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Quantifying MCPA load pathways at catchment scale using high temporal resolution data

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ABSTRACT

Detection of the agricultural acid herbicide MCPA (2-methyl-4-chlorophenoxyacetic acid) in drinking water source catchments is of growing concern, with economic and environmental implications for water utilities and wider ecosystem services. MCPA is poorly adsorbed to soil and highly mobile in water, but hydrological pathway processes are relatively unknown at the catchment scale and limited by coarse resolution data. This understanding is required to target mitigation measures and to provide a framework to monitor their effectiveness. To address this knowledge gap, this study reports findings from river discharge and synchronous MCPA concentration datasets (continuous 7 hour and with additional hourly sampling during storm events) collected over a 7 month herbicide spraying season. The study was undertaken in a surface (source) water catchment (384 km^2—of which 154 km^2 is agricultural land use) in the cross-border area of Ireland. Combined into loads, and using two pathway separation techniques, the MCPA data were apportioned into event and baseload components and the former was further separated to quantify a quickflow (QF) and other event pathways. Based on the 7 hourly dataset, 85.2 kg (0.22 kg km^{-2} by catchment area, or 0.55 kg km^{-2} by agricultural area) of MCPA was exported from the catchment in 7 months. Of this load, 87.7 % was transported via event flow pathways with 72.0 % transported via surface dominated (QF) pathways. Approximately 12 % of the MCPA load was transported via deep baseflows, indicating a persistence in this delayed pathway, and this was the primary pathway condition monitored in a weekly regulatory sampling programme. However, overall, the data indicated a dominant acute, storm dependent process of incidental MCPA loss during the spraying season. Reducing use and/or implementing extensive surface pathway disconnection measures are the mitigation options with greatest potential, the success of which can only be assessed using high temporal resolution monitoring techniques.

1. Introduction

Meeting food demand through intensive agriculture without further environmental degradation is recognised as a global challenge (Cassman and Grassini, 2020). To meet production targets, for example, pesticide application has become a fundamental component of modern agriculture to maximise yields and to protect crops (Pretty, 2018). However, residual losses of agro-chemicals following application increase ecological and human health risks (Yadav, 2010) when transferred to adjacent water bodies from point and diffuse sources (Malaj et al., 2014). Consequently, vital ecosystem goods and services that are provided by freshwater systems can be compromised (Bunn, 2016) including provision and access to safe drinking water (Swartjes and Van der Aa, 2020).

National and international legislation is designed to counteract potential residual pollutant losses from agricultural chemical applications. For example, the European Union (EU) has implemented statutory policies to protect and secure Member States' water resources. The Water Framework Directive (WFD—OJEC, 2000), Drinking Water Directive (DWD—OJEU, 2015) and other sister directives (also covering European Economic Area states, and transposed into United Kingdom law following departure from the EU) have provided common policy frameworks for water management and environmental protection based on the concept of river basin planning.

Water utilities are required to ensure water supplied to consumers

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Glossary

MCPA	2-methyl-4-chlorophenoxyacetic acid
QF	qucikflow
IF	interflow
eBF	elevated baseflow
BF	baseflow
WFD	Water Framework Directive
DWD	Drinking Water Directive
WTW	water treatment works
FDC	flow duration curve
LMM	Local Minimum Method
LRA	Loadograph Recession Analysis
GUS	Groundwater Ubiquity Score

meets regulatory standards. Treatment to reduce and remove contaminants, including pesticides, is therefore routine and particularly so for supplies derived from surface sources, which may have reduced natural geological filtration. However, conventional flocculation treatment processes may not be efficient in the removal of pesticide compounds and can require an augmented treatment process with expensive granular activated carbon filters (Pirsaheb et al., 2014). Furthermore, pesticide removal planning and efficiency at water treatment works (WTW) is based on data from sparse monitoring, most often on a weekly basis (Behmel et al., 2016) and may not account for high concentrations during storm events, especially in hydrologically responsive (flashy) catchments.

Phenoxyalkanoic acid herbicides have received attention from research and policy communities due to their global distribution, extensive use in agriculture, and mobility (Costa et al., 2013). MCPA (2-methyl-4-chlorophenoxyacetic acid), for example, is a systemic, polar herbicide that is used for post-emergence control of rushes (*Juncus* spp.), and annual and perennial broad-leaved weeds in grasslands and cereal fields (Piwowarczyk and Holden, 2013). Due to its potentially high solubility in water (29.4 g L^{-1} at 20°C) and poor adsorption to the soil matrix (log K_{OC} 1.73 - 2.07) (PPDB, 2021) (but see Oberleitner et al., 2020 for adsorption potential to riverbank materials and seasonal redox boundaries) MCPA is susceptible to mobilisation and transfer to adjacent water bodies by runoff and leaching (Hiller et al., 2010). As a result, the compound can be widespread in the water environment and has been detected in surface water (Sandin et al., 2018), groundwater (McManus et al., 2017), and drinking water supplies (Donald et al., 2007; EPA, 2019).

MCPA degrades in the environment following application and Hornsby et al. (1996) reports that the degradation half-life (DT_{50}) of MCPA is 7-60 days in oxic environments. PPDB (2021) reports a typical DT_{50} of 24 days in soil and 13.5 days in the water phase. Thorstensen and Lode (2001) found MCPA half-lives of 4 days in organic soils and 16 days in mineral soils. However, seasonal usage and rainfall events largely influence MCPA transfers from land with incidental losses occurring before the compound has fully degraded (Müller et al., 2003). Furthermore, it is likely the degradation rate of MCPA slows once in anoxic sub-surface environments such as groundwater and sediments (McManus et al., 2017; Gamhewage et al., 2019). Correspondingly, concentrations of MCPA in water bodies can frequently be high and place pressures on WTWs not to exceed the maximum permissible limits for treated drinking water of 0.1 μg L^{-1} for a single pesticide compound, and 0.5 μg L^{-1} for the sum of total pesticide compounds (DWD—OJEU, 2015). In Ireland, for example, where MCPA is widely used to control *Juncus* (spp.) on marginal and improved agricultural land on poorly drained soils, a comprehensive review of water quality from 2013-2018 noted that 80 of 144 rivers (55.6 %) monitored for MCPA recorded positive detections of the compound (EPA, 2019). Furthermore, 42 drinking water supplies had exceedances above the limit of 0.1 μg L^{-1} and MCPA accounted for 75 % of these failures (EPA, 2019).

Despite its widespread use and growing detection in water bodies, MCPA transport mechanisms following mobilisation, its biological impacts, and its synergistic interactions with other pesticides and nutrients remain relatively unknown (Morton et al., 2020). Indeed, in a wide-ranging review, Morton et al. (2020) identified major knowledge gaps in terms of the dynamics, apportioning and persistence of MCPA transfers via surface and sub-surface hydrological pathways, and progress has been hindered by the limited insights provided by a paucity of monitoring data (e.g., Lefrancq et al., 2017). It follows that for highly soluble and mobile pesticides such as MCPA, which are susceptible to transfer during rainfall events, a higher resolution sampling approach is required. This type of empirical research has precedence at lysimeter (Bergström, 1990), and plot scale (Ulrich et al., 2013). However, beyond catchment modelling approaches to estimate pesticide transport routes (e.g. Holvoet et al., 2007), other catchment scale research has focussed more on the extent and pattern of pesticide losses (e.g. Blanchoud et al., 2004) rather than using data to assess flow pathway dynamics. An exception is reported in Lefrancq et al. (2017) where high temporal resolution sampling of pesticides in storm events in a very small (2.2ha) catchment indicated a dominant overland flow pathway. For other surface water contaminants, such as nutrients, using high temporal resolution catchment scale datasets of synchronous river discharge and concentration has demonstrated that phosphorus (P) pathways could be apportioned from the recession characteristics of P loads during storm events (Mellander et al., 2012). This mass apportionment approach has subsequently been used in agricultural catchment studies to understand the dynamics and magnitude of P loads delivered via dominant pathways, and to monitor the effect of agri-environmental policies on those magnitudes (Murphy et al., 2015).

Therefore, this study was based on a recognised knowledge gap and an empirical method to apportion pesticide pollution pathways from higher resolution synchronous river discharge and chemical concentration data. The specific aim was to provide a deeper understanding of MCPA hydrological pathways at the catchment scale. Using a high temporal sampling resolution to obtain datasets of synchronous river discharge and MCPA concentration, and in combination with other secondary datasets, the objectives were to:

1 Investigate MCPA concentrations and load dynamics in the river during a spraying season.
2 Using a mass apportionment approach, quantify catchment scale MCPA load and concentration pathways.

2. Methods and Materials

2.1. Study Area

The cross-border River Derg catchment (384 km^2; elevation 32-450 m) is located in the north-west of the island of Ireland. Two principal tributaries start from Lough Derg and Lough Mourne and flow in an easterly direction. For this investigation, the catchment outlet was delineated at the Northern Ireland Water (NI Water) WTW abstraction point, approximately 7 km east of Castlederg in Northern Ireland (Figure 1). The Derg river joins the Strule, becoming the Mourne river, and joins the wider Foyle catchment flowing north into the Foyle estuary and the North Atlantic Ocean. The Derg catchment has developed on a post-glacial landscape with rolling hills and a wide valley (maximum width approximately 18 km). River channels are characterised by cascade step pools and pool riffle glide type sections. Catchment geology is comprised of metamorphosed schistose sandstone, shale, limestone and basic igneous intrusive and extrusive rock overlain with extensive glacial till, sands, gravels and alluvium in the channel valleys (NRFA, 2022). Aquifers are poorly productive. Soils are naturally poorly drained on surface-water gleys and, with drained peat areas, high rainfall and

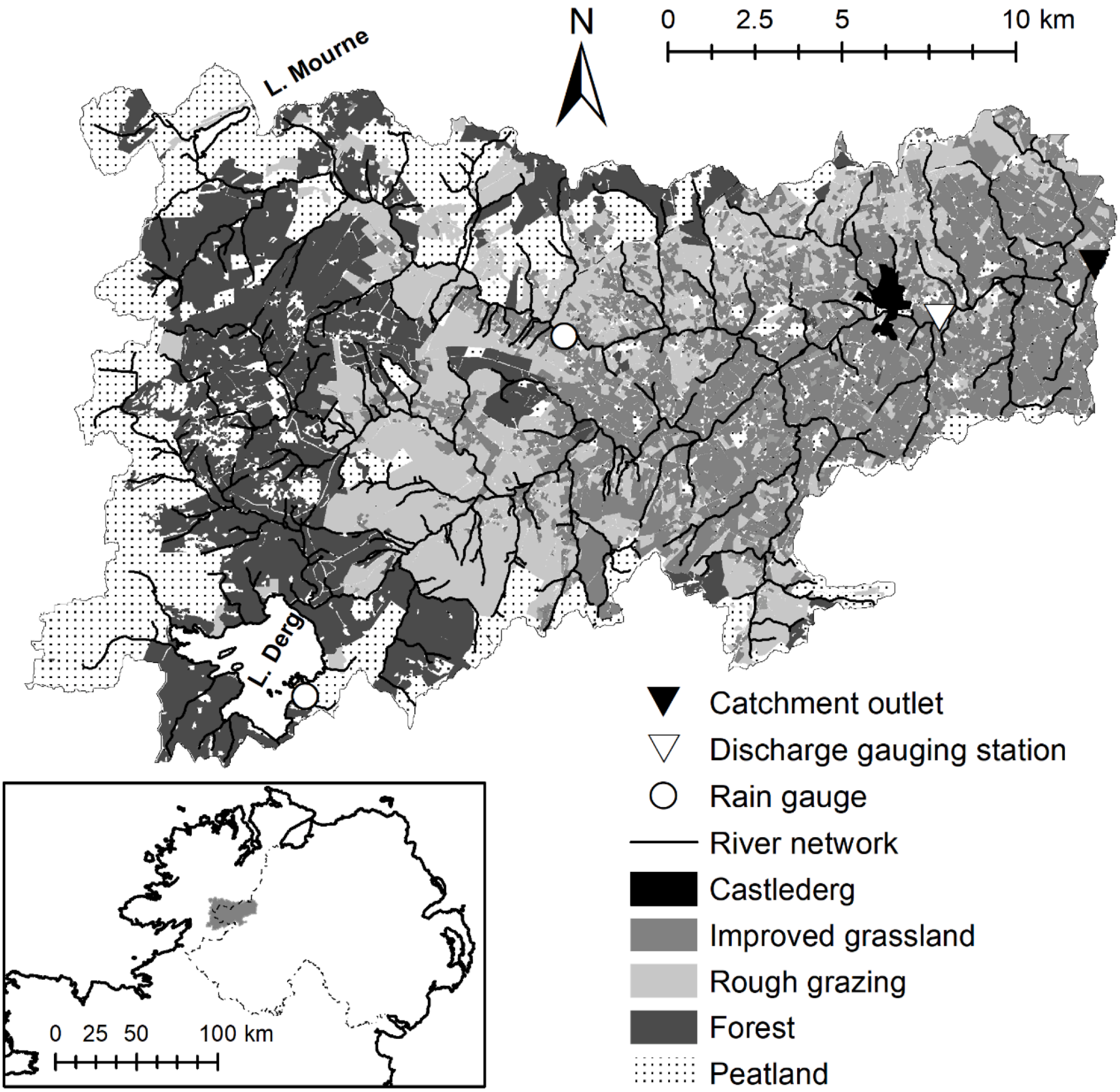


Figure 1. Map of the River Derg catchment area in the Irish border region (inset) showing major land uses and the catchment outlet at 384km^2. Water is abstracted at this point for treatment and domestic water supply.

valley gradients, result in the catchment contributing to flashy storm hydrology (Smyth, 2007). Extensive coniferous forest plantations, peatlands, scrubby wet woodland, and open moorland dominate the western headwaters and upland areas. Rough, extensive, and improved grassland land uses transition from west to east in the mid to lower reaches of the catchment. This transition is typical for the island of Ireland and elsewhere in NW Europe where upland land uses are different from the lowlands in post-glacial landscapes, and where runoff is influenced by organic, heavy and often drained soils, and Atlantic weather systems (Ulén et al., 2007).

Data on individual farm MCPA use were not available in the Derg catchment and so any measured exports are only contextualised with national statistics for application to grasslands and catchment assumptions on inputs. For example, total annual MCPA load to grass and fodder crops in Northern Ireland is estimated to be 3.81 kg km^{-2}, and in the Republic of Ireland 2.39 kg km^{-2} (DAFM, 2017; Lavery et al., 2017). Using published MCPA input loads for the main grassland uses in each jurisdiction, and collated to the majority improved and rough grazing grassland classes (Morton et al., 2021), approximate area-based annual MCPA inputs (149.3 km^2 in NI, and 5.1 km^2 in RoI—154.4 km^2 in total) for the Derg catchment were estimated to be 5.38 kg km^{-2} (Supplementary Material SM1).

2.2. *Hydrometry and hydrological pathways*

Stage height (m) and rated discharge data were measured at 15 minute intervals at the Department for Infrastructure (DfI) hydrometric station at Castlederg (335 km^2). For this investigation, data for the hydrological year 2018-2019 were used and also compared with longer term data. Stage height was also measured downstream at the abstraction point (384 km^2) using a water level logger (Level Troll 500, In-Situ, USA). In the absence of a rating equation for this downstream hydrometric station it was assumed that discharge was approximately similar to the upstream station following Morton et al. (2021). However, to provide reference points for the extra 49 km^2, area-based estimates of river discharge were taken from the upstream gauging station and a downstream station (1,844 km^2) using long-term records (SM2). These reference points were used as models to account for potential underestimates of total discharges, total loads, and pathway loads at the 384 km^2 site due to the use of upstream hydrological data. Furthermore, thirty storm event water levels (May - Oct 2018) were compared at both 335 km^2 and 384 km^2 stations to establish the time lag peaks between each. The average time between water level peaks was 105 minutes (range 75-240 minutes, ± standard error 6.38 minutes) and so the upstream discharge data were adjusted as a proxy for downstream station instantaneous discharge (albeit with the uncertainty of the extra 49 km^2—SM2). Rainfall (mm) data were collected by a tipping bucket rain gauge (ARG-100, EML, UK) and logged at 15 minute intervals (TGP-4901, Tinytag, UK), 15 km from the WTW abstraction point (in the approximate centre of the catchment). These were compared with long-term data from a weather station at Lough Derg (Met Éireann (2020), station number 1042).

To assess the hydrological response of the river during the study period, deviations from long term mean daily discharges (10 and 5 year) were investigated. Discharge data were obtained from the hydrometric station at Castlederg over the three timescales (10 yr, 5 yr, sampling year). These were ranked, and percentile discharge ranges from each timescale were extracted (Q1-Q99) for flow duration curves (FDC) and seasonal comparisons. Following Kolmogorov–Smirnov tests of normality, Kruskal-Wallis tests (SPSS v26—IBM corp., 2019) were conducted on the FDC data to test for differences ($p < 0.05$) between each period (Ssegane et al., 2012).

Turbidity was measured at the WTW abstraction point every hour using a water quality sonde (C3 Submersible Fluorometer, Turner Designs, USA). These data were intended to provide an independent reference point between event and baseflow hydrological pathway conditions during storm discharges. Despite MCPA having a low affinity with particle bound transport (PPDB, 2021), it was assumed that a change point in turbidity recessions would occur between more energetic event flow pathways and those at baseflow as post-storm conditions establish (Mellander et al., 2012). Moreover, hydrological flow paths were further conceptualised using the terminology adapted from Archbold et al. (2010). Quickflow (QF) from overland flow and near surface sources, interflow (IF) as lateral flow through the soil profile, and elevated baseflow (eBF) as a transition zone to groundwater, were assumed to be components of event discharges in pathways from the surface to shallow sub-surface. Baseflow (BF) was assumed to be from deeper aquifer groundwater sources, sustaining river flows between storm events and low rainfall periods (Kelly et al., 2019).

2.3. *MCPA Monitoring*

To monitor MCPA concentrations in the river, a 24/7 (one 350 ml sample every 7 hours, 24 samples per week) monitoring regime was implemented at the WTW abstraction point following the method described by Halliday et al. (2012) and applied by Morton et al. (2021). To complement these data and to characterise hydrological event pathways of MCPA, further samples were collected hourly during storms. The monitoring period encompassed a 7 month spraying season from 1st April to 31st October 2019. For each sampling arrangement automatic refrigerated samplers (6712, ISCO, USA with silicone pump tubing and vinyl intake tubing) with 24 bottle carousels were housed in a GRP kiosk adjacent to the river. The 24/7 method was a continuous programme within which the sampler carousel and bottles were switched weekly. For the hourly method, the sampler was actuated using a conductivity probe which initiated the sampling programme following a rise in water level that completed the electrical circuit (1640 Liquid Level Actuator, ISCO, USA). To prepare for storm events the conductivity probe was set to 1 cm above current water levels in the 24 hours prior to a forecast event. Once actuated, the sampler was programmed to take a sample every hour until all bottles were filled. The passage of storm peaks was monitored remotely by telemetry (HydroVu, In Situ, USA) to view the Troll500 water level data and plan sample retrieval (within a maximum of 12 hours of the event concluding). Following retrieval, all water samples were transported to the laboratory and stored at 4 °C prior to chemical analysis. Sample bottle material (polyethylene) and storage temperature tests were undertaken prior to analysis to ensure acceptable recoveries (described in Morton et al., 2021).

To further contextualise MCPA hydrological patterns, a secondary MCPA concentration dataset from regulatory grab samples at the catchment outlet was obtained from NI Water (analysis by LC-MS in an independent UK Accreditation System laboratory—limit of detection 0.0005 μg L^{-1}). This monitoring coincided with the sampling period of the high-resolution datasets and, on average, samples were taken every seven days, generally between 08:00 and 12:00 UTC.

2.4. *Chemical Analysis*

The method used for MCPA extraction and concentration on the 7 and 1 hourly samples was adapted from Gervais et al. (2008). To save resources, where 1 hour and 7 hour samples coincided, the 7 hour sample was analysed and the data shared with the 1 hour dataset. The method was based on solid phase extraction (SPE; Bond-Elut ENV, 200 mg, 6 ml, Agilent Technologies), separation (Shimadzu Nexera X2 UHPLC/HPLC system and an InfinityLab Poroshell 120 EC-C18 column), and analysis (Sciex 6500 Q-Trap instrument - Sciex UK Ltd). MCPA concentrations below the limit of detection, <0.0005 μg L^{-1}, were treated as half this value (USEPA, 2000). Further detail on the MCPA extraction method, including uncertainty analysis, is provided as Supplementary Material (SM3 and SM4) and in Morton et al. (2021).

2.5. *MCPA concentration and discharge analysis*

MCPA concentrations (μg L^{-1}), for both 7 hourly and 1 hourly datasets, were synchronised to instantaneous river discharge (m^3 s^{-1}). Instantaneous MCPA and 7 hour loads (mg s^{-1} and kg, respectively) were calculated as the product of MCPA concentrations and river discharge. Subsequent pathway load apportionment was based on the summary equations described in Supplementary Material (SM5).

Automated filtering algorithms are used to estimate event and baseflow contributions to hydrographs from time-series records of discharge (Sloto and Crouse, 1996) and can be used to identify hydrological processes that are useful for water quality assessment (Eckhardt, 2008). Some recursive filters assume baseflows incorporate an element of elevated baseflow due to specific catchment conditions. The Local Minimum Method (LMM), however, reduces the baseflow separations to the lowest conditions by identifying minimum discharge values in a set interval (N). These are compared to neighbouring minima and if less than a proportion (i.e., < 1) of these values (f), are classed as turning points. These turning points are then connected as the baseflow contribution (O'Brien et al., 2013).

Here the BFI+ software (Gregor, 2010) was adapted for use on the 7 hour time series using the LMM to identify very low contributions from the aquifer. Two adaptions were: first, the time step was reduced to 7 hourly rather than daily and second, in addition to the method being used to separate baseflow from total flow, the MCPA baseload was also separated from total load. As N is normally empirically derived in days as a function of catchment area (O'Brien et al., 2013), change to a 7 hourly interval could not use this relationship. However, as the intention was to quantify the lowest possible baseflows and baseloads from total discharge and loads, trials with several coarse representative f and N values were undertaken to separate the time-series (20 combinations) starting at one increment higher than the default $f = 0.5$ (Bayou et al., 2021). The combinations covered the range $f = 0.6$ and $N = 5$, to $f = 0.9$ and $N = 9$. Subsequently, four combinations of $f = 0.6$ to 0.9 with $N = 9$

were judged to provide the lowest baseflow and baseload conditions, and an average was used in subsequent analysis. Total discharge and total load, minus baseflow and baseload, provided estimates of event discharge and event load (also providing estimates of flow weighted mean MCPA concentrations in total, base and event flows). Event load conditions were consequently used in further pathway separations as follows.

The 1 hourly storm hydrology and MCPA mass load data were separated into event pathways and MCPA mass transfer pathways using the heuristic hydrograph separation and Loadograph Recession Analysis (LRA) methods. This is the graphical separation of flow and pollutant time-series loads and can only be produced with enhanced river discharge and synchronous pollution concentration datasets (Mellander et al., 2012). Inflection points on the recession limb of the hydrographs and loadographs were visually identified in storm event time-series. The section between two inflection points indicates dominant hydrological and MCPA transfer pathways. In this case the pathways were interpreted using the QF, IF and eBF conceptualisation. Pathways were separated logarithmically from the start of the rising limb to inflection points assuming a logarithmic pathway response to the rainfall event (Mellander et al., 2012). Event flow and MCPA mass loads for each conceptualised pathway (QF, IF, eBF) were then quantified by summing the flow and load for the active time and then subtracting that for other concurring pathways (Mellander at el., 2016—and Supplementary Material for further references, SM6). The average proportion of flow and load for each pathway was applied to the full 7 hourly event load dataset to estimate the event pathway loads (kg). The proportion of baseflow and baseload in the BF pathway was estimated independently using the LMM method as noted previously. A work-flow diagram of the data handling process is shown in Supplementary Material (SM7)

3. Results

3.1. Hydrometeorology

A cumulative precipitation total of 1779 mm was measured in the River Derg catchment for the 2018-2019 hydrological year and was comparable to long-term rainfall recorded at Lough Derg (i.e., <3 % difference to the 30 year annual average of 1739 mm). Normalised discharge for the 2018-2019 hydrological year, calculated from the Castlederg hydrometric station, was 1306 mm.

Ten- and five-year FDCs, constructed from long-term mean daily discharge data recorded at the Castlederg hydrometric station, are presented in Figure 2 with corresponding data from the 2018-19 hydrological year. Despite small differences at higher discharges, Kruskal-Wallis tests indicated that there was no statistical difference between FDCs ($p = 0.66$). However, mean daily discharges during the monitoring period (1st April to 31st October 2019) were found to be 16 % higher than the ten-year record and 28 % higher than the five-year record. These data indicated lower discharges over the sampling period during the spring (April, May). Conversely, summer (June onwards) and early autumn conditions were found to have higher discharges in comparison to the ten- and five-year periods (Figure 3).

3.2. MCPA concentration and load analysis

Over the monitoring period, 7 hour sampling resulted in a dataset of $n = 734$. Thirteen rainfall events were also captured at 1 hour resolution (Figure 4a), providing a second dataset of $n = 330$. Also shown in Figure 4a are the MCPA concentrations from NI Water regulatory sampling during the period ($n = 30$). A summary of MCPA concentrations is presented in Table 1 and, with Figure 4a and a concentration duration curve in Figure 4b, shows the extent of higher magnitude concentrations as storm peaks were sampled.

By focusing on sampled storm events, the hourly dataset had 80.3 % of samples above the maximum concentration threshold of 0.1 μg L^{-1} for a single pesticide in treated water as regulated in the DWD. Furthermore, 43.4 % of samples exceeded 0.5 μg L^{-1}. In total, 158 samples (47.9 %) were captured on rising limbs of storm hydrographs, of which 125 (37.9 %) were over 0.1 μg L^{-1} and 65 (19.7 %) exceeded 0.5 μg L^{-1}, highlighting the pressures on WTW treatment during these periods.

The product of 7 hour MCPA and discharge data over the seven

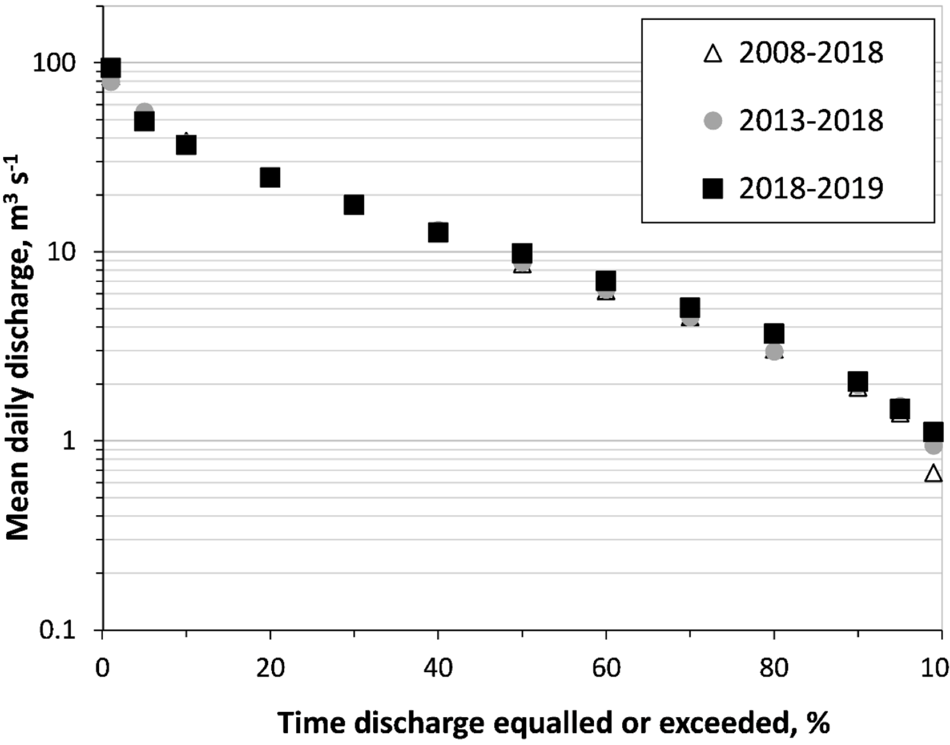


Figure 2. Flow duration curves for the River Derg indicating low deviations between the hydrological year of the sample period compared with long-term records.

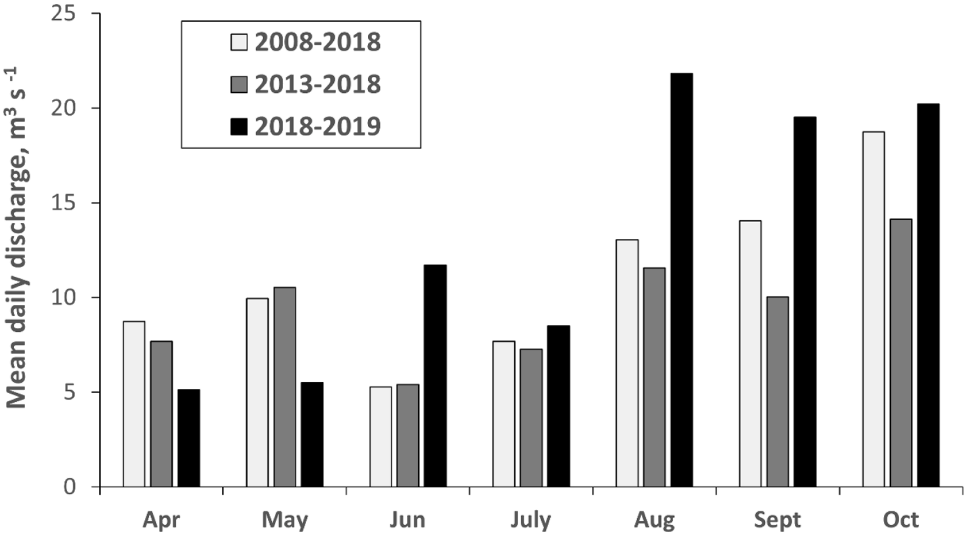
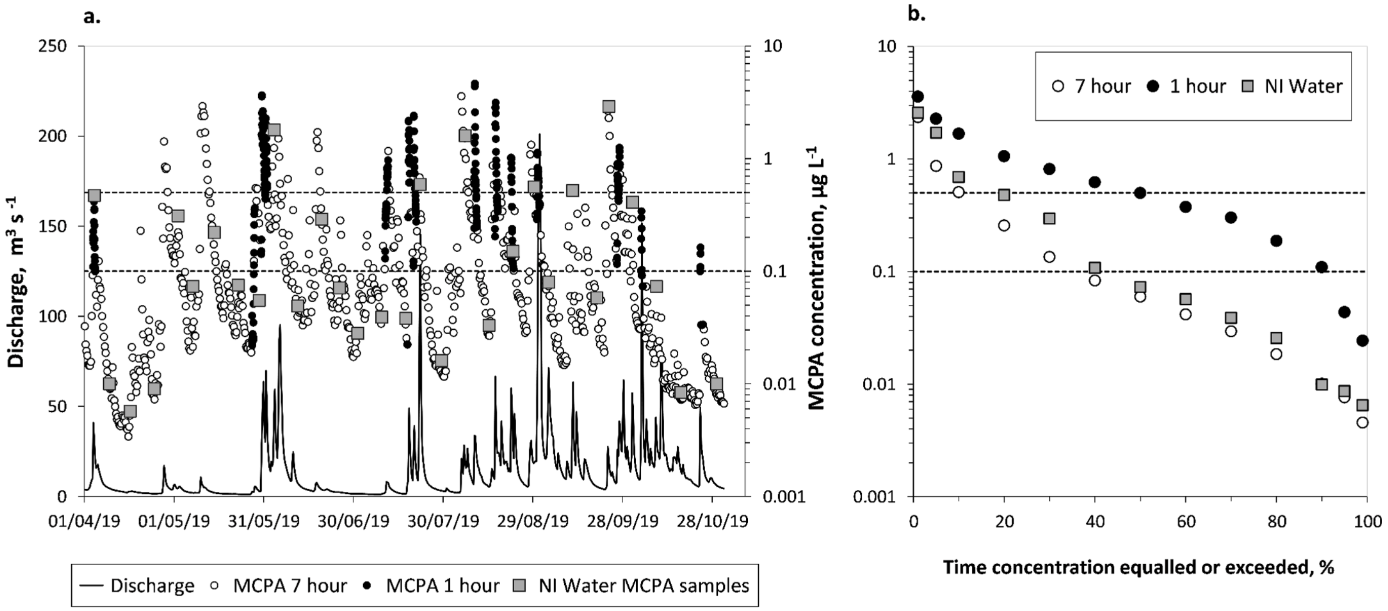


Figure 3. Monthly River Derg discharge indicating a seasonal hydrological deviation during the sample period compared with long term records.



Figures 4. a,b. Time series record of River Derg (a) discharge and MCPA concentrations over a 7 month sampling period. The dashed lines indicate target water treatment concentrations (following treatment) of 0.1 µg L^{-1} for a single pesticide and 0.5 µg L^{-1} for the sum of all pesticides. Concentrations above these lines in source water represent a burden on water treatment processes. Concentration duration curves (b) for the different sampling approaches indicate a higher burden during storm flows captured with enhanced (1 hour) sampling.

Table 1

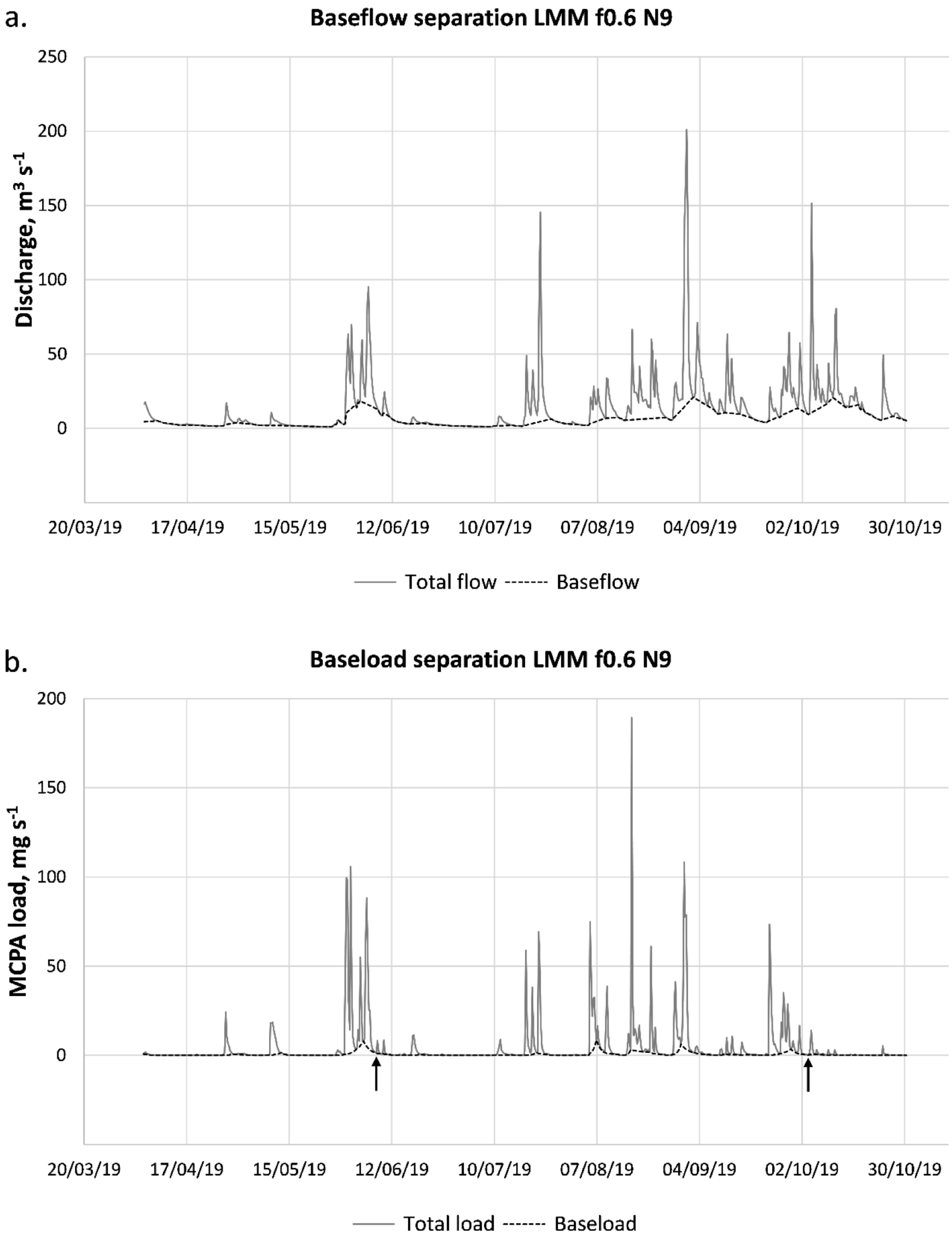
Summary of MCPA concentration data gathered at the River Derg WTW abstraction point from 1st April to 31st October 2019. The number of samples exceeding a threshold for a single pesticide (0.1µg L^{-1}) and the sum of all pesticides (0.5µg L^{-1}) indicate WTW pressures to mitigate through activated carbon filtration.

MCPA concentration, µg L^{-1}	1 hourly in thirteen storm events	7 hourly full season	NIW monitoring full season
n	330	734	30
Maximum	4.64	3.59	2.9
Minimum	0.0003	0.0034	0.0057
Median	0.40	0.06	0.07
Mean	0.63	0.20	0.35
n > 0.1µg L^{-1}	265	265	12
n > 0.5µg L^{-1}	143	76	6

month spraying/sampling period yielded an MCPA load of 85.5 kg (0.22 kg km^{-2}, or 0.55 kg km^{-2} by agricultural land use area). The thirteen storm events had a combined load of 34.7 kg. Substituting the storm periods in the 7 hour dataset for those data captured in the hourly sampling, the estimated load for the sampling period was 87.1 kg.

3.3. MCPA load separations

The four coarse LMM filter outputs separated total discharge (flow) on the 7 hour data into event flows and baseflows—the median proportion of baseflow was 0.37 (0.47, 0.38, 0.36, 0.32) and compares with a long-term (1975-2020) Baseflow Index of 0.31 (NRFA, 2022). Similarly, MCPA load on the 7 hourly data was separated into event and baseload proportions—the median proportion of the baseload was 0.13 (0.129, 0.129, 0.129, 0.086) of the total load (see Fig. 5a and b for baseflow and baseload separation example using LMM parameters of f =



Figures 5. a,b. Example of LMM separations on (a) river discharge time-series and (b) MCPA load time-series using $f = 0.6$ and $N = 9$ filters. Two features are highlighted in Fig. 5b which show small increases in event load due to (left arrow) the presence of MCPA during receding or low flow, and (right arrow), small MCPA event loads due to MCPA depletion during latter season events. Such small event loads are incorporated within the longer time-series.

0.6 and $N = 9$). The dividend of the sum of MCPA total load (85.2 kg), event load (74.7 kg) and baseload (10.9 kg) with total flow (2.43×10^8 m^3), event flow (1.53×10^8 m^3) and baseflow (8.94×10^7 m^3) provided an estimate of flow-weighted mean concentrations over the monitoring period which were 0.351 μg L^{-1}, 0.487 μg L^{-1} and 0.122 μg L^{-1}, respectively.

Storm hydrographs can be complex and may include multiple peaks associated with successive rainfall events in the catchment. As the LRA requires a reasonably stable recession curve for analysis the sampled storm events were screened for suitability to omit recessions with further rainfall. An overview of MCPA concentration datasets and instantaneous discharge identified four, near-consecutive storm events of similar magnitude that were applicable to hydrograph separation and LRA (Table 2—and Supplementary Material SM8 for a full rainfall-runoff sequence). The four storms exported 11.5 kg of MCPA, which was over 30 % of the total exported across the 13 storm events sampled in the hourly dataset. The maximum event load occurred during Storm 8 (4.1 kg) with Storms 7 and 6 contributing 3.2 kg and 2.6 kg,

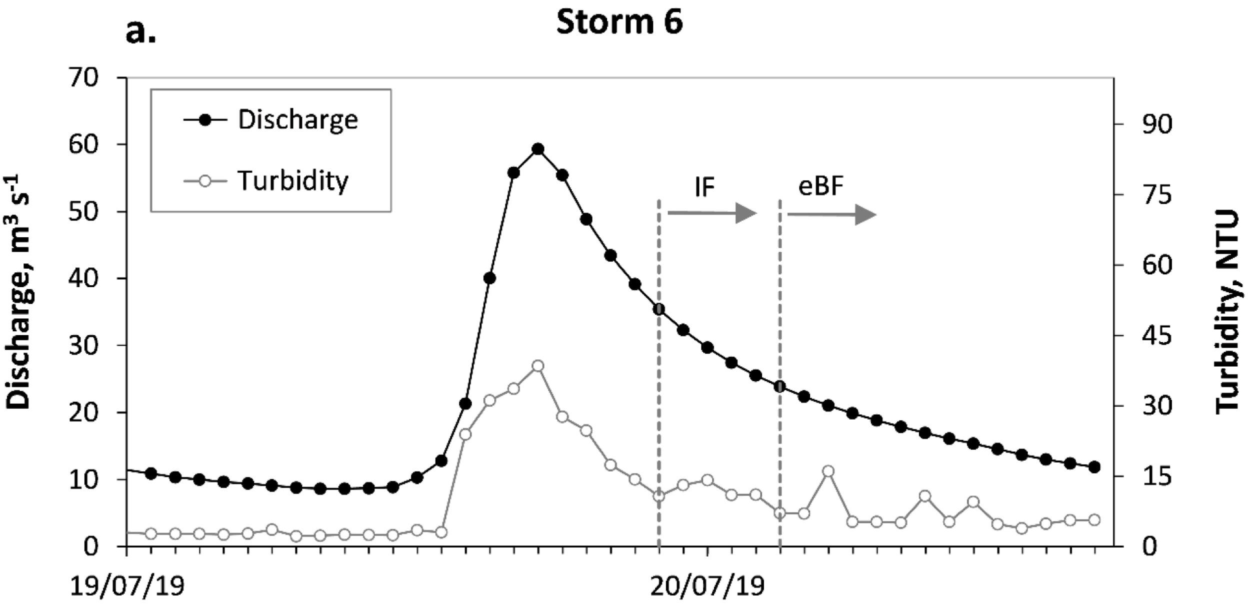
Table 2
Summary data from four discrete storm events monitored at the River Derg WTW abstraction point and used for Loadograph Recession Analysis.

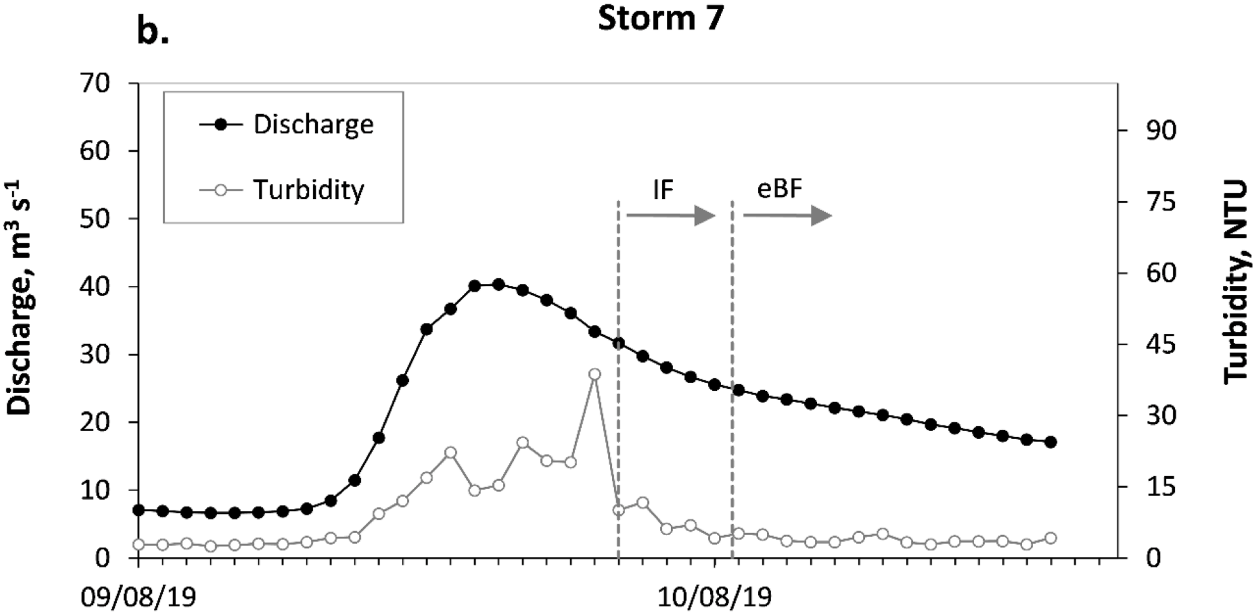
	Storm 6	Storm 7	Storm 8	Storm 9
Date of storm event	20-21/07/19	09-10/08/19	16-17/08/19	21-22/08/19
Rainfall, mm	16.0	13.6	23.4	24.2
Discharge* - total, mm	6.43	6.06	7.92	8.94
Discharge - maximum, $m^3\ s^{-1}$	59.33	40.34	71.72	75.74
Discharge - minimum, $m^3\ s^{-1}$	14.57	20.48	13.88	18.53
Discharge - mean, $m^3\ s^{-1}$	30.47	29.37	37.26	41.51
Maximum MCPA concentration, μg L^{-1}	2.41	4.64	3.15	1.02

* Normalised to catchment area

respectively.

Over the four storms, graphical analysis of the flow and MCPA event load time-series identified a faster load component comprising of most of the storm peaks, and two slower event load components. The QF flow and load pathway dominated up to 10 hours into storm events and maximum MCPA loads were noted between 2 hours and 5 hours from the first sample. An inflection point was also noted some hours before 10 hours and this may indicate a faster flow pathway within the QF component. Slower event flow and load components were separated into IF pathways 10 hours after the first sample and eBF pathways after 14 hours to 15 hours (Supplementary Material SM9 and SM10). Of the four storms, the C3 fluorometer captured turbidity time-series data in just two owing to sensor logging malfunctions. Despite this, Figure 6 (a and b) indicates an approximate change point in turbidity after approximately 14-15 hours in transition from IF to eBF. While this adds some support to the method (following Mellander et al., 2012), further data





Figures 6. a,b. Total discharge and turbidity time-series of storm 6 (a) and storm 7 (b). Dashed vertical lines indicate the approximate change point periods identified by recession analysis as transitions from quickflow to interflow (IF) and elevated baseflow (eBF).

would be required for validation in future investigations.

Averaging the graphical separations across the four storms, the event flow and load proportions for QF, IF and eBF were 0.712, 0.169, 0.119 and 0.822, 0.123, 0.056, respectively (Supplementary Material SM11). Using these to partition the four LMM event load outputs, the median QF pathway exported 61.4 kg (72.0 %) of the total MCPA load during the monitoring period, and the IF and eBF pathways exported 9.2 kg (10.8 %) and 4.1 kg (4.9 %), respectively. The baseload proportion (LMM) was estimated to be 10.9 kg (12.3 %). The dividend of the sum of QF, IF and eBF MCPA event load pathways, with each (median) event flow pathway (1.10×10^{8} m^{3}, 2.59×10^{7} m^{3} and 1.83×10^{7} m^{3}, respectively) provided an estimate of flow-weighted mean concentrations over the monitoring period which for QF, IF and eBF were 0.558 μg L^{-1}, 0.355 μg L^{-1} and 0.227 μg L^{-1}, respectively (Fig. 7).

For NI Water samples taken for regulatory monitoring ($n = 30$; Fig. 4), 60 % were taken during BF conditions (63 % during combined eBF and BF conditions) despite this pathway only accounting for 12.3 % of the MCPA load. Thirty-seven percent were taken during QF conditions, despite this pathway accounting for 72.0 % of the load.

4. Discussion

4.1. Hydrometeorology

There was little variation in River Derg catchment rainfall during the sampling year when compared to the long-term average. This translated into low deviations from long-term average FDCs despite an apparent increase in median discharges and a decrease in high discharge (up to 11 %) during the sampling year. However, seasonal hydrological variability indicated lower than average (5 and 10 year means) discharges in spring periods and higher than average discharges in summer and early autumn for the sampling year. These two conditions have the potential to increase trafficability on farmland for spring/summer spraying, and to increase the potential for soil anoxia (Vink and van der Zee, 1997) and hydrological flushing in summer/autumn. The impact on MCPA use and loss in the sampling season has, therefore, to be viewed in the context of potentially increased applications of MCPA in spring/summer (relative to long term average conditions) and, in summer/autumn lower potential for attenuation due to soil anoxia and higher potential for mobilisation due to higher discharge. This may have resulted in a higher risk of MCPA delivery from land to water in the year of sampling than in long-term average years. It is worth noting, however, that these variations in hydrological conditions measured in this study are likely to be similar to those proposed for Irish catchments in climate change scenarios (Steele-Dunne et al., 2008). Seasonal (and future) variations in hydrometeorological conditions are also noted as being particularly important vectors for increased agricultural pollutant transfers in NW Europe (Ockenden et al., 2017).

4.2. MCPA concentration dynamics and loads

The discharge and MCPA datasets in Figures 4a and 4b reveal a number of features. First, the close agreement with the NI Water sample results and the 7 hour sample results (i.e. from two laboratories) in Figure 4a provide an informal inter-laboratory comparison and confidence in a complex analysis and different sample handling methods. Second, the distribution of data in Figure 4a highlight storm dependent MCPA loss from land to water that is acute in nature and with concentrations, indicated by the hourly and 7 hourly sampling, that would cause pressure at WTWs treating abstracted water into drinking water. For example, the maximum concentration in the hourly dataset is almost double that in the NI Water dataset and over 1 μg L^{-1} higher than the 7 hour dataset (Table 1). Third, Figure 4b shows that the NI Water dataset reasonably falls within the range of the 7 hour dataset with a similar pattern across all percentiles and so a useful indicator of a descriptive river concentration range. For example, both datasets indicate that the 0.1 μg L^{-1} threshold is exceeded for 40 % of the time and the 0.5 μg L^{-1} threshold between 10 % and 20 % of the time. Despite this, the hourly

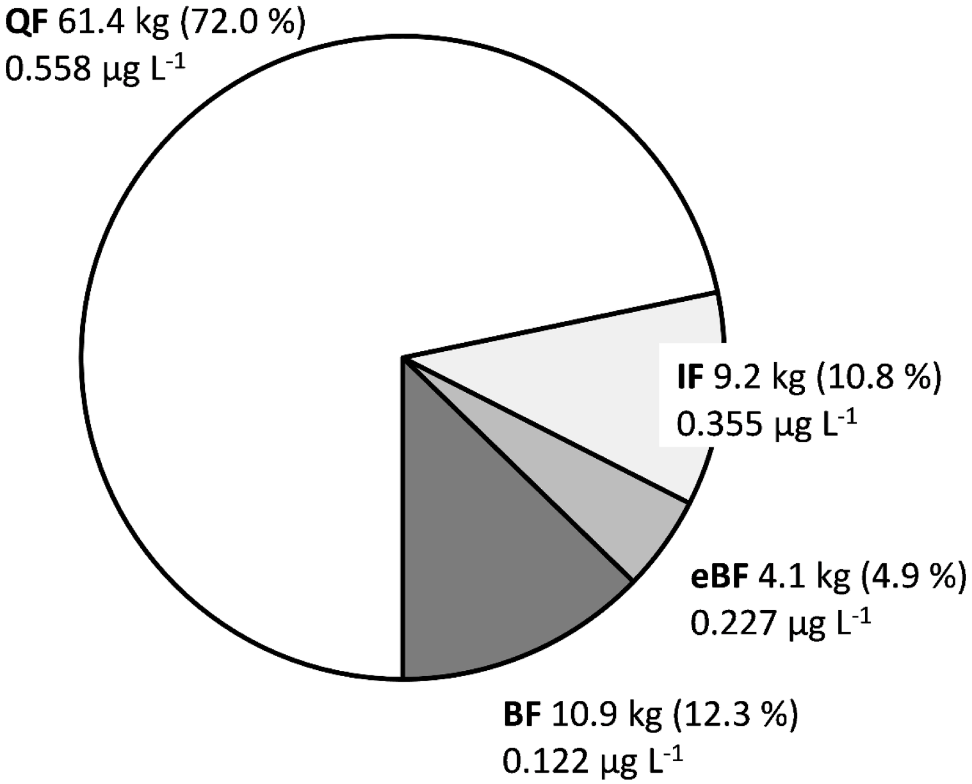


Figure 7. Pie chart showing MCPA pathway loads (kg), the percentage of the total exported MCPA load contributed by each flow pathway, and the pathway flow-weighted mean concentration (μg L^{-1}). QF—quickflow; IF—interflow; eBF—elevated baseflow; BF—baseflow.

dataset demonstrates that, even at seven hourly and at large catchment scale, acute, storm dependent MCPA transfers are better captured at higher resolution. This 1 hour dataset demonstrates that, during storm conditions, the 0.1 μg L^{-1} threshold can be exceeded for up to 90 % of the time and the 0.5 μg L^{-1} threshold up to 50 % of the time of storm periods. This has implications for water treatment works design for abstraction and pesticide removal as this is generally based on a low temporal resolution dataset and where concentration is the parameter of concern. Finally, this last point has also to be considered in the context that not all storm events were sampled at the higher 1 hour rate and, particularly early in the season, storms were mostly captured using the 7 hour rate. Therefore, the MCPA concentrations were likely to be higher than indicated (i.e., undetected) and a higher burden on treatment facilities.

However, the datasets did not clearly show concentration complexity as a result, for example, of the full connection of all storm runoff pathways, proximal/distal sources (e.g. Phillips and Bode, 2004), or incidental losses independent of storm events (Bruen et al., 2021). Such patterns are likely to be important in terms of spraying opportunity (trafficability pre-condition) and the frequency/intensity of storms in the future as noted previously.

The high concentrations captured with all three sampling methods follow similar findings in Canadian water reservoirs (0.37 μg L^{-1}; Donald et al., 2007) and German surface waters (0.06 to 4.17 μg L^{-1}; Müller et al., 2002), although higher concentrations have been reported elsewhere in Ireland (EPA, 2019). There are fewer studies on MCPA (or other pesticide) catchment loads and none with enhanced datasets. For example, when normalised to the Derg catchment area the 7 hour load data over the 7 month period of 85 kg (0.22 kg km^2 by catchment area, or 0.55 kg km^2 by agricultural land use area) is two orders of magnitude higher than those annual losses reported in Germany (0.002 kg km^2, Huber et al., 2000) and Canada (0.004 kg km^2, Poissant et al., 2008). Zhang et al. (2016) used two different monthly sampling approaches in a comparable sized river catchment in Scotland—the highest annual flux recorded from the sum of six pesticides, including MCPA, was 0.013 kg km^{-2}. Considering that a 25 litre container of MCPA product has an equivalent 12.5 kg MCPA content, the load estimated by the 7 hour Derg dataset is the equivalent of almost seven full containers of a single pesticide being lost from land to water over the seven month period—or approximately 10% of the estimated input (by agricultural land use area—see SM1). This excludes all MCPA degradation products and other pesticides and represents a very high single pesticide export on a sub-annual basis. Moreover, when factoring in the extra discharge modelled from the 49 km^2 of ungauged catchment, the total MCPA load and individual pathway loads could increase by 9 % to 15 % above that measured and apportioned. This will, however, need to be verified with the development of a specific stage-discharge rating curve for the 384 km^2 site.

4.3. MCPA in hydrological pathways and implications

The separation of event and baseloads was demonstrated using two methods (LRA and LMM) and an approximate validation of changing storm pathways using the turbidity datasets. There is, therefore, some confidence applied to the major pathway load estimates using a method that is applicable to catchments dominated by surface water runoff processes. However, use of the LMM to separate baseloads from total loads (and hence event loads) would benefit from further testing with similar high temporal resolution datasets, but particularly in combination with daily time-step data over a longer time-period. This will provide a theoretical basis for deriving the N parameter rather than optimising this and in combination with the turning point parameter (f). While the LRA method cannot be easily applied as a full time-series baseload filter due to the longer time-step and interruptions to recessions, isolation of some discrete events comparing the LMM separation with a heuristic approach does support the filter method (SM12). However, further validation of the baseload separation could be done with time-series groundwater chemical concentrations from borehole clusters (e.g., Rivas et al., 2017; Khan et al., 2020) in combination with baseflow separation data. A challenge here would be the investment required for high-temporal resolution data at the outlets of river catchments, combined with high-spatial resolution data from borehole clusters within the catchments.

Furthermore, it was found that the QF component of event flow delivered most MCPA to the catchment outlet and the load in the BF component accounted for approximately 12.3 % (Fig. 7). Further understanding of the partitioning of event loads into faster QF pathways as well as IF and eBF pathways, and particularly the role these have in the transition from QF to BF, would benefit from further higher resolution datasets and a complete picture would be gained from inclusion of data from other catchments. Likewise, the similarly fast runoff patterns and pathways in karst zones of contribution, where LRA has been used to partition below ground P load pathways (Mellander et al., 2013), could also be investigated with higher resolution pesticide datasets. Together, this would provide a benchmark for alternative physical modelling approaches (e.g. Pullan et al., 2016).

Targeted, catchment-based interventions aimed at reducing diffuse pollution at source are being increasingly adopted as a sustainable alternative to traditional water treatment methods (Mohamed Ibrahim et al., 2019). These alternatives include catchment pesticide pollution mitigation measures (Bloodworth et al., 2015) and system redesign from simple changes to practice (Deffontaines et al., 2020). The QF and other event load pathways provide an indication of how the bulk of MCPA can be lost in the higher storm conditions and how mitigation should be targeted. Both source related (MCPA use) and transport related (the hydrological connections between land and water) management is the foundation of addressing acute, diffuse pollution issues in critical source areas as demonstrated for other diffuse pollutants (Doody et al., 2012). Beyond statutory obligations in both Irish jurisdictions and in place for several years (Statutory Instruments 155 2012; Statutory Instruments 1657 2012), source measures may include stricter regulation of MCPA use for rush control and promotion of alternative treatments, such as cutting and weed wiping with other, less mobile products. Measures focussed on transport should consider intercepting the pathways to watercourses through, for example requiring wider buffer zones along drains and rivers and prohibiting use in areas of peaty or poorly drained soils. A useful review is provided by Reichenberger et al. (2007) for both ground and surface water systems. These measures are essential in combination with better advice and training for farmers on the proper use, disposal and risks of pesticide use (Harrington and Ghanizadeh, 2017; Damalas and Koutrabas, 2018). Morton et al. (2021) also consider periods of reduced abstraction or abstraction from different sources during periods of acute, high magnitude pesticide loads and concentrations. They propose an empirical approach based on catchment pre-conditions and river discharge rate of change to predict such periods.

Using the Groundwater Ubiquity Score (GUS) of Gustafson (1989), MCPA has a groundwater contamination potential of 2.98 (PPDB, 2021) where the boundary between moderate and high is 3.0. The 12.3 % of MCPA load transferred in the BF pathway in this study is a catchment reflection of this contamination potential. It is likely to be from the presence of pesticide that has not degraded following application and has infiltrated to the aquifer via sub-surface pathways and subsequently been released into surface water. This persistence has been noted elsewhere in groundwaters (McManus et al., 2017; Munira et al., 2018) and calls into question the degradation rates published for MCPA in the literature (e.g., Hiller et al., 2010). As this is likely to be a chronic signal in flowing water, it will be an urgent next phase in determining residual ecotoxicological impacts in isolation or with multiple stressors (von Stackelberg, 2013; Jackson et al., 2016). It will also be important to assess these signals in terms of the mitigation required for below-ground pesticide reduction (e.g., Della Rossa et al., 2017). Moreover, the estimation of MCPA pathway loads in Figure 7 provides an important cautionary benchmark for using low temporal resolution data to monitor, for example, the effectiveness of pesticide mitigations that have a storm dependency. In this example, the use of NI Water data for monitoring purposes indicates that 60 % of samples were taken during BF conditions and so not during QF conditions when i) the bulk of MCPA is lost and ii) MCPA mitigation should be targeted. Here, at least, the 7 hour method will likely provide a more robust sampling alternative for monitoring the effectiveness of MCPA catchment mitigation measures. To complement this, the 1 hour storm method would be a more robust dataset for WTW abstraction and the design of filters for pesticide removal or alternative abstraction periods for pesticide avoidance (Morton et al., 2021).

5. Conclusions

This study provided new insights on the dynamics and persistence of the acid herbicide MCPA in a large scale, surface source water catchment. Over a 7 month period that spanned a spraying season, a combination of continuous (7 hour, $n = 734$) and focused storm (13 storms 1 hour, $n = 330$) samples indicated a high incidence of undesirable concentrations (0.1 μg L^{-1}) of 36.1 % and 80.3 %, respectively, and with concentrations up to 4.6 μg L^{-1}. This shows a seasonal system where MCPA losses are incidental, storm dependent and acute. As loads, the 85 kg of MCPA lost from the catchment occurred during hydrometeorological conditions that were ideal for both application and losses (drier spring-summer transitioning to wetter summer-autumn). While variable from longer term records, these conditions may be more prevalent under future climate scenarios.

Using a combination of methods, pathway load separations indicated that approximately 87.7 % of the MCPA was lost in storm event pathways and 12.3 % in baseflows. These event load pathways were dominated by quickflow (QF – 72.0 %) and, therefore, mitigation should focus on limiting herbicide use at the catchment scale for source water protection. Alternatives would be the large-scale disconnection of quickflow pathways, or reduced abstraction during critical times. A combination of these three solutions would be desirable.

Deep baseflow loads indicated a persistence of MCPA in the subsurface environment—processes and chronic impacts of which should be research priorities. Moreover, regulatory monitoring (weekly) indicated that over 60 % of samples were taken during baseflow conditions and so cannot be used to effectively monitor the immediate impacts of mitigation measures designed to limit MCPA use or pathway disconnection.

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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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2022.118654.

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