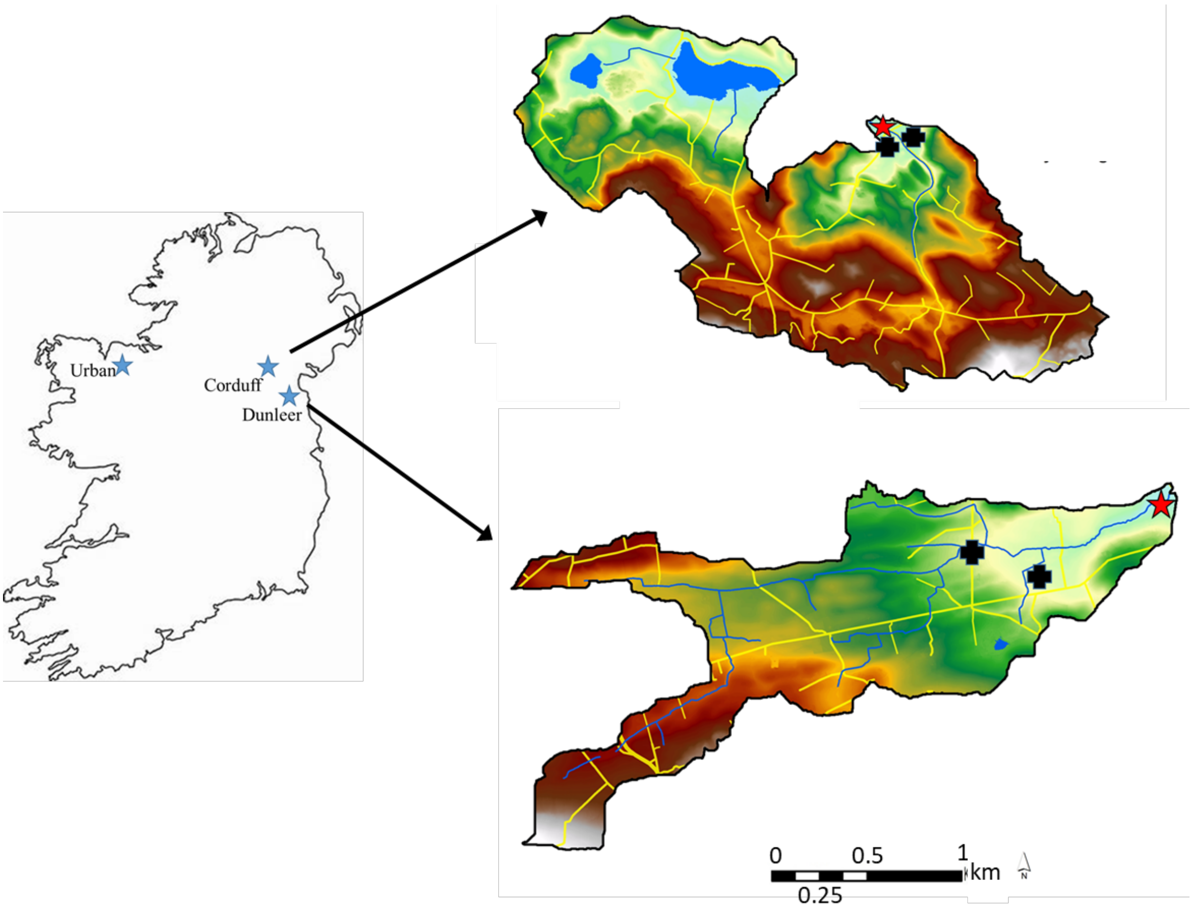


Figure 1. Map of Ireland showing location of the three sampling sites with blue stars. The outlet points at the two agricultural catchments are denoted with red stars, while the locations of the interventions in Year 2 are marked with black crosses.

2.2 *Identification of monitoring locations and interventions used*

High risk locations for pollution impact potential were identified at the agricultural catchment sites, based on an online Irish Environmental Protection Agency (EPA) Geographical Information System (GIS) application that contains information for flow delivery paths (WMS Layer: “PIP-P Flow Delivery Paths”) and entry points (WMS Layer: “PIP-P Flow Delivery Points”) for phosphorus (https://gis.epa.ie/EPAMaps). As these map layers were primarily generated based on topography and overland flow, the identified flow delivery paths and entry points were considered to be likely routes for herbicide movement from land to waterways. From these delivery paths and points, optimal locations for the placement of the interventions were selected following visual inspection and taking cognisance of physical accessibility and willingness of the farmers to grant access. Two locations were selected for Corduff and Dunleer: in both cases, these locations included a main stream and a tributary upstream (ca. 200 m and 1000 m, respectively) of the outlet. One location within the drain, ca. 10 m upstream of the outlet, was used in the Urban site.

Two configurations of interventions were investigated at each study site. Both configurations used CAC (Nova-Q, Ireland), sieved to a particle size > 2mm, as it had been shown to have a high adsorption affinity (>97 %) for acid herbicides (McGinley et al., unpublished work). One configuration used filter bags (2 mm netten 400G bags, 100 × 40 cm; Triskell Seafood, Ireland) containing 16 kg of CAC (hereafter referred to as “filter bags”). The second configuration used the same filter bags, but in this case they were filled with 12 kg of sieved CAC, and fitted into a polyethylene pipe (0.3 m wide × 0.8 m long) to fill the full diameter of the centre 0.4 m section of the pipe (hereafter referred to as “filter pipe”) (Fig. 2). At each intervention site, three staggered filter bags were placed perpendicular to the flow of the water, in order to maximise contact of the media with the water but not cause flooding (Fig. 2). Just downstream of the filter bags, the filter pipe was placed in line with the flow of the water, so an aliquot of water passed through the filter. The filter pipe was not placed in parallel with the filter bags, due to the width constraints of the streams and drains, which required sequential placement of the systems. The impact of placing the filter pipe after the filter bags was expected to be minimal as pesticide concentrations were measured before and after each system.

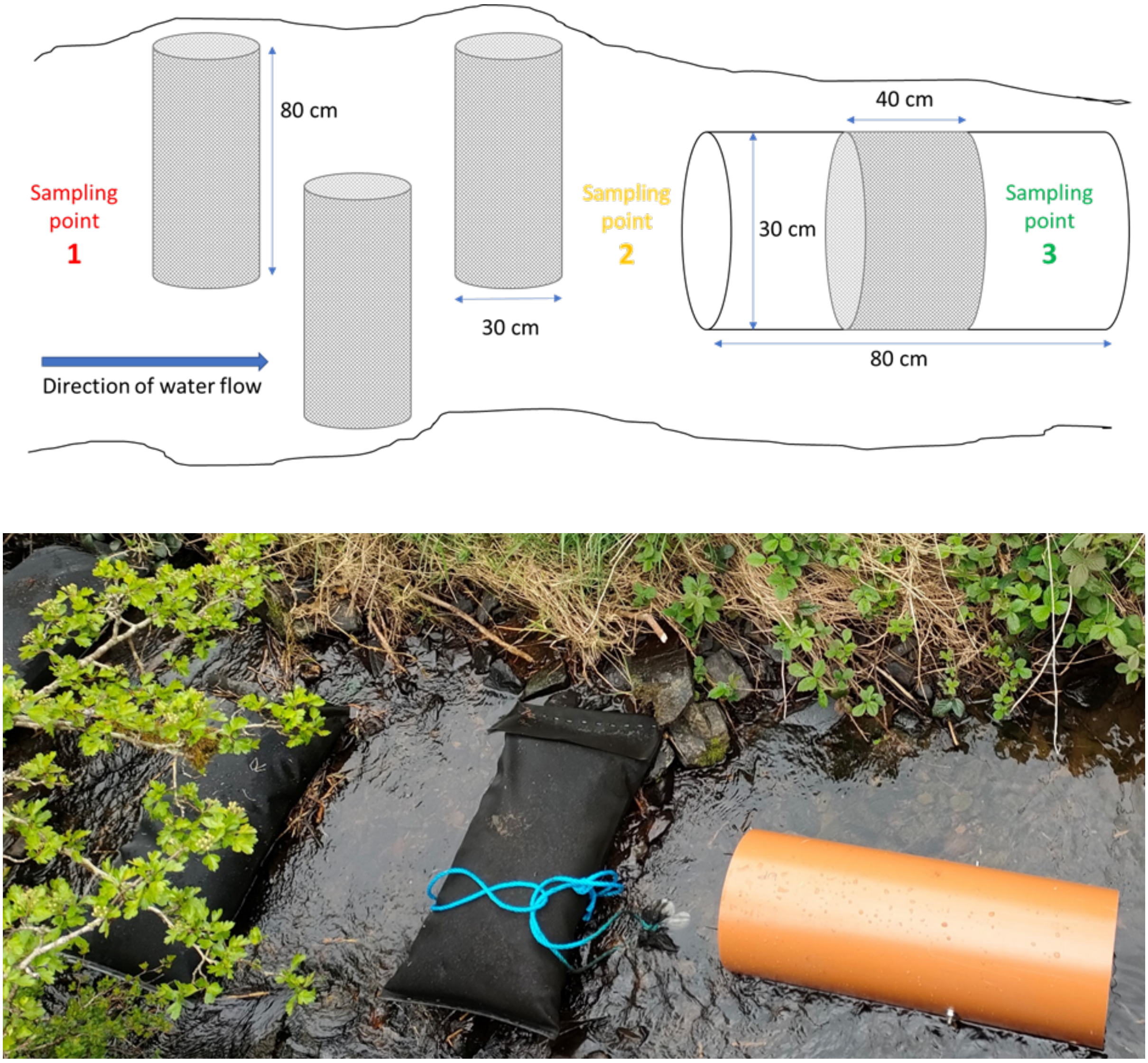


Figure 2. Schematic of different configurations of the intervention positioned in the stream. The blue arrow indicates direction of water flow. Filter bags are upstream from the filter pipe. Sampling points, colour-coded (see Section 2.4), are also indicated on the scheme. Photo shows actual configurations in one of the streams, with first bag of three in the top left hand corner of photo.

2.3 *SEM microscopy and CAC characterisation*

A Hitachi S4700 Scanning Electron Microscope (SEM, Hitachinaka, Japan) equipped with a Bruker X-Flash EDX detector was used to image gold-coated (Emitech K550) samples of the CAC and to determine its elemental composition. The analyses were performed at an acceleration voltage of 15 kV, and a working distance of 11 - 12 mm. Physical and morphological analyses of the CAC, including pore volume, pore diameter and surface area, were carried out by Glantreo Ltd (Cork, Ireland).

2.4 *Herbicide sampling and analysis*

Herbicide sampling was carried out using Chemcatcher® passive sampling devices that were placed in the water, in duplicate, for two-week periods. For both years 1 (2021) and 2 (2022), monthly herbicide sampling was conducted at the outlet of each of the three sites from April to October. In Year 2, additional monthly herbicide sampling was undertaken to assess the efficiency of the two intervention configurations at three sampling locations: (1) immediately (< 1m) upstream of the filter bag interventions (red sampling point 1 in Fig. 2), (2) between the filter bags and the filter pipe (yellow sampling point 2 in Fig. 2), and (3) within the filter pipe (green sampling point 3 in Fig. 2), downstream of the adsorbent. This allowed for determination of the herbicide removal by each of the intervention configurations independently, where the concentration difference between sampling points 1 and 2 indicated removal by the filter bags, and the difference between sampling points 2 and 3 indicated removal by the filter pipe.

Details on the preparation of the Chemcatchers® have been previously reported (Grodtke et al., 2021; Taylor et al., 2022). During each deployment, an additional Chemcatcher® was exposed to serve as a blank at each site, so that any contamination occurring during deployment of the devices could be readily identified. Once retrieved from the water, they were stored at 4 °C prior to being disassembled for removal of the filter disk. When dry, the herbicides were extracted from the disks with 25 ml of a 9:1 ethyl acetate/formic acid mixture. Chromatographic separation was carried out on a C18 LC Column using a Thermo scientific Dionex UlitMate 3000 system equipped with a binary pump, a vacuum degasser and an autosampler. The column oven was maintained at 25 °C. Samples were analysed using a Thermo scientific Exactive Plus LC-MS Orbitrap® mass spectrometer. TraceFinder 4.1 EFS LC software was used for data acquisition and analysis.

2.5 *Statistical analysis and assessment of groundwater contamination potential*

MS Excel™ 2016 was used for all statistical analysis, including calculations of the means and standard error of replicated herbicide data, and the analysis of the variance. Data were initially tested to determine the normality and homogeneity of variances. A one-tailed *t*-test was used to determine statistical significance of the reduction of herbicide concentration by the interventions. Results were considered significant at $p \leq 0.05$.

For a preliminary assessment of groundwater contamination potential, the Groundwater Ubiquity Score (GUS) was estimated using Eq. (1),

$$GUS = \log(T_{½}) \times (4 - \log(K_{OC}))$$

where $T_{½}$ is the half-life of the pesticide and K_{OC} is the organic-water carbon partition coefficient (Gustafson, 1989).

3. Results and Discussion

3.1 *Outlet monitoring*

At each study location, a suite of eighteen acid herbicides were analysed (limit of detection ($ng.l^{-1}$) is given in brackets): 2,3,6-trichlorobenzoic acid (3.571); 2,4-D (0.446); 2,4-DB (2.143); 2,4,5-T (0.5); benazolin (5.714); bentazone (5); bromoxynil (5); clopyralid (1.623);

dicamba (2.435); dichlorprop (0.478); fenoprop (0.714); fluroxypyr (0.978); MCPA (1.325); MCPB (1.728); mecoprop (0.759); pentachlorophenol (1.429); picloram (1.429) and triclopyr (0.876). The acid herbicides used and detected across the locations were 2,4-D, clopyralid, fluroxypyr, MCPA, mecoprop and triclopyr. Table 1 shows the minimum, maximum, mean and frequency of detection of the detected herbicides at the catchment outlets over the two-year study period. In total, 298 detections of individual herbicides were recorded across all three outlets, of which 131 were over the MAC of 100 ng.l^{-1} (EU, 1998). The MAC of 500 ng.l^{-1} (EU, 1998) for total cumulative herbicides was exceeded on 38 occasions (Table 1).

Table 1. Minimum, maximum and mean concentrations and frequency of detection of the studied herbicides at the outlet points in the sampling areas.

Outlet	Herbicide	Year 1					Year 2				
		Concentration (ng.l^{-1})			Frequency		Concentration (ng.l^{-1})			Frequency	
		Min	Max	Mean	Detection (%)[a]	Exceedance (%)[b]	Min	Max	Mean	Detection (%)[a]	Exceedance (%)[b]
Corduff	2,4-D	5.02	23.61	10.81	5 (36)	0 (0)	39.29	47.10	39.89	4 (29)	0 (0)
	Clopyralid	21.11	86.04	42.61	8 (57)	0 (0)	14.61	108.77	47.89	4 (29)	1 (7)
	Fluroxypyr	3.43	968.2	200.22	12 (86)	6 (43)	2.45	29.84	12.23	5 (36)	0 (0)
	MCPA	4.67	33973.96	4513.81	14 (100)	6 (43)	5.01	245.33	96.72	11 (79)	4 (29)
	Mecoprop	1.01	4.68	2.33	3 (21)	0 (0)	0	0	0	0 (0)	0 (0)
	Triclopyr	36.86	1630.66	230.51	10 (71)	4 (29)	41.71	131.94	83.84	5 (36)	2 (14)
	Total	111.69	34147.15	4878.79	14 (100)	5 (36)	2.45	357.13	135.38	14 (100)	0 (0)
Dunleer	2,4-D	4.52	2008.04	261.75	14 (100)	5 (36)	28.12	1675.22	449.80	14 (100)	10 (71)
	Clopyralid	28.41	1349.84	427.11	10 (71)	7 (50)	21.92	386.36	125.44	11 (79)	4 (29)
	Fluroxypyr	156.56	1215.75	358.19	13 (93)	13 (93)	43.05	3593.44	949.12	14 (100)	11 (79)
	MCPA	3.05	724.37	118.38	9 (64)	2 (14)	12.15	1540.55	474.21	14 (100)	10 (71)
	Mecoprop	4.55	81.61	16.38	10 (71)	0 (0)	4.84	47.25	15.84	6 (43)	0 (0)
	Triclopyr	106.47	1139.08	426.67	10 (71)	10 (71)	13.34	772.78	173.92	10 (71)	3 (21)
	Total	364.63	4356.87	1295.66	14 (100)	11 (79)	174.31	5712.19	2104.26	14 (100)	12 (86)
Urban	2,4-D	9.88	319.81	100.76	12 (86)	4 (29)	6.64	6697.88	2488.47	14 (100)	10 (71)
	Clopyralid	7.31	819.81	271.79	8 (57)	4 (29)	1070.62	1070.62	1070.62	1 (7)	1 (7)
	Fluroxypyr	5.38	113.50	44.81	9 (64)	2 (14)	6.36	384.54	103.29	8 (50)	2 (14)
	MCPA	5.47	155.99	47.64	10 (71)	2 (14)	5.07	41.13	18.84	9 (64)	0 (0)
	Triclopyr	19.14	5057.55	1358.89	8 (57)	6 (43)	9.84	2629.58	760.39	7 (50)	2 (14)
	Total	33.34	5259.4	1228.00	12 (86)	4 (29)	37.84	9317.88	3016.79	14 (100)	6 (43)

[a] Number of positive samples with percentage of positive samples from a total number of 14 sampled in parentheses.

[b] Number of exceedances (MAC = 100 ng.l^{-1} for individual herbicides and 500 ng.l^{-1} for total herbicides), with percentage of exceedances from a total of 14 sampled in parentheses.

At the three sites, the most frequent herbicide exceedances at the outlets over both years were, from highest to lowest, fluroxypyr (n = 34), 2,4-D (n = 29), triclopyr (n = 27), and MCPA (n = 24). Herbicide persistence is categorised by DT_{50} values, which is the time required for the chemical concentration under defined conditions to decline to 50% of the amount at application. The DT_{50} values of the detected herbicides ranges from 3 days (fluroxypyr) to 28.8 days (2,4-D) under field conditions (Lewis et al., 2016). All of the herbicides detected in the current study were categorised as non-persistent (defined as having a DT_{50} <30 days; Silva et al., 2019). There are two potential reasons why these herbicides were detected: (1) the detection of the herbicides in the waterways can be attributed to their desorption from soils or sediments, where they may have accumulated during previous applications (Postigo et al., 2021; McGinley et al., 2023), and (2) the detection can be indicative of recent herbicide application. DT_{50} values do not consider the organic carbon-water partitioning coefficient (K_{OC}) of herbicides, so a more accurate parameter to use when considering herbicide movement from soil to water would be the Groundwater Ubiquity Score (GUS) leaching values. The GUS score is an indicator of the potential leaching of a chemical into groundwater, based on the herbicides K_{OC} and DT_{50} (Gustafson, 1989), and is one of the most widely used indicators for herbicide leaching from soil to water. A value above 2.8 indicates that the herbicide is a potential leacher, below 1.8 indicates non-leacher, and those between 1.8 and 2.8 represents moderate mobility in soil or a transition between leacher and non-leacher (Gustafson, 1989). The GUS scores of 2,4-D, MCPA, and triclopyr are >2.8 (Table S1), indicating that they are potential leachers, while fluroxypyr was <1.8, indicating that it was a non-leacher. This implies that 2,4-D, MCPA and triclopyr are more likely to be found in waterways than in soils, while the opposite would be the case for fluroxypyr. This further suggests that, particularly in the case of fluroxypyr, the detection of the herbicide in the waterways was due to recent application. This is in agreement with the work of Prosser et al. (2020), who reported that surface run-off following rain events, which is one of the main drivers for herbicide discharge from soil to waterways, occurs mainly with soils having low porosity and low water draining capacity. Given the prevalence of slopes within the topography of both Corduff and Dunleer, surface run-off is a likely pathway for herbicide transport from the application site to these water courses. Overall, the balance between the impact of topography and GUS index must be considered, as the GUS index does not take into account electrostatic interactions, and may not fully correlate with the observed mobility of herbicides (Butkovskyi et al., 2021).

Fig. 3 shows the exceedances at the outlets, as well as the rainfall over the two-year sampling period. The majority of the exceedances occurred during April to June of each year, with several also observed in early autumn (September/October). This corresponds with the application times for herbicides, which should occur in early to mid-spring of each year, when there is rapid growth of the weeds, as well as in early autumn, at which point the weeds are transporting food from their foliage to their roots in preparation for the winter (Turf and Till, 2023). The herbicides that showed exceedances are used to control broadleaf weeds, as well as rushes and thistles. They are commonly used on grasslands and where cereal crops are grown (Lewis et al., 2016), and would be expected to be found at the both the Corduff and Dunleer sites, as well as a recreational space such as the urban golf course site. Table S2 shows the optimal spraying time and conditions for the herbicides with exceedances found at the outlets.

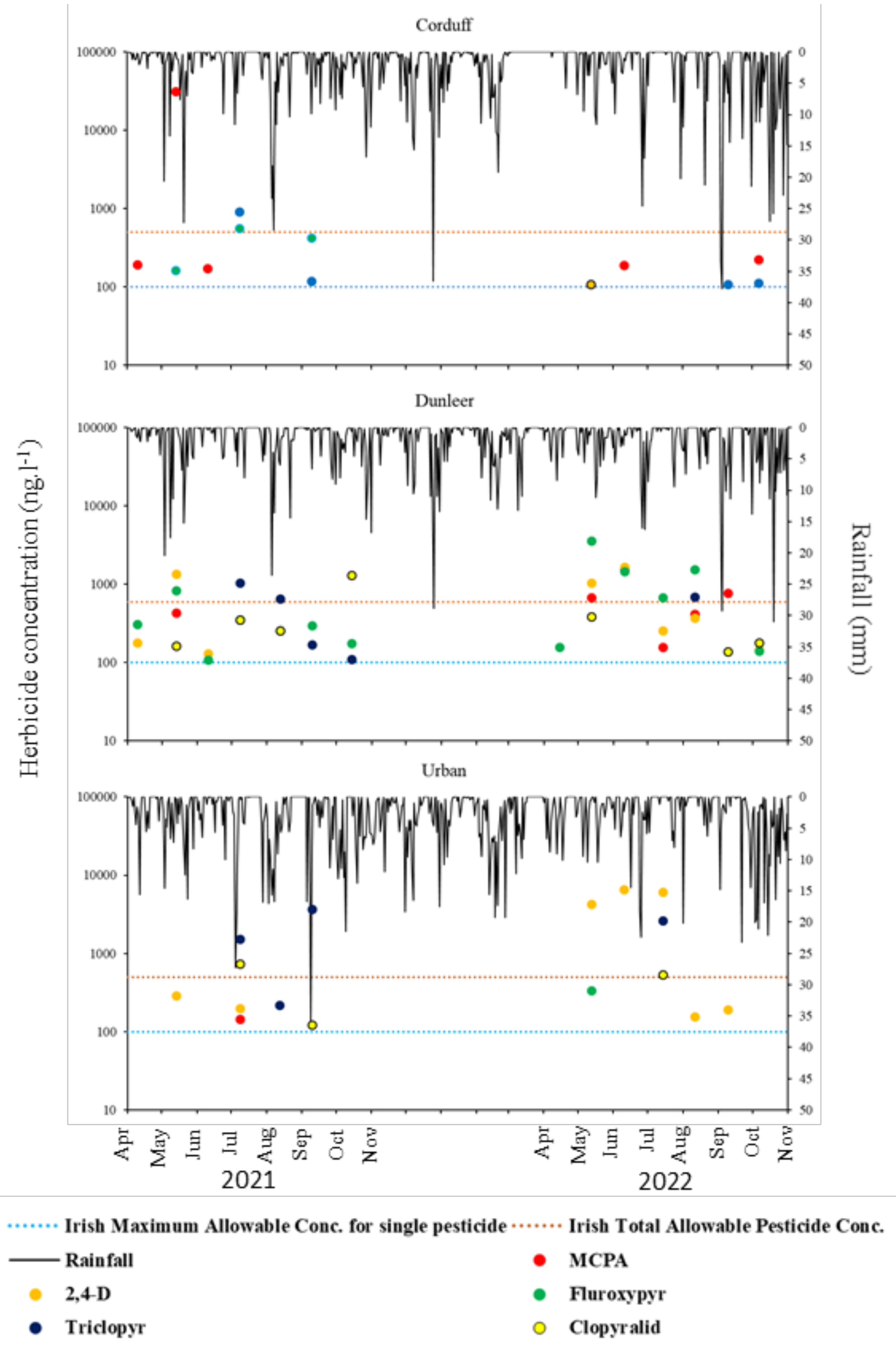


Figure 3. Exceedances of herbicides at outlet points in Corduff, Dunleer and Urban sampling areas for Year 1 (2021) and Year 2 (2022) of the study.

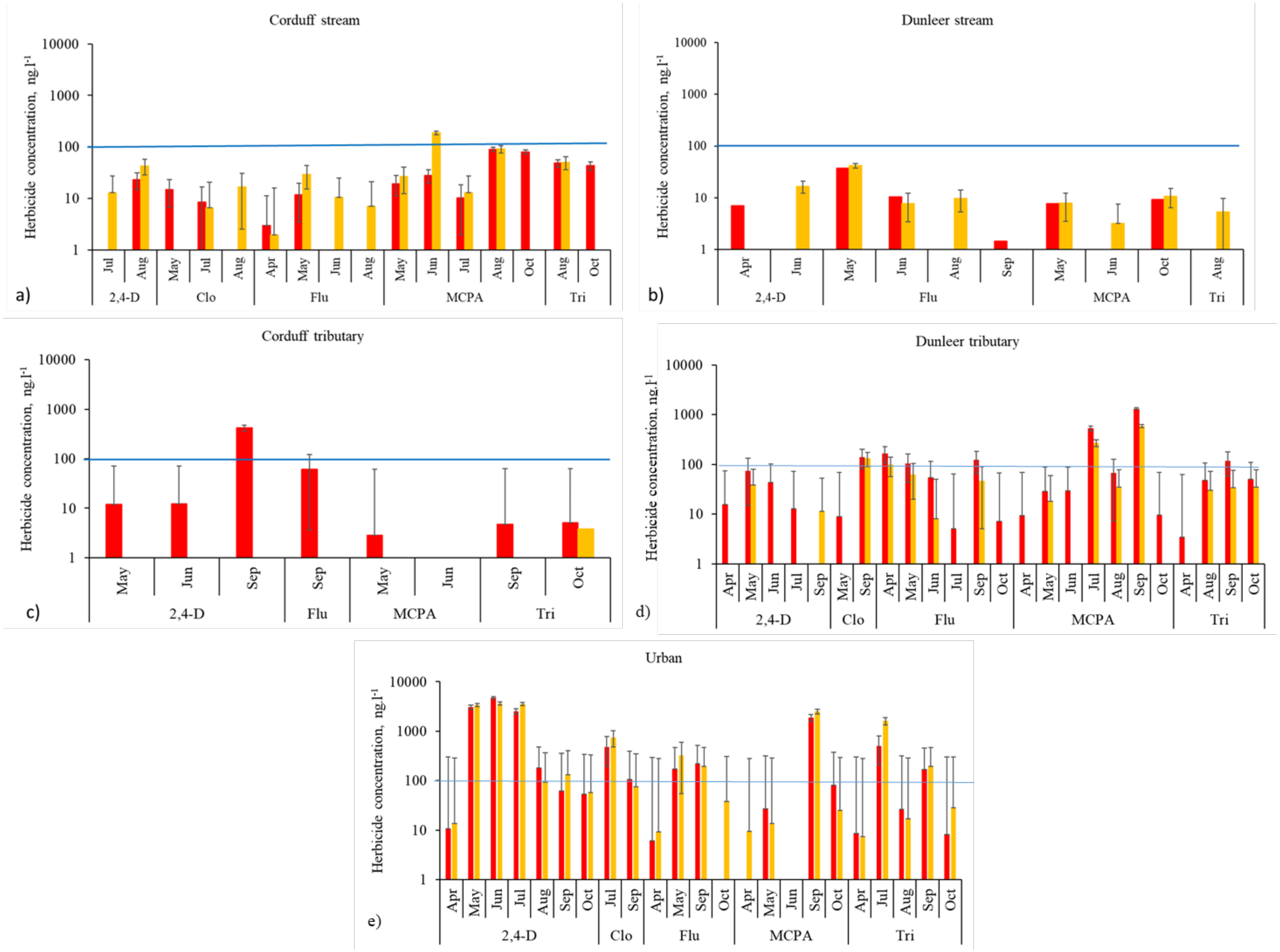
The rainfall distribution was similar between the Corduff and Dunleer catchments, but different for the Urban site (Fig. 3), which was not surprising given that the latter was located in the west of Ireland (Fig. 1). The average rainfall for the Belmullet weather station in Co. Mayo (on the west coast of Ireland) was 1258.9 mm.y^{-1}, while that for Dublin Airport (on the east coast of Ireland) was 607.6 mm.y^{-1} (Met Éireann, 2023). In all cases, where rainfall exceeded 15 mm.day^{-1}, the concentrations of herbicides detected at the outlets greatly exceeded the MAC value of 100 ng.l^{-1}. This supports evidence that heavy rainfall triggers an increase in overland flow, causing loss of applied herbicides and the subsequent contamination of surface waterways (Khan et al, 2020; Prosser et al, 2020; Liu et al., 2021).

3.2 *Media characterisation*

We have previously shown, in a laboratory setting, that GAC is capable of removal of the herbicides, 2,4-D, fluroxypyr, MCPA, mecoprop-P and triclopyr, from aqueous solutions with >95% removal reported (McGinley et al., 2022). We have also found that CAC is as efficient at removal of the same suite of herbicides as GAC, with >97% removal observed (McGinley et al., unpublished work). The surface of the GAC was not smooth but, instead, had small clusters distributed over smooth platelets (Fig. S1a and b). The surface of CAC, on the other hand, was smooth, with visible indentations in the surface (Fig. S1c and d). Adsorbent materials can be categorised according to pore size distribution, as macroporous (>50 nm), mesoporous (2-50 nm) or microporous (<2 nm) (Feng et al, 2022; Gao et al., 2023). Mesoporous materials have large specific surface areas (>500 m^2.g^{-1}; Xu et al., 2020; Plohl et al., 2021; Kouchakinejad et al., 2022), which facilitate the adsorption of guest molecules. GAC is at the lower end of the mesoporous range, with a pore diameter of ca. 6 nm, resulting in a high surface area (579 m^2.g^{-1}) and a high pore volume (ca. 0.496 cm^3.g^{-1}), which is optimal for adsorption (McGinley et al., 2022). On the other hand, CAC has a lower surface area (10.52 $m^2.g^{-1}$) and pore volume (0.028 $cm^3.g^{-1}$) than GAC, which would suggest reduced adsorption capacity. However, CAC has a larger pore diameter than GAC (ca. 14.5 nm), which would better facilitate herbicide adsorption. Full media characterisation for CAC is given in Table S3 while the full characterisation of GAC has been previously reported (McGinley et al., 2022). EDX imaging of GAC and CAC are shown in Fig. S1e and f. While both materials primarily contained carbon and oxygen, GAC also contained the elements aluminium silicon, sodium and titanium, while CAC also contained calcium. As CAC and GAC had comparable abilities to adsorb herbicides, but as CAC was more cost-effective than GAC, it was selected as the adsorbent for the interventions in Year 2.

3.3 *Herbicide removal by filter bag configuration*

Fig. 4 shows the herbicide detections before and after the filter bags at each site, thereby indicating the ability of the filter bags to remove the herbicides investigated, while Table S4 (a-c) shows the minimum, maximum, mean and frequency of detection of the herbicides detected before and after the filter bags in the three sampling areas. In Corduff stream, there were 31 detections of herbicides and one exceedance before the filter bags, compared to 29 detections of herbicides and three exceedances after the filter bags (Fig. 4a; Table S4a), while in Dunleer stream, there were 17 detections of herbicides and no exceedances before the filter bags, compared to 22 detections of herbicides and no exceedances after the filter bags (Fig. 4b; Table S4b). In the majority of samples from the Corduff and Dunleer streams, the concentrations of the herbicides before the filter bags was less than the MAC of 100 $ng.l^{-1}$. Overall, in the two streams, there was a slight, but not statistically significant ($p > 0.05$), decrease in the average concentrations detected after the filter bags, with a reduction of 24% and 17% in Corduff and Dunleer streams across all measured herbicides (Fig. 4a and b; Table S4a and b). Incomplete removal of the herbicides is probably due to the wide body of water (< 1m in width) in both streams, which meant that a single filter bag could not span the stream. Although the three filter bags were put in a staggered position, there was still room for the water to flow around the filter bags, rather than passing through the adsorbent material. This ability to circumvent the filter bags could account for the incomplete removal of herbicides by this configuration. It is possible that what is causing the increases in herbicide detections is sediment particulate matter that has pesticides adsorbed to it, circumventing the first Chemcatcher® and intervention, but being picked up by the post-intervention Chemcatcher®. So, it is not dissolved pesticides, but an outlier of some kind.


Corduff stream
Herbicide concentration, ng.l-1
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Dunleer stream
Herbicide concentration, ng.l-1
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Corduff tributary
Herbicide concentration, ng.l-1
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MCPA
Tri
d)
Urban
Herbicide concentration, ng.l-1
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Figure 4. Herbicide detections for the filter bag interventions across all sampling areas. Clo = clopyralid, Flu = fluroxypyr and Tri = triclopyr. Red columns indicate herbicide concentrations before the filter bag interventions, and yellow columns indicate herbicide concentrations after the filter bag interventions. Average values of the two Chemcatchers® have been displayed for each monthly detection. Error bars show standard error where n = 2. The blue line is the maximum allowable concentration for individual herbicides (100 ng.l^{-1}).

In the Corduff tributary, there were 12 detections of herbicides and three exceedances before the filter bags, compared to one detection of herbicides and no exceedances after the filter bags (Fig. 4c; Table S4a). The filter bags were very effective in the Corduff tributary (average 89% reduction, $p > 0.05$), with only one detection of triclopyr after the filter bags, which was below the MAC of 100 $ng.l^{-1}$ (Fig. 4c; Table S4a). There was a complete removal of 2,4-D from an average initial concentration of 422.6 $ng.l^{-1}$ (Fig. 4c; Table S4a), indicating that the CAC adsorbent was capable of dealing with incoming herbicide concentrations up to 500 $ng.l^{-1}$. Zafra-Lemos et al. (2021) reported that coconut-based activated carbon completely removed the herbicide 2,4-D, at a concentration of 10 $mg.l^{-1}$, from water, but no pilot-scale experiments were undertaken. Two possible reasons for this complete removal were (1) the low level of water that was present in the tributary, with the level of water never rising above 0.15 m over the base of the stream from April to October, and (2) the tributary was also only 0.40 m wide at its widest point, so that the bag interventions completely filled the path of the stream, thereby forcing the polluted water through the CAC-filled bags and allowing time for the adsorption of the herbicides to occur. The height of the filter bags was approximately 0.15 m, which meant that the water could not flow over the bags. Furthermore, the flow of water in the tributary was quite slow, so that the water had time to flow through the bag and allow adsorption to take place.

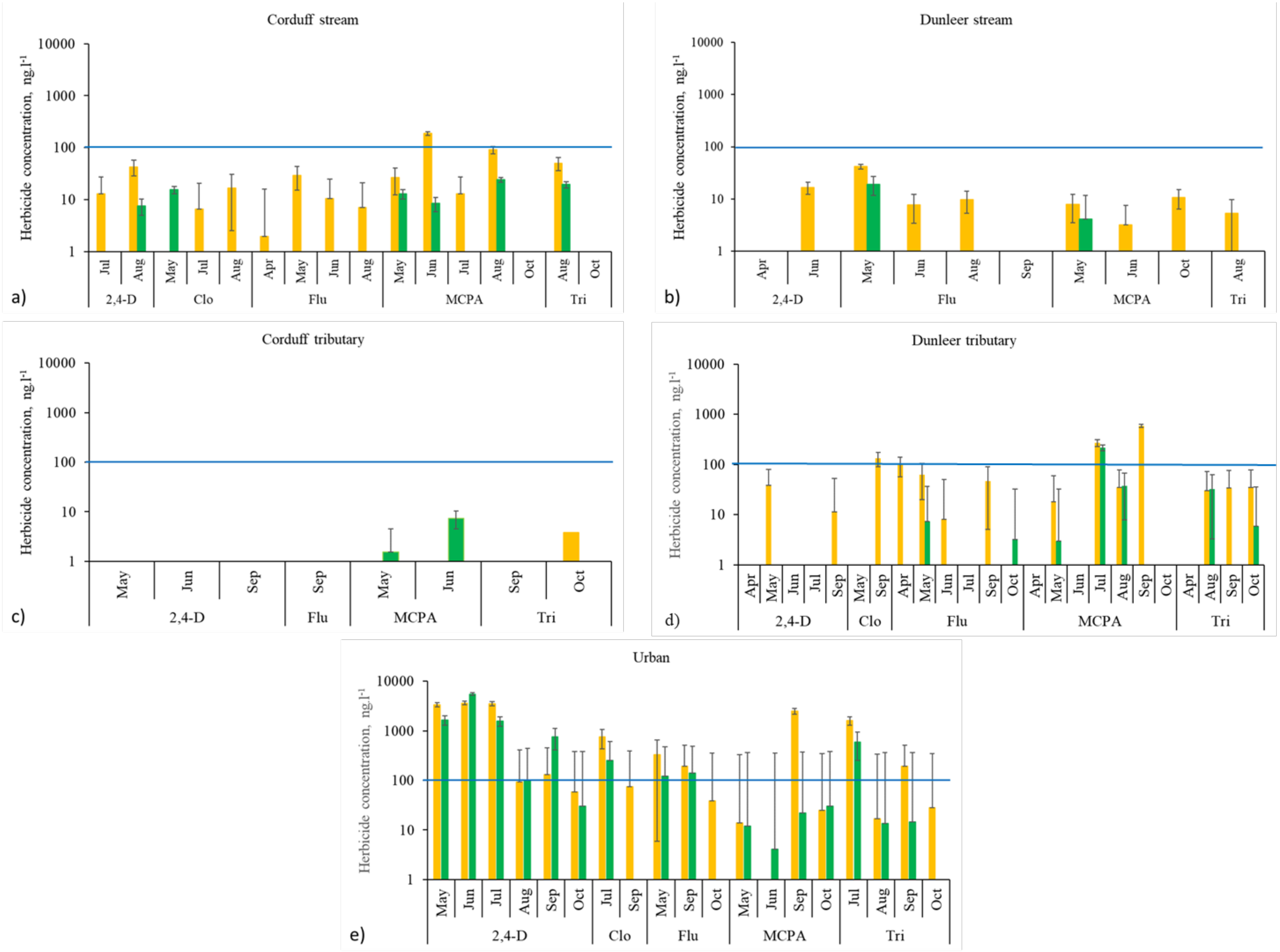
In the Dunleer tributary (Fig. 4d; Table S4b), the number of detections before the filter bags was 56, of which seventeen were exceedances, while after the bags, there were 39 detections and eight exceedances. At the Dunleer tributary, the filter bags were effective for herbicide removal on the majority of occasions (an average reduction across all herbicides of 67.1%; Fig. 4d), with either minimal or no detections of the herbicides observed after the bags ($p > 0.05$). However, for MCPA in July and September, the incoming concentrations of 536.8 and 1334 ng.l^{-1}, respectively, were reduced to 270.1 and 593.7 ng.l^{-1}, which were considerably above the MAC. This would suggest that the CAC adsorbent does not have the capacity to deal with very high concentrations of herbicides in the waterways. The tributary was also slow moving and the filter bags were able to almost completely span the width of the waterway, with only a few centimetres on either side available for the water to circumvent the filter bags.

The number of herbicides detected in the Urban area before the filter bags was 53, of which 29 were exceedances, while after the bags, there were 56 detections and 27 exceedances (Fig. 4e; Table S4c). Across all herbicides measured in the Urban area, there was no significant difference ($p > 0.05$) between detections before and after the filter bags (Fig. 4e; Table S4c). The water was slow moving, which helped the removal of the herbicide by the treatment system. However, the drain was over 1 m in depth, and the water level was consistently >0.5 m, even during the summer months. This reduced the amount of water that was passing through the filter bags and making contact with the CAC material. Overall, the filter bags reduced the exceedances from n=50 to n=38 (Tables S4(a-c)).

Based on these observations, the filter bags adsorbed the herbicides most efficiently when the water flow was slow, the filter bags spanned the entire width of the waterway and the water level present in the waterway was lower than the height of the filter bags. In the cases where the water covered the filter bags, or where the water can easily bypass above or around the bags, then the filter bags did not reduce the herbicides concentrations as effectively. Fig. 4 also shows that, where the concentrations of herbicides before the bags are <500 ng.l^{-1}, then the media are better able to remove those herbicides completely in the majority of cases. However, where the concentrations exceed 500 ng.l^{-1}, particularly in the case of the Urban area, then complete adsorption is more difficult to achieve.

3.4 *Herbicide removal by filter pipe configuration*

Fig. 5 shows the herbicide detections before and after the filter pipes at each site, indicating the ability of the filter pipe to remove the herbicides under investigation, while Table S4 (a-c) shows the minimum, maximum, mean and frequency of detection of the detected herbicides before and after the filter pipes in the three sampling areas. The filter pipes typically had a lower influent concentration as the water had already passed through the filter bags. In the Corduff stream (Fig. 5a; Table S4a), there were 29 detections of herbicides before the filter pipes, of which 3 were exceedances, which were reduced to 14 detections and no exceedances after the filter pipes, while in Dunleer stream (Fig. 5b; Table S4b) there were 22 detections and no exceedances before the filter pipes, which were reduced to 5 detections and no exceedances after the filter pipes. Except for the case of the detection of MCPA at the Corduff stream, the concentrations of the herbicides before the filter pipes in both Corduff and Dunleer streams were below the MAC of 100 ng.l^{-1}. Overall, in the two streams, there was a large, statistically significant ($p < 0.05$), decrease in the concentrations of herbicides, with an average reduction of 83% and 88%, respectively, across the herbicides measured (Fig. 5a and b). These reductions included a 95% reduction for MCPA from 186.9 ng.l^{-1} to 8.4 ng.l^{-1} in the Corduff stream (Fig. 5a).


Corduff stream
Herbicide concentration, ng.l-1
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Dunleer stream
Herbicide concentration, ng.l-1
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Corduff tributary
Herbicide concentration, ng.l-1
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Dunleer tributary
Herbicide concentration, ng.l-1
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Clo
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MCPA
Tri
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Urban
Herbicide concentration, ng.l-1
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Clo
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Figure 5. Herbicide detections for the filter pipe interventions across all sampling areas. Clo = clopyralid, Flu = fluroxypyr and Tri = triclopyr. Yellow columns indicate herbicide concentrations before the filter pipe interventions, and green columns indicate herbicide concentrations after the filter pipe interventions. Average values of the two Chemcatchers® have been displayed for each monthly detection. Error bars show standard error where $n = 2$. The blue line is the maximum allowable concentration for individual herbicides (100 $ng.l^{-1}$).

In the Corduff tributary, only one detection was measured before the pipe, while two were measured after the pipe (Fig. 5c). None of these detections were above the MAC. In the Dunleer tributary, there were 39 detections of herbicides before the pipe, of which eight were exceedances, while there were only 14 detections and two exceedances after the filter pipe (Fig. 5d; Table S4b). The filter pipes greatly reduced the herbicide concentrations ($p < 0.05$), with an average reduction of 64% (Fig. 5d). In almost all the cases, the starting herbicide concentration was lower than the MAC, except for MCPA in July and September, and clopyralid in September. There was a measured reduction of MCPA in July from 270.1 ng.l^{-1} to 216.7 ng.l^{-1} (which was above the MAC; Fig. 5d). However, in September, the pipe was moved from its original position by the force of water coming down the tributary as a result of heavy prolonged rainfall earlier that month, so no readings were obtained after the pipe for that month. This month of data was, as a result, discounted from the overall reduction calculations. In the case of the Dunleer tributary, the herbicide concentrations before the filter pipe were reduced ($p <0.05$) from 8.1 – 593.7 ng.l^{-1} to between below the LOD and 216.7 ng.l^{-1}.

At the Urban site, the number of herbicides detected decreased from 56 to 42, while the number of exceedances decreased from 27 to 22 after the filter pipes (Fig. 5e; Table S4c). There was a decrease in concentration detection ($p > 0.05$), after the filter pipe, with an average reduction of 47% (no herbicides were detected after the filter pipe on several occasions; Fig. 5e). The herbicide concentrations varied from 7.5 – 3645 ng.l^{-1} before the filter pipe to between below the LOD and 5503 ng.l^{-1} after the pipe. When the concentrations of the herbicides were greater than 3000 ng.l^{-1}, the filter pipe was unable to reduce the concentration to below the MAC (Fig. 5e).

Overall, the filter pipes reduced the exceedances from n=38 to n=24 (Table S4 (a-c)). The pipe containing the intervention was 0.3 m in diameter and so could easily fit into all the waterways. The filter pipes adsorbed the herbicides most efficiently when the water flow was slow. From Fig. 5, it is clear that, when the concentration of herbicides is < 2500 ng.l^{-1}, the pipe intervention is quite capable of reducing the concentration to below the MAC.

3.5 *Comparison of the filter bag and filter pipe configurations*

There are both similarities and differences between the filter bags and the filter pipes. In terms of similarities, both configurations adsorbed herbicides most effectively when both the water flow and the incoming herbicide concentration were low (< 500 ng.l^{-1}). Since both configurations used the same adsorption-based process, this is not surprising. The major difference between both types of intervention was that the filter pipe was better at removing herbicides than the filter bags. There was a 13% reduction in the number of detections and a 24% reduction in exceedances across all sampling sites when considering the filter bag interventions. This was compared to a 48% reduction in detections and a 37% reduction in exceedances across all the sampling sites for the filter pipe interventions. The number of reductions was statistically significant ($p < 0.05$) for the filter pipes.

Varying the shape and size of the filter pipe may be an option to improve the configuration of the interventions: they could be smaller and have a rectangle-shape rather than a circular shape, so that multiple pipes could be used across the streams.

Alternatively, a larger bag within the pipe may increase the volume of the adsorbent and therefore the operational life-span of the system. A second option could be to physically adapt the stream environment to suit the filter pipe, by creating a narrow section of the stream in order to funnel the water through the intervention.

4. Conclusions

This study showed that herbicides are present in high concentrations (frequently above the MAC) in two agricultural catchments and one urban area in Ireland, and that the majority of the exceedances occurred in April to June and September/October, corresponding to the application times for these herbicides.

Two different CAC-based *in situ* remediation systems, filter bags and filter pipes, capable of herbicide removal close to the source of contamination, were designed and installed at the agricultural catchment areas and the urban area. Both systems operated effectively when the water flow in the waterways was slow, which allowed time for the adsorption of the herbicides to occur. The reduction in herbicide concentrations was better for the filter pipes than for the filter bags ($p < 0.05$).

While further work on the design of the interventions is envisaged, including increasing the size of the filter bags and modifying the shape of the pipe, this investigation into the use of a CAC-based adsorption system for the removal of herbicides at source, rather than treatment at a drinking water treatment facility, has shown good potential. This further suggests that, by choosing strategic points in streams and slow moving rivers for the placement of interventions, the levels of herbicide contamination of water can be significantly reduced, prior to reaching drinking water treatment facilities.

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