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Article Title: **A review of the pesticide MCPA in the land-water environment and emerging research needs**

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Abstract

Due to its high solubility and poor adsorption to the soil matrix, the post-emergence herbicide MCPA is susceptible to transport into surface and groundwater bodies, where it can result in compromised water quality and breaches of legislative standards. However, there is still poor understanding of catchment scale dynamics and transport, particularly across heterogeneous hydrogeological settings. Whilst it is known that MCPA degrades under aerobic conditions, negligible breakdown can occur in anaerobic environments, potentially creating a legacy in saturated soils. Fast runoff pathways post application are likely transport routes, but the relative contribution from the mobilisation of legacy MCPA from anaerobic zones has yet to be quantified, making the delineation of MCPA sources encountered during monitoring programmes challenging. Whilst ecotoxicological effects have been examined, little is known about the interaction of MCPA (and its degradation products) with other pesticides, with nutrients or with colloids, and how this combines with environmental conditions to contribute to multiple stressor effects. We examine the state of MCPA knowledge, using case study examples from Ireland, and consider the implications of its widespread detection in waterbodies and drinking water supplies. Research themes required to ensure the sustainable and safe use of MCPA in an evolving agricultural, social and political landscape are identified here. These include the need to identify mitigation measures and/or alternative treatments, to gain insights into the conditions governing mobilisation and attenuation, to map pathways of migration and to identify direct, synergistic and antagonistic ecotoxicological effects.

Graphical/Visual Abstract and Caption

The soluble herbicide MCPA is poorly understood, yet frequently used in agriculture and causes breaches in legislative water quality standards. Identification of mitigation measures requires further insights into MCPA's degradation and transportation pathways and ecotoxicological effects.

1. Introduction and scope

The selective herbicide 2-methyl-4-chlorophenoxyacetic acid (MCPA) is used to control broadleaf weeds in arable and horticultural crops (Mackay, Shiu, Ma, & Lee, 2006), as well as reduce rush (*Juncus* spp.) cover in areas of rough grazing and pasture (Moran, 2015). MCPA is, however, susceptible to both fast and slow surface and sub-surface pathway loss from land to water and may be remobilised from sediment stores, which can compromise drinking water quality. The World Health Organisation gives a guideline value of $2 \mu\text{g L}^{-1}$ of MCPA in drinking water (WHO, 2003). Beyond acute to long-term exposure toxicology experiments with animals, MCPA is considered to show limited evidence of carcinogenicity. However, the EU Drinking Water Directive 98/83/EC, which concerns the quality of water intended for human consumption, stipulates that the maximum concentration of any individual pesticide in drinking water is $0.1 \mu\text{g L}^{-1}$ and maximum concentration of the total sum of all pesticides present is $0.5 \mu\text{g L}^{-1}$ (Bailey, Reade, Burn, & Zappala, 2017; Council

of the European Commission, 1998). Despite these measures and guidelines, MCPA is regularly detected in abstracted water and can sometimes breach the EU limits and require treatment (e.g. Kreuger, 1998; McManus et al., 2014, 2017).

MCPA use is particularly prevalent in areas of marginal and upland agricultural land but here it is also most vulnerable to loss due to soil and drainage characteristics. In these areas, grass sward growth is in competition with broadleaf weed – and especially rush – growth due to high rainfall and low soil permeability. North Atlantic Europe is particularly vulnerable and Ireland, for example, has reported a trend where MCPA is the most widely observed of all pesticides recently detected in freshwater, with concentrations still increasing (EPA, 2017b, 2017a). Moreover, we incorporate primary and secondary data from Ireland to place experiences here into a global context. Ireland's upland catchments comprise areas of surface-derived source drinking water, areas with high occurrences of pristine or near-pristine water bodies and areas of marginal agricultural land where climate and soil/geology factors constrain agricultural production. As such, MCPA use on upland grassland may be regarded as a pressure of competing land use resources - symptomatic of a “wicked” or complex problem (e.g. L. E. D. Smith & Porter, 2010).

To aid the study and management of MCPA, an emerging contaminant in freshwater posing potential risks wherever it is used, the aim of this review was to provide a science-management-policy overview in one document consisting of five key areas:

- Chemical constituents, history, use and trends
- Soil-water partitioning, mobilisation and fate
- Hydrological dynamics
- Ecotoxicology
- Standards, legislation and mitigation

Due to a paucity of recent sources, the review was based on an open-ended (no limit to start/end dates, no limit to number of references, no set search strings) method where word combinations from the key areas above were combined with “MCPA” and used as search strings. Google Scholar and Web of Knowledge were the two main academic databases used, with the World Wide Web as a general source. In total, 83 MCPA/acid herbicide related references (out of 95 used) were consulted and these were published between 1942 and 2018. As a general rule, the older references were focused on MCPA development and followed by soil-water studies. More environmental focused studies were published more recently, and standards/legislation references were mostly sourced from the grey literature. A final section draws from the review findings to suggest emerging research themes.

2. Chemical constituents, history, use and trends

MCPA (4-chloro-2-methylphenoxy acetic acid (CAS number 94-74-6) and also named 4-chloro-o-tolyloxyacetic acid by IUPAC) is a phenoxyalkanoic acid herbicide, which belongs to a group of chemicals related to the plant growth hormone, auxin. Phenoxyalkanoic acid herbicides are compounds containing either a 2,4-dichlorophenoxy or a 4-chloro-2-methylphenoxy group substituted onto a carbon of acetic, butyric or propanoic acid (Paszko et al., 2016). Chemically, MCPA is a carboxylic acid joined by an alkoxy group to an aryl group, which is a chlorinated phenoxy group, and has the chemical formula $C_9H_9ClO_3$. Usually, MCPA is formulated as a dimethylamine salt

(Gimeno, Plucinski, Kolaczowski, Rivas, & Alvarez, 2003), which takes the chemical form $C_{11}H_{16}ClNO_3$.

The growth-regulating effects of various phenoxy acids were first published in the early 1940s by Zimmerman and Hitchcock (1942), although investigations mainly centred around inducing the growth of plants rather than being used as a herbicide. The most potent chemical trialled in the USA was 2,4-dichlorophenoxyacetic acid (2,4-D), used to induce seedless tomatoes. Whilst 2,4-D was being developed in the USA as a substance to promote plant growth, it and other plant-growth substances were being trialled as selective weed-killers and herbicides in the UK (Nutman, Thornton, & Quastel, 1945; Peterson, 1967). Subsequently, MCPA was first described by Templeman and Sexton (1946) during an investigation for compounds which had a similar or greater selective growth-regulating effect than α -naphthylacetic acid. MCPA was synthesised by condensation of the parent phenol, 2-methyl-4-chlorophenol (described as 5-chloro-o-cresol in the paper), with chloroacetic acid and a dilute base (unspecified) and purified by crystallisation with benzene (Templeman & Sexton, 1946). The widespread use of MCPA in agriculture dated from the 1950s (Mackay et al., 2006; Paszko et al., 2016).

MCPA is approved for use in all EU countries (except Cyprus) and is also available for use in the USA, Australia (AERU, 2016), China (Fu et al., 2009), Canada and New Zealand (The Dow Chemical Company, 2015). In the EU market between 1995 and 2016, the amount of pesticide produced varied by an order of magnitude (12 million kg to 160 million kg), although the total monetary value did not (European Commission, 2017). In 2008, MCPA and other phenoxyalkanoic herbicides accounted for nearly 16% of the total value of all herbicides sold in the EU and 17.5% of the amount produced (European Commission, 2017). In contrast, in 2000 only 6% of herbicides sales and 2% of herbicides produced were phenoxyalkanoic herbicides, with the proportion produced falling to just over 1% the following year, despite the total amount produced being nearly eight times as much (reason not given - European Commission, 2017). In most years between 1995 and 2008, the UK, Denmark and Poland were responsible for much of the production and sales of phenoxyalkanoic herbicides, with just Denmark, France, Poland and the UK accounting for 80% of the sales in 2012 (European Commission, 2017). Between 2012 and 2016, both the value and amount of phenoxyalkanoic herbicides produced fell gradually but steadily. However, sales and production data are either unavailable or classified as confidential for many EU countries which sell and/or produce MCPA products (European Commission, 2017). By 2015, all rush control products available within the EU contained MCPA and were sold under a variety of brand names (see Table S1).

MCPA has been detected in surface water, groundwater and drinking water (which is derived from surface or groundwater) around the world, illustrating the international context and scale of its environmental occurrence (Bach & Frede, 2012; Birch, Drage, Thompson, Eaglesham, & Mueller, 2015; Donald, Cessna, Sverko, & Glozier, 2007; Environment Canada, 2011; Köck-Schulmeyer et al., 2014; Kreuger, 1998; Loos et al., 2017; Lundbergh, Kreuger, & Johnson, 1995; McManus et al., 2017, 2014; Palma et al., 2014; Rawn, Halldorson, Woychuk, & Muir, 1999; Rippy et al., 2017; Schreiner, Szöcs, Bhowmik, Vijver, & Schäfer, 2016; Spycher et al., 2018).

In a review of Canada's national water quality surveillance programme, MCPA was found to be one of the most commonly encountered herbicides, with detections in approximately 90% of surface water samples taken from 2003-2005 in the Lower Fraser Valley and Okanagan Basin areas of British

Columbia (Environment Canada, 2011). Similarly, in the regions of Alberta, Saskatchewan and Manitoba, MCPA was detected in 92% and 99% of rivers and reservoir water samples, respectively. In another Canadian study, MCPA was detected in 65% of samples taken over a three year period from the Red River (Rawn et al., 1999), while it was detected in essentially all 15 drinking water reservoirs assessed by Donald et al. (2007).

In Australia, MCPA was detected in over 50% of samples taken in a study of urban storm water (Rippy et al., 2017). Furthermore, Birch et al. (2015) investigated subsequent MCPA occurrence (among other parameters) in 30 sites adjacent to storm water outlets across the entire Sydney estuary. MCPA was widely distributed (23 sites) and was present in considerably higher concentrations in the upper estuary rivers.

Schreiner et al. (2016) analysed routine national monitoring data for herbicides, insecticides and fungicides from Germany, France, the Netherlands and the USA comprising a total of 4532 sites. Herbicides were the most frequently detected pesticide group in the study, of which MCPA (and isoproturon and atrazine) were the most frequent. Overall, MCPA was detected at 22.5%, 43.2%, 0.4% and 44.4% of sites in Germany, France, the USA and the Netherlands, respectively.

In other European studies, MCPA was detected in 36-42% of samples (depending on the monitoring site) from the Alqueva reservoir in Portugal, making it one of the most frequently encountered pesticides (Palma et al., 2014). Higher levels were observed in June and July after the first runoff-producing rainfall in May and soon after their application, namely in vineyards and in the intensive olive crops. In Spain, MCPA was detected at a 7% frequency in 112 wells monitored over a four year period (Köck-Schulmeyer et al., 2014), while it was detected in 93% of the samples taken at 68 sites along the Danube, the longest river in the European Union (Loos et al., 2017). Additionally, MCPA has been detected in Swiss surface waters to a maximum concentration of $1.6 \mu\text{g L}^{-1}$ with detection frequencies ranging from 7-65% in five studied agricultural catchments (Spycher et al., 2018).

During the period 2013-2015, the Irish Environmental Protection Agency (EPA) identified MCPA as the most widely observed pesticide, with detections in almost two-thirds of all rivers surveyed (EPA, 2017b). Correspondingly, regulatory monitoring of drinking water supplies in Ireland in particular has shown increasing trends in MCPA occurrence, although the reasons for these trends are currently unknown. At the end of 2016, 63 supplies serving over 900,000 people had open investigations due to failures to meet the pesticide standard ($0.1 \mu\text{g L}^{-1}$), with 61 reported in 2015 and 44 in 2016 (Figure 1a) (EPA, 2017a). Despite similar data summaries being unavailable in Northern Ireland, the increase in average MCPA concentrations in raw water indicates a similar trend (Figure 1b).

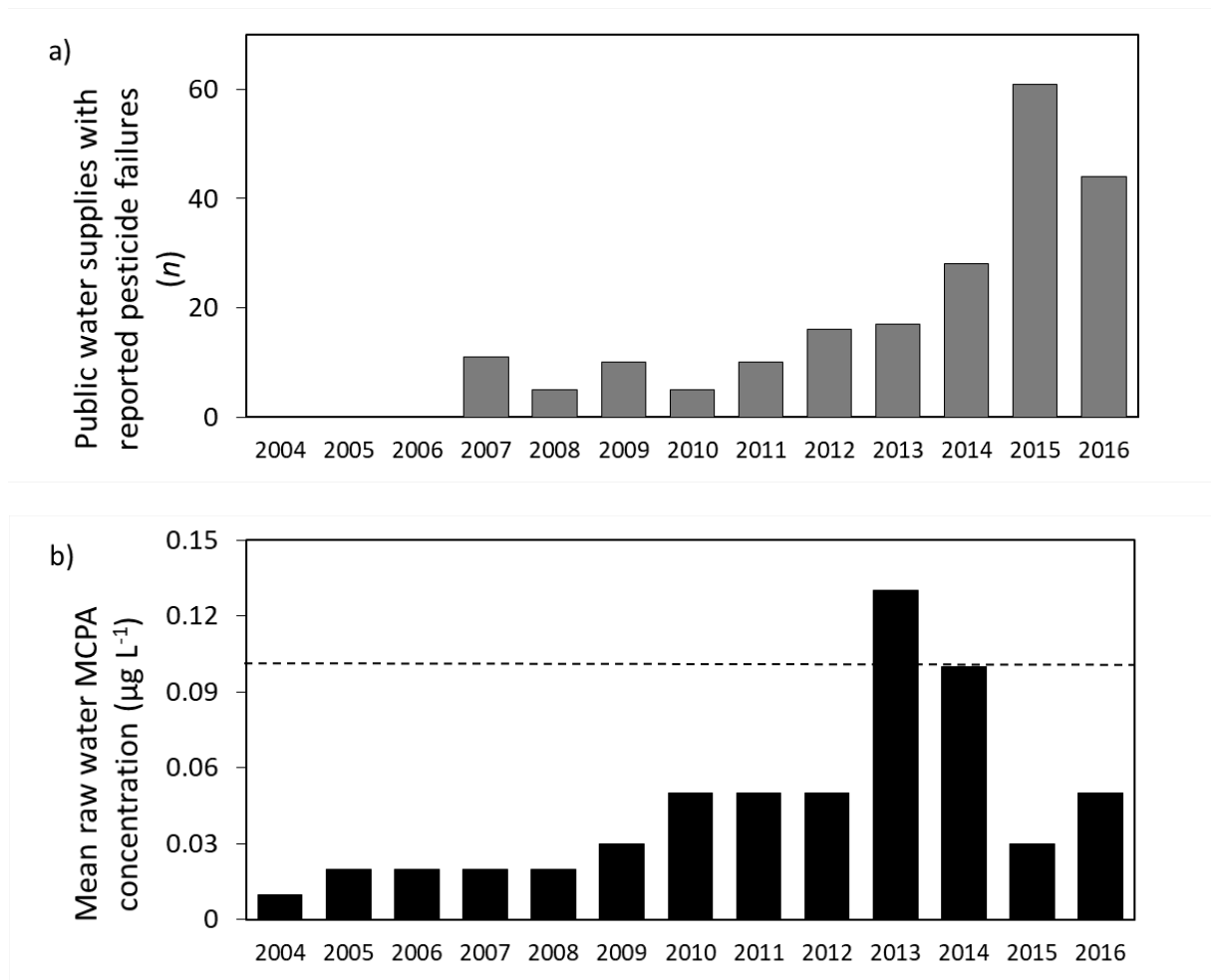


Figure 1 Trends between 2004 and 2016 in a) the number of reported pesticides failures for public water supplies in the Republic of Ireland (reproduced from EPA, 2017a) of which 81% are sourced from surface water (EPA, 2017a) and b) the mean raw water concentration of MCPA in Northern Ireland (data provided by Northern Ireland Water). The dashed line on b) represents the drinking water standard limit of 0.1 µg L⁻¹.

3. Soil-water partitioning, mobilisation and fate

The soil-water partitioning, breakdown and ultimate fate of most pesticides depends on many factors including soil type, structure and depth to bedrock, subsoil geology, hydrogeological conditions, soil pH, soil microbial community, soil moisture, pesticide application mode, application timing and pesticide formulation, although the impact of some of these is not fully understood (Bailey et al., 2017; Hornsby, Wauchope, & Herner, 1996; McManus et al., 2017). MCPA can be formulated as either an ester of the parent acid (usually either ethylhexyl or butoxyethyl esters; (Paszko et al., 2016) or as alkali metal or amine salts and the formulation can greatly affect the behaviour of the herbicide in different media (Hornsby et al., 1996).

The formulation is of particular importance before the pesticide contacts the soil or plant surfaces. Like all phenoxyalkanoic pesticides, MCPA has very low volatility (Paszko et al., 2016), but esters are more volatile than the free acid, which are more volatile than salt forms (Hornsby et al., 1996). However, MCPA is often applied by spraying which creates “spray drift”, broadcasting droplets to

the atmosphere that can combine with rain or fog (Freiberg & Crosby, 1986), as well as increasing the chances of MCPA entering streams and lakes (Kreuger, 1998). Based on a modelling study by Comoretto et al. (2008), about 0.3% of the MCPA applied to soil could be volatilised to the air. Whilst this is a small amount, MCPA was detected in 50% of high-volume air samples in a study in Canada, with concentrations up to 1.9 ng m^{-3} , and greater concentrations higher in the atmosphere, indicating long-range atmospheric transportation (Waite et al., 2005).

Once in the atmosphere or on plant leaves, sunlight exposure causes MCPA degradation (Freiberg & Crosby, 1986). Whilst this can be a slow process, with authorities stating a soil photolysis DT_{50} (degradation half-life) for MCPA between 9 and 67 days (European Union, 2005; US EPA, 2004), Mackay et al. (2006) report a half-life of 4.6 days for $14700 \text{ } \mu\text{g mL}^{-1}$ MCPA to degrade in spray droplets in the air in natural sunlight. In natural sunlight (in autumn) in river water (from the Thames), Stangroom et al. (1998) estimated that the photolysis DT_{50} of MCPA was about 14 days.

The majority of MCPA applied, even when considering spray drift, reaches the soil where the formulation becomes much less important. Esters are fairly insoluble and non-ionic, with only about 5 mg L^{-1} of MCPA esters dissolving in water, whilst the salt and free acid forms are much more soluble, with up to 866,000 mg of MCPA salt able to dissolve in a litre of water (Hornsby et al., 1996). However, once in soil, esters are hydrolysed to the salt or free acid form within hours or days (Hornsby et al., 1996), meaning that the formulation applied has very little effect on the breakdown or dissipation rate of phenoxyalkanoic acids since all forms are rapidly converted to anionic form (A. E. Smith, Aubin, & Biederbeck, 1989). The actual proportion of anions and neutral molecules is dependent on the soil pH (Kah & Brown, 2006) and the pK_a value (the acid dissociation constant at logarithmic scale) of the herbicide: MCPA has a pK_a of 3.09 (values of 3.05-3.13 have been reported) (Mackay et al., 2006), meaning that 89% of the compound is in anionic form – and 11% in neutral form – at pH4 and 100% in anionic form at pH7 (Paszko et al., 2016). In practical terms, this means that MCPA is a weak acid that is highly soluble and mobile, except under very acidic conditions (Bailey et al., 2017; Hornsby et al., 1996).

Pesticides which adsorb strongly to soil have high soil-organic-carbon-to-water partitioning coefficients (K_{oc} values) of 1000 to 5000 L kg^{-1} (corresponding to $\log K_{oc}$ values of 3-3.7) (Bailey et al., 2017). Conversely, the K_{oc} value of MCPA is generally about 54 to 118 L kg^{-1} (or $\log K_{oc}$ 1.73-2.07), depending on the conditions under which it was measured, meaning that MCPA has low adsorption to soils and is highly mobile (Mackay et al., 2006). As K_{oc} values depend largely on the soil organic matter (OM) content and soil pH, they are site- and depth-specific, with adsorption being negatively correlated with pH and greater in soils with higher OM content (Hiller, Tatarková, Šimonovičová, & Bartaľ, 2012; Kah & Brown, 2006).

Humic and fulvic acids, typical in high OM soils, are reported to increase the sorption potential of MCPA (Hiller et al., 2012). However, in sandier soils, Haberhauer, Temmel, & Gerzabek (2002) reported dissimilar sorption capacities of humics and fulvics, with humic acids increasing, and fulvic acids decreasing, MCPA mobility. An additional complication in predicting the mobility of MCPA is that liming can be used in conjunction with herbicide spraying and cutting to decrease establishment of rushes (Moran, 2015). As liming increases the soil pH (Blake & Goulding, 2002), MCPA will dissociate more towards the anionic than neutral form (Paszko et al., 2016), thus reducing its affinity for OM (Werner, Garratt, & Pigott, 2013), and hence decreasing its adsorption in the soil (Paszko,

2011). This outweighs the slight increase in adsorption caused by Ca^{2+} ions from the lime, which create a Ca-bridging mechanism, because the affinity of MCPA in anionic form to OM is 10 times lower than that of MCPA in neutral form as soil OM is negatively charged (Tülp, Fenner, Schwarzenbach, & Goss, 2009). Hiller et al. (2012) reported similar relationships with phosphorus (P) and low molecular weight organic acids which, when present, decreased the soil sorption potential of MCPA.

As previously discussed, where light can penetrate, MCPA can undergo photodegradation (Freiberg & Crosby, 1986). However, the main method of breakdown in the soil is microbial degradation (Helweg, 1987; Paszko et al., 2016). The speed of this degradation varies greatly and is largely controlled by the amount of available oxygen, which is usually linked to the soil moisture (Helweg, 1993). Soil temperature, soil pH and nutrient content also influence MCPA breakdown, as these factors regulate the growth and activity of soil microbial communities (Kah & Brown, 2006; McGhee & Burns, 1995). The field DT_{50} of MCPA is usually between 7 and 60 days (Hornsby et al., 1996), although a DT_{50} of less than 7 days has been recorded in groundwater (Mackay et al., 2006) and in salt media in the laboratory (A. E. Smith, Mortensen, Aubin, & Molloy, 1994). As degradation tends to follow an exponential decay, MCPA can persist for more than three months in the soil (Mackay et al., 2006) and almost indefinitely in constantly anaerobic soils (Vink & van der Zee, 1997). The depth at which MCPA undergoes degradation also affects the speed at which it breaks down. For example, Juhler, Henriksen, Ernstsén, Vinther, & Rosenberg (2008) measured the average DT_{50} of MCPA at 15 cm depth as 9 days, whereas in the same soil it was 15 days at 45 cm depth and 28 days at 105 cm depth, which is likely due to changes in microbial communities, available oxygen and soil moisture down the soil profile.

Additionally, soils that have previously been treated with phenoxy acid herbicides usually exhibit much more rapid degradation when these herbicides are added than soils that have never been directly exposed to phenoxy acids (Bælum, Prestat, David, Strobel, & Jacobsen, 2012). In some cases, even if a soil has previously been treated with one phenoxy acid herbicide, the degradation rate of a different phenoxy acid herbicide will be very slow or non-existent as the microbial strains present are unable to adapt (A. E. Smith et al., 1994). Where phenoxy acids have previously been applied, degradation usually follows an s-shaped curve, reflecting the growth of the microbial community, whereas microbes in soils without a history of phenoxy acid application exhibit either no growth or slow linear growth (Bælum et al., 2012). Some fungi also have the ability to break down MCPA (Poll et al., 2010), albeit much more slowly than microbial communities (Paszko et al., 2016).

When MCPA breaks down, it can form other compounds that have different properties and toxicity to MCPA molecules. The main breakdown product of MCPA formed by direct photolysis is 4-chloro-2-methylphenyl (4C2MP) (Zertal, Sehili, & Boule, 2001). Breakdown products in soil and water include phenoxyacetic acid (PAC) (McManus et al., 2017), 4-chlorophenol (4CP), 2-methylphenol (2MP) and phenol (Crespín, Gallego, Valcárcel, & González, 2001). As PAC has no chlorines, its ability to transfer into aquatic environments is much higher than that of MCPA (El-Naas, Mousa, & Gamal, 2017), and it has been detected across a range of sampling depths and soils (McManus et al., 2017). However, the occurrence of PAC is not always indicative of MCPA usage as 2,4-D is the chlorinated version of PAC (Vroumsia, Steiman, Seigle-Murandi, & Benoit-Guyod, 2005). The metabolite 4C2MP may have a higher toxicity than MCPA (Zertal, Jacquet, Lavédrine, & Sehili, 2005; Zertal et al., 2001),

although little is known about its persistence in the environment but, in a study in Ireland, it was detected in 17% of groundwater samples tested (McManus et al., 2017).

4. Hydrological dynamics

Notwithstanding soil OM type and soil chemical co-relationships, MCPA in soil is largely dissolved within the soil pore water (Hornsby et al., 1996), making it very susceptible to being washed out of the soil into streams and rivers, which could be exacerbated by artificial drainage networks, or percolating through into groundwater (Lundbergh et al., 1995). The more recently MCPA has been applied, the closer it is to the surface and so the more likely it is to be carried in runoff water during storms or heavy precipitation events that are incidental to application (Kreuger, 1998). In a study in Sweden, MCPA was detected in over 50% of the streamwater samples taken, with most of the detection occurring shortly after application or after storm events (Kreuger, 1998). MCPA can also appear in soil and watercourses in areas where it has not been applied but is instead a degradation product of methylchlorophenoxypropionic acid (mecoprop or MCP) (Vink & van der Zee, 1997). This, combined with large loss events during storms, can lead to concentrations in streams and rivers spiking (McManus et al., 2017).

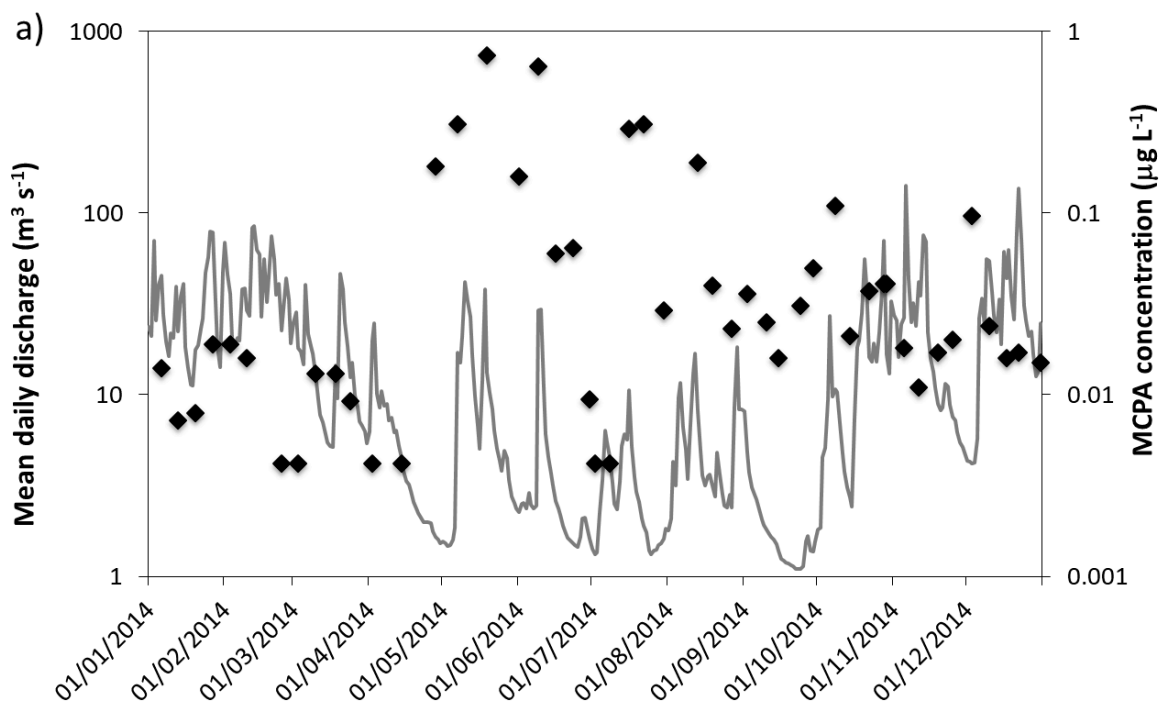
In groundwater, the aquifer type, underlying quaternary deposit and soil type are more closely associated with pesticide occurrence (McManus et al., 2014). Under anaerobic conditions, there is virtually no degradation of MCPA and low soil and groundwater oxygen concentrations (3×10^{-6} M O₂) can reduce degradation by more than an order of magnitude compared to environments where oxygen readily diffuses (Vink & van der Zee, 1997). There is some evidence that pesticides may persist in shallow groundwater for extended periods (Kreuger, 1998) – and therefore MCPA may also persist in highly saturated soils where it is commonly used, but further research is required.

In Ireland, data collected for the EU Drinking Water Directive, and reported under Article 7 of the EU Water Framework Directive results during the period 2013–2015, focused on the screening of 14 substances totalling 9,464 measurements (EPA, 2017b). Overall, 395 samples had pesticide detections (4.2%) affecting 72 of the 85 rivers assessed (EPA, 2017b). MCPA was the most widely observed substance, detected in almost two-thirds of all rivers surveyed (EPA, 2017b). Whilst most values (86%) were $<0.1 \mu\text{g L}^{-1}$, six exceeded $0.2 \mu\text{g L}^{-1}$. The highest value was $18 \mu\text{g L}^{-1}$, recorded in 2013 in the Banoge River (Co. Wexford) (EPA, 2017b). Conversely, in a groundwater screening study, 210 samples were analysed from 204 monitoring sites, with 35,671 individual results reported for a suite of parameters, including MCPA. Only 0.25% of results were above the limit of quantification and of these, there were only four individual exceedances of the relevant standards (0.01% of results), although none of these were attributable to MCPA (EPA, 2017b).

In contrast, regulatory monitoring of drinking water supplies has encountered widespread MCPA occurrence. At the end of 2016, 63 supplies in Ireland serving over 900,000 people had open investigations due to failures to meet the pesticide standard, the vast majority of which failed on MCPA concentrations (EPA, 2017a). A seasonal pattern in detections has emerged, with exceedances mostly evident during May, June and July and again in September and October. This coincides with periods when MCPA is commonly applied to grassland for the control of ragwort, rush and thistle (EPA, 2017a).

Catchment scale MCPA dynamics have received relatively little attention to date, although a useful comparison can be made with typologies that describe the relationship between river discharge and P. There is a seasonality element where extreme loss occurs via diffuse surface pathways during storm events (Jordan, Melland, Mellander, Shortle, & Wall, 2012). High solubility and low affinity with the soil adsorption process means that MCPA transfers are generally higher following application, i.e. incidental transfers similar to slurry losses following recent applications (Preedy, McTiernan, Matthews, Heathwaite, & Haygarth, 2001). Unlike P, which can accumulate and be stored in topsoil, the legacy issues of MCPA are more complex, relating to degradation rates and also transfers to environments where anaerobic conditions prevail (Vink & van der Zee, 1997). Perched (including soil water) and deep groundwater and lake/river sediments are environments where retarded degradation may occur and provide conditions for transfers of legacy MCPA.

Largely unknown at the catchment scale is the partitioning of MCPA from recent to legacy applications in the soil-surface to groundwater spectrum and how these transfer in the pathways of each catchment type. Figures 2 and 3 show this link to diffuse discharge events and seasonality, with MCPA concentration data taken approximately weekly from a raw water river source in Northern Ireland (Northern Ireland Water, pers. comm.). Higher discharges appear to show higher MCPA concentrations but only in those spring and summer months that are coincident with application periods (Figure 2b). In autumn and winter, this is less apparent. Diffuse, seasonal and incidental transfers typify these patterns. The MCPA loads for the same period in Figures 3a and 3b indicate, with lower loads during the winter (but higher discharges), that the patterns reflect MCPA degradation and flushing from spring-summer applications. Importantly in these data however, MCPA concentrations do not fully deplete (to zero) and in summer recessions and winter periods, concentrations are still mostly in the $0.01 \mu\text{g L}^{-1}$ range. This indicates persistence is likely in a groundwater pathway and is consistent with findings of McManus et al. (2014) in Irish rivers and groundwater.



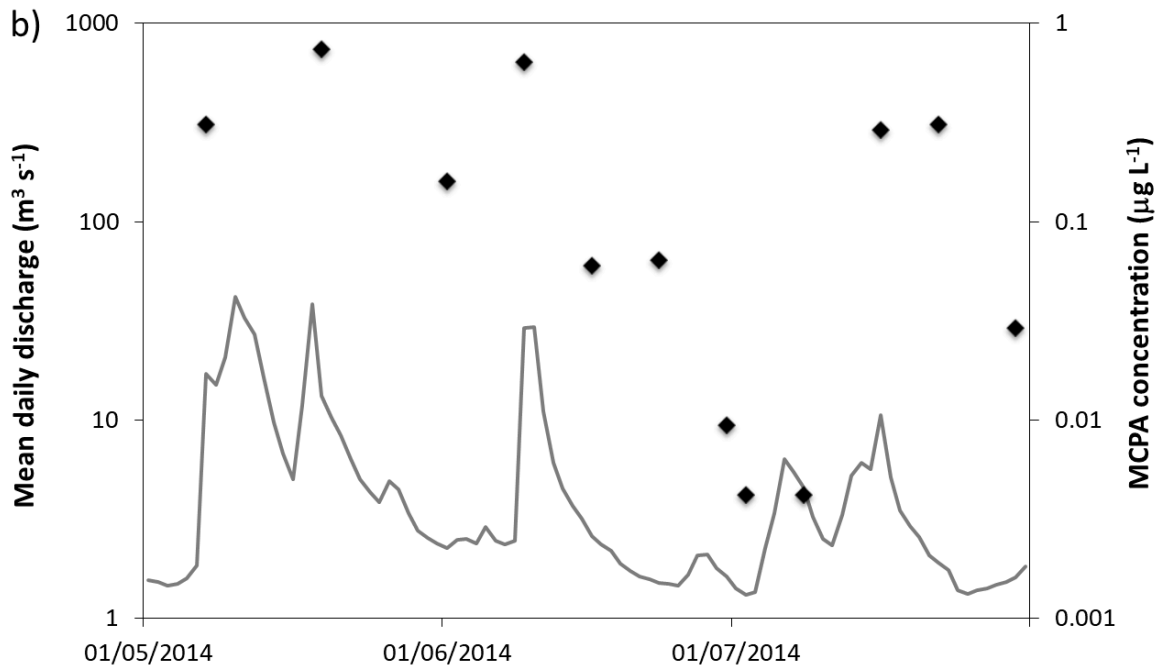
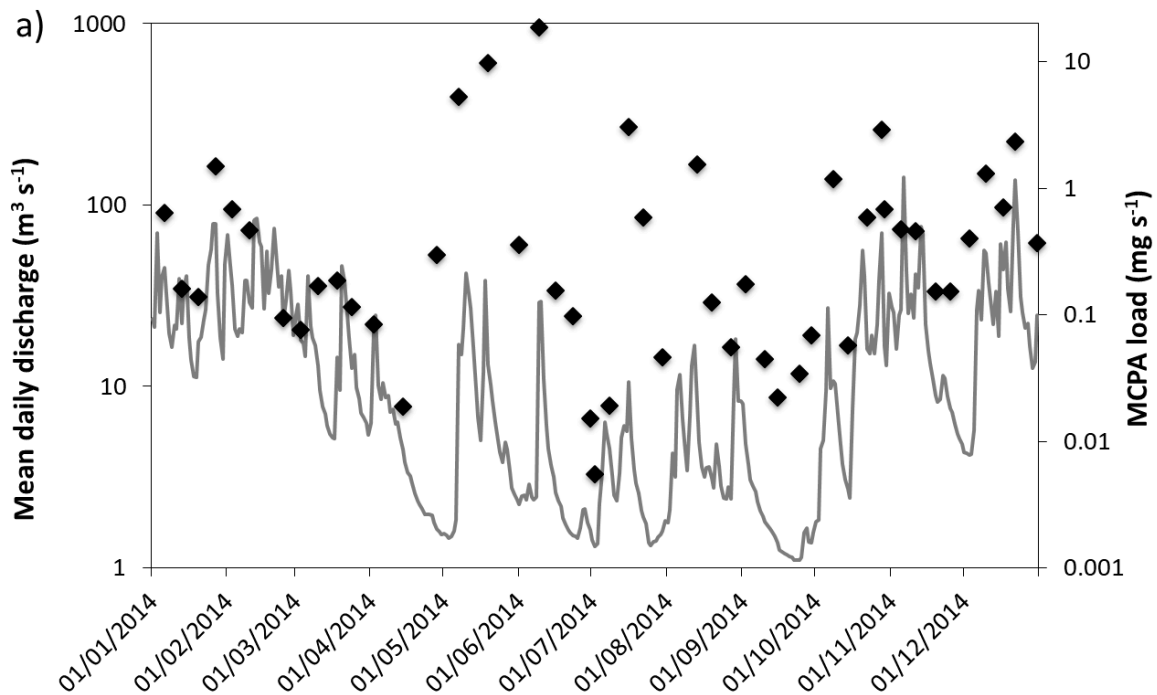


Figure 2 River discharge (15 minute frequency; data from Department for Infrastructure NI) and MCPA concentrations (data provided by Northern Ireland Water) in a river in Northern Ireland shown for a) a full year (2014) and b) the summer period only, when high concentrations are likely coincident with application and rainfall/runoff events. River discharge is shown as a grey line and MCPA concentrations are black diamonds. Note that both discharge and MCPA concentrations are displayed on a logarithmic scale.



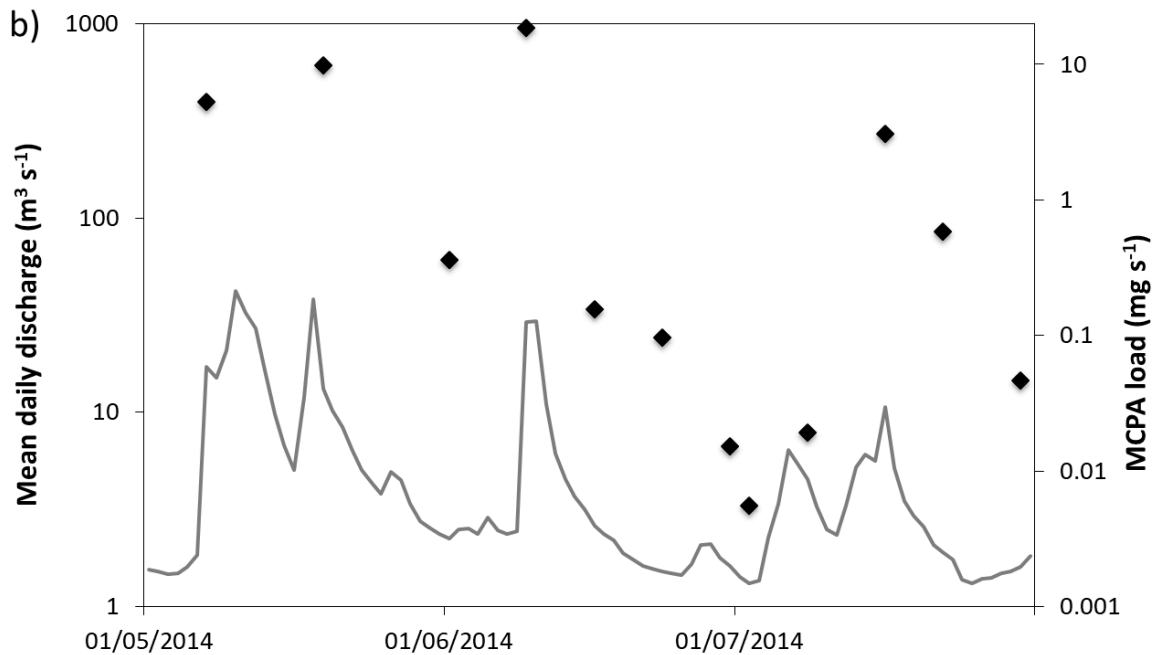


Figure 3 River discharge (15 minute frequency; data from Department for Infrastructure NI) and MCPA loads (data provided by Northern Ireland Water) in a river in Northern Ireland shown for a) a full year (2014) and b) the summer period only, when high loads are likely coincident with application and rainfall/runoff events but do not reduce to zero during inter-storm periods throughout the year. River discharge is shown as a grey line and MCPA loads are black diamonds. Note that both discharge and MCPA loads are displayed on a logarithmic scale.

Cassidy & Jordan (2011) showed how higher resolution monitoring (sub-daily) was required for a full appraisal of concentration patterns and load estimates of P leaving river catchments. Similarly, and reflecting on MCPA's i) high water solubility and ii) affinity to runoff in diffuse events, the weekly data presented in Figures 2 and 3 may be hiding important MCPA transfer patterns. Increasing the resolution of data capture may provide some definitive information that are not currently available on i) maximum concentration magnitudes, ii) hydrological dependence and pathways (Mellander et al., 2012), and iii) persistence in the water environment. Even from a regulatory and management perspective, Figure 4 provides an example of better insights of MCPA magnitude and storm dependency during vulnerable times and which is not identified with weekly sampling, contrasting with data reported in the same river by Jess et al. (2014).

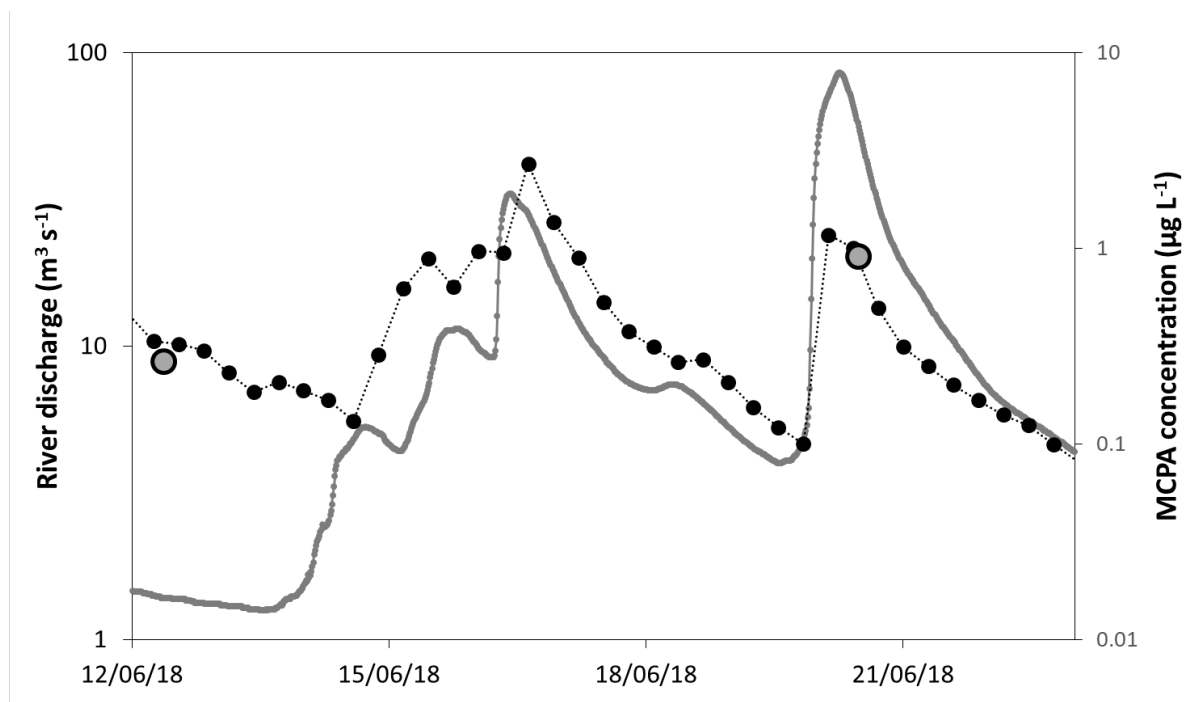


Figure 4 River discharge (15 minute frequency; data from Department for Infrastructure NI), weekly MCPA concentrations (data provided by Northern Ireland Water) and 7-hourly MCPA concentrations (data provided by AFBI) in a river in Northern Ireland during the summer period of 2018. River discharge is shown as a grey line, weekly MCPA concentrations are grey circles and 7-hourly MCPA concentrations are black circles. Note that both discharge and MCPA concentrations are displayed on a logarithmic scale. The data highlight the importance of sample resolution for insights on MCPA magnitude and process relationships.

5. Eco- and human toxicology

The toxicity of MCPA is dependent on its formulation and the species affected, as well as the method by which an organism is exposed to the pesticide. However, MCPA has a very low bioconcentration factor (BCF) between 1 (AERU, 2016) and 14 (Mackay et al., 2006) meaning that, regardless of its toxicity, the bioaccumulation rate is low and any organism killed by MCPA is unlikely to be toxic to another organism (a BCF of less than 1000 is not considered bioaccumulative; US EPA, 2016).

Nevertheless, MCPA is reported as highly toxic to aquatic organisms according to The Dow Chemical Company (2015), although AERU (2016) classify MCPA as having low toxicity to aquatic algae and invertebrates, and low to moderate toxicity to fish and aquatic plants. These differences are most likely due to use of different ecotoxicology classification systems (e.g. UN, 2015). The EC_{50} (half maximal effective concentration, i.e. reduces cell growth or density by half) for aquatic algae is between 32.9 and 392 mg MCPA L⁻¹, depending on the species, and is just 152 µg L⁻¹ for *Lemna gibba*, a common aquatic plant species (AERU, 2016; European Commission, 2008). Acute toxicity (LC_{50} ; lethal concentration required to kill 50% of the population) for fish is 50-72 mg L⁻¹, although is over 190 mg L⁻¹ for aquatic invertebrates, with a long term NOEC (no observable effect concentration) of 15 mg L⁻¹ for fish and 50 mg L⁻¹ for aquatic invertebrates (AERU, 2016; European

Commission, 2008). For comparison, the maximum concentration at which MCPA can legally be applied to fields is 6.75 g L⁻¹ (Nufarm UK Limited, 2016).

For birds, The Dow Chemical Company (2015) state that MCPA is virtually non-toxic whereas AERU (2016) state that MCPA is moderately toxic. The lethal dose (LD₅₀) for birds on an acute basis is 270 mg kg body weight⁻¹ and on a dietary basis is more than 983 mg kg diet⁻¹ day⁻¹ (AERU, 2016; European Commission, 2008). For amphibians, MCPA toxicity is very low, with NOECs of over 12 mg L⁻¹ reported (Kegley, Hill, Orme, & Choi, 2016). Toxicity of MCPA to honeybees is low (AERU, 2016; Kegley et al., 2016) with an LD₅₀ of more than 200 µg bee⁻¹ (AERU, 2016; European Commission, 2008). However, MCPA is moderately toxic to earthworms (AERU, 2016) with an LC₅₀ over 14 days of 325 mg kg dry soil⁻¹ (European Commission, 2008). MCPA is toxic to some soil arthropods (e.g. 100% mortality for *Aphidius rhopalosiphi* at a dose of 2.1 L ha⁻¹) but has no effect on others (e.g. 0% mortality for *Typhlodromus pyri* at a dose of 2.0 L ha⁻¹) (AERU, 2016).

Data reported for mammals indicate that MCPA is moderately toxic at an acute level (AERU, 2016), with an LD₅₀ for rats of 962 mg kg body weight⁻¹ (European Commission, 2008). Short-term oral or dietary toxicity to rats may be high, with one reported NOEC of 60 mg kg body weight⁻¹ (AERU, 2016) and another of 37.8 mg kg body weight⁻¹ day⁻¹ from a 90 day study at 450 ppm (European Commission, 2008). The majority of toxicity information reported for humans appear to be extrapolated from other studies on mammals that are not reported under toxicity to mammals (AERU, 2016; European Commission, 2008; The Dow Chemical Company, 2015) or else for which the data source is unclear (Kegley et al., 2016; The Dow Chemical Company, 2015; US EPA, 2016).

MCPA is classed as a slightly to moderately hazardous acute toxin to humans if ingested orally (AERU, 2016; Kegley et al., 2016). According to the US EPA (2004), the levels of MCPA which humans are exposed to through diet (food and water) are not of concern, although young children are at the most risk due to their lower body weights, and the WHO (2017) give an acceptable daily intake of 0.7 mg L⁻¹ on the basis of a 60 kg adult drinking 2 L day⁻¹. MCPA is not a skin irritant, although prolonged skin contact may cause slight irritation with local redness (The Dow Chemical Company, 2015). However, MCPA formulated as the parent acid, sodium salt or dimethylamine salt is a strong eye irritant (AERU, 2016; European Commission, 2008; US EPA, 2004). Inhalation of MCPA may cause some irritation in the nose, throat and lungs (The Dow Chemical Company, 2015) but toxicity is low (US EPA, 2004).

MCPA is not classed as a carcinogen (AERU, 2016; Bond & Rossbacher, 1993; European Commission, 2008; The Dow Chemical Company, 2015) or endocrine disruptor (AERU, 2016) although it has been shown to cause birth defects, low birth weight and maternal toxicity in laboratory animal studies (European Commission, 2008; The Dow Chemical Company, 2015). However, there are some non-conclusive epidemiological studies which suggest that exposure to MCPA may be associated with increased risk of non-Hodgkins lymphoma, Hodgkin's disease, leukaemia, and soft-tissue sarcoma (see von Stackelberg (2013) for a review of these studies). Whilst the evidence suggests that MCPA does not have a genotoxic mode of action, little is known about any potential interaction between exposure to MCPA and genetic polymorphisms, which increase the risk of developing non-Hodgkins lymphoma (von Stackelberg, 2013).

The majority of toxicity data for MCPA is based on studies involving MCPA formulations for spraying or as it is sold. However, as discussed previously, MCPA breaks down to form other compounds but

the toxicity and persistence of these metabolites is relatively unknown (McManus et al., 2017). Additionally, MCPA is often sold in a mixture with other pesticides (see Table S1; DAFM, 2017; HSE, 2017) and is likely to mix with other pesticides if it runs off into waterbodies or percolates through to groundwater. There is a paucity of data on toxicity effects of pesticide mixtures to any organisms (McKnight, Rasmussen, Kronvang, Binning, & Bjerg, 2015) although this is an increasing field of research (e.g. Gustavsson, Kreuger, Bundschuh, & Backhaus, 2017; Schreiner et al., 2016; Spycher et al., 2018).

There are also cases where MCPA itself is not toxic to the species involved but can form complexes that result in toxic effects. Phenoxyalkanoic acid herbicides can be adsorbed to mineral or organic ions in the soil and can react with metal ions within the soil solution (Kobyłecka, Turek, & Sieroń, 2009). MCPA has been shown to form complexes with Pb, Cd, Cu, Co, Mg (Kobyłecka, Ptaszynski, Rogaczewski, & Turek, 2003), Zn (Nefedov, Struchkov, Konnik, & Shulgin, 1991) and Mn (Tangoulis et al., 1996). As these complexes are sparingly soluble in water, this can increase the mobility of heavy metals within the soil and alter the resistance of MCPA to degradation (Kobyłecka et al., 2009).

While MCPA ecotoxicological studies report dosage responses that would be likely under acute pollution exposures and with the limits and guidelines for human health and environmental quality (see section 6) set well below these, there still remain issues with exposure in multiple stressor environments. Research to understand the impact of multiple stressor effects is ongoing. For example, Jackson, Loewen, Vinebrooke, & Chimimba (2016), in a study of multiple stressor effects in freshwater environments, indicated a more antagonistic interaction (impact is less than the sum of individual potential impacts) of multiple stressors rather than synergistic (greater than the sum of individual potential impacts) – but excluded pairing with pesticides. Baker, Bancroft, & Garcia (2013) reviewed studies on the synergistic impacts of pesticides and fertilizers, suggesting that the survival and growth rates of amphibians were significantly impacted.

6. Standards, legislation and mitigation

Whilst the EU Drinking Water Directive threshold of MCPA is set at $0.1 \mu\text{g L}^{-1}$, there is less consistency (at least among EU and affiliated member states) on assigning limits for Environmental Quality Standards (EQS) or similar under the EU Water Framework Directive. These standards are generally based on the biological responses to individual chemicals and, in the case of pesticides, related to ecotoxicity. For example, EQS based on annual average MCPA concentrations (AA-EQS) in some EU member states range from $0.01 \mu\text{g L}^{-1}$ to $1.6 \mu\text{g L}^{-1}$ (European Communities, 2012). Switzerland (non-EU but following similar methods) stipulates a Chronic Quality Standard (equivalent to AA-EQS) of $0.66 \mu\text{g L}^{-1}$ and an Acute Quality Standard (equivalent to a Maximum Allowable Concentration EQS) of $6.4 \mu\text{g L}^{-1}$ (Oekotoxzentrum, 2019). Other member states and affiliates (such as the Irish jurisdictions) rely instead on targets set by the Drinking Water Directive.

Due to the potential of many pesticides to cause toxicological effects or other damage to humans and the environment, all pesticides on the EU market are legally required to obtain authorisation in compliance with the EU Regulation (EC) No 1107/2009 (DAFM, 2017; HSE, 2017). There are two layers of authorisation required: firstly, an EU-wide assessment of active ingredients (a.i.) resulting in a “positive” list of substances, i.e. those that are approved for use; secondly, authorisation by individual EU Member States of plant protection products, i.e. formulated products which contain an a.i. (Bailey et al., 2017). An a.i. is usually approved for an initial period of 10 years, after which it

must be reassessed to ensure it complies with the latest standards of assessment relating to human health and environmental risks (HSE, 2017). The authorisation of formulated products contains conditions for the product use, application and storage and these are shown on product labels to ensure users are aware of and comply with these conditions (HSE, 2017).

Conditions of authorisation include application rates, timing of application, amount of time between applications or between treatment and harvesting, worker protection measures and measures to protect the environment (HSE, 2017). For MCPA, the maximum application rate is 1350 g a.i. ha⁻¹ (Hygeia Chemicals Ltd, 2017; Moran, 2015), which was reduced from 1650 g a.i. ha⁻¹ (Nufarm UK Limited, 2011) due to lower application rates being almost as effective as higher ones (Moran, 2015). Regardless of the marketed product concentration, MCPA should always be applied in at least 200 L of water per hectare (Hygeia Chemicals Ltd, 2017; Moran, 2015; Nufarm UK Limited, 2016). MCPA must not be applied between the end of September and the beginning of March (Hygeia Chemicals Ltd, 2017). Where rushes are the target weed, rush stems should be cut and removed either four weeks before or after treatment and MCPA should be sprayed only between April and June (Hygeia Chemicals Ltd, 2017; Nufarm UK Limited, 2011, 2016) in order to target the rushes when they are at their most vigorous growth stage.

Environmental protection measures include timing of application and the designation of statutory no-use and vegetated buffer zones where pesticide spraying cannot occur. As MCPA is highly soluble under most conditions (Bailey et al., 2017; Hornsby et al., 1996), it should only be applied when the ground is dry and when no rain is forecast in the proceeding 48 hours (Moran, 2015). Statutory no-use (safeguard) zones vary in size depending on the status of the waterbody (European Communities, 2012; Moran, 2015). For any waterbody where more than 100 m³ of water is abstracted per day for human consumption or which serves more than 500 people, there is a statutory no-use zone of 200 m (European Communities, 2012). Additionally, pesticides should not be used within 15 m of landscape features such as sinkholes, karst areas and collapse features that are known to be associated with areas of groundwater (European Communities, 2012).

Buffer zones include hedgerows, as well as waterbodies from which drinking water is not extracted, and vary between 1 m and 70 m (Moran, 2015). These buffer zones differ from safeguard zones in that their size depends on the type and concentration of pesticide used and the width can be reduced under certain conditions, although the methods used differ between countries. In Ireland, STRIPE (Surface water Tool for Reducing the Impact of Pesticides on the Environment) can be followed to determine the possible reduction in buffer width (DAFM, 2015), whilst a LERAP (Local Environmental Risk Assessment for Pesticides) is used in the UK (Defra & PSD, 2001). For both schemes, buffer zones can be reduced by reducing the pesticide dose applied, by using approved low drift spraying nozzles to apply the pesticide or by applying both measures (DAFM, 2015; Defra & PSD, 2001). Until recently, MCPA had a buffer zone of 5 m, which could be reduced if a LERAP or STRIPE assessment permitted a reduction based on the dose and equipment used (Nufarm UK Limited, 2011), but the buffer zone is now 5 m regardless of dose and equipment in order to protect aquatic organisms (Hygeia Chemicals Ltd, 2017; Nufarm UK Limited, 2016).

More recently, unpublished data from Northern Ireland Water show how the selective *application* of a broad-spectrum systemic herbicide, such as glyphosate using weed-wipers, as a replacement for the selective *treatment* of rush using MCPA, may be an effective alternative for rush control

(Northern Ireland Water, pers. comm.). This will, however, require further experimental research to gauge the potential for pollution swapping (e.g. Guilherme, Gaivão, Santos, & Pacheco, 2010) and must be cognisant of political debates on the future use of glyphosate and similar herbicides (European Parliament, 2017). Whilst rushes have historically been controlled by non-chemical means, such as raising pH by liming, drainage and cutting (Morse & Palmer, 1925), and rush prevalence can be reduced by avoiding poaching and overgrazing (Backshall, Manley, & Rebane, 2001), pesticides provide farmers with a quicker, easier and more effective method of rush reduction. However, modern farm machinery could facilitate a return to these traditional non-chemical methods.

Conclusion

7. Implications for emerging research

From this collation of information, research and action themes emerge relating to MCPA transfer in agricultural catchments. A useful template to illustrate these is the nutrient transfer continuum conceptual model described by Haygarth, Condon, Heathwaite, Turner, & Harris (2005) but here adapted as a herbicide transfer continuum:

1. Source – research into alternative MCPA use to minimise overall applications is required. Experiments on selective application of broad-spectrum herbicides require a formalised experimental approach using before-after-control-impact designs. Utility of alternatives combined with potential pollution swapping are important considerations.
2. Mobilisation – specific to soil, geology and land use type and with regard to varying OM content, further mobilisation experiments are required to disentangle hydrological and biogeochemical time lags, especially with regard to chemical bridging influences such as soil amendments of lime and nutrients (especially P) which may alter mobilisation dynamics. As liming and nutrient amendments are generally performed to augment the suppression of rush growth in marginal areas, and liming is a recommended longer-term measure, the effects on MCPA mobility under these conditions are unknown. Additionally, mobilisation experiments in highly organic soils are required.
3. Pathways – MCPA is highly mobile and the likelihood of incidental loss during storm events following applications is high in fast surface hydrological pathways, possibly including artificial drainage. Degradation is also high under aerobic conditions. However, degradation under anaerobic conditions is low and the transport of MCPA to these environments may contribute to legacy issues and distribution to a spectrum of hydrological pathways. There is emerging evidence of persistence in groundwater and this may be due to different MCPA ages based on oxic conditions. These processes at the catchment scale require untangling as well as the relative contributions of each pathway during hydrological events.
4. Delivery – despite the high mobility of MCPA and its seasonal use and loss, there is a paucity of higher resolution data, especially during high river discharge events when mobility will be greatest. These data will provide the best risk assessment in terms of concentration magnitudes and inform research on persistence and pathways. Increasing the resolution to at least sub-daily data capture through targeted investment will provide these insights.
5. Impact – ecotoxicological impacts of MCPA are well documented for lethal and sub-lethal effects. Guidelines and regulations for drinking water are clear. However, EQS targets for

MCPA among countries are less consistent and this may require further research. Furthermore, in the natural environment, knowledge on raw water multiple stressor effects is emerging on a global scale. As many of the environments where MCPA is applied also support higher water quality rivers and lakes (in addition to compliance with EQS), there is a need to research the potential synergistic and antagonistic effects of MCPA with other stressors (such as other pesticides and nutrients).

This empirical information will inform catchment scale herbicide models but also the debate on herbicide use in marginal agricultural areas. The suppression of rush growth in such areas is linked to the absolute soil function of primary production. As governments move to agricultural planning with political consultation of 'public goods for public services' (Bateman & Balmford, 2018), other functions such as carbon sequestration, water regulation and biodiversity may provide the conditions where MCPA use reduces.

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