02- Herbicides in Irish rivers – Hydrology is only part of the picture

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Abstract

Analysis of three separate sources of herbicide data (from EPA, Teagasc-ACP and APHA) and relating them to hydrological fluxes in an EPA-funded project has shown a range of different herbicides in Irish rivers. The percentages of analyses exceeding the S.I. 122 drinking water limit for each herbicide is mainly low but there are some higher herbicide concentrations, predominantly in the period from March to October that includes the main spraying period. These have a bimodal temporal distribution with more exceedances at the beginning and towards the end of this period.

For the ACP catchment data, where corresponding local flow and precipitation data was available, the higher 14-day average herbicide concentrations are not always strongly associated with the highest average flows or high rainfall peaks in the averaging period. Thus, the high herbicide concentrations in the river are not always the result of high surface runoff alone. This means that while rainfall events can and do deliver high concentrations of some herbicides, there are other times in which equally high concentrations are measured that are not associated directly with storm events and for which alternative explanations are needed. The high herbicide concentrations sometimes coincide with periods of high average potential evapotranspiration (PET). This could be because of (i) these good-weather periods tend to be chosen for the application of herbicides and the very high concentrations are due to accidents when mixing or spray drift or (ii) less dilution of herbicide in baseflows.

The analysis of the EPA Water Framework Directive herbicide monitoring data indicated an inverse relationship between high herbicide concentrations and suspended sediment, OrthoPhosphate and TON. This also suggests that there is an association of some of the high herbicide concentrations with dry weather and low flows.

The AHPA data, which has clusters of monitoring stations close together in each of its focus areas, suggests that the timing of high concentrations of a widely used herbicide (MCPA) is similar in stations close together. This is understandable for multiple stations on the same river, but also occurs for different rivers in the same general area. This could be caused by similar choice of suitable days for application of herbicides or a local weather event affect all sampling areas.

Overall, the analysis of Irish data indicates that many occurrences of high herbicide concentrations in rivers are intermittent and not exclusively associated with high water fluxes. The timing link of very high herbicide concentrations with periods of high PET suggest that timing is, at least partly, related to the choice of good weather periods for application of the herbicides and to the application process.

This attests to the complex and multiple-drivers character of the episodic concentration peaks. This means that modelling requires more than just hydrological and chemical processes and must include a characterisation of the incidents that cause the high peak concentrations and possibly human behaviour in relation to application of pesticides.

1. PESTICIDE MODELS IN THE LITERATURE

Models and Preferential Flow

Most models of pesticides and water describe vertical, 1-Dimensional, leaching and retention of pesticides through soil profiles [e.g. Sichani et al., 1991; Kannan et al., 2006; Sabbagh et al., 2007]. Several models of pesticide leaching describe chromatographic leaching, that is leaching without preferential flow, thereby predicting chemicals with stronger sorption to travel slower through soils [e.g. Vanclooster et al., 2000; Liestra et al., 2001; Scorza Júnior & Boesten 2005]. The significance of preferential water flow to pesticide movement however is now generally accepted to occur in most soils [Flury et al., 1994]. Preferential flow allows chemicals with strong sorption to move rapidly through soil profiles via macropores or other preferential flow mechanisms [Ghodrati and Jury, 1992]. Preferential flow is now an essential component of such leaching models, implemented as a dual-domain approach, i.e. modelling with two overlapping domains, one with chemical transport dominated by advection and the other dominated by slower diffusion [Feehley et al, 2000;Roulier and Jarvis, 2003; Larsbo and Jarvis, 2005; McGrath et al, 2008, 2009] as in the model MACRO, or as dual-permeability models such as is implemented in HYDRUS [e.g. Gerke and Köhne, 2004; Gärdenäs et al., 2006].

The impact of preferential flow at catchment scales is still unclear. Spatial variability is known to increase the susceptibility of catchment-scale groundwater to experience diffuse contamination [Christiansen et al., 2004]. So too, preferential flow at these scales is thought to increase the risks to groundwater [Stenemo et al., 2005]. Nevertheless, preferential flow is thought to impact water quality in streams via the loading of groundwater as well as from rapid sub-surface contributions from areas adjacent to streams [Kladivko et l., 1991; Gächter et al., 1998; Weilera et al., 2003; Leu et al., 2004; Lehmann et al., 2007].

Catchment-scale models tend to conceptualise preferential flow, e.g. due to macropores, as fast flow [e.g. Bertuzzo et al., 2013]. This event-based consideration in the models reflects perceptions that even at the catchment-scale pesticide transfer is largely the result of particular rainfall events. Indirect evidence for this comes from the US for pesticide loading to the Mississippi River [Capel et al., 2001]. They observed the annual load as a percentage of use remained almost the same irrespective of where in the large watershed the calculations, based upon data, were performed, further suggesting small scale events were propagating through the system. Some attempt at stochastic modelling of short duration events has been attempted for other types of chemicals. For instance, Whelan, Ramos et al. 2020 report successful modelling of export of the molluscicide Metaldehyde from an agricultural catchment in the UK in porewater drained following storm events. Applications of the chemical were modelled as a stochastic process with a Poisson distribution. In contrast to the herbicides studied here, their measured Metaldehyde concentrations showed a strong positive relationship with high river flows.

Catchment Scale Processes

Catchment-scale processes are somewhat neglected in the pesticide modelling literature. Indeed, an analysis of the literature, (Bruen, McGrath et al. 2021) suggests that empiricists have not yet found the means to express catchment-scale effects in pesticide transport. This is surprising since, at the catchment scale, the geomorphological structure of the landscape imparts spatial organisation to soils, the channel network, water storage and water flow [Schidegger 1968; Troutman and Karlinger, 1984; Mesa and Mifflin 1986; Rodriguez-Iturbe and Rinaldo, 2001; Grayson et al., 2002; Botter et al., 2007; McGrath et al., 2012; Bertuzzo et al., 2017]. Some of these patterns in the ways in which catchments are organised are universal, having been observed in all rivers on earth and all known extra-terrestrial rivers valleys such as those of Mars and Titan [Rodriguez-Iturbe and Rinaldo, 2001]. Catchments are now thought of as archetypes of self-organisation and contain statistical properties which are indicators of this. The ratios of the areas of successive stream orders in a basin follows an exponential relationship with stream order, so-called Horton's Area Law, and similarly the Law of Stream Numbers, stream slope etc. The probability distribution of cumulative contributing area scales as a power-law with an exponent of 0.43±0.01 for many catchments [Rinaldo, Rigon et al. 2014] even artificially engineered sewer networks tend towards this scaling [Yang et al., 2017]. Thus, it is surprising that this hydrological understanding has not been used to develop more catchment scale models of pesticide export from catchments (there are a small number of exceptions, e.g. SWAT as mentioned above). Again, with in-stream transport, the hydrological understanding has been applied to other pollutants, but less so to pesticide transport. For instance, there have been some recent general contributions to understanding transport in river networks using network and scaling concepts [Gooseff et al., 2008; Riml and Wörman, 2011; Harvey and Gooseff, 2015]. The scaling of in-stream processing of dissolved organic carbon was assessed by Bertruzzo et al., [2017] by determining how the topology of the river network structure contributed to the change in DOC concentrations along it. River network structure impacts the spatial organisation of biodiversity and ecological processes [Campbell et al., 2007; Muneepeerakul et al., 2011]. More recently, in a move away from complex models with many parameters, simple conceptual field-scale models have been applied, e.g. for herbicides in Switzerland [Ammann, 2020] and for Metaldehype (a Molluscicide) in the UK [Whelan, 2020].

2. HERBICIDE DATA ANALYSIS AND MODELLING IMPLICATIONS

Here, measurements of herbicide concentrations are analysed seeking information on the factors involved in their movement that can inform modelling efforts. Three major sources of data were available to the DiffuseTools project;

(i) One year of 14-day average herbicide concentrations in two Agricultural Catchments Programme (ACP) catchments, collected as part of the EU Horizon 2020 WaterProtect project, together with local precipitation and flow measurements. Using a Chemcatcher instrument, this provides a picture of the low-frequency variation of concentrations over the year and were compared with contemporaneous river flows and rainfall.

(ii) Water Framework Directive Monitoring: Environmental Protection Agency (EPA) data on concentrations in rivers of 19 herbicides. There was 15,463 analytical results from 162 surface water sampling sites in the dataset analysed.

(iii) Monitoring of herbicide concentrations undertaken by the Animal and Plant Health Association (AHPA) at priority catchments as defined by the National Pesticide and Drinking Water Action Group, Deel, Feale, Lough Forbes, Nore and Upper Erne.

Analysis of Agricultural Catchments Programme Data

As part of the Horizon 2020 project WaterProtect, a one-year time series of herbicide measurements was collected by Teagasc in the outlet of two ACP catchments, Ballycanew (dominated by grassland on poorly drained soils) and Castledockrell (dominated by arable land on well drained soils) covering the period 6/11/2018 to 21/11/2019. These catchments were not chosen for being “problem areas” for herbicides, but because they are hydrologically different and have different land uses.

The average annual runoff for that period was similar for both catchments and was 719 mm for Ballycanew and 694 mm for Castledockrell. However, the annual rainfall totals were different, i.e. 1180 mm for Ballycanew and more than that (1316 mm) for Castledocerell, showing naturally different hydrological behaviour between the catchments.

A Chemcatcher ® passive sampler was used to produce 14-day time-weighted mean concentrations of a range of herbicides but here we concentrate on MCPA, Fluroxypyr and Mecoprop. In most cases, while these were found in both catchments, the concentrations tend to be greater in the poorly drained, grassland dominated, Ballycanew catchment compared to the well-drained Castledockrell, dominated by arable crops. Minimum values for these herbicides throughout the year are not zero and generally (with some exceptions) are above detection limits. As the pesticide is not applied all year round, this implies some contribution from base flows, i.e. through subsoil pathways. However, the minimum concentrations are small compared to the annual mean or median concentrations.

A key question is to what extent the delivery of herbicides to rivers is via the hydrological pathways (surface runoff, interflow and baseflows). To examine this question, the 14-day measured pesticide concentrations were plotted against the flows (mean and maximum), precipitation (mean and maximum), Potential evapotranspiration (mean and maximum) and estimates of the soil moisture deficits (mean and maximum) for the corresponding 14-day periods.

Looking at Ballycanew first, Figure 1 (a) and (c) shows the Fluoxypyr and MCPA concentrations vary with the corresponding 14-day mean flows. High concentrations of all herbicides are strongly associated with low mean flows and there are no high herbicide concentrations associated with high river flows. Similar patterns occur for the relationship between rainfall and these herbicides (not shown). However, when these herbicide concentrations are plotted against Potential Evapotranspiration (PET) there is a strong indication that high concentrations are associated with high values of average PET, (Figure 1e,g)) for Ballycanew and, only marginally for Fluroxypyr in Castledockrell, (Figure 1f), but not for MCPA.

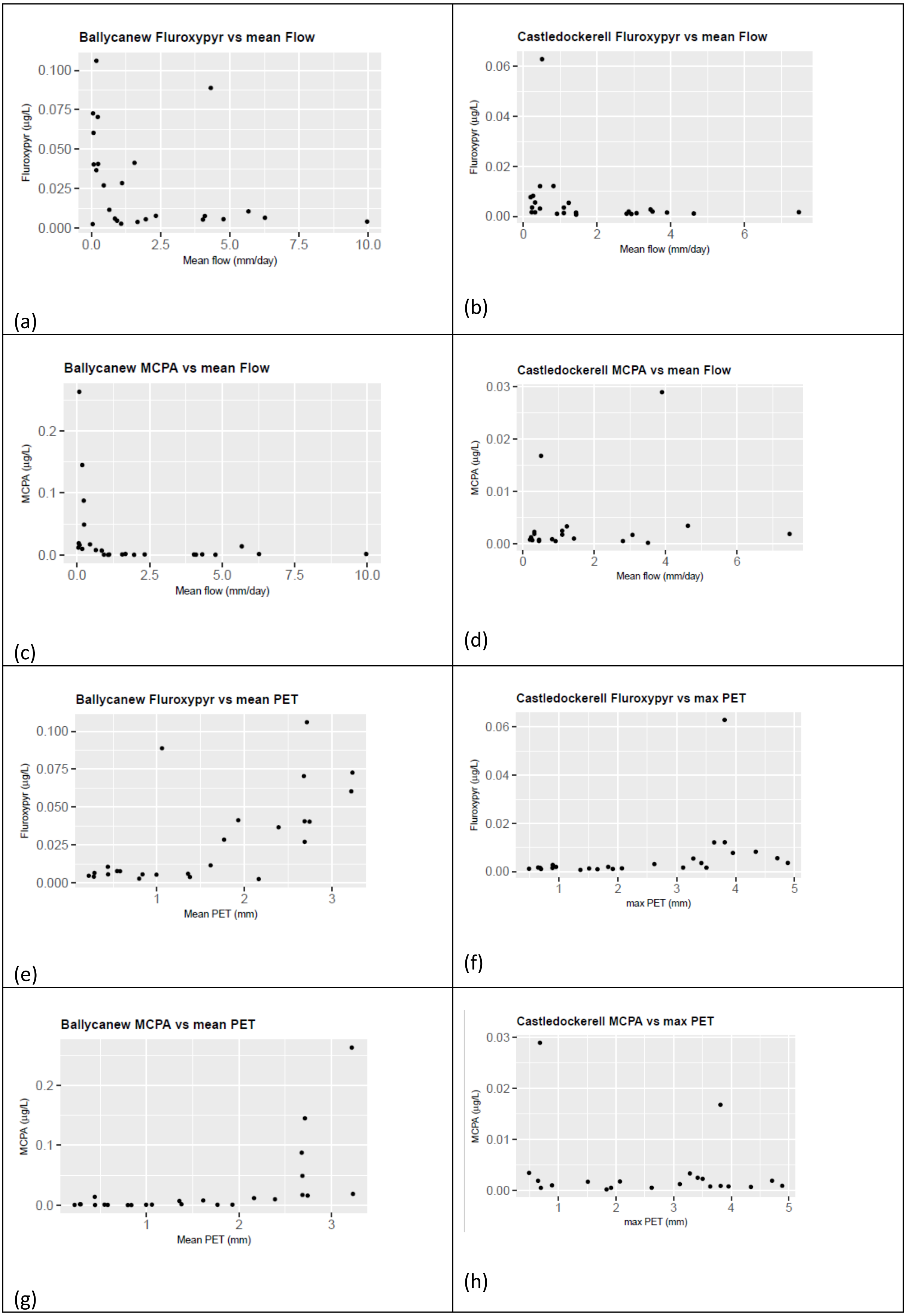


Figure 1: Herbicide concentrations, flow and PET for Ballycanew and Castledockrell.

Thus, high herbicide concentrations are not always the result of high surface runoff. This means that while rainfall events can and do deliver high concentrations of some herbicides, there are other times in which equally high concentrations are measured that are not associated directly with storm events and for which alternative explanations are needed. However, the 14-day averaging in the Chemcatcher data collection must be taken into account. Concentration data of higher temporal resolution may be required to resolve the various contributions from hydrological process from other factors. In Northern Ireland, preliminary reports of data with high temporal resolution (Source to Tap project) does show that high MCPA concentration peaks can occur both during periods of high river flows but also, and just as frequently, during periods when river flows are much lower (Jordan, 2019). This attests to the complex and multiple-drivers character of the episodic concentration peaks.

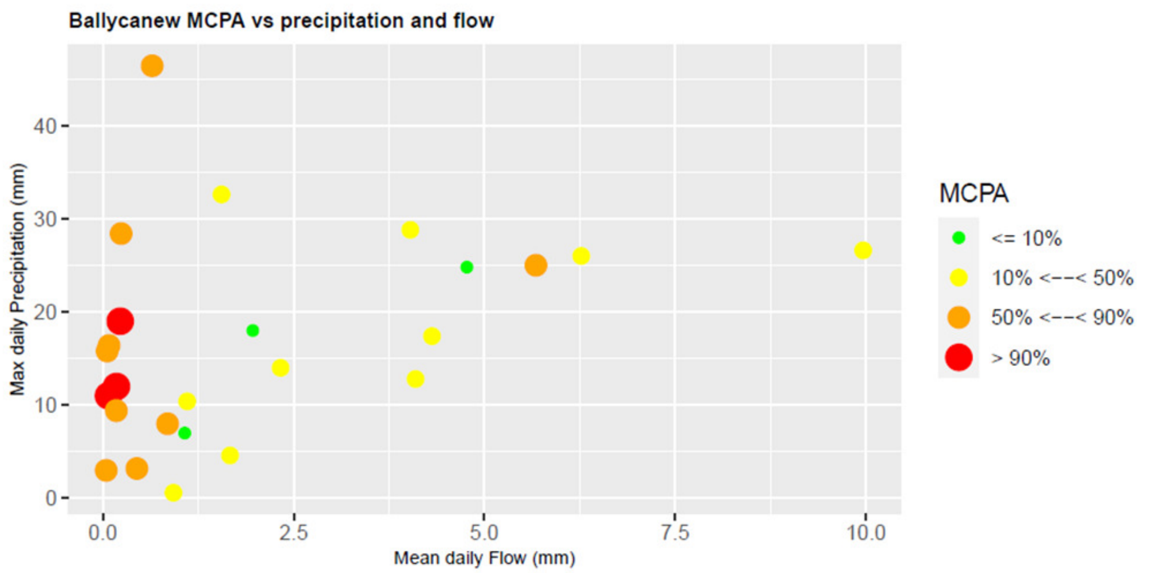
The strong relationship between high 14-day average herbicide concentrations and high PET (and to a lesser extent soil moisture deficit) means these high concentrations occurred in good weather and mostly with no rain. This is consistent with these high concentrations occurring during preparation (spills or washing) or spray drift during application on dry, warm periods (i.e. high PET). However, other explanations, including dilution, etc. may also play a role.

Combined effect of rainfall and flow

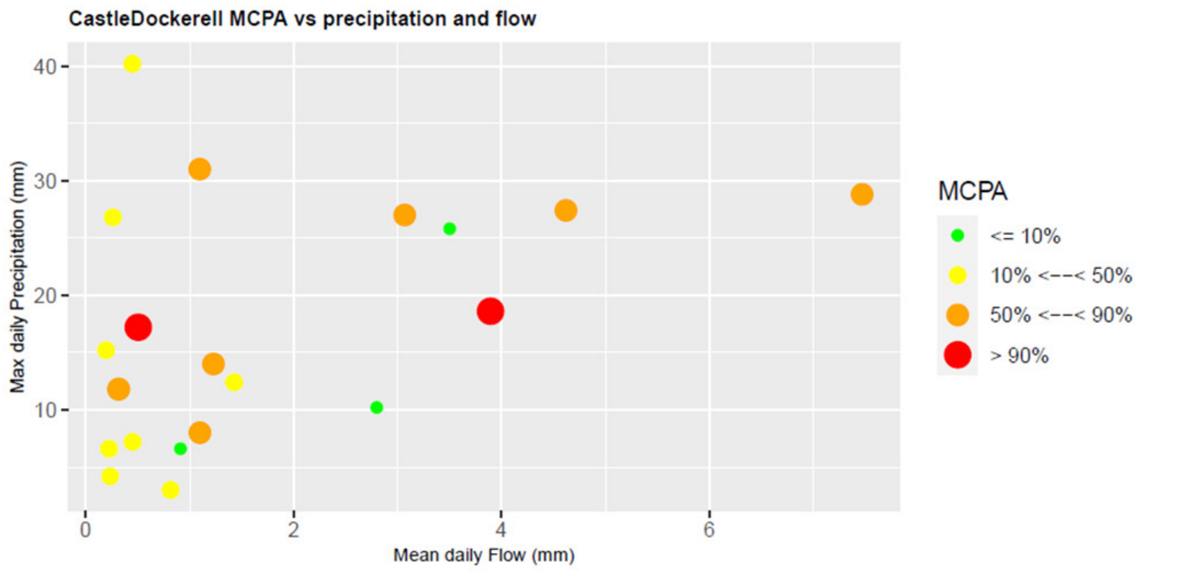
While there appears, from Figure 1 above, some herbicide may be exported through subsurface flows (i.e. high concentrations during low flows), it is curious that there is not a stronger indication in the data of a mechanism due to surface runoff from high intensity rain. Dilution in the resulting higher or intermediate flows occurs and may be a factor. It is also likely that herbicides are leached to groundwater (it was present in many private drinking water wells in the catchments) and transferred to the streams via shallow groundwater [Khan, Costa et al. 2020]. Also, there may be some in-stream storage of herbicide in sediments that are mobilised under certain conditions.

To investigate further the possible drivers of herbicide concentrations, plots of peak daily rainfall in each 14-day data interval versus the corresponding mean flow in the same period and the average MCPA concentrations were overlain (subdivided by size and colour into quartiles), The peak daily rainfall is used instead of the fortnightly average because if surface runoff transport is a dominating factor then high herbicide concentrations can be expected to be generated by severe events rather than average rainfall. In these figures, the position of each dot, irrespective of size and colour, represents maximum daily precipitation in each two-week period plotted vs. the mean daily flow for the corresponding period. The size and colour of the dots represent the magnitude of the average herbicide concentration in the same period. To determine the size and colour of the dots, the herbicide concentrations are divided into classes, i.e. less than the lowest 10% of the herbicide data (green), between 10% and the median of the data(yellow), between the median and the higher 90% of the data (orange) and higher than 90% of the data (red).

For Ballycanew, Figure 2 (a) there are no 14-day periods in which large average herbicide concentrations are associated with the highest quantile of sample averaged river flows and this supports baseflow as a source, or a dilution effect or that there is little storm runoff export from land in those periods. The more intensive rainfalls are mostly associated with the lower river flows (probably occurring as thunderstorms in summer), but the highest concentrations in the river occur for a very wide range of peak rainfalls. However, there are many high concentrations of herbicide associated with periods of low river flow and low peak rainfall (lower left-hand side of plots). This implies an important non-hydrological influence in addition to any hydrological transport. This may include subtle influences of timing, spatial distribution and methods of herbicide application.



(a)



(b)

Figure 2: MCPA concentration relationship with rainfall and flows at Ballycanew and Castledockrell

For the well-drained Castledockrell catchment, Figure 2 (b) there is not a clear relationship between most herbicide concentrations and flows or precipitation variables. About half of the high MCPA values are associated with high precipitation and flows, while the other half occur during low flow periods, typical of the main herbicide application period, and all bar one of these also had low rainfall. This also suggests that higher stream concentrations have multiple influential drivers not simply related to river flow and precipitation intensity.

EPA monitoring

An important question is whether the results, described above, derived from the two intensively monitored ACP catchments are representative of the herbicide situation in the Republic of Ireland. To answer this a more spatially extensive dataset is required. The EPA monitor water quality at 9399 sites across Ireland for purposes that include their Water Framework Directive related responsibilities. The data for pesticides typically is one day per month from the period 2013-2019 includes samples from 194 of these stations, on rivers or streams distributed across the country, with slightly better coverage in the Midlands than in the West and South of Ireland. Only a small percentage (less than 3%) of samples exceeded the S.I. 122 maximum limit, except for MCPA for which less than 8% exceeded the limit. There were no exceedances of that limit for Simazine and Terbutryn. In all these, the concentration median and 75% quartile are well below the S.I. 122 limit, Figure 3 and the exceedances are typically an order of magnitude, or even more, greater than the median, suggesting they are caused by exceptional events. In that figure, the red dots show large number of high concentration outliers

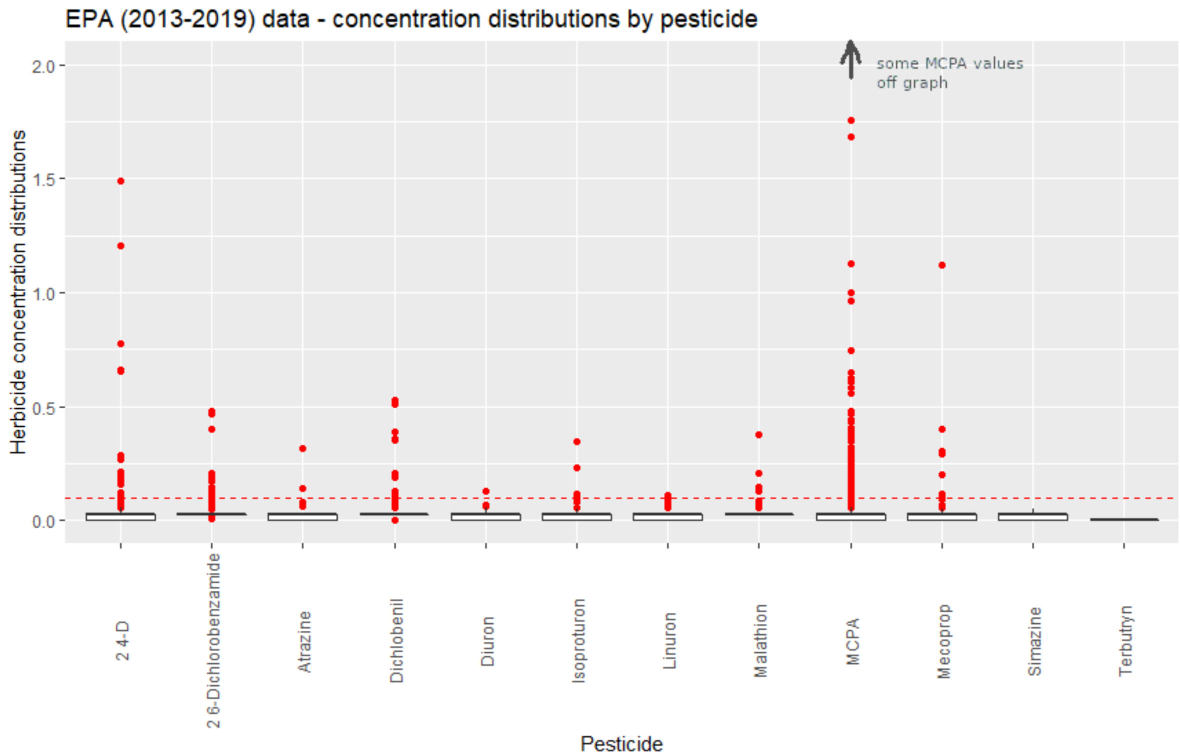


Figure 3: Box plots of EPA herbicide data concentration distributions (µg/L) of key pesticides. Note: red dots show high concentration outliers and values below Limit of Reporting are treated as concentrations half that limit.

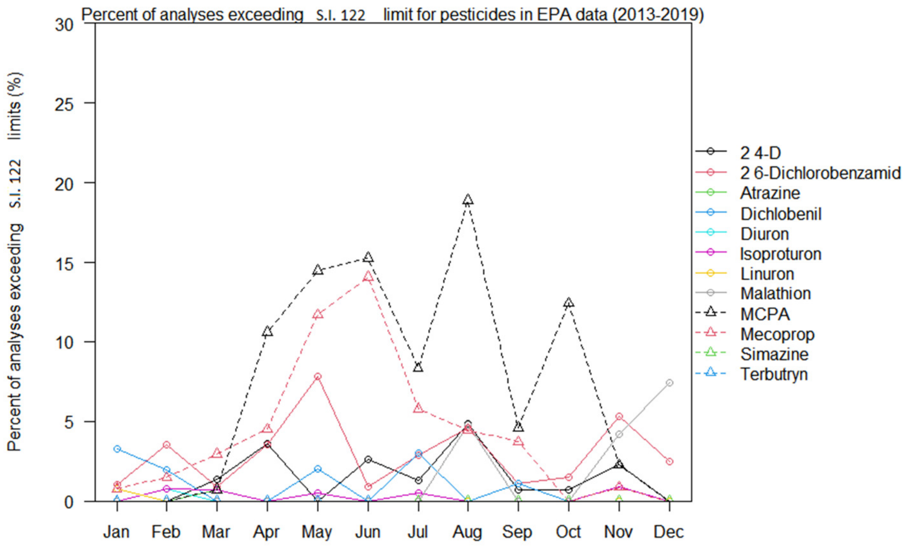


Figure 4: Monthly distribution of analyses exceeding S.I. 122 by month in EPA data (2013-2019)

The most frequently detected chemicals are Dichlobenil, MCPA, Clopyralid, Mecopropo and Diuron. The percentage of analyses each month that exceeded the S.I. 122 limit are shown in Figure 4. Here we do see, as expected, a tendency for many exceedances of S.I. 122 maximum limits to cluster in the summer/autumn period, particularly for MCPA and Mecoprop. This is consistent with the previous analysis of the ACP data and tends to support the conclusions made from that data. However, the percentage of samples exceeding the limits is smaller for 2.4-D and 2.6-Dichlorobenzamide, and they are more evenly spread over the year.

There are a larger number of analyses below the LOR in the EPA dataset when compared with the ACP data for some herbicides. Several reasons could be proposed, but one possibility is that the continuous 14-day average produced by the Chemcatcher picks up short duration pulses of herbicide that less frequent grab sampling may miss. Nevertheless, such averaging techniques have been recommended in the literature from an ecotoxological perspective, [Ashauer, 2020].

Relationship of herbicide concentrations with hydrological processes

Unfortunately, river flow and catchment rainfall data are not readily available for the EPA monitoring stations used for herbicide sampling. So, an indirect approach is therefore used to investigate the strength of the relationship between herbicide concentration and hydrological processes. It is generally accepted that sediment concentrations [Rymszewicz, Bruen et al. 2018], and to some extent phosphorus concentrations [Nasr, Bruen et al. 2007], in rivers are related to heavy rain events and high flows and both are associated with the quick-flow response of catchments. In contrast, nitrate concentrations are generally associated with less variable subsurface pathways. Nitrate pulses can also follow drought periods because the moisture stress means less root uptake and more leaching when the drought ends. If the processes involved in producing high herbicide concentrations in rivers were the same as those of suspended sediment and phosphorus or alternatively were like those of nitrates this would support an argument that the processes of mobilisation and transport were also similar. To examine this, measurements of suspended sediment, phosphorus, and nitrate for the same days as herbicide measurements were extracted from the EPA dataset and correlated with the individual herbicide concentrations. This was done for all the individual monitoring locations for which there is herbicide data. There is considerable scatter in the data, understandable because of the multitude of factors that influence the concentrations of herbicide and other water quality parameters and many graphs were not used if dominated by a single outlier. Nevertheless, there is some indication of an inverse relationship between high herbicide concentrations and suspended sediment, Figure 5, and for OrthoPhosphate and TON (not shown here). This suggests that there are some differences in the processes producing high concentrations of each. In particular, the association of some high herbicide concentrations with dry weather and low flows from the analysis of the two ACP catchments does seem to apply more widely.

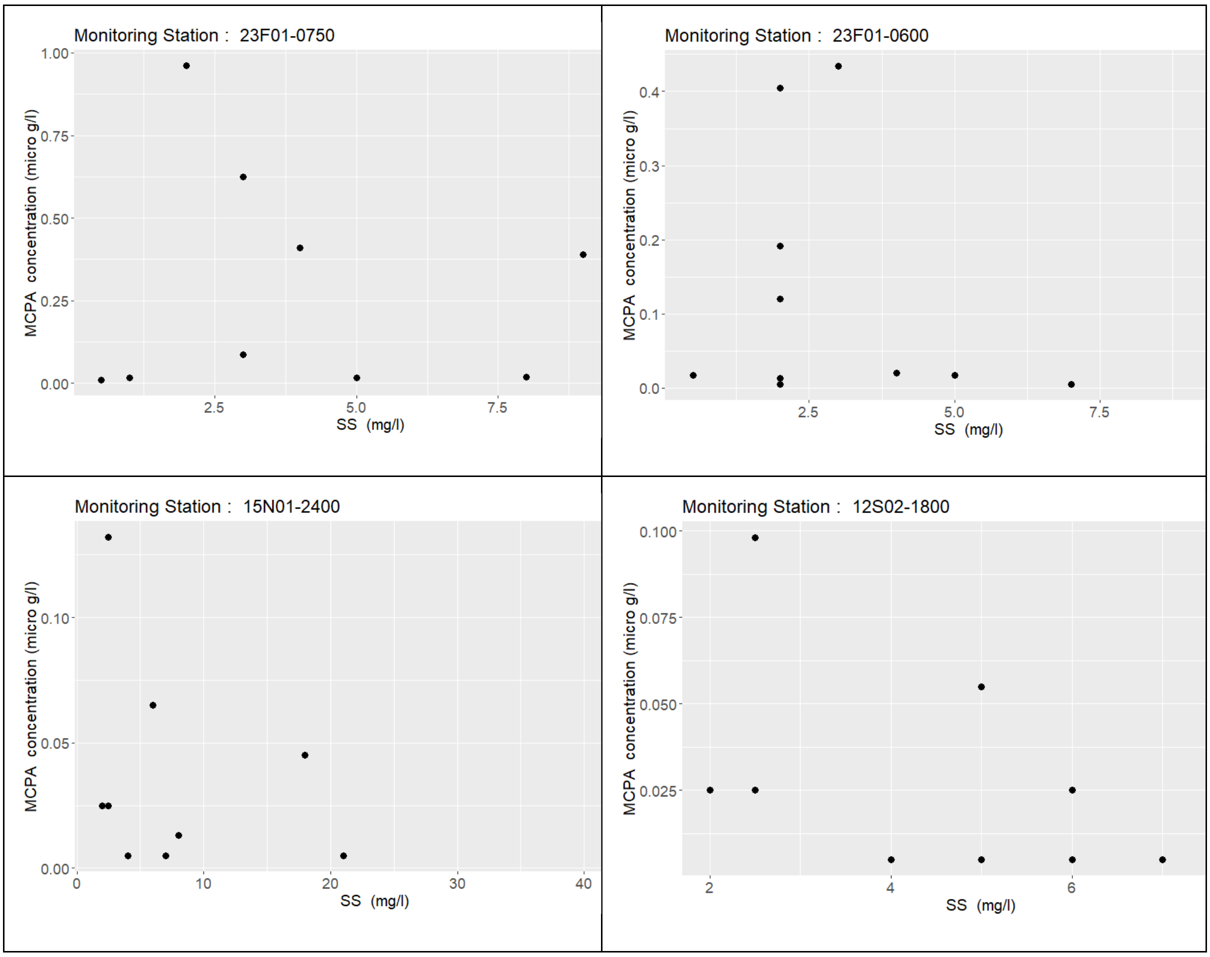


Figure 5: Examples of MCPA vs SS (EPA data 2013-2019)

Data from APHA

The Animal and Plant Health Association (APHA) is the representative body for manufacturers and sole distributors of veterinary medicines and agrochemicals, including pesticides and herbicides. Part of its remit is to provide information about these products and to inform policy and legislation in relation to their effects on the environment. The APHA has undertaken monitoring of pesticides in waterbodies in four areas in 2018 and 2019, near Lough Forbes together with the upper reaches of the Deel, Feale, and Nore. In 2020, the Nore sites were not sampled and areas in the upper Erne system near Belturbet was added to the monitoring. Monitoring was either weekly or fortnightly and most sites were sampled from week 14 to week 42 with a reduced number of sites in other weeks. Therefore, while all available data is used in summaries, the analysis below focusses on weeks 14 to 42. Also, although a small number of the Lough Forbes sites were monitored during the winter of 2019, this data was not used in this analysis as there were no corresponding measurements for the other areas. These sites were chosen because of their history of pesticide related issues and so are not necessarily representative of the overall national situation.

All samples were analysed for MCPA, MCPB, 2,4-D, 2,4-DB, Mecoprop and Dicloroprop 24DP. Only a small percentage of samples exceeded the S.I. 122 limit of 0.1 µg/L for MCPA, 2,4-D, 2-4-DB and Mecoprop, Table 1. For MCPA the percentage exceedence (15%) is approximately double that of the EPA dataset, but this is understandandable as the areas in the APHA dataset were chosen because of their herbicide issues and also here the APHA data is not averaged over the entire year but over weeks 14 to 42 covering the main spraying season.

Table 1: Summary of AHPA analyses for all five study areas (2018-2020)

Herbicide	Percent exceeding S.I. 122 limit	Herbicide	Percent exceeding S.I. 122 limit
MCPA	15 %	Mecoprop	0.6%
2,4-D	2 %	2,4-DB	0.2 %
		Overall	**4.4 %**

Sampling at all monitoring points typically took place from week 14 (mid-April) until about week 42 (end-September) corresponding to the application period expected to be of highest risk. This is the period analysed here. Table 1 shows a box and whisker plot of the results for all analyses by week. The horizontal black bar shows the overall median concentrations for each week, lumping all analysis together for each week, was well below the S.I. 122 limit (shown as a dotted red line) for all weeks. However, there are many very high concentration outliers (exceeding 1.5 times the inter-quartile range above the upper quartile, shown as red dots) in each week sampled, (up to 5 µg/L) suggesting the episodic nature of the higher concentrations. Note that some of the sampling sites are small streams with reduced dilution capacity and this may be reflected in the concentrations. The earlier summer weeks, particularly from week 18 to week 22 tend to have higher exceedances than the later parts of the year.

3. DISCUSSION AND CONCLUSIONS

Analysis of three separate sources of data on herbicide concentrations in Irish rivers has detected a range of different herbicides. The most frequently detected are MCPA, MCPP (Mecoprop), 2,4-D, with a smaller number of detections of Fluroxypyr, Bentazone, Triclopyr, 2,4-DB, 2,6-Dichlorobenzamide, Atrazine, Dichlobenil, Isoproturon, Linuron, Malathion and Simazine. The full details of the analysis is reported in [Bruen, McGrath et al, 2021] and only an overview is given in this paper.

The higher concentrations, and exceedances of the drinking water limit set out in S.I. 122 are predominantly in the March to October period that includes the main spraying period and have a bimodal distribution with a higher number of exceedances at the beginning and towards the end of this period. The percentages of analyses exceeding the S.I. 122 limit for each herbicide is mainly low and is in single digits nationally but higher in the APHA data which focusses on the main spraying period in areas with known herbicide issues. At most monitoring points the distributions of concentrations are heavily positively skewed with some intermittent extremely high values. This necessitates a frequent monitoring regime to capture the full variability and to estimate loads.

In general, where local flow and precipitation data was available, (the ACP catchments) the higher herbicide concentrations are often seen to coincide with low 14-day average flows and low rainfall amounts but interestingly do tend to correspond to periods of high average PET and to a lesser extend high average soil moisture deficits. Triclorpyr in the Castledockrell ACP catchment is the exception. This could be because of (i) these good-weather periods tend to be chosen for application of herbicides and the very high concentrations are due to accidents when mixing or application or spray draft or (ii) less dilution of herbicide in baseflows. This means that modelling requires more than just hydrological and chemical processes and must include a characterisation of the incidents that cause the high peak concentrations and possibly human behaviour in relation to application of pesticides.

The AHPA data, which has clusters of monitoring stations close together in each of its focus areas, suggests that the timing of high concentrations of a widely used herbicide (MCPA) is similar in stations close together. This is understandable for multiple stations on the same river, but also occurs for different rivers in the same general area. This could be caused by similar choice of suitable days for application of herbicides or a local weather event affecting all sampling areas.

The association of high herbicide concentrations with periods of high PET suggest it may be related to the choice of good weather periods for application of the herbicides and/or related to the application process. This study considered the endpoint of the solute transport process by focussing on concentrations in streams and rivers. The starting point, the application process, its exact timing, the rates of application and its spatial distribution are much less documented. This is a significant challenge for interpreting transport pathways and mechanisms of pesticide mobilisation and has implications for the modelling of herbicide concentrations in rivers. Data collection that includes use may be key to improving water quality in Irish rivers. The high variability of observed concentrations suggests that a stochastic model for applications linked together with a process-based hydrological model for transport, dilution and attenuation is required to better understand the interplay of climate, environmental chemistry, and hydrology. The available data collection is insufficient for the development of clear conceptual models of dominant transport processes, let alone the validation of a complex process based model.

The results presented here suggest several mechanisms during the warmer months may be significant contributors to high MCPA concentrations in Irish rivers. Research activities to identify and mitigate these may prove beneficial for water quality improvement. Human behaviour or common methods of herbicide application could be assessed for their risks to water quality. Additionally, to assess if subsurface flow is a significant source of MCPA a survey of riparian groundwaters should be able to test such a hypothesis. High resolution pesticide monitoring can also shed light on a variety of controls such as soils, climate and land management as has been elucidated for nitrogen and phosphorous in the ACP catchments. Critically, for understanding how to improve water quality at catchment scale, the spatial and temporal distribution of pesticide applications needs to be measured in order to be able to better interpret ongoing water quality monitoring.

Note: The conclusions from this empirical analysis do not necessarily apply to other herbicides not mentioned, particularly those with significantly different properties.

4. ACKNOWLEDGEMENT

This paper arises from the DiffuseTools project which was funded as part of the EPA Research Programme 2014–2020. The EPA Research Programme is a Government of Ireland initiative funded by the Department of Environment, Climate and Communications. It is administered by the Environmental Protection Agency, which has the statutory function of co-ordinating and promoting environmental research.

Special thanks go to the data providers, the Agricultural Catchments Programme, the Environmental Protection Agency and the Animal and Plant Health Association.

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