Science of the Total Environment 838 (2022) 156080

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Reducing MCPA herbicide pollution at catchment scale using an agri-environmental scheme

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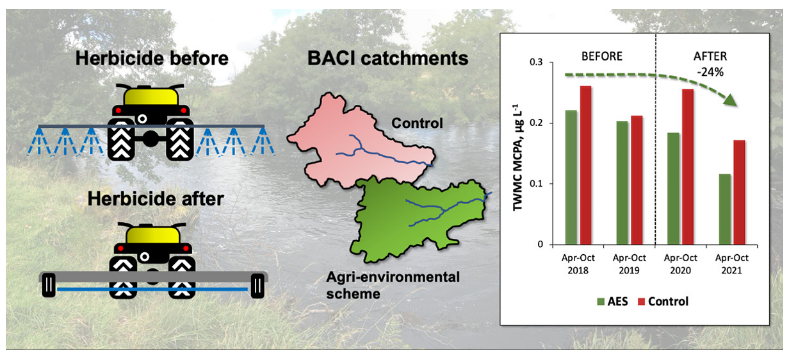
HIGHLIGHTS

- MCPA is highly mobile in the soil-water environment following application.
- A catchment agri-environmental scheme aimed to reduce MCPA in source water.
- A full BACI framework with enhanced monitoring was employed over 4 years.
- MCPA concentrations and loads of up to 5.8 μg L^{-1} and 106 kg yr^{-1} were measured.
- The scheme catchment indicated reduced MCPA concentrations up to 24%.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Damià Barceló

Keywords:
MCPA
Drinking water
Before-after-control-impact
Herbicides
Agri-environmental scheme
Water quality monitoring

ABSTRACT

In river catchments used as drinking water sources, high pesticide concentrations in abstracted waters require an expensive treatment step prior to supply. The acid herbicide 2-methyl-4-chlorophenoxyacetic acid (MCPA) is particularly problematic as it is highly mobile in the soil-water environment following application. Here, an agri-environmental scheme (AES) was introduced to a large-scale catchment (384 km^2) to potentially reduce the burden of pesticides in the water treatment process. The main measure offered was contractor application of glyphosate by weed wiping as a substitute for boom spraying of MCPA, supported by educational and advisory activities. A combined innovation applied in the assessment was, i) a full before-after-control-impact (BACI) framework over four peak application seasons (April to October 2018 to 2021) where a neighbouring catchment (386 km^2) did not have an AES and, ii) an enhanced monitoring approach where river discharge and MCPA concentrations were measured synchronously in each catchment. During peak application periods the sample resolution was every 7 h, and daily during quiescent winter periods. This sampling approach enabled flow- and time-weighted concentrations to be established, and a detailed record of export loads. These loads were up to 0.242 kg km^{-2} yr^{-1}, and over an order of magnitude higher than previously reported in the literature. Despite this, and accounting for inter-annual and seasonal variations in river discharges, the AES catchment indicated a reduction in both flow- and time-weighted MCPA concentration of up to 21% and 24%, respectively, compared to the control catchment. No pollution swapping was detected. Nevertheless, the percentage of MCPA occurrences above a 0.1 μg L^{-1} threshold did not reduce and so the need for treatment was not fully resolved. Although the work highlights the advantages of catchment management approaches for pollution reduction in source water catchments, it also indicates that maximising participation will be essential for future AES.

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http://dx.doi.org/10.1016/j.scitotenv.2022.156080
Received 28 March 2022; Received in revised form 16 May 2022; Accepted 16 May 2022
Available online 20 May 2022

1. Introduction

With agriculture the primary land use in most western European countries it is inevitable that polluting materials of agricultural origin will be found in freshwater systems (Evans et al., 2019; Mateo-Sagasta et al., 2017). Depending on the levels that occur these may impact water quality and pose a threat to both aquatic ecosystems and downstream human users. Once a contaminant has entered a waterbody, removal is difficult (Rathi et al., 2021). Where water is abstracted for human consumption the presence of contaminants, particularly complex compounds such as pesticides, necessitates complex and expensive treatment processes to ensure supplies meet regulatory standards (Teodosiu et al., 2018). This is particularly the case for surface water abstractions from rivers or lakes, which lack the natural filtration afforded by aquifers to groundwater sources.

For pesticides, limits are set on acceptable concentrations in drinking water (Dolan et al., 2013). For example, the Drinking Water Directive (DWD) in the European Union (EU) (OJEU, 2015), and transposed into UK law following Brexit, sets a precautionary principle limit for single pesticide compounds in treated water of 0.1 $\mu g\ L^{-1}$, and 0.5 $\mu g\ L^{-1}$ as a combined total for all pesticides. The herbicide 2-methyl-4-chlorophenoxyacetic acid (MCPA) is a particular issue in water supplies world-wide due to its mobility in the soil-water continuum (Caux et al., 1995; Morton et al., 2020).

MCPA has long been promoted as an effective solution to rush (*Juncus* spp.) inundation in agricultural grasslands. In Irish jurisdictions, for example, MCPA is the most used pesticide by weight, with 45 t yr^{-1} used in Northern Ireland and 95 t yr^{-1} in the Republic of Ireland according to the most recent census reports (Lavery et al., 2017; Pesticide Control Division DAFM, 2017). In terms of potential for loss from land to water, MCPA is highly soluble and does not bind well to soils compared to other herbicides, with a low K_{oc} range (soil-organic-carbon-to-water partitioning coefficient) of 54–118 L kg^{-1} (Mackay et al., 2006). This mobility potential is problematic, as rushes tend to proliferate in low pH, poorly drained soils that are generally hydrologically well-connected to waterbodies (e.g. Holden et al. (2006)).

Treatment of source water to remove pesticide residues involves, amongst other methods (El-Nahhal and El-Nahhal, 2021), the use of granular activated carbon (GAC) filter technology which can be expensive to install and maintain to ensure that regulatory standards are met (Larasati et al., 2022). Alternatives to drinking water treatment technologies include integrated catchment management strategies to improve water quality prior to treatment and involve improving pesticide management over wide areas, including agri-environmental schemes (AES). However, evaluating the impact such approaches have on water quality can be challenging (Mohamad Ibrahim et al., 2019).

Operating a full before-after-control-impact (BACI) assessment for such strategies is rarely undertaken at large catchment scale owing to the timescale required to interpret results (Melland et al., 2018). Finding similar paired catchments may also be difficult at larger scales, and the cost of analysis for pesticides that have an acute, storm transfer dependency can be prohibitive. However, paired catchments including a control help to ensure that trends or stepped changes in water attributes are not primarily associated with variations in inter-annual climate/weather factors over the period of the AES assessment (Brown et al., 2005).

In the current investigation an AES was established in the Irish cross-border River Derg catchment used for drinking water abstraction. Frequent detections of MCPA in untreated water had been made in this catchment and in similar grassland catchments throughout the island of Ireland (Khan et al., 2020; Morton et al., 2020). The 100% funded AES was designed to reduce MCPA in river water, in addition to providing mitigation for other water quality pressures. These MCPA measures included contractor-delivered weed wiping with glyphosate as a substitute to boom spraying MCPA, provision of pesticide storage and disposal facilities, and a programme of education and outreach to the local community. To assess the impact of the AES a water quality monitoring programme was designed. Following a scoping exercise a BACI approach was adopted where the AES was implemented in the River Derg and a comparison catchment, the River Finn (386 km^2), acted as a business-as-usual control for periods prior to and after the implementation of AES measures (e.g. Van Loon et al. (2019)).

The overarching aim of the work was to improve water quality through pesticide reduction in a drinking water source catchment. The objectives were to:

1. Review the impact of a voluntary AES on MCPA losses in the Derg cross-border river catchment through a BACI water quality monitoring programme
2. Examine the implications of any changes associated with the AES for water treatment in the catchment
3. Examine the potential for pollutant swapping where the alternative management strategies offered to farmers included weed wiping with glyphosate as an alternative

2. Methods

2.1. River Derg AES catchment

The catchment is predominantly rural, flowing eastward from the headwaters in the Bluestack and Pettigo Mountains before crossing the border between the Republic of Ireland and Northern Ireland (Fig. 1), then joining the River Mourne within the wider Foyle river basin. Monitoring was undertaken at a drinking water abstraction point (managed by Northern Ireland Water) close to Castlederg (54.722 N, 7.497 W) with a catchment area of 384 km^2 at this point. Most of the western catchment is superficially covered by peat or blanket bog, sand, silt and alluvium outline the river channels, and brown earths (Cambisol) and brown podzolic (Umbrisol) soils dominate the wide valley floors in the east of the catchment. The catchment is underlain by Dalradian metasediments and later Silurian-Devonian granites. The CORINE dataset (European Environment Agency (EAA), 2018) records that agricultural land (mainly grassland) occupies 35.4% of the land area, woods and forest 17.6% and marginal land and peat bogs 44%. On average, over the period October 2017 to 2021, average river flows were 1499 mm per annum at Castlederg hydrometric station (DFI, 2022). Long-term data shows the river has a Q5:Q95 ratio of 50.7, based on the 1976–2016 period (NRFA, 2017).

2.2. River Finn control catchment

The River Finn is an adjacent and similarly rural catchment, also within the Foyle river basin (Fig. 1). It was chosen following an assessment of several catchments in the region of similar size magnitude, and where there was a long term hydrometric station. Long term flow duration curve (FDC) records were compared for similarity, with the River Finn best matching the River Derg (Supplementary Material Fig. S1) indicating similar rainfall-runoff patterns over the discharge range, and over similar land uses.

The headwaters are located in the Bluestack and Derryveagh mountains and the river flows eastward until it meets the River Mourne. The studied area of the catchment lies in County Donegal with the monitoring station located at Killygordon (54.795° N, 7.686° W). The study catchment has an area of 386 km^2 at this point. Most of the western catchment is superficially covered by peat or blanket bog, alluvium outlines the river channels, and brown earths (Cambisol), brown podzolic (Umbrisol) and gleyed (Gleysol) soils dominate the wide valley floors in the east of the catchment. The catchment is underlain by Dalradian metasediments, predominantly psammitic and pelitic schists, quartzite and Silurian-Devonian granites. The land cover (European Environment Agency (EAA), 2018) is 26% agricultural land (mainly grassland), 62% marginal land and peat bog and 11.2% woods and forestry. On average, over the period October 2017 to 2021, river flows were 1865 mm per annum. The River Finn has a Q5:Q95 ratio of 42.92 over 1972–2016 (OPW, 2017). Beyond monitoring no MCPA mitigation activities or farmer engagements were undertaken in the River Finn catchment over the course of the project. Characteristics of each catchment are summarised in Table 1.

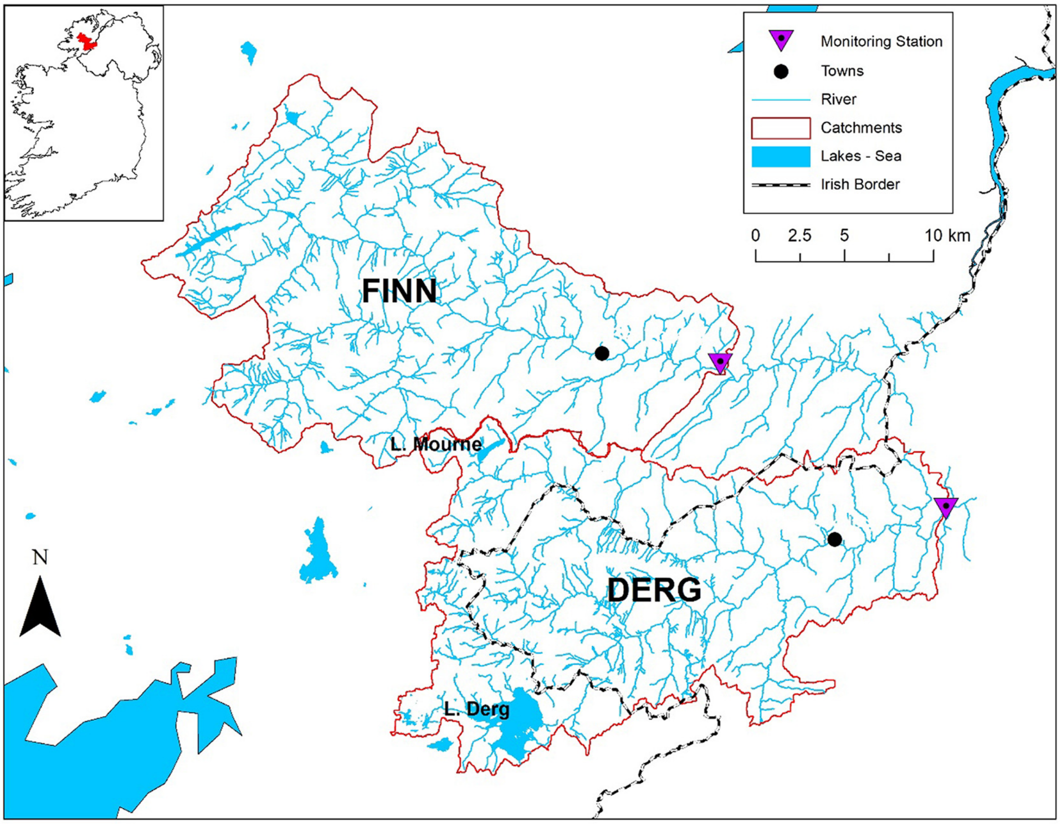

Fig. 1. Overview map of the study area and Finn and Derg catchments.

Table 1
Characteristics of the Derg and Finn catchments.

Catchment characteristics	Derg	Finn
Monitoring station locations	54.722303, −7.4967152	54.794676, −7.6861891
Downstream distance from hydrometric station	8.9 km	9.1 km
Catchment Area	384 km^2	386 km^2
Land use (source: CORINE 2018)		
Woods/forestry	17.6%	11.2%
Agricultural land	35.4%	25.8%
Marginal land/peat bogs	44.0%	61.6%
Q_{50} (median)	7.852 $m^3 s^{-1}$	8.254 $m^3 s^{-1}$
Q_5:Q_{95}	50. 7	42.92
Q_5	50.006 $m^3 s^{-1}$	50.259 $m^3 s^{-1}$
Q_{10}	36.132 $m^3 s^{-1}$	38.316 $m^3 s^{-1}$
Q_{95}	0.987 $m^3 s^{-1}$	1.171 $m^3 s^{-1}$

Sources: Finn (period 1972–2016) https://waterlevel.ie/hydro-data/stations/01043/station.html?1637625315; Derg (period 1976–2016) https://nrfa.ceh.ac.uk/data/station/meanflow/201008

2.3. Agri-environmental scheme

The River Derg AES was implemented in the catchment by a team of project officers employed by the Rivers Trust and Irish Water. The project officers visited each of approximately 350 farms in the catchment, all of whom were entitled to participate under the terms of the scheme, and offered a range of measures to address water quality issues linked to colour, turbidity and MCPA. Where farmers expressed an interest in the scheme the project officers visited and, following a survey of the farm, provided guidance on appropriate measures based on the issues identified. A list of measures with potential to reduce MCPA use for treatment of rushes and reduce accidental losses is provided in Table 2, all provided at 100% of cost.

Table 2
Incentivised measures relating to MCPA loss mitigation offered to farmers within the AES.

Measure	Potential impact on MCPA use
Weed wiping	Provides an alternative to boom spraying of MCPA, by substituting glyphosate applied by wiping to the growing plant. Delivered by a contractor.
Rush topping	Used in tandem with weed wiping, removing old rush and encouraging regrowth more susceptible to subsequent treatment by weed wiper.
Pesticide handling and storage	Biobeds/biofilters, loading and wash down areas, and safe storage units protect against accidental spills or leaks.

Estimates of treated areas by weed wiping were made based on hourly costs per unit area data submitted by AES contractors. These were, on average, €50 h^{-1} for 0.81 ha^{-1} treated (NI Water, 2022). All claimed costs were therefore converted using this relationship to a km^2 spray area estimate (Supplementary Material Fig. S2) which provides an initial indication of the level of uptake and timing. Although some weed wiping did take place during 2019 as part of trials and demonstrations, the main AES measures were implemented from 1st April 2020 onward. In total 75 farm businesses participated in weed wiping or preparatory activities towards weed wiping (mechanical topping of rushes), and on weed wiping alone a total of €60,226.62 was spent over an area of approximately 9.75 km^2; 6.32 km^2 in April 2020–21 and 3.43 km^2 from April 2021 on. It is expected that following treatment rushes will take ~3 years to re-establish before requiring further interventions.

2.4. Herbicide water quality monitoring

Water quality monitoring began in April 2018 and provided a two year baseline prior to the implementation of AES measures on the ground from April 2020.

Water samples from both rivers were collected using programmed ISCO 6712FR refrigerated automatic water samplers (Teledyne ISCO, Lincoln, USA) installed in mains powered kiosks at the catchment outlets (Morton et al., 2021).

Monitoring for MCPA followed a combination of 7 hourly sampling (the 24-7 "Plynlimon" approach—Halliday et al. (2012)) during the peak periods for MCPA applications (April–November) and at least daily through winter. The use of this approach through the peak MCPA period was judged appropriate to capture the dynamic changes in concentrations expected to be caused by short duration, high magnitude storm events in the catchments for contaminants in primarily surface pathways. This was based on an evaluation undertaken for phosphorus in Irish rivers by Jordan and Cassidy (2011) and the supposition that MCPA concentrations exhibit similar mobilisation dynamics to phosphorus, and are primarily sourced in diffuse losses from the soil surface by energetic hydrological flow pathways (based on Ulén et al. (2014)).

Samples for MCPA analysis were taken from 27th April 2018 in the River Derg and 22nd May 2018 in the River Finn until 31st October 2021. All samples were refrigerated within 8 h of collection from the automatic sampler and were analysed for MCPA within 3 days of receipt. Following Gervais et al. (2008) and McManus et al. (2014) unfiltered aliquot were extracted and concentrated, then analysed by LC-MS/MS (see Morton et al. (2021) for storage tests and analysis details). The limit of detection for MCPA was 0.0005 μg L^{-1}.

Glyphosate was analysed from 9th July 2019 and taken as a weekly composite extracted from the samples collected by the automatic sampler (either 24 or 7 samples/week depending on time of year). These were analysed by a sub-contracted laboratory of Northern Ireland Water using Off-Line FMOC-CL derivatisation, followed by direct injection LC-MS. The limit of detection for glyphosate varied through the analysis period due to changing operations within the laboratory (values were <0.017 (n = 14), <0.0034 (n = 1), <0.006 (n = 1), 0.06 (n = 3), 0.0077 (n = 2) and < 0.0084 (n = 50) μg L^{-1}) and were changed to half that LOD for analysis.

River discharge time series (15 min frequencies) were obtained from the closest hydrometric stations to the monitoring locations (Table 1); at Castlederg ("Rivers Agency Hydrometric Network-000020100815"; 54.705451 N, 7.589423 W) for the River Derg, and Ballybofey ("OPW Station 01403"; 54.799930 N, 7.7907343 W) for the River Finn.

2.5. Pesticide concentrations and loads

MCPA time-weighted and flow-weighted mean concentrations (TWMC and FWMC, respectively) were calculated for full peak periods (here standardised to 1st April–31st October) and quiescent periods (1st November–31st March) within each year of observation.

The TWMC weights the concentration by the time period it represents and is indicative of the concentrations monitored where there is a steady rate of abstraction from a source, such as a pumped abstraction for drinking water treatment and supply. It is calculated as:

$$TWMC = \frac{\sum_{i=1}^{n} c_i t_i}{\sum_{i=1}^{n} t_i} \tag{1}$$

where:

c_i is the pesticide concentration in the ith sample (μg L^{-1})
t_i is the time period represented by the sample (s)
n is the total number of samples in the data set.

The FWMC weights the concentration at each time step by both the time period it represents and the flow, or river discharge, occurring during that time. This is more representative of the dynamics of a surface-water driven river system where there is a high flow dependency of concentrations. This is calculated as:

$$FWMC = \frac{\sum_{1}^{n}(c_i t_i q_i)}{\sum_{1}^{n}(t_i q_i)} \tag{2}$$

where:

c_i is the instantaneous pesticide concentration in the ith sample (μg L^{-1})
t_i is the time period represented by the sample (s)
q_i is the flow in the ith sample period (interpolated from hourly data) (m^3)
n is the total number of samples in the data set.

Only periods with synchronous samples available for both catchments were used in the analysis of loads, dropping 82 records from the Derg and 47 records from the Finn time series where records were missing in the other catchment (n = 3081 total).

Loads were calculated by linear interpolation of the time series as

$$L = \sum_{1}^{n}(c_i t_i q_i) \tag{3}$$

where:

L is the load over a sampling period
c_i is the instantaneous pesticide concentration in the ith sample (μg L^{-1})
t_i is the time period represented by the sample (s)
q_i is the flow in the ith sample period (interpolated from hourly data) (m^3)
n is the total number of samples in the data set.

MCPA concentrations and loads were compared for application peak periods (1st April–31st October) and quiescent periods (1st November–31st March) before and after the AES was implemented in both catchments.

Composite weekly samples of glyphosate were compared between catchments from July 2019 onward, examining both trends and occurrences of concentrations above the 0.1 μg L^{-1} limit. As this data collection started later, the comparisons were made on an ACI, rather than a BACI framework.

2.6. Hydrometric analysis

Hydrometric observations at fifteen minute intervals were reduced to hourly averages and matched with the concentration time series for all analyses of FWMCs and loads.

Additionally, to examine concentration characteristics at different flow conditions, the discharge time series for each river was logged and split into four equal intervals across the discharge range (−0.227–2.307 $m^3 s^{-1}$ for Derg; 0.109–2.320 $m^3 s^{-1}$ for Finn) for the period 2018–2021. Concentrations were then partitioned according to the flow interval at the time of sampling according to the thresholds (Table 3) with lowest discharge concentrations in Q1 and highest discharge concentrations in Q4. The use of logged discharge data enabled approximately the same number of concentration values in each flow interval.

2.7. Data handling and analysis

Data handling and statistical analysis were undertaken in R (R Core Team, 2022) using the *stats* package (version 4.0.3) and *lubridate* library, and in MS Excel using Real Statistics Resources (Release 7.6) (Zaiontz, 2020).

Comparisons of MCPA concentration data between pre- and post-AES periods were undertaken as linear regressions and t-tests on the difference between slopes, and changes in variance using Kruskal-Wallis tests. Concentrations partitioned into the four flow intervals were compared in pre- and post-AES periods using Kruskal-Wallis tests. Following Wenng

Table 3
Intervals of logged discharge in the Derg and Finn catchments over the monitoring period 2018–2021.

	Discharge (Q)	
	Log Q m^3 s^{-1}	Q, m^3 s^{-1}
Derg		
Interval 1 (Q1)	−0.227–0.329	0.592–2.133
Interval 2 (Q2)	0.329–0.693	2.133–4.926
Interval 3 (Q3)	0.693–1.119	4.926–13.159
Interval 4 (Q4)	1.119–2.307	13.159–202.833
Finn		
Interval 1 (Q1)	0.109–0.546	1.285–3.518
Interval 2 (Q2)	0.546–0.812	3.518–6.486
Interval 3 (Q3)	0.812–1.201	6.486–15.902
Interval 4 (Q4)	1.201–2.320	15.902–209.020

et al. (2021), a statistical significance level was set at $\alpha = 0.05$ and a (non-significant) tendency at $\alpha = 0.05$–0.10.

The comparison of pre- and post-AES concentrations in instantaneous data was used to show where in the concentration range any detected change had occurred. The analysis of concentration data within specific flow intervals (Section 2.6) was used to show where in the flow range any detected change had occurred.

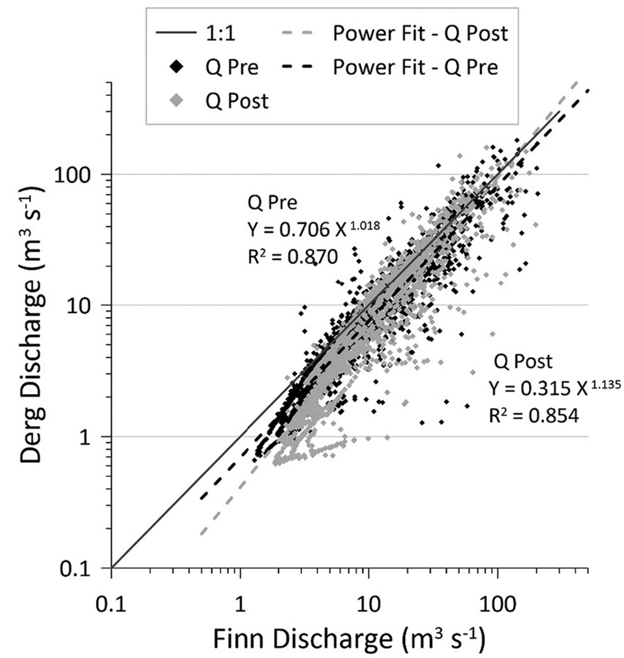

Fig. 3. Comparison of paired discharge pre- and post-AES for the River Derg AES and River Finn control catchments.

3. Results and discussion

3.1. Chemistry and hydrology over four years

Over the monitoring period a total of 3406 samples were collected and analysed from the River Derg and 3144 samples from the River Finn. A total of 3081 samples were synchronous to both stations (Supplementary Material Table S1). The full time series are shown in Fig. 2 and cover four peak application seasons; two years preceding implementation of AES measures in the River Derg catchment and two summer periods post-AES.

Over the four years, although the rivers compared well at higher flows, with storm flows often well-matched in magnitude between catchments, base flows in the River Derg were lower than in the River Finn (Fig. 3). Power law fits to the pre- and post-AES period data also indicate lower base flows in the River Derg relative to the River Finn in the post-AES period (and with a significant difference between slopes ($p < 0.05$)). Peak application season and quiescent period river discharges are summarised in Supplementary Material (Fig. S3).

3.2. Pre- and post-AES MCPA comparisons

3.2.1. Instantaneous concentrations

All instantaneous MCPA concentration data from peak season application (7 h) and quiescent (at least daily) periods for pre- and post-AES periods in both catchments are shown in Fig. 4. Power curves were best fitted to each dataset across the concentration range and were significantly different between pre- and post-AES datasets ($p < 0.05$). The post-AES dataset variance was also significantly higher than the pre-AES dataset ($p < 0.05$). Therefore, at face value, there were indications that MCPA

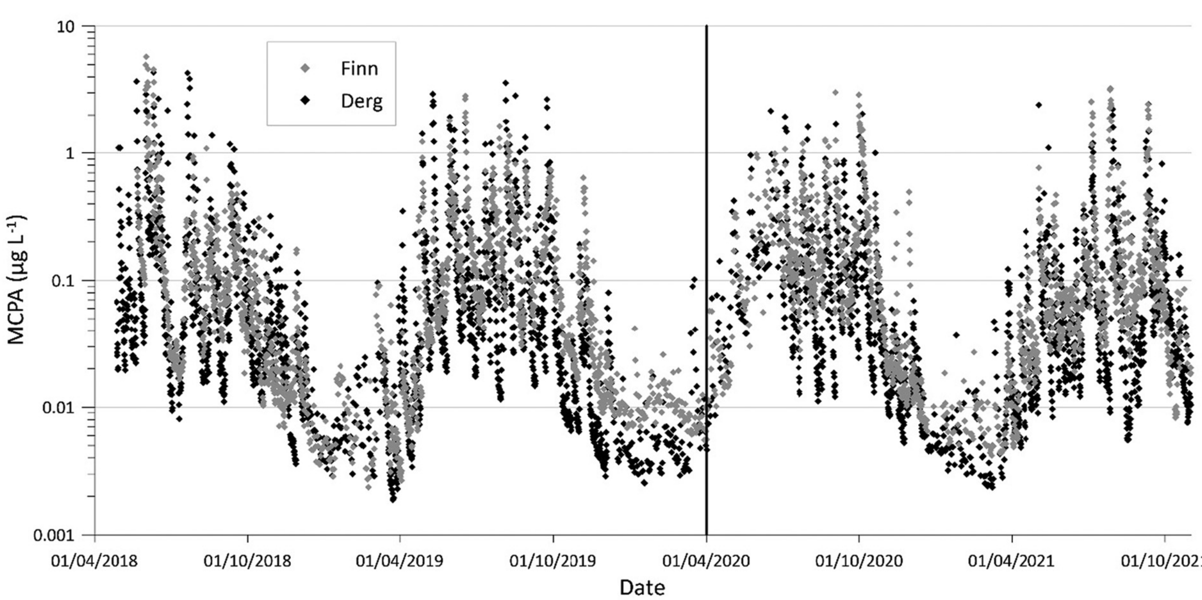

Fig. 2. Full MCPA concentration time series for the Derg and Finn catchments with the start of the AES indicated by a black vertical line.

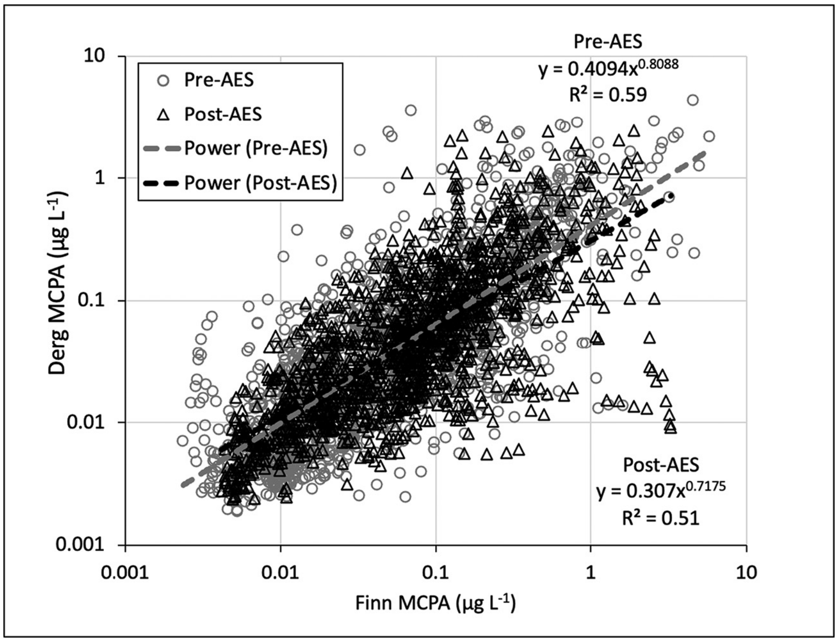

Fig. 4. Instantaneous MCPA concentrations from the pre- and post-AES periods for the River Derg AES catchment and the River Finn control catchment.

concentrations had reduced in the post-AES catchment river compared to the control catchment—particularly in the higher concentration range.

3.2.2. Seasonal MCPA loads and flow-weighted mean concentrations

Based on the synchronous data, MCPA loads indicated small differences between catchments prior to the AES commencing (Fig. 5). Prior to the AES, the River Derg load was lower during the peak application season by 1.3% and 6.8% for 2018 and 2019, respectively (i.e. excluding quiescent periods). Following the implementation of the AES in 2020 the River Derg load was 13.9% lower than that of the River Finn, (105.7 kg), and in 2021 was 39.5% lower than that of the River Finn. Of note in Fig. 5 is the discharges for all seasons showing a similar proportional discharge between the River Derg and River Finn in both peak application and quiescent periods of 82% to 88%, The exceptions are the first (2018) and last (2021) peak application season discharges where this proportion was 65% in each. However, the first of these periods (pre-AES) shows a matched MCPA load

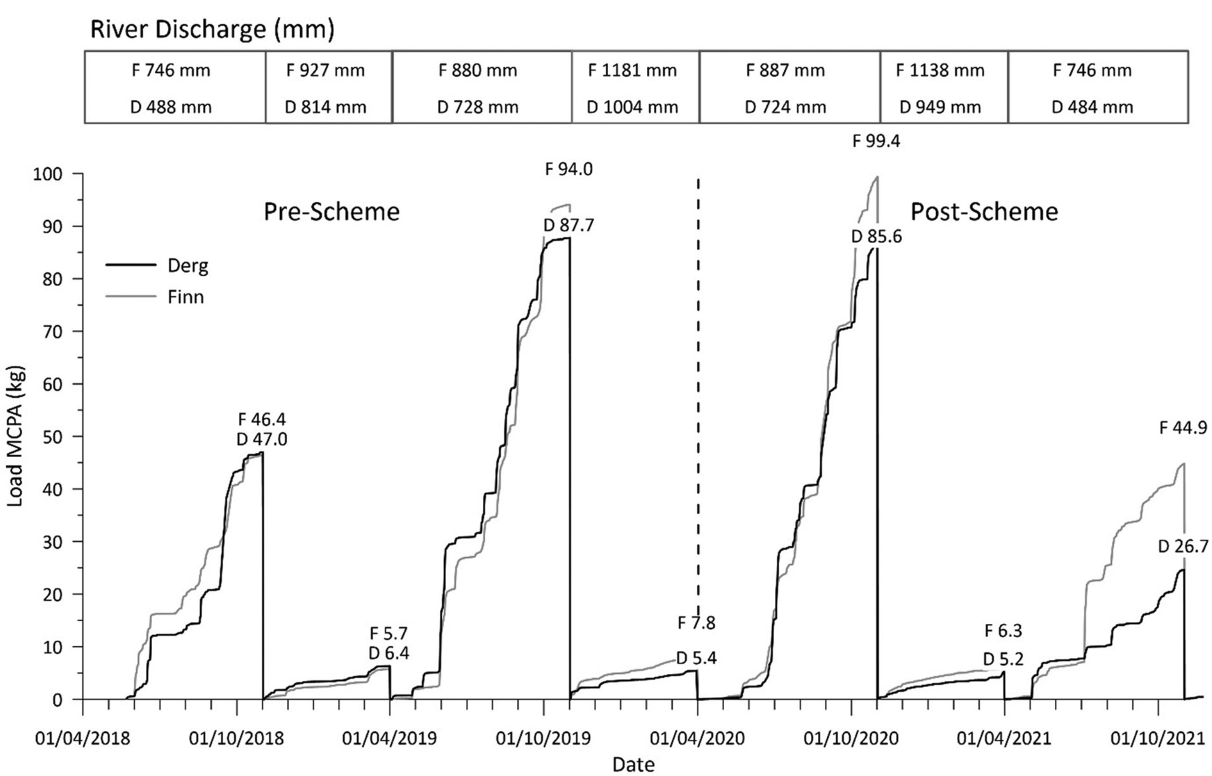

Fig. 5. Load summaries for peak (April–October) and quiescent periods (November–March) over the monitoring period. Dashed line indicates start of AES implementation (1st April 2020). The bar at top indicates the total discharge (mm) in each peak application and quiescent period for the River Derg (D) and the River Finn (F).

between the two catchments, and the second period (post-AES) a large reduction in MCPA load, suggesting a reduction in MCPA concentration post-AES.

Chemical and sediment loads from catchments are influenced by variations in seasonal and interannual hydrometeorological conditions (causing dilution and magnification, for example) and so flow-normalising enables these effects to be filtered out in FWMCs. Using the data in Figs. 5 and S3 the River Derg catchment FWMC concentrations (Fig. 6) showed a decline between the pre- and post-AES periods, switching from slightly higher concentrations before the AES was implemented. These reductions in MCPA FWMC during the peak application seasons were 5.3% in the first year of the AES and 29.3% in the second year (between AES and control catchments). With most incentivised measures to target MCPA implemented during September and October 2020 (Fig. S2), and then through summer 2021, a greater impact was expected in the second peak application season after the start of the AES. Areas treated with weed wiping by glyphosate in 2020 did not need further treatment in 2021 (usually treatment follows a two-to-three-year repeat period) so a cumulative effect in terms of areas not requiring boom spraying with MCPA was expected in 2021. This possibly explains the increased difference in FWMCs between catchments in the second year of the AES. Over the period of two peak applications and one quiescent period pre- and post-AES (i.e., equal time periods 01/04/18 to 31/10/19 and 01/04/20 to 31/10/21, respectively), there was a reduction of FWMC in the River Derg of 20.9% (0.207 μg L^{-1} to 0.146 μg L^{-1} in the River Derg—not shown but from analysis of the combined time series data in Fig. 6), and which accounts for the changes in the River Finn control catchment (0.187 μg L^{-1} to 0.170 μg L^{-1}).

3.2.3. Flow interval concentrations

The peak application season concentrations partitioned into flow intervals (Table 3) are summarised as box-plots for both river catchments in Fig. 7. In both catchments, the highest MCPA concentrations occurred during peak flows (the upper flow interval—Q4). Comparing peak season concentrations pre- and post-AES in the River Derg indicates reductions in median and maximum values across all flow intervals. Reductions in concentration were also noted in the Q2, Q3 and Q4 intervals in the River Finn for the same period. Analysis of variance indicated that the only significant decrease ($p < 0.05$) in MCPA concentration occurred in the River Derg AES catchment during the Q2 flow interval (2.133–4.926 $m^3 s^{-1}$).

3.3. Glyphosate substitution

The pre-AES monitoring period was short (July 2019–April 2020) and did not cover a full peak season hence, using an ACI framework, the data were examined for trends, with the glyphosate data best fitted by a power-law regression model for each catchment time series (Fig. 8).

Concentrations were generally lower in the River Finn, with 62% of samples analysed at the LOD compared to 18% of samples in the River Derg. General linear trends to both time series were weakly positive (Derg: $\log(Concentration) = 4.042 \times 10^{-9}\,Time - 8.168$; Finn: $\log(Concentration) = 2.225 \times 10^{-9}\,Time - 5.607$). Slopes were not significantly different ($p > 0.05$) and did not show a tendency to diverge over time ($p > 0.10$) indicating no greater rate of increase in the River Derg than the River Finn.

There was one glyphosate exceedance of the 0.1 μg L^{-1} DWD threshold in the weekly composite samples from River Derg in 2019; in 2020 there was a single exceedance for the River Finn and two exceedances in the River Derg; in 2021 three exceedances in the River Derg and one in the River Finn. The estimated areas sprayed as part of the AES (Fig. S2) were similar in 2020 (7.3 km^2) and 2021 (8.8 km^2). The relatively short period of (July 2019–April 2020) monitoring prior to the AES implementation limits references to the baseline period. Having a longer time pre-scheme time series and a higher sampling frequency through storm events in particular would have been beneficial in this regard. However, the weekly glyphosate composite sample data are likely to disproportionately emphasise any instantaneous exceedances of the 0.1 μg L^{-1} limit. This was confirmed for a similar analysis of MCPA data (not shown), where instantaneous exceedances of 27% and 36% for the Derg and Finn, respectively, translated to 36% and 44% exceedances when a weekly arithmetic average (equivalent to composite) was taken. Therefore, on balance and with the data available, there did not appear to be pollution swapping of glyphosate for MCPA due to the AES.

3.4. MCPA exceedances and impacts on treatment

A constant abstraction rate, such as at a water treatment works, is better represented by the TWMC and more indicative of the likely treatment needs within the plant filtration processes. Seasonal differences in TWMCs pre- and post-AES implementation are shown in Fig. 9 and a widening gap between the Finn and Derg in terms of concentration is noted in the period 1st April 2020 onward. Prior to the April 2020 peak application season, concentrations in the River Derg were 15.3% lower than the River Finn in 2018 and 4.5% lower in 2019. In 2020 and 2021 this increased to 28.3% and 32.9% lower, respectively. Over the period of two peak applications and one quiescent period pre- and post-AES (i.e., equal time periods 01/04/18 to 31/10/19 and 01/04/20 to 31/10/21, respectively), there was a reduction of TWMC in the River Derg of 23.7% (0.158 μg L^{-1} to 0.114 μg L^{-1} in the River Derg—not shown but from analysis of the combined

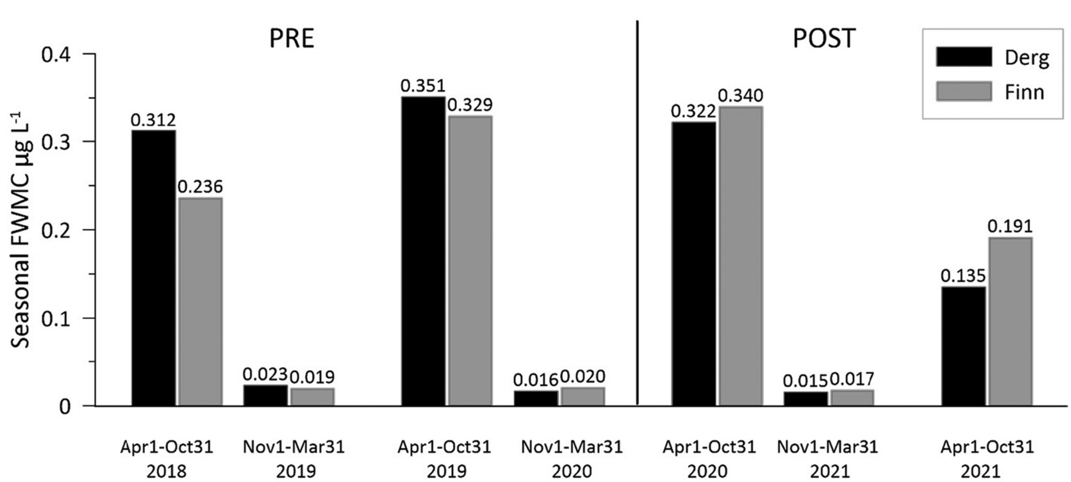

Fig. 6. Seasonal FWMC MCPA (μg L^{-1}) for the River Derg and Finn catchments for the pre- and post-AES implementation periods in the Derg catchment. Vertical line indicates start of AES implementation. April to October represents the peak application season in each year.

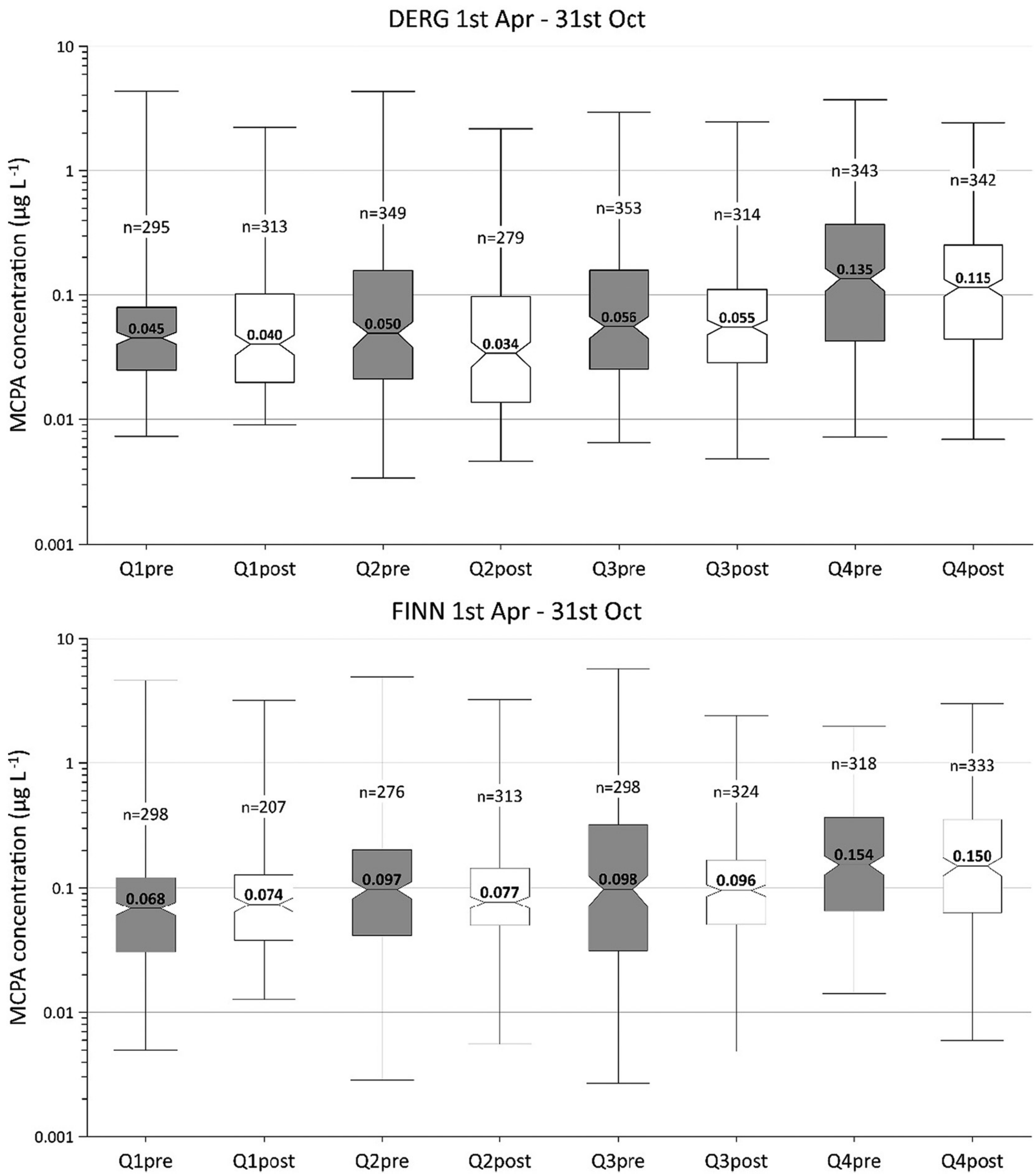

Fig. 7. Notched boxplots of flow partitioned MCPA concentrations in the River Derg AES catchment and River Finn control catchment over four peak pre- and post-AES application seasons 2018–2021. Median values and sample numbers are labelled. The most significant reduction in concentration occurred in the River Derg Q2 flow interval between pre- and post-AES periods (p < 0.05).

time series data in Fig. 9), accounting for changes in the River Finn control catchment (0.170 μg L^{-1} to 0.163 μg L^{-1}).

To examine changes in MCPA concentrations above the DWD limit (used here to indicate the need for treatment before supply) the number of sample concentrations >0.1 μg L^{-1} were enumerated for each peak and quiescent period, pre- and post-AES implementation in both catchments and compared (Fig. 10). Overall, and despite the reductions noted in TWMC concentrations there was no discernible difference in the pattern of concentrations above 0.1 μg L^{-1} in the River Derg relative to the River Finn in peak application periods following implementation of the AES. However, exceedances in quiescent periods reduced annually in the Derg whilst increasing in the Finn.

4. Discussion

The time-series MCPA concentration data in Fig. 2 indicate a striking seasonality with higher concentrations in the two rivers concurrent with the peak application season (up to 5.8 μg L^{-1}). The individual concentration peaks are also concurrent with storm flow peaks (not shown) and concentrations subsequently decrease in winter storm peaks during quiescent periods. This shows an acute incidental, transport limited system for MCPA mobilisation and delivery through the summer when storm events occur, similar to incidental losses reported for recently applied slurry and manure (Bloodworth et al., 2015). However, this transitions quickly to a source limited system during the winter as MCPA either degrades in the soil or is reduced through mobilisation. Nevertheless, this source limitation does not fully subside during the quiescent period for applications or between summer storm periods. These residual MCPA concentrations in the river during winter therefore indicate a persistence beyond complete degradation. Morton et al. (2020) propose that knowledge gaps still exist on the ecotoxicology of MCPA in natural waters and a persistence between storms during low flows in ecologically sensitive summer periods is likely to be when such impacts could occur (Vaj et al., 2011).

Conservative estimates of MCPA export loads in this study reached up to 93.1 kg yr^{-1} (April 2019–2020) in the River Derg and 105.7 kg yr^{-1} in the River Finn (April 2020–2021), with lower loads linked either to

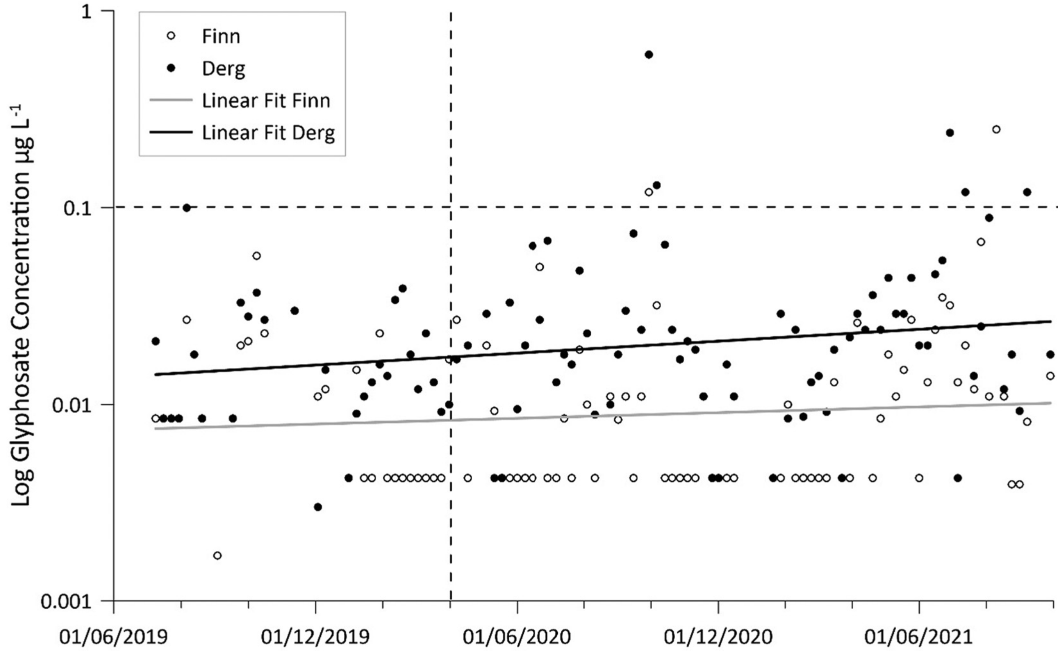

Fig. 8. Glyphosate composite sample concentrations for the River Derg and River Finn over the monitoring period from July 2019. The start of the AES is indicated by a vertical dashed line at 1st April 2020 and the 0.1 μg L^{-1} DWD threshold by a horizontal dashed line.

variations in weather (rainfall-runoff) or, indeed, to the AES. As a function of agricultural area (136 km^2 of the Derg and 100 km^2 of the Finn, Table 1), maximum annual normalised loads were 0.685 kg km^{-2} yr^{-1} in the River Derg and 1.061 kg km^{-2} yr^{-1} in the River Finn or as catchment (384 km^2 and 386 km^2) export loads of 0.242 kg km^{-2} yr^{-1} and 0.274 kg km^{-2} yr^{-1}, respectively. These loads are likely to be a function runoff regime (i.e., consistently higher runoff in the Finn—Sections 2.1 and 2.2) and possible differences in spray area within areas of agricultural land use, and realised through the enhanced monitoring approach used to capture the data. For example, the next highest MCPA export load reported in the literature is 0.013 kg km^{-2} yr^{-1} by (Zhang et al., 2017) in a similar sized Scottish agricultural catchment based on monthly sampling. Khan et al. (2020) also reported a combined acid herbicide export load of 0.026 kg km^{-2} yr^{-1} in a smaller (12 km^2) catchment in south-east Ireland where MCPA was one of five herbicides measured using a passive sampling approach. For highly mobile pollutants, the current work and high measured loads exemplifies the requirement for enhanced water quality monitoring approaches to establish the *state* of the water environment, and also the *impacts* of mitigation *responses* as reviewed by Westerhoff et al. (2022).

A combination of BACI experimental design (Van Loon et al., 2019) and enhanced water quality monitoring were innovations in this study and particularly at the large scale studied. For example, out of twenty reviewed studies on pesticide trends in river systems, Chow et al. (2020) noted that only four included mitigation monitoring in a full BACI design. Enhanced monitoring of pesticides in catchment rivers is rarer (but see Holvoet et al., 2007 and Baets et al., 2018 for enhanced monitoring in small catchments), with other studies reporting enhanced datasets of up to eighty samples per year (e.g. Brown et al. (2002)) or with annual coverages using passive samplers (Townsend et al., 2018). The experimental design here indicated a measure of success with the AES and a reduction of the MCPA pressure in terms of catchment export and the burden on GAC filtration following abstraction. These reductions are summarised as a 20.9% decrease in FWMC and a 23.7% decrease in TWMC compared across 18 months pre- and post-AES when accounting for the control catchment. These decreases

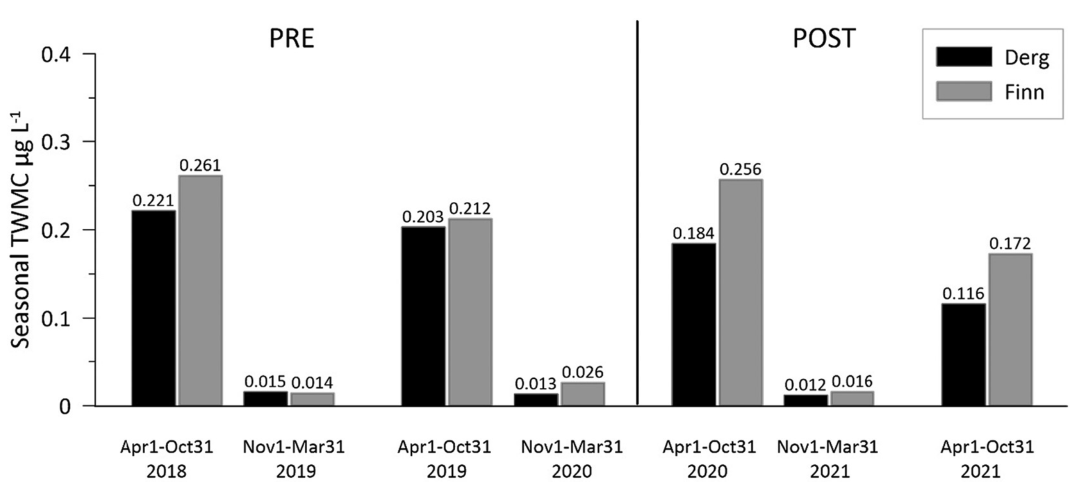

Fig. 9. Seasonal TWMC MCPA (μg L^{-1}) for the River Derg and River Finn catchments for the periods pre- and post-AES implementation in the Derg catchment. Vertical line indicates start of AES implementation.

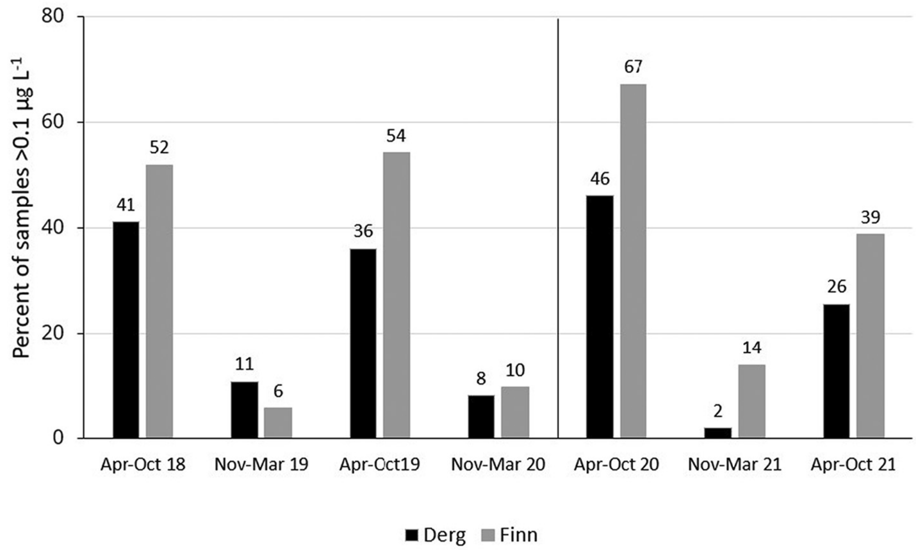

Fig. 10. Percentage number of concentrations higher than the 0.1 μg L^{-1} DWD threshold (and so indicating the need for treatment prior to supply) by catchment and monitoring periods, pre- and post-introduction of AES measures in April 2020. Vertical line indicates the start of AES measures.

were found to be due to a change in MCPA concentrations with fewer high concentrations and a higher variance post-AES in the River Derg (Fig. 4), and significantly during the 2.133–4.926 $m^3\ s^{-1}$ (Q2) flow interval (Fig. 7).

Despite the AES indicating reductions in the MCPA burden to any abstracted water, there remained a high percentage of concentrations above the 0.1 μg L^{-1} limit (Fig. 10) and so indicative of continued treatment requirements. Participation in the direct measures (MCPA substitution) was approximately 21% of catchment farmers but does not include those farmers who may have altered practice due to AES education and outreach activities. In this regard, further engagement and buy-in would likely have reduced the MCPA burden further. Nevertheless, the results here will be important in boosting farmer behaviour and belief in future schemes that utilise farmer knowledge to the highest level (Shahvi et al., 2021).

Trend analysis of glyphosate data (limited to pre-AES data) indicated that pollution swapping was not significant (Fig. 8) and hence a suitable substitute in a weed-wiping application. This assumes the same or better performance at rush control (Ghanizadeh and Harrington, 2019) and lower mobility in water (k_{oc} = 884–50,660 mL g^{-1} (Lewis et al., 2016)). However, other studies have found residual glyphosate in soils can lead to subsequent transfer to rivers (e.g. Carles et al. (2019)) via slower routes and there is also a question over the future of this herbicide for general agricultural use (Davoren and Schiestl, 2018). Furthermore, although MCPA degradation can be fast (Bech et al., 2022), the main metabolite, 4-chloro-2-methylphenol (Rahemi et al., 2015), was not considered in this investigation. These factors will need to be considered in this and future AES.

The very high MCPA concentrations found in river water because of herbicide spraying (both pre- and post-AES) on wet, often marginal, grasslands may also need to be reviewed. A driver of use in such areas is the need to maintain fields as "agriculturally active" and therefore eligible for area-based subsidy payments. Acknowledging the other environmentally beneficial functions that such grasslands have to offer (Reed et al., 2014) and supporting those through policy change and actions within future AES could lead to source reductions. There is also a debate on precautionary principle pesticide limits (Dolan et al., 2013) and the burden this places on the drinking water treatment process to meet these targets.

5. Conclusions

Evidence from a BACI and enhanced water quality monitoring framework indicates that a voluntary agri-environmental scheme (AES) had a positive impact on MCPA reduction in the River Derg drinking water catchment.

The assessment identified improvements following the implementation of scheme measures from 1st April 2020 using an alternative herbicide (glyphosate) and application method. Seasonal flow-weighted mean MCPA concentrations in the post-AES catchment were up to 20.9% lower than the pre-AES period and accounting for the control catchment. Time-weighted mean concentrations were up to 23.7% lower. Load and concentration reductions were more pronounced in 2021, potentially due to the cumulative effects of two successive years of substitute glyphosate weed wiping (a total estimated area of 9.75 km^2) where areas treated will not require re-applications within ~3 years. This effectively doubled the area removed from potentially being boom sprayed with MCPA, compared to 2020. There was no indication of pollution swapping using the glyphosate substitute.

In terms of water treatment burdens, the percentage number of occurrences of MCPA concentrations above 0.1 μg L^{-1} did not change proportionally between AES and control catchments. This means a continued need for activated carbon filters at the point of source water treatment, but the reduction in concentration suggests better filter longevity and reduces the chances of very high concentrations not being adequately treated and entering public supply.

The work provides a strong evidence-based endorsement for using agri-environmental schemes to reduce the pesticide burden on water treatment processes, and a justification for further stakeholder engagement.

CRediT authorship contribution statement

Rachel Cassidy: Conceptualization, Methodology, Formal analysis, Writing – original draft, Visualisation, Funding acquisition. **Phil Jordan**: Conceptualization, Methodology, Formal analysis, Writing - review & editing, Visualisation, Supervision, Funding acquisition. **Stewart Floyd**: Methodology, Validation. **Colin McRoberts**: Writing - review & editing, Supervision, Funding acquisition. **Luke Farrow**: Investigation, Writing - review & editing. **Phoebe Morton**: Investigation, Methodology, Writing - review & editing. **Donnacha G. Doody**: Conceptualization, Writing - review & editing, Supervision, Funding acquisition, Project Administration.

Declaration of competing interest

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.

Acknowledgements

We thank AFBI technical staff Briege McCarney and Carmel McBarron for help with field work. We also acknowledge contributions to this work from staff at Northern Ireland Water, Irish Water and The Rivers Trust. This work was carried out as part of *Source to Tap* (IVA5018), a project supported by the European Union's INTERREG VA Programme, managed by the Special EU Programmes Body (SEUPB). The views and opinions expressed in this paper do not necessarily reflect those of the European Commission or the SEUPB.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.156080.

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