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Approaches to herbicide (MCPA) pollution mitigation in drinking water source catchments using enhanced space and time monitoring

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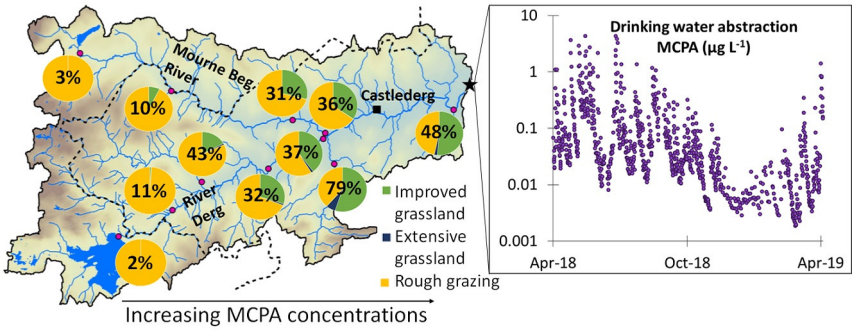
HIGHLIGHTS

- Our research developed an enhanced spatial and temporal MCPA water quality dataset.
- Spatial catchment data implicated Improved Grassland in high MCPA concentrations.
- 25% of source water samples exceeded the drinking water limit of 0.1 μg L^{-1}.
- Hydrometeorological scenarios were used to reduce MCPA intake in abstractions.
- Ecosystem services may need revaluing, especially in source water catchments.

GRAPHICAL ABSTRACT



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ABSTRACT

Freshwater occurrences of the selective acid herbicide 2-methyl-4-chloro-phenoxyacetic acid (MCPA) are an ongoing regulatory and financial issue for water utility industries as the number and magnitude of detections increase, particularly in surface water catchments. Assessments for mitigating pesticide pollution in catchments used as drinking water sources require a combination of catchment-based and water treatment solutions, but approaches are limited by a lack of empirical data. In this study, an enhanced spatial (11 locations) and temporal (7-hourly to daily sampling) monitoring approach was employed to address these issues in an exemplar surface water source catchment (384 km^2). The spatial sampling revealed that MCPA was widespread, with occurrences above the 0.1 μg L^{-1} threshold for a single pesticide being highly positively correlated to sub-catchments with higher proportions of 'Improved Grassland' land use ($r = 0.84$). These data provide a strong foundation for targeting catchment-based mitigation solutions and also add to the debate on the ecosystems services provided by such catchments. Additionally, of the 999 temporal samples taken over 12 months from the catchment outlet, 25% were above the drinking water threshold of 0.1 μg L^{-1}. This prevalence of high concentrations presents costly problems for source water treatment. Using these data, abstraction shutdowns were simulated for five scenarios using hydrometeorological data to explore the potential to avoid intake of high MCPA concentrations. The scenarios stopped abstraction for 4.2–9.3% of the April–October period and reduced intake of water containing over 0.1 μg L^{-1} of MCPA by 16–31%. This represents an important development for real-time proxy assessments for water abstraction in the absence of more direct pesticide monitoring data.

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1. Introduction

In Europe, 37% of all drinking water is sourced from surface waters (Völker and Borchardt, 2019) such as rivers, lakes and impounding reservoirs, with proportions varying among countries depending upon geology, climate and legacy practices. In countries such as Ireland, Greece, the UK and Bulgaria, this proportion is much higher, accounting for >65% of source allocation (EPA, 2017a; European Topic Centre, 2016a, 2016b, 2016c, 2016d), while in Northern Ireland 99.9% of the public supply is sourced from surface water (NI Water, 2018). Treatment of public drinking water varies between source water supplies. Whilst groundwater generally only tends to require disinfection prior to distribution, surface waters lack the natural filtration provided by the soil and bedrock and, consequently, complex and costly additional treatment is often required before use (Völker and Borchardt, 2019).

Across Europe, pesticides and nitrate have been identified among the main chemical contaminant issues for drinking water supplies, with these problems mostly attributed to agriculture (Glavan et al., 2019). In the European Union (EU) for example, agricultural land accounts for nearly 50% of the land area (Stoate et al., 2009), to which pesticides and chemical fertilisers are routinely applied. The EU Drinking Water Directive (DWD) stipulates that the maximum allowable concentration of a single pesticide in treated drinking water is 0.1 μg L^{-1} and the limit for the sum of all pesticides is 0.5 μg L^{-1} (Council of the European Commission, 1998).

Herbicide applications greatly outweigh those of fungicides or insecticides in many countries (Schreiner et al., 2016) and either target a broad spectrum of plant weed species or selectively target specific plants, or plant groups, in tilled or grassland settings. The selective acid herbicide, 2-methyl-4-chlorophenoxyacetic acid (MCPA) is widely used, and applied by broadcast spraying to reduce weeds (Loos et al., 2017; Schreiner et al., 2016; Spycher et al., 2018). This can – despite statutory buffer zones – result in the herbicide directly entering watercourses via spray drift (Kreuger, 1998). However, whilst MCPA has been found in watercourses in countries where it is often used on arable crops (e.g. Kreuger, 1998), it is of greater concern for drinking water in countries where it is primarily used on grassland to reduce the cover of soft rush (*Juncus effusus*) and docks (*Rumex* spp.) (EPA, 2017b; Lavery et al., 2018). This is because soils supporting such weeds are often prone to saturation and the majority of MCPA applied is highly soluble (i.e. the salt forms of MCPA), and thus mobile (Bailey et al., 2017; Hornsby et al., 1996), making it very susceptible to loss from soil surfaces through leaching and fast runoff after rainfall. Whilst ester forms of MCPA can be used in commercial applications and are only poorly soluble, they tend to rapidly hydrolyse in soil (Hornsby et al., 1996; Paszko et al., 2016), thus becoming mobile in water.

MCPA has a reported soil photolysis degradation half-life (DT50) of between 9 and 67 days (European Union, 2005; US EPA, 2004), a soil water DT50 of between 7 and 60 days (Hornsby et al., 1996) and a DT50 of fewer than seven days in groundwater (Mackay et al., 2006). This suggests that high MCPA concentrations should rapidly diminish and consequently have little effect on biological organisms present in watercourses. However, research data has brought the accuracy of degradation estimates in natural catchment settings into question. For example, a national campaign in Ireland detected MCPA in over 8% of 845 groundwater samples (McManus et al., 2014), indicating transport and persistence. Similarly, a four year Spanish survey found MCPA in 7% of samples from 112 groundwater wells (Köck-Schulmeyer et al., 2014). Furthermore, the high solubility and leachability of MCPA is strongly evident in surface waters. For example, Loos et al. (2017) detected MCPA at 93% of the 68 sites surveyed along the length of the Danube, whilst Spycher et al. (2018) found MCPA in 33% of their samples taken from five small stream catchments in Switzerland. Across the island of Ireland, MCPA is considered to be the most problematic pesticide in source drinking waters both in terms of its distribution and concentration levels (Morton et al., 2019).

Knowledge of the transport pathways and persistency of MCPA is still limited, which is partly attributed to a paucity of data, both spatial and temporal (Morton et al., 2019). This has consequences for understanding pressures on aquatic biology and also the efficacy of source water treatment. Furthermore, in order for agricultural mitigation measures to be targeted correctly and cost-effectively, knowledge of the variability in MCPA concentrations across catchments is a necessity. Regulatory frameworks, such as the DWD, allow for the definition of monitoring frequencies specific to each country but the maximum resolution available for regulatory checks is unlikely to exceed weekly in many countries. For example, in Northern Ireland, the minimum frequency for checks on treated drinking water is eight times per year for abstractions up to 50 ML day^{-1} (Statutory Rules of Northern Ireland No. 212; DAERA, 2017). There is only a requirement to monitor pesticides in abstracted water prior to treatment if a catchment risk assessment determines their use in the catchment. The monitoring frequency is then determined based on the level of risk identified: Northern Ireland Water samples every 4–10 days in high-risk areas (Northern Ireland Water, pers. comm.). However, high concentration pulses of pesticides in rivers can pass within days or even hours (Spycher et al., 2018).

Pesticide concentrations can be reduced in source water abstractions at water treatment works (WTWs) using, for example, ozonation or granulated activated carbon (GAC) filters, which also remove taste- and odour-causing compounds and organic materials (Ridal et al., 2001), at a cost to water utilities. However, these filters tend not to remove all the pesticide present and have finite capacity before effectiveness is reduced and regeneration is necessary. Whilst some parameters, such as ammonia or oil, are continuously monitored and trigger an abstraction shutdown once concentrations exceed a WTW-defined threshold (Northern Ireland Water, pers. comm.), pesticides cannot currently be monitored in real-time, thus very high concentrations may cause statutory drinking water limits to be exceeded even with the use of GAC filters or other contaminant removing processes.

Optimising treatment of surface source water to reduce treatment costs requires a two-part risk assessment approach. Firstly, there is a need to reduce the magnitude and frequency of pollution transfer events from land to water in source catchments. This requires an understanding of *where* the contaminants are originating from, enabling catchment-based solutions to be targeted. Secondly, there is a need to optimise treatment at WTWs. This requires a detailed understanding of *when* the issues are most problematic. In the case of pesticides, optimising treatment is difficult as all water passes through GAC filters regardless of pesticide concentration. Therefore, this second assessment may instead include modelling of optimal abstraction times. For highly mobile pesticides such as MCPA, both spatial and temporal assessment approaches require a highly empirical evidence base.

Consequently, the aim of this research was to increase understanding of MCPA transfer processes in source water catchments (i.e. a recommendation from Morton et al., 2019), and develop approaches using these data to reduce the risk to drinking water supplies. In an exemplar catchment, the objectives were to 1) build an enhanced spatial dataset to aid in land use mitigation planning and 2) build an enhanced temporal dataset and apply these data to a proxy real-time risk framework for source water abstractions (i.e. temporarily shutting down abstraction).

2. Methods

2.1. Study area

The study was undertaken in the River Derg catchment, part of the cross-border Foyle catchment in the north-west of Ireland (Fig. 1). The headwaters of the Derg rise in the Republic of Ireland in Lough Mourne and Lough Derg and flow eastwards into Northern Ireland in two main tributaries, the River Derg and the Mourne Beg River. The catchment

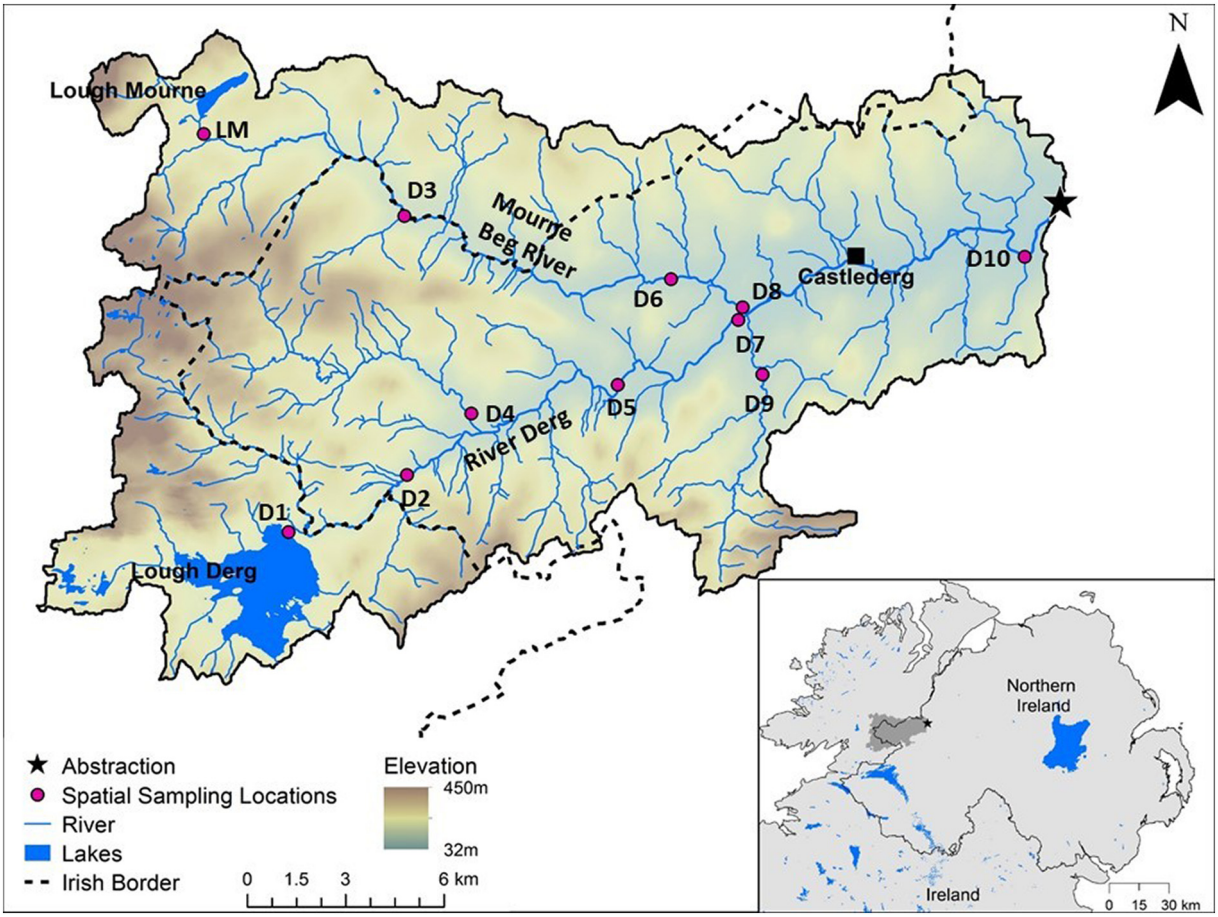

Fig. 1. Map of the Derg catchment, with the inset showing its cross-border location on the island of Ireland (grey shaded area). The two main tributaries, the River Derg and the Mourne Beg River, and their minor tributaries are shown with spatial sampling locations. The main town of Castlederg is on the River Derg after the confluence. The drinking water abstraction point is also the catchment outflow and the location of the temporal sampling.

area to the drinking water abstraction point on the River Derg is 384 km^2 and the connected WTW treats approximately 16 ML day^{-1} for 30,000 people. This includes the rural population surrounding and including Castlederg and the town of Strabane.

The catchment is underlain by Dalradian metasediments and later Silurian-Devonian granites. The region was extensively glaciated during the Quaternary and, from the rolling hills of the uplands (maximum elevation 450 m), the river enters a broad valley of mixed land use (elevation at abstraction point 32 m). Blanket bog covers 25.1% of the catchment and coniferous forestry plantations underlain by peat cover 22.2% of the catchment, both mainly in the western upland areas. Sand, silt and alluvium outline the river channels, and brown earths (cambisol) and brown podzolic (umbrisol) soils dominate the valley floors. In the lower eastern parts of the catchments, extensive grassland gives way to more intensive agriculture, dominated by permanent pastures and silage meadows. Arable land use accounts for just 0.2% of land cover and this is almost all on the floodplain in the most easterly part of the catchment. MCPA use is seasonal, with spraying permitted between March and September. Where rushes are predominantly the target species, spraying generally peaks in the April to June period each year (Hygeia Chemicals Ltd, 2017, Nufarm UK Limited, 2011, 2016), although timings depend on weather (growing) and soil (trafficability) conditions.

2.2. Spatial sampling and land use assessment

Spatial sampling was carried out on a weekly basis at 11 locations through the Derg catchment (LM and D1-D10; Fig. 1) between 27th March 2018 and 26th June 2018 (excluding 3rd April 2018). This period of spring and early summer was targeted for spatial sampling due to the majority of MCPA application usually occurring at this time of year and because MCPA concentrations within the Derg catchment have historically been higher during these months (Northern Ireland Water, pers. comm.). The majority of sampling locations were along the two main catchment tributaries (LM, D1-D3 and D5-D8), or at the end of a minor tributary, just before it joined the River Derg (D4 and D9), in order to pinpoint which tributaries had high MCPA occurrence. Samples were taken from the rivers in 750 mL HDPE bottles attached to TeleScoop Sample Dippas (bottle-holders on extendable poles; Bürkle GmbH, Bad Bellingen, Germany) and decanted into 1 L amber glass bottles.

The total agricultural area was determined for the full sub-catchment area upstream of each spatial sampling monitoring location using agricultural field maps (polygon shapefiles) that included all land with defined field boundaries and thus excluding any commonage holdings. Land use types within those fields were identified from aerial imagery (OSNI, 2020) and classified as Improved Grassland (fertilised productive pasture and meadow), Extensive Grassland (low input pasture where rush growth is common), Rough Grazing (poor quality pasture used primarily for sheep and boggy ground with dense rush or scrub cover) and Arable. Data were collated and archived in a GIS database.

2.3. Temporal sampling

An ISCO 6712FR refrigerated autosampler (Teledyne ISCO, Lincoln, NE), with a 24-bottle configuration of 1 L polypropylene bottles, was installed at the Derg WTW abstraction point. It was necessary to use polypropylene instead of glass bottles to ensure a full 24-bottle configuration

(not available in glass) and so a storage test on this material was undertaken prior to the sampling campaign (Supplementary Material – Storage). The autosampler was mostly programmed to draw water up from the river once every 7 hours, following the 24/7 "Plynlimon" approach (Halliday et al., 2012) evaluated by Jordan and Cassidy (2011). While this approach was originally assessed for phosphorus (P) transfers from land to water, it was chosen because MCPA was assumed to exhibit similar dynamics to P (based on details in Ulén et al., 2014). This is because both are surface sourced, highly mobile and primarily lost in surface and near-surface flow pathways during storm events in these landscapes, particularly as incidental losses following application. Sampling covered the period 27th April 2018 to 30th April 2019 in order to obtain a full year of concentrations. Between 11th December 2018 and 12th March 2019, sampling was reduced to once per day at 14:00 GMT due to the expectation that little MCPA would be detected during this period as land applications had ceased. Three small gaps in sampling occurred throughout the year due to power failures, all during the 24/7 sampling (record 96% complete). The longest gap was 6.5 days.

2.4. Water sample analysis

All samples were refrigerated within 8 hours of collection from the autosampler (temporal samples) or rivers (spatial samples). Samples were analysed within 3 days of receipt, with storage tests demonstrating good recovery in MCPA concentrations during this storage period (Supplementary Material – Storage). Samples were extracted and concentrated (Gervais et al., 2008) then analysed by LC-MS/MS (Supplementary Material – Analysis). This method of analysis measures MCPA as multiple reaction monitoring transitions from the $[M\text{-}H]^-$ of MCPA. As MCPA esters hydrolyse in soil to salt or free acid forms (Hornsby et al., 1996) and both MCPA salts and the free acid dissociate in water to form anions of the parent acid (Muszyński et al., 2020), the analysis using negative electrospray ionisation detection captures the majority of MCPA present within the samples. Additionally, although soil pH can affect the speed at which phenoxy acid esters hydrolyse (Waite et al., 2002), 99% of the MCPA applied in Northern Ireland in 2017/18 was in salt form (Lavery et al., 2018; Lavery et al., 2019), meaning that most of the applied MCPA would have dissolved in the water and thus dissociated to anions.

The limit of detection (LOD) for MCPA was estimated from the calibration curve as <0.0005 μg L^{-1}. Values below the LOD are included and presented here as half the LOD value, following the recommendation by Helsel (2006) for large datasets.

2.5. Hydrometeorology

River discharge data were obtained from the only long-term gauging station within the Derg catchment, situated at Castlederg (54°42′19.6″ N 7°35′21.8″ W) and covering 335.4 km^2 of the catchment (NRFA, 2018). River levels were recorded once every 15 minutes and converted to discharge using established rating curves from DfI Rivers (Department for Infrastructure, Northern Ireland, pers. comm.). Long term discharge as well as study period data were used. Soil moisture deficit (SMD) estimates were obtained for the closest synoptic weather station at Malin Head, Co. Donegal (55°22′20″N 7°20′20″ W – 75 km from Castlederg) and calculated for well-, moderately- and poorly-drained classifications following Schulte et al. (2005). The SMD model uses combinations of rainfall and weather parameters used for evapotranspiration estimates in a cumulative daily calculation. SMD predictions for the moderately-drained soil class were used in the analysis.

2.6. Data analysis

Descriptive statistics were calculated for spatial and temporal samples in Microsoft Excel. Further analyses were undertaken in R (R Core Team, 2020). Pearson correlation coefficients were calculated for spatial sampling concentrations relative to agricultural land use using the "stats" package (version 3.5.3). Prior to analysis, the existence of linear relationships was visually inspected using bivariate scatterplots, and normality of the dependent variables was determined using the Shapiro–Wilks test.

Rates of change in river discharge (dQ/dt) were calculated in R and included in a critical period analysis, which examined the potential of using real-time hydrometric observations to trigger abstraction shutdowns and minimise periods when high MCPA concentrations pass through the WTW. The period for simulated shutdowns was restricted to 1st April–31st October, when peak in-stream MCPA concentrations were observed. The 7-hourly concentrations measured at the Derg WTW abstraction point were linearly interpolated to hourly timestamps and paired with average hourly discharge as water utilities are most likely to operate and evaluate abstraction shutdowns at an hourly resolution.

Five scenarios were simulated, using combinations of soil moisture (trafficability and growth) and rising discharge (surface and near-surface flow pathways) as conditions to trigger shutdowns. Abstraction shutdown periods of 8-hour and 12-hour durations were modelled by treating these periods as non-abstractions (i.e. removing the concentrations for these periods from the dataset). The 8-hour periods were chosen as very few MCPA peaks lasted fewer than 8 hours, and 12-hour durations were chosen as this is usually the maximum shutdown the Derg WTW can handle for ammonia avoidance. The scenarios were:

(1) Discharge rising (+dQ/dt) and above 9.3 $m^3\ s^{-1}$ (median discharge over 3 years),
(2) Discharge rising (+dQ/dt) at a rate exceeding 0.8 $m^3\ s^{-1}\ h^{-1}$ (rapid increase in discharge),
(3) Discharge rising (+dQ/dt) and above 2.0 $m^3\ s^{-1}$ (90th percentile discharge over 3 years) where the five-day antecedent SMD was above 5.0 mm (dry ground conditions for moderately-drained soils),
(4) Conditions (a) where river discharges were rising (+dQ/dt) and above 9.3 $m^3\ s^{-1}$ (median discharge over 3 years) or (b) where discharge exceeded 2.0 $m^3\ s^{-1}$ and the five day antecedent SMD was above 20 mm (very dry ground conditions)
(5) Discharge rising (+dQ/dt) at a rate exceeding 0.8 $m^3\ s^{-1}\ h^{-1}$ (rapid increase in discharge) and 24 hour antecedent discharge was less than 21.1 $m^3\ s^{-1}$ (excluding highest 20% of discharges, which dilute concentrations) where both conditions were met for 3 hours or more.

In all cases, the simulated abstraction shutdown was started in the first hour after the conditions for that scenario ceased to be met as peak MCPA concentrations tended to occur after the discharge peak was reached. The scenarios were assessed on their ability to reduce overall MCPA concentration intake and to avoid intake of concentrations above 0.1 μg L^{-1} (the DWD limit for a single pesticide in drinking water), 0.5 μg L^{-1} (the DWD limit for total pesticides in drinking water) and 0.9 μg L^{-1} (a concentration over which treatment could not reasonably reduce concentrations to less than 0.1 μg L^{-1} assuming a best-case scenario treatment performance removing 80–95% of MCPA). The practicalities associated with these scenarios were evaluated.

3. Results

3.1. Spatial water quality and land use assessment

A total of 143 samples were analysed from the spatial sampling in the Derg catchment, 13 from each location. Median MCPA concentrations at all spatial locations were below the drinking water limit of 0.1 μg L^{-1}, with the highest median concentrations observed at D6 and D8, both on the Mourne Beg River (Table 1). However, across all sampling locations, 26 samples (18.2%) contained more than 0.1 μg L^{-1} of MCPA and seven

(4.9%) contained over 0.5 μg L^{-1} of MCPA, indicating that the quantity of this herbicide alone could exceed the maximum regulatory threshold for the sum of all pesticides. The highest MCPA concentration detected at any location was 8.97 μg L^{-1}, which was on 5th June 2018 at D9 (Fig. 2), a small tributary that entered the main river at the confluence of the River Derg and Mourne Beg River. D10, situated on the main River Derg just upstream of the temporal monitoring location (and abstraction point), had the most samples above 0.1 μg L^{-1} and the number of samples exceeding 0.1 μg L^{-1} increased with distance from the headwaters (Table 1).

The collation of land use types in each sub-catchment are summarised in Table 1 and show an increase in proportions of agricultural land and Improved Grassland from the headwaters to the abstraction point. Strong linear relationships between the median concentrations and sub-catchment land use characteristics were revealed. Median MCPA concentrations were positively correlated to the percentage of agricultural land upstream of each sampling point ($r = 0.71$, $p < 0.02$), irrespective of land use. When agricultural land use was categorised, the percentage that was Improved Grassland (0–54.97% of agricultural land) in a sub-catchment was a significant predictor of the median MCPA concentration ($r = 0.86$, $p < 0.001$). There was also a strong negative correlation between median MCPA concentrations and percentage area of Rough Grazing ($r = -0.85$, $p < 0.001$). Extensive Grazing and Arable were positively correlated but not significantly ($r = 0.42$ and $r = 0.29$; $p > 0.1$ and $p > 0.3$, respectively). At least four samples from each location contained MCPA above the LOD (0.0005 μg L^{-1}), demonstrating the widespread nature of MCPA presence throughout the catchment.

3.2. River discharge and SMD

Long-term mean river discharge (1975–2018) recorded at Castlederg hydrometric station was 14.52 m^3 s^{-1}, with 5th and 95th percentile discharges of 49.71 m^3 s^{-1} and 0.98 m^3 s^{-1}, respectively, and a base flow index of 0.32 (NRFA, 2018). Over the year of temporal sampling (2018–19), the mean discharge was 13.60 m^3 s^{-1}, and the 5th and 95th percentile discharges were 48.19 m^3 s^{-1} and 1.08 m^3 s^{-1}, respectively. The 2018 annual rainfall of 1100 mm was similar to the annual long-term average (LTA) rainfall of 1076 mm at the Malin Head synoptic station (1981–2010). However, rainfall during May, June and July was lower in 2018 (41.5 mm, 51.1 mm and 60.3 mm, respectively) compared to the LTA (56.9 mm, 69.1 mm and 76.8 mm) (Met Éireann, 2020). Similarly, mean summer temperatures were higher than average (11.7 °C, 13.5 °C and 14.9 °C, respectively, for May, June and July, relative to the LTA of 10.5 °C, 12.7 °C and 14.5 °C) and ground conditions were drier – SMD for moderately drained soils was 28 mm (range: 12–44 mm) in May–August 2018, compared to 11 mm (range: −1–21 mm) in May–August 2019.

3.3. Temporal monitoring and abstraction shutdown scenarios

In total, 999 samples from the Derg catchment were analysed for MCPA during the temporal monitoring period. In contrast to the spatial data, MCPA was detected in all samples, with concentrations spanning three orders of magnitude. The highest MCPA concentration was 4.33 μg L^{-1}, whilst the lowest was 0.0019 μg L^{-1}, nearly four times higher than the LOD. Whilst the median MCPA concentration over the full year of sampling was 0.034 μg L^{-1}, the mean was 0.151 μg L^{-1}. The majority of high MCPA concentrations occurred in May, June and September 2018, although concentrations over 0.1 μg L^{-1} occurred frequently throughout spring, summer and autumn (Fig. 3). Between 30th November 2018 and 3rd April 2019, all measured concentrations were below 0.1 μg L^{-1}, with the median concentration for this period being 0.0085 μg L^{-1} (mean was 0.014 μg L^{-1}). However, in the first week of March 2019, MCPA concentrations reached 0.096 μg L^{-1} (Fig. 3). Overall, MCPA exceeded 0.1 μg L^{-1} in 25.1% of the samples analysed (Fig. 3). Whilst the majority of those samples contained between 0.1 μg L^{-1} and 0.5 μg L^{-1} of MCPA, there were 65 (6.5%) samples containing more than 0.5 μg L^{-1} of MCPA, with 13 (1.3%) containing over 2 μg L^{-1} of MCPA. Considering only the period when MCPA can be applied (March to September), 34.3% of the samples exceeded 0.1 μg L^{-1}, with all samples exceeding 0.5 μg L^{-1} falling within this period. MCPA concentrations exceeded 0.1 μg L^{-1} in 34.7% of the samples during the period used for the simulated abstraction shutdowns.

For the majority of the time, increases in river discharge corresponded to increases in MCPA concentrations (Fig. 3), with the peaks in river discharge often occurring before the peaks in herbicide concentrations. Seventy-seven percent of MCPA concentrations over 0.1 μg L^{-1} occurred during the falling limb of the hydrograph, although this may have been an artefact of rapidly increasing concentrations occurring between the 7-hourly sampling occasions that were unsampled. However, the magnitude of the increase in river discharge did not necessarily match the magnitude of the increase in MCPA, with some relatively small discharge increases triggering high concentrations of pesticide. Probably the most notable of these was the eight-fold increase (0.79 to 6.29 m^3 s^{-1}) in discharge on 20th July 2018, which led to a thirty-fold increase in MCPA in a 14 hour period (Fig. 3). Longer durations between rainfall events, which would cause SMD to rise, appear to influence the size of the pesticide peak more than the quantity of rainfall (mm) associated with an individual event. However, there were some very high MCPA concentrations that were recorded during periods when the river discharge remained constant or was decreasing, indicating that not all herbicide loss was caused by rainfall-generated runoff.

The simulated abstraction shutdown modelling resulted in a range of outcomes, both for total length of shutdown and time when water containing high MCPA concentrations was abstracted. Whilst the simulated 12-hour shutdowns all performed better at MCPA reduction than the 8-hour shutdowns of the same scenario, as expected, the 8-hour shutdown for Scenario 3 outperformed the 12-hour for Scenario 5 in terms of reducing intake of the highest MCPA concentrations and the 8-hour shutdown for Scenario 4 outperformed the 12-hour shutdown for both Scenario 2 and 5 (Table 2).

The reduction in annual mean MCPA concentration ranged from 9.8% (8-hour shutdowns Scenario 5) to 24.4% (12-hour shutdowns Scenario 4) (Table 2). Scenario 4 also had the greatest reduction in the number of hours MCPA concentrations exceeded 0.1 μg L^{-1}, 0.5 μg L^{-1} and 0.9 μg L^{-1} (31.1%, 40.2% and 41.3%, respectively) but this required the intake to be shut down for 9.3% of the year (Table 2). Additionally, the length of the longest shutdown was 36 hours. Scenario 5 (for both lengths of shutdown) produced the smallest reduction in both annual average MCPA concentration and intake of concentrations above 0.1 μg L^{-1} and 0.5 μg L^{-1} (Table 2). However, the number of hours that intake concentrations exceeded 0.9 μg L^{-1} was the same as for Scenario 1 when comparing the 8-hour shutdowns and lower than Scenario 1 and only 3 hours more than Scenario 2 when comparing the 12-hour shutdowns (Table 2), suggesting a more targeted approach. Moreover, Scenario 5 was the only scenario in which none of the shutdowns overlapped (hence producing maximum shutdowns of just 8 and 12 hours, respectively), had the fewest shutdown triggers, the shortest total length of shutdowns and the fewest unnecessary shutdown events (i.e. when none of the excluded concentrations exceeded 0.1 μg L^{-1}).

4. Discussion

Around the world, MCPA has been detected in rivers, lakes and groundwater (Bach and Frede, 2012; Birch et al., 2015; Environment Canada, 2011; Köck-Schulmeyer et al., 2014; Kreuger, 1998; Lindahl et al., 2005; Loos et al., 2017; Lundbergh et al., 1995; McManus et al., 2017; Palma et al., 2014; Rawn et al., 1999; Rippy et al., 2017; Schreiner et al., 2016). However, the maximum sampling frequency did not exceed daily in any of these studies (although Lindahl et al.

Table 1
The number of samples (out of 13) containing more than 0.1 μg L^{-1} of MCPA and the median MCPA concentration for each location in the spatial sampling program as shown in Fig. 1. The percentage of agricultural land and percentage of those areas under each agricultural land use category in each sub-catchment are also shown.

Site code	No. samples > 0.1 μg L^{-1}	Median conc., μg L^{-1}	Agricultural land in sub-catchment, %	Agricultural land categories			
				Improved grassland, %	Extensive grassland, %	Rough grazing, %	Arable, %
LM	0	0.0010	2.91	0	0	100	0
D1	0	0.0003	1.95	0	0	100	0
D2	0	0.0003	10.57	0.79	0.23	98.98	0
D3	1	0.0106	10.07	7.43	0	92.57	0
D4	3	0.0099	42.64	16.96	0.92	82.12	0
D5	3	0.0410	32.15	30.01	0.90	69.03	0.06
D6	3	0.0568	31.25	29.10	0.09	70.82	0
D7	3	0.0352	36.62	39.70	1.47	58.78	0.05
D8	4	0.0560	36.30	34.41	0.11	65.48	0
D9	4	0.0507	78.84	54.97	6.27	38.76	0
D10	5	0.0426	47.57	51.08	2.06	46.65	0.21

(2005) used 10-minute to hourly sub-samples composited into weekly and bi-weekly samples) and the majority did not sample regularly, if at all, over winter. There are no published studies that combine the spatial distribution of MCPA throughout a catchment with high resolution MCPA monitoring. This makes the data presented in this study novel in contaminant monitoring of surface waters. It demonstrates the scale of the problem of MCPA contamination to watercourses in that, whilst high concentrations can be very transient, they can also be much higher than the drinking water limits – and, indeed, than the environmental quality standards based on annual average MCPA concentrations for some EU countries (range: 0.01–1.6 μg L^{-1}; European Communities, 2012) – and that MCPA contamination exists year-round. The spatio-temporal framework used here is equally valid for other contaminants where pollution patterns are dependent on catchment land use and hydrological processes. As methods of pollutant quantification improve, especially the ability to monitor at a higher temporal resolution, contaminant risk assessment and, ultimately, pollution mitigation are both likely to be more effective (Rode et al., 2016).

The insights provided by the spatial sampling campaign demonstrate the prevalence of MCPA throughout a typical Irish surface water source catchment, with low concentrations even observed in a headwater sub-catchment (D1) containing no Improved Grassland and having only 1.9% agricultural land (Fig. 2; Table 1). Rainfall data did indicate that May–July 2018 was drier than average, and so some careful consideration of spatial MCPA concentrations may be required. For example, as rushes tend to proliferate in damp soils, and dry periods provide an opportunity for farmers to access normally non-trafficable areas with spraying machinery, the drier weather may have encouraged MCPA applications. Conversely, the lower rainfall and higher temperatures may have reduced losses through fewer storm runoff events. This will need an analysis of longer term data to examine interannual variability from this and other surface water source catchments.

Nevertheless, the significant positive correlation between higher concentrations of MCPA and the proportion of Improved Grassland provides a strong evidence base for spatially optimising catchment-based mitigation solutions. These solutions may include farmer led initiatives, such as alternative rush treatments (e.g. Backshall et al., 2001), or policy led initiatives, such as valuing the wider functions that wetter land (i.e. prone to rush growth) can provide to society (Bateman and Balmford, 2018). Implicating Improved Grassland with higher MCPA occurrences using these discrete spatial data will, however, require further validation using a higher-frequency temporal monitoring approach in river

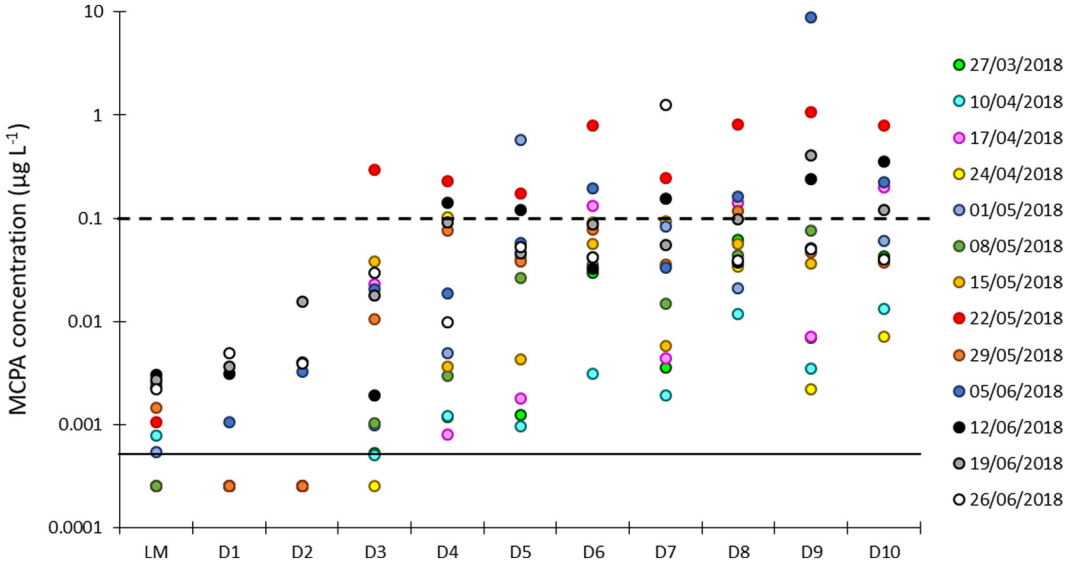

Fig. 2. MCPA concentrations at each spatial sampling location for each of the 13 sampling occasions (as shown in Fig. 1). The drinking water limit for treated water is shown for reference as a dashed line and the LOD is shown as a solid line (points below this line were determined as below LOD and have been included as half LOD concentrations). Note that MCPA concentrations are shown on a log scale.

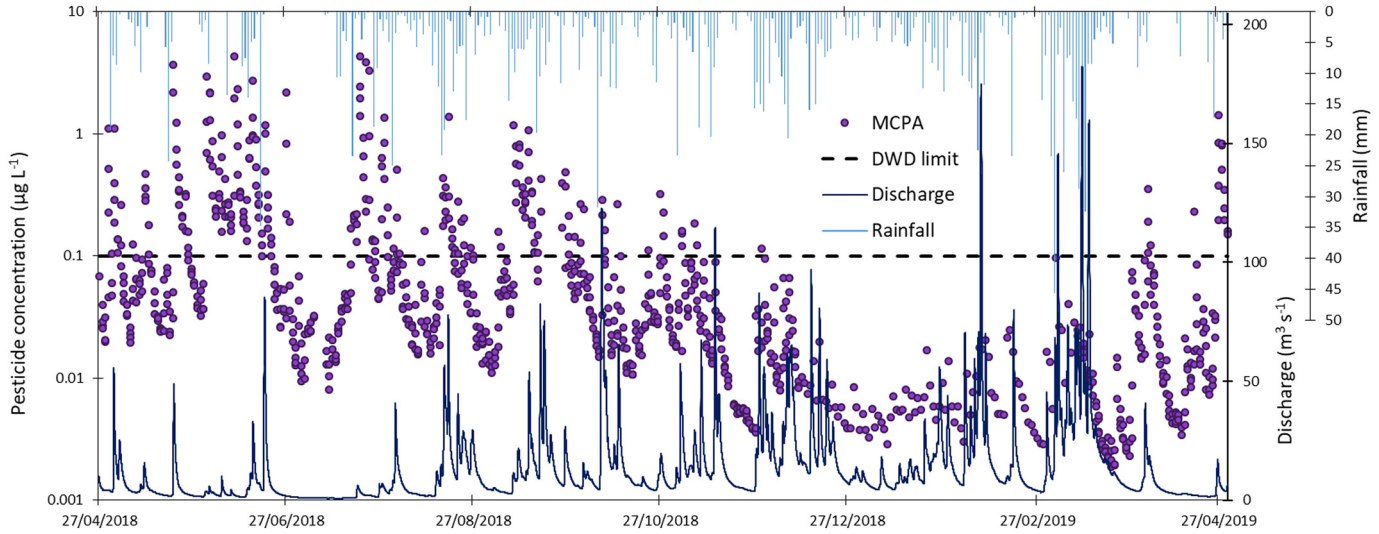

Fig. 3. Concentration of MCPA in the River Derg at the catchment outlet and abstraction point, the River Derg discharge 7 km upstream of the monitoring point at Castlederg, and Malin Head daily rainfall between 27/04/18 and 30/04/19. The single pesticide drinking water limit for treated water is shown for reference as a dashed line. Note that the pesticide concentrations are shown on a log scale on the left y-axis.

locations with other major land uses. This will be to ensure that the spatial concentration data are fully reflective of MCPA loss linked to specific land uses and not a legacy of specific pathways (as the importance of these may change during different hydrological conditions).

Elsewhere, spatial sampling of a Sydney estuary catchment by Birch et al. (2015) detected MCPA at 23 of their 30 sites. The pattern of their detections was the opposite to that in the Derg catchment in that the highest concentrations of MCPA occurred in the upper reaches of the Sydney estuary catchment (Birch et al., 2015). Although Birch et al. (2015) linked the distribution of another pesticide in their study to numbers of parks and golf courses, these were more prevalent in the lower catchment: they suggested that MCPA in the upper catchment was due to reduced flushing times further up the catchment. Loos et al. (2017) found that MCPA concentrations varied by more than an order of magnitude across parts of the Danube River catchment (71 samples) but did not comment on any association with land use nor repeat samples throughout the season.

The method of temporal sampling used here was based on a principle that a higher-resolution approach, especially for highly mobile contaminants, provides clearer insights of pollution patterns and enables better analysis potential to understand pollution transfer processes. This utility is reviewed, for example, by Rode et al. (2016) and demonstrated, for example, by Bowes et al. (2015) and Cassidy et al. (2018) for nutrient pollution. However, there are passive sampling methods that can capture the range of hydrological conditions in a single time-weighted pollution concentration over a deployment period and these have been applied to MCPA detection in a large river catchment (Townsend et al., 2018). Nevertheless, the discrete approach used in this study provides new insights and also enables scenario testing that could not be achieved with passive sampling approaches, due to the highly transient nature of the MCPA peaks.

One important feature of the temporal MCPA data from the Derg catchment was that concentrations never fell below the LOD, even during the winter months (Fig. 3) when spraying was highly unlikely to occur. The frequent and sometimes heavy rainfall in the Derg was expected to promote dilution and flushing of MCPA from the catchment system, resulting in concentrations rapidly falling below the LOD during the winter months. The fact that this did not occur suggests that further investigation is required into the conditions under which MCPA is stored and degrades in this type of environment. Indeed, the majority

Table 2
Results of the simulations for 8-hour and 12-hour shutdowns for five scenarios. Scenario conditions were: (1) positive dQ/dt (rising discharge) and discharge >9.3 $m^3 s^{-1}$, (2) dQ/dt >0.8 $m^3 s^{-1} h^{-1}$, (3) positive dQ/dt, discharge >2.0 $m^3 s^{-1}$ and five day antecedent SMD >5.0 mm, (4) either positive dQ/dt and discharge >9.3 $m^3 s^{-1}$ or discharge >2.0 $m^3 s^{-1}$ and five day antecedent SMD >20 mm, and (5) dQ/dt >0.8 $m^3 s^{-1} h^{-1}$ and 24 hour antecedent discharge <21.1 $m^3 s^{-1}$ where both conditions were met for 3 hours or more. The number of unnecessary shutdown events is where none of the excluded concentrations exceeded 0.1 µg L^{-1}. Length of longest shutdown is included as shutdown events overlapped on occasion creating longer total shutdowns than the 8-hour or 12-hour periods used.

	Scenario 1 (8 h)	Scenario 1 (12 h)	Scenario 2 (8 h)	Scenario 2 (12 h)	Scenario 3 (8 h)	Scenario 3 (12 h)	Scenario 4 (8 h)	Scenario 4 (12 h)	Scenario 5 (8 h)	Scenario 5 (12 h)
No. shutdown triggers	54	54	46	46	64	64	76	76	31	31
No. unnecessary shutdown events	12	10	5	4	23	21	16	12	3	2
No. hours shutdown (% reduction intake)	409 (4.6%)	593 (6.7%)	345 (3.9%)	504 (5.7%)	472 (5.4%)	669 (7.6%)	569 (6.5%)	815 (9.3%)	248 (2.8%)	372 (4.2%)
Length of longest shutdown (hours)	12	25	18	23	19	36	16	36	8	12
Average MCPA conc. (and % reduction)	0.114 (10.3%)	0.109 (14.0%)	0.113 (11.1%)	0.107 (15.9%)	0.109 (14.3%)	0.101 (20.6%)	0.105 (17.1%)	0.096 (24.4%)	0.115 (9.8%)	0.109 (14.3%)
No. of hours (and % reduction) MCPA >0.1 µg L^{-1}	1644 (15.5%)	1517 (22.0%)	1665 (14.4%)	1537 (21.0%)	1661 (14.6%)	1538 (21.0%)	1517 (22.0%)	1341 (31.1%)	1738 (10.7%)	1632 (16.1%)
No. of hours (and % reduction) MCPA >0.5 µg L^{-1}	388 (17.4%)	358 (23.8%)	388 (17.4%)	351 (25.3%)	342 (27.2%)	290 (38.3%)	333 (29.1%)	281 (40.2%)	399 (15.1%)	359 (23.6%)
No. of hours (and % reduction) MCPA >0.9 µg L^{-1}	196 (18.3%)	181 (24.6%)	193 (19.6%)	175 (27.1%)	173 (27.9%)	143 (40.4%)	171 (28.8%)	141 (41.3%)	196 (18.3%)	178 (25.8%)

of studies on the degradation and persistence of MCPA have been conducted in soils with low organic matter content (see Morton et al. (2019) and Paszko et al. (2016) for reviews on the topic), whereas soils in the Derg catchment are mainly highly organic and prone to waterlogging. Higher organic carbon contents have been shown to increase the retention of MCPA in the soil by increasing its sorption potential (Hiller et al., 2012). In addition, waterlogging decreases the amount of oxygen available to pesticide-degrading microbes (Vink and van der Zee, 1997) and may also reduce the mobility of MCPA by increasing its sorption (López-Piñeiro et al., 2019). Therefore, in the scenarios when these conditions are combined, there is likely to be an increased degradation time of MCPA (López-Piñeiro et al., 2019) and, in addition to immediate incidental losses, a secondary slower passage to watercourses, hence it can be detectable beyond published degradation times.

While this persistence has implications beyond water treatment and may have hitherto not been investigated, the high MCPA concentrations and high proportion of concentrations over 0.1 μg L^{-1} are particularly noteworthy. Whilst MCPA concentrations greater than 4.33 μg L^{-1} have been found in Irish rivers (EPA, 2017b), the extent of the problem was not previously evident. The 25% of temporal samples above the EU drinking water limit represents a significant challenge to drinking water utilities abstracting from the River Derg and similar surface water source catchments. Although the World Health Organisation recommends a maximum value for MCPA in drinking water twenty times that of current DWD thresholds (WHO, 2017), little is known about the toxicological effects of MCPA to humans long-term, nor to aquatic organisms. Additionally, almost nothing is known about the interaction of MCPA with other compounds and the toxicological effects of this – this may be particularly problematic as MCPA is often sold in a mixture with other herbicides (for a review of MCPA (eco)toxicity, see Morton et al., 2019). These considerations and pesticide thresholds are likely to receive further focus in UK source water catchments as the UK reviews EU Directives post-Brexit and this will be particularly challenging on the new EU frontier in Northern Ireland if new thresholds are considered (Hendry, 2018). Considering that data in this study implicate Improved Grassland in greater losses of MCPA (notwithstanding the need for further temporal data assessments), a revaluing of this land use function in source water catchments post-Brexit could include a sustainability debate on what society can gain from optimising food production. In this regard, conversations should include what other functions wetter soils and landscapes can provide for society such as water purification and regulation, carbon sequestration and biodiversity (e.g. Schulte et al., 2019). Here, at least, Rough Grazing could be a more optimum fit.

4.1. Critical periods of concern for drinking water utilities

The simulated shutdowns, tested here, demonstrate that relatively simple use of discharge and modelled SMD conditions can identify periods when abstractions could be shut down to avoid intake of some of the high concentrations of MCPA. However, the choice of a method to avoid high MCPA concentrations would depend on individual considerations for each WTW and every scenario represents trade-offs for the water utility. For example, to minimise intake of high MCPA concentrations, the 12-hour shutdowns under Scenario 4 would be the best choice (Table 2). This would only be possible for a WTW with a minimum treated water storage capacity of three days (to account for the longest shutdowns of 36 hours, which were sometimes followed by another shutdown within a day) and the ability to abstract and treat surface water rapidly between shutdowns. Alternatively, another water source would have to be substituted, either from a different river or using groundwater abstractions, for example, to temporarily bridge the shutdown periods. For WTWs with limited treated water storage capacity, a scenario that minimised the length of each individual shutdown whilst providing more targeted shutdowns to avoid the highest MCPA concentrations, such as Scenario 5, may prove more beneficial.

These abstraction shutdown scenarios represent an important proxy for 'now-casting' pollutants of concern where there is no current method for real-time data monitoring. Here, the shutdown scenarios to minimise MCPA treatment use a limited number of hydrometeorological variables and provide an early warning system as the rates of river discharge change are situated several kilometres upstream from the abstraction point. Further data which include interannual variation of MCPA concentrations, are likely to yield more conclusive relationships with river discharge, SMD and perhaps rainfall, and allow for fine-tuning of conditions to enable greater reduction of MCPA intake without negatively impacting the supply of drinking water. Deliberate or accidental losses, unrelated to hydrological drivers, will continue to require stakeholder engagement and education, to improve pesticide handling and eliminate cases of poor disposal and spillages within drinking water catchments.

5. Conclusions

The herbicide MCPA is highly mobile following application on agricultural land and is susceptible to losses in rainfall-runoff events. Assessing the magnitude of these incidental losses required an enhanced sampling approach, which was undertaken here on a spatial and temporal scale to help inform mitigation strategies for catchment-based and water treatment solutions. This research found in an exemplar 384 km^2 surface source water catchment that:

- In enhanced spatial sampling across 11 locations ($n = 143$), 18% of samples contained MCPA over the 0.1 μg L^{-1} (and 5% over the 0.5 μg L^{-1}) threshold. The distribution of MCPA concentrations was highly positively correlated with Improved Grassland ($r = 0.86$) and highly negatively correlated to Rough Grazing ($r = -0.85$). This indicates that Improved Grassland (up to 55% of sub-catchment agricultural land area) is the main land use contributor to MCPA loss, and should be targeted for catchment based mitigation solutions. Further enhanced temporal data will be required to validate this finding.
- At the catchment outlet and source water abstraction point, 25% of the 999 samples from a year-long enhanced (7-hourly to daily) temporal monitoring programme contained more than 0.1 μg L^{-1} of MCPA (and 6.5% contained more than 0.5 μg L^{-1}). High MCPA concentrations were mostly related to high river discharges with 77% of all samples over the 0.1 μg L^{-1} threshold found on the falling limbs of storm hydrographs – conditions that could be targeted by water utility industries. Furthermore, MCPA concentrations never fell below the limits of detection (0.0005 μg L^{-1}), suggesting persistence in the soil-water system, and secondary pathways beyond the more immediate incidental rainfall-runoff pathways.
- In the absence of direct real-time pesticide monitoring, scenario testing undertaken using the enhanced temporal data to predict optimum periods of abstraction shutdown, resulted in potential 12-hour abstraction shutdowns covering of 4.2–9.3% of the April–October period and a potential reduction of 16–31% of MCPA concentrations above the 0.1 μg L^{-1} (and 24–40% over the 0.5 μg L^{-1}) threshold. Abstraction shutdown criteria used seasonal hydrometeorological datasets of river discharge and SMD, both of which could be measured or obtained in near real-time by water utilities. This approach will require fine tuning and be catchment specific but, based on this study, shows potential to benefit drinking water utilities and water quality.

This research demonstrates the benefits of using enhanced monitoring approaches for highly mobile pollutants such as MCPA in source water catchments: benefits to society include reduced burdens for drinking water treatment and supply. However, the results also question the sustainability of certain land uses, in particular where Improved Grassland is competing with drinking water supplies since it appears from data presented here to be the main source of MCPA to water bodies. Identifying ecosystem services, such as water purification (as well as

water regulation, carbon sequestration and biodiversity) from agricultural land uses (such as Rough Grazing), and balancing these against optimising food production is a debate that is urgently required in drinking water source catchments.

CRediT authorship contribution statement

Phoebe A. Morton: Methodology, Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Visualization. **Rachel Cassidy:** Conceptualization, Methodology, Formal analysis, Writing - review & editing, Visualization, Funding acquisition. **Stewart Floyd:** Methodology, Validation, Writing - review & editing. **Donnacha G. Doody:** Conceptualization, Writing - review & editing, Supervision, Funding acquisition. **W. Colin McRoberts:** Conceptualization, Writing - review & editing, Supervision, Funding acquisition. **Philip Jordan:** Conceptualization, Methodology, Investigation, Writing - review & editing, Supervision, Funding acquisition.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.142827.

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