CatchmentCARE
Final Report on Chemical Escape from Land Use

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Disclaimer:

The views and opinions expressed in this report do not necessarily reflect those of the European Commission or the Special EU Programmes Body (SEUPB).

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Executive Summary

As part of the CatchmentCARE Project, Loughs Agency was responsible for investigating the Control of Chemical Export from Land Use in the Finn Catchment. This task was put forth in Activities A.T1.7 & A.T2.4, both of which were titled "Control of Chemical Export from land use activities". Several deliverables formed these Activities which, broadly, directed Loughs Agency to investigate chemicals of concern, their source, and methods to help mitigate or eliminate their introduction to the aquatic environment.

To address these deliverables, Loughs Agency produced a desktop literature review which identified key areas of concern related to chemical export which were identified as Agriculture and Forestry in the Finn Catchment. Four chemicals of concern were identified. The four chemicals of concern were; Cypermethrin, Acetamiprid, Organophosphates and MCPA. The literature review investigated the impact that these chemicals had on the aquatic environment and flora and fauna therein as well as how introduction to that environment could be reduced or eliminated.

Following on from recommendations contained within the literature review, Loughs Agency carried out two large scale surveys in the Finn Catchment. One was to identify all known public and private forestry plantations in the Catchment and the other was to identify all public and private sheep dipping facilities. In both surveys, information was gathered on how these activities interacted with the watercourse, whether measures were in place to help avoid any negative impacts upon the river environment and what could potentially be implemented at locations that were seen to be a high risk for chemical export to the river.

A third survey was also devised which used passive sampling equipment to determine the extent of chemical export in the Catchment. Passive sampling devices were deployed continuously over a twelve month period for a month at a time and allowed for continuous monitoring of selected sites in the Finn Catchment. This survey facilitated the capture of chemical export events over a set time period.

Data collected during the forestry survey resulted in a suite of mitigating measures being devised and an infographic was produced showing these measures and how they should be implemented on any newly planted forest crops. Discussions held with representatives of Coillte on these mitigation measures revealed that all public forestry planted after 1991 had mitigating measures in place similar to those suggested by CatchmentCARE. The main issue was with any crops planted before this period.

Investigations into sheep dipping facilities revealed that a significantly higher number of dipping facilities existed in the Catchment than was previously known from historical records. Additionally, it was determined that the dipping facilities which were highest risk for chemical export to local water bodies were multi-user publicly available dipping facilities.

To remedy this, Loughs Agency and Donegal County Council identified three publicly owned, regularly used facilities and installed Integrated Constructed Wetlands (ICW's) at each of these sites. These wetlands were planted with a mix of plants that were known to be able to remove chemicals from polluted water.

In addition to installing the ICW's, Loughs Agency and Donegal County Council held a sheep dip demonstration day that showcased to farmers how to properly dip sheep, proper disposal methods for spent sheep dip and the negative impacts that sheep dip can have on water quality and the aquatic flora and fauna. This demonstration was filmed and distributed via social media as well as by Teagasc.

An infographic was also produced with the same information that was contained in the demonstration day video and these were distributed at numerous CatchmentCARE events held in the Finn Catchment.

Results for the Passive Sampling survey indicated that exceedances occurred at different points in the year at different locations for Acetamiprid, Diazinon & MCPA. No exceedances occurred that could be attributed to Cypermethrin although Cypermethrin levels on field blanks were exceptionally high.

Overall, chemical export to water from land use in the Finn River Catchment can mainly be attributed to agricultural activity, particularly sheep dipping, and the improper disposal of spent dip. There are also still some residual risks from forestry plantations planted prior to 1991 but, as these are cleared and replanted with proper measures in place, this issue should be mitigated over time.

The efforts to raise awareness in the Finn about proper use and disposal of pesticides and herbicides, through the production of infographics and holding demonstration days, will help reduce the introduction of these chemicals to the aquatic environment.

Similarly, the installation of three Integrated Constructed Wetlands at three publicly used dipping facilities will help eliminate any chemical export from these facilities related to sheep dipping.

1. Introduction

The Finn Catchment is situated in the North West of the Island of Ireland and the majority of the Catchment (approx. 95%) lies within Co. Donegal with the rest falling in Co. Tyrone. It consists of 21 waterbodies, 20 of which occur in Ireland and 1 in Northern Ireland and is incorporated in to the North Western River Basin District.

The Catchment runs West to East from Lough Finn, where the river rises, to the town of Lifford where the river joins the River Mourne and ultimately the Foyle. The Catchment is 498km^2 in size with 478.3km^2 located in Ireland and the remaining 19.5km^2 occurring in Northern Ireland. Due to the cross border nature of the river, and the fact that it ultimately enters the sea via Lough Foyle, Loughs Agency is the competent authority with remit to protect and monitor the river and its tributaries.

The River Finn and its tributaries, the Corlacky, Reelin sub-Catchment, Sruhamboy, Elatagh, Cummirk and Glasagh as well as the spawning grounds of the Mourne and Derg Rivers, Loughs Derg and Belshade and the tidal stretch of the Foyle north of Lifford to the border are all included in the River Finn Special Area of Conservation (SAC) (Site Code 002301). The site was designated for the following habitats and species listed on Annex I/II of the E.U. Habitats Directive (* = priority):

- [3110] Oligotrophic Waters containing very few minerals;
- [4010] Wet Heath;
- [7130] Blanket Bogs (Active)*;
- [7140] Transition Mires;
- [1106] Atlantic Salmon (*Salmo salar*);
- [1355] Otter (*Lutra lutra*).

Several other designations exist within the catchment and these are:

- Meenaguse Scragh SAC (Site Code: 001880);
- Meentygrannagh Bog SAC (Site Code: 000173);
- Cloghernagore Bog and Glenveagh National Park SAC (Site Code: 002047);
- River Foyle and Tributaries SAC (Site Code: UK0030320);
- Moneygal Bog SAC (Site Code: UK0030211);

- Derryveagh and Glendowan Mountains SPA (Site Code: 004039).

Lough Finn also supports a population of Arctic Char (*Salvelinus alpinus*) which is listed in the Red Data Book as threatened.

Corine Land Cover Data 2018 shows that the Western half of the Finn Catchment is made up of mostly upland blanket bog and peat land. Areas of bare or sparsely vegetated rock are common and drier more well drained areas support heath and moor habitats. Peat harvesting and associated drainage are widespread in this area although relatively intact bog still covers large areas. Commonages are an important feature in this area and sheep grazing is widespread.

Significant areas of commercial forestry have been planted in the western area of the catchment, largely made up of coniferous plantations. Sitka Spruce is most commonly planted although Lodgepole Pine, Larch and Scots Pine are also planted. Several relatively small areas of hardwood forests also exist consisting of beech, alder, sycamore, oak and ash.

Rough grazing occurs in the transitional areas between the west and east of the catchment however in the eastern half of the catchment agriculture dominates land use. The lowland alluvial ground in this area gives rise to productive pastures as well as some limited tillage land. Much of the grassland is unimproved although improved grasslands and silage pastures are also present, particularly east of Ballybofey. Spreading of slurry and fertiliser in these areas is one of the main threats to water quality in the Finn, particularly as this area is prone to extensive flooding.

Data collected during the scoping phase of the Catchment CARE project, which was used as a baseline for carrying out targeted mitigation measures in the Finn Catchment, revealed that, while a number of the headwaters in the Catchment were of Good status (the upper Finn, the Cummirk), many of the headwater rivers were significantly impacted and of a Poor ecological status. These include the Elatagh, Reelin, Rough Burn and Burn Daurnett. Large sections of the main stem of the Finn were also classified as of Poor status and thus below the Water Framework Directive (WFD) objective of Good status. A comparison of data between 2015 and 2018 showed that nine water bodies had deteriorated in status whereas only two had improved in status. The remaining nine waterbodies status (of which there was monitoring data available) remained unchanged during this period.

Of the parameters comprising the status assessment for the Finn for the scoping study, general chemical and nutrient conditions were satisfactory in many areas, and in a number of cases total ammonia, ortho-phosphate and total oxidised nitrogen levels showed modest decreases in the years prior to the scoping study. Therefore, in many of the waterbodies macroinvertebrate status was the driving factor – i.e. the status element with the lowest rating – in determining overall status. Macroinvertebrate sampling has been a long-standing element of river monitoring programmes in the Finn and lengthy datasets enable long term trends to be assessed. In almost all instances in the Finn catchment there was a steady decline in macroinvertebrate biotic quality indices (Q-value).

In some waterbodies indications of toxic effects on the macroinvertebrate communities were noted, e.g. in the Elatagh River and in the Finn downstream of its confluence with the Elatagh, and in the lower Reelan River and its tributary the Clogher River. The herbicide MCPA was highlighted as an issue in the Stranagoppogue, as well as forestry pressures. Indications of heavy siltation were also noted in the Elatagh River.

Pesticide use and the potential impact it could have on water quality on the Finn was highlighted as a particular concern for the Catchment and a possible cause of the decline in macroinvertebrate populations in the area. The Stranagopoge, Clogher, Reelin & Finn_040 were listed by the EPA as being particularly vulnerable to negative impacts from pesticide use, particularly from sheep dipping activities.

This report, produced by Loughs Agency, for the SEUPB funded CatchmentCARE project, is being presented as a requirement of work packages T1 "*Scoping and Action Targeting*" & T2 *"Waterbody Actions in Catchments"* which define Activity A.T1.7 & A.T2.4 as "*Control of Chemical Escape from land use*". Work package T1 details two deliverables and these are D.T1.7.1 "*Report on areas that are most likely to be impacted upon by chemical export*" and D.T1.7.2 "*Report outlining possible actions to prevent chemical export from land use in the identified areas*". Work package T2 details three deliverables and these are D.T2.4.1 "*Investigative monitoring as directed by WP3*", D.T2.4.2 "*Implement recommendations from WP3*" and D.T2.4.3 "*Develop best practice solutions*".

To address the above deliverables, and adequately quantify and mitigate against chemical export from land use in the Finn Catchment, Loughs Agency took a multipronged approach.

The initial phase involved a desktop evaluation of the potential sources of chemical export in the Finn as well as of the chemicals of concern. Also, three field based surveys were carried out to ensure that all potential sources of chemical export from forestry and sheep dipping activities were recorded and up to date, and a passive sampling survey was conducted to determine the scale of chemical export in the catchment, time periods when it occurred more frequently and which of the four chemicals targeted was the most prevalent.

Once the initial data collection had been completed, Loughs Agency, along with Donegal County Council, developed several knowledge transfer initiatives to spread understanding of issues related to chemical export to the wider Finn Community.

Finally, three publicly used sheep dipping facilities were selected for implementation of mitigating measures designed to eliminate the introduction of spent sheep dip in to the Finn and its tributaries.

This report gives detailed information on each aspect of these activities and presents the findings of each.

2. LITERATURE REVIEW OF HERBICIDE AND PESTICIDE CHEMICALS

2.1. Introduction

The introduction of pesticides into the aquatic environment is of great concern both for ecosystem conservation and human health. Poorly managed agricultural & forestry operations can lead to the contamination of surface and groundwater by nutrients and pesticides (Spalding & Exner 1993, Kolpin et al, 1998, Pereira et al, 1996, Novotney 2005, Gunningham & Sinclair, 2005). Due to the potential for harm to the aquatic environment and associated biota, there is an increasing need for monitoring of these chemicals to ensure the protection of aquatic ecosystems.

The impacts of pesticide introduction to the aquatic environment can be severely detrimental and can include; macroinvertebrate and fish mortality, species behaviour change as well as impacting the fauna of the adjacent riparian zone.

As part of the CatchmentCARE Activity A.T1.7, 'Control of Chemical Export from Land Use Activities', a desktop chemical export literature review was carried out on commonly used agricultural & forestry pesticide and herbicide chemicals and these included; Cypermethrin, Acetamiprid, Organophosphates and MCPA.

Cypermethrin was historically used in treatment of forestry crops however this chemical is being replaced with Acetamiprid by Coillte and the changeover began in 2018.

The aim of the literature review was to help identify the potential impacts of these chemicals on the aquatic environment with focus on, among other aspects; potential pathways of introduction to the environment, persistence within the environment and effects on macroinvertebrates and fish. The literature review was intended to aid in the selection of the most appropriate measures to help eliminate or, at the very least, reduce the potential for the introduction of these chemicals to the aquatic environment.

Cypermethrin is a widely used insecticide within the agricultural sector, primarily as a component of sheep dip. It is a lithospheric neuropoison which works by terminating the functions of the nervous system in parasites by interacting with the sodium channels of the target organism (WHO 1989). This has long-lasting effects on the permeability of the nerve membrane in target parasitic groups causing problems within the sense organs and nerve impulses of tissue fibre. It has the same effect on non-target macroinvertebrate species.

Acetamiprid is an insecticide and part of the neonicotinoid substance group. It is ideally used to control Hemiptera spp. (True Bugs) particularly aphids. It is extremely soluble in water and can be volatile. It does not show great penetration when absorbing into soils (Smith et al 2008) although studies have found that it may pose a risk of transference to surface and ground water (Dujaković et al., 2010). As stated, Acetamiprid is replacing Cypermethrin use in forestry treatments for pine weevil.

Organophosphates are commonly used pesticides within the agricultural sector, particularly sheep dips. Organophosphates are a cholinesterase-inhibiting pesticide which work by terminating the functions of the acetylcholine neurotransmitter within the nervous system of the target parasite, however the chemical is not target specific and affects non-target macroinvertebrate species in the same way. Organophosphates have very toxic effects on both animals and humans. Organophosphate exposure pathways overlap for many wildlife species and humans and contamination of well water can harm humans, long after the adverse impact of spraying on wildlife has occurred. (Vermeire et al 2003).

Organophosphates are relatively non-persistent in the environment, particularly in dry conditions, however introduction to the aquatic environment can greatly increase the half-life of these chemicals, causing them to persist for longer. They generally show very little adsorption to soils but if they do they can persist bonded to soil particles years after their initial application (Ragsnardottir, Vala K., 2000).

MCPA is one of the main phenoxy herbicides used on permanent grassland. It has no effect on grass yield and is an effective treatment of broadleaf weeds and rushes. It is used as an herbicide for control of annual and perennial weeds in crops (URL 2). Phenoxy herbicides were first identified in the 1940s (Moran, 2015). These Phenoxy hormones regulate the growth of the plant and one of their functions is to cause the plant to grow towards sunlight. When the Phenoxy herbicide is applied it travels throughout the plant causing an overdosing impact through uncontrolled growth with severe thickening and twisting which in turn causes the plant to overgrow itself to death (Moran, 2015). MCPA is prone to leaching directly into watercourses or through land drains due to its inability to bind to soil particles. When introduced to watercourses it can take between 3 to 4 weeks to be broken down in untreated areas.

All of the above chemicals have the potential to negatively impact on the aquatic environment by impacting on macroinvertebrate populations either directly or indirectly. The three pesticides can cause death of macroinvertebrates in high enough concentrations and, in low concentrations, can cause downstream drift of these populations. MCPA can eliminate instream or emergent flora in any watercourse that it is introduced, which has indirect impacts on macroinvertebrate populations by removing a source of food and refuge. These factors combined lead to an environment in which macroinvertebrate population success is reduced.

Any negative impacts upon the macroinvertebrate populations in a waterbody can have numerous knock on consequences for fish species as well as other macroinvertebrates and the overall ecological health of the river. This is because macroinvertebrates are a key food source for many fish species and also carry out numerous crucial activities in a river that help maintain its ecological health.

Different macroinvertebrates fill different niches in the river ecosystem as they are divided into "Functional Feeding Groups" which are numerous in variety but, at the highest level, can be broken down in to Scrapers, Shredders, Collectors (Gatherers and Filterers) and Predators. Scrapers feed on algae and microorganisms present on rocks, submerged trees and plants in a river. Shredders break down organic material introduced to the river such as leaves and wood, Collector Gatherers collect fine particulate organic matter from the river bed and Collector Filterers collect fine particulate organic matter from the water column. Finally, predators feed on other macroinvertebrates.

These macroinvertebrate ecosystem functions are all crucial to maintaining an overall healthy aquatic ecosystem so if any one are impacted by chemical export in to a waterbody, then this will create an imbalance that will negatively impact upon plants and animals within that ecosystem.

In order to better understand the four target chemicals and the way that they interact chemically with the aquatic environment and the flora and fauna within, as well as the most likely pathways for these chemicals to enter the watercourse, a detailed desktop literature review was compiled. This review gave overviews on several aspects of each chemical and made recommendations on what measures should be taken to eliminate or greatly reduce their introduction to the aquatic environment in the Finn.

Several recommendations were put forward and these influenced the subsequent steps taken by Loughs Agency CatchmentCARE team to help address chemical export from land use in the Finn. The full literature review can be found in **APPENDIX I** of this document.

3. SHEEP DIP SURVEY

3.1. Introduction

The literature review conducted into chemical export in the Finn Catchment identified that the main potential source from agriculture was from improper disposal of spent sheep dip.

Sheep dipping occurs in specially built structures known as sheep dipping baths. Although each may vary slightly they generally consist of several components including an initial holding pen for sheep, a race which leads to the bath, the bath itself which is filled with dip, an exit ramp and then a final holding pen where the sheep should be allowed to drip dry.

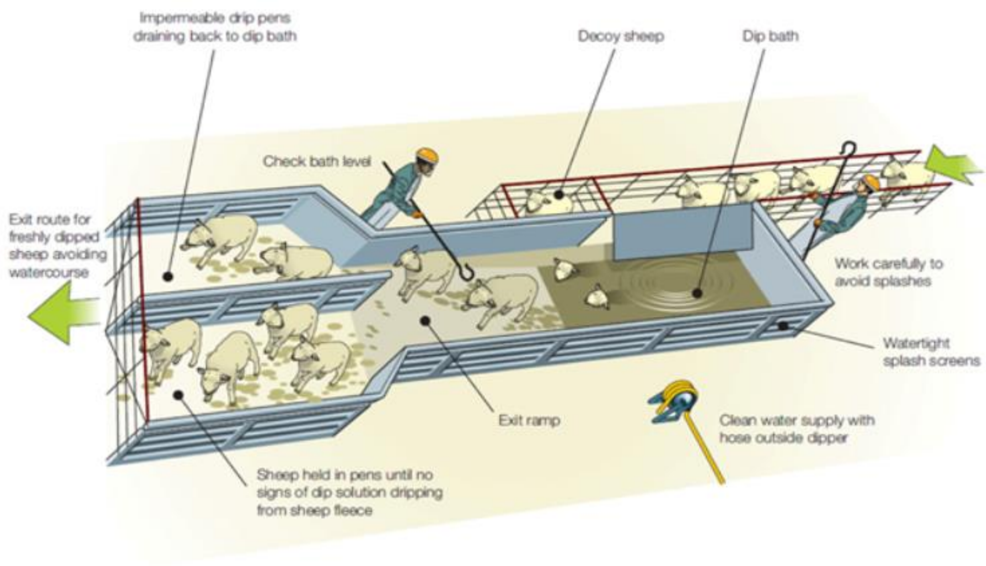


FIGURE 1, IMAGE OF SHEEP DIPPING BATH FACILITY (IMAGE TAKEN FROM GROUNDSURE.COM)

Historically many baths were built with a bung in the bath where the farmer could allow the spent dip to drain into the local watercourse however this is no longer permitted today due to the negative impacts that spent dip can have on the aquatic environment. Nevertheless, structures still remain that have the bung for releasing spent dip into watercourses.

In order to determine the scale of sheep dipping activity in the Finn Catchment, and the potential for it to negatively impact upon the aquatic environment, Loughs Agency decided to gather additional data using several methods.

This report outlines how this was carried out and presents the results produced.

3.2. Methodology

Initial data gathering focused on already available data of existing sheep dipping facilities in the Finn Catchment. These data were sourced from historical records available to Loughs Agency from their data archives.

During this stage, conversations with Loughs Agency Fisheries Inspectors posted in the Finn indicated that many dipping facilities existed in the Catchment that were not recorded in the historical records.

To ensure that these additional dipping facilities were included in the overall data set, Loughs Agency designed a survey to locate and document as many dips as possible in the Catchment.

This survey was carried out as follows:

- Donegal County Council GIS Officer set up an ArcGIS platform on the Survey123 App which would allow recording of all dipping facilities - This was named “Sheep Dip Survey”;
- Survey123 App with “Sheep Dip Survey” was installed on a Galaxy Note tablet;
- The “Sheep Dip Survey” included several recording metrics and these were:
  - Ability to GPS mark location of dipping facility on a map;
  - To mark whether the dip was active, inactive or unsure;
  - Whether the structure was permanent or temporary;
  - A comment section to state where the dip was being discharged to;
  - Whether the facility was sealed or had a bung/ cracks;
  - A comment section to list any empty dip bottles present on site;
  - Whether the land was publicly or privately owned;
  - Whether the dip was inside or outside a farm yard; and
  - A feature which allowed the capture of images of the dip and any empty dip bottles.

- The extensive local knowledge of Loughs Agency Fisheries Officers was used to identify the locations of as many dips in the Catchment as possible;
- Fisheries Officers would approach farmers on CatchmentCARE officers behalf and arrange for the survey team to visit the dipping facility, if located on privately owned land;
- If located on publicly owned land, Fisheries Officers would bring CatchmentCARE Officers directly to a site to record its status;
- CatchmentCARE Officers would record all the required information at each site, including GPS location, and these data would feed in to the “Sheep Dip Survey” ArcGIS Programme;

- If a landowner/ dip owner was present on site at time of inspection, the CatchmentCARE Officers would ask them to complete a questionnaire that had been created to ascertain local knowledge and practices around use of sheep dip (see below for more details);

- In addition to carrying out the sheep dipping facility survey, a Sheep Dip Questionnaire was created which the CatchmentCARE Officers asked local sheep farmers to fill out either when inspecting dipping facilities on the farmers land or at marts that the team attended occasionally in the Finn Catchment. Information gathered on the questionnaire included:
    - Approximately how many head of sheep did the landowner possess;
    - What time of year does the landowner treat his stock for pests;
    - Which type of treatment did they use (Sheep dip, pour on, injection, spray or a combination of these);
    - Does the landowner use a sheep dipping tank on their farm, a communal tank, a mobile sheep dip or a mobile sheep sprayer;
    - What are the names of the pest control products that the landowner uses;
    - How does the landowner dispose of the spent dip - Local stream/ river, landspread, Slatted tank, other - if other give details;
    - Does the landowner think discharge of spent dip would have an effect on the local water course - Yes or No;
    - If Yes, what impact do they think the dip would have;
    - Have they heard of the CacthmentCARE Project on the River Finn;

- Data collected were used to determine the overall scale of sheep dipping activity in the Catchment and the awareness of farmers on the proper methods for disposing of spent dip.

This information led to several different options for addressing chemical export to water and these included; creation of a best practice infographic for sheep dipping and disposal of spent dip, holding of a demonstration day to show local farmers how to properly dip sheep and dispose of spent dip, and selection of three publicly used sheep dipping facilities for implementation of measures to ensure spent dip is not introduced to the local water course from them.

3.3. Results

The results from the survey of sheep dipping facilities in the Finn Catchment revealed that a total of 103 dipping facilities are present in the Catchment. The historical archive held by

Loughs Agency had, before conducting of the survey, only recorded 43 locations so an additional 60 facilities were identified.

Of the 103 locations visited, 60 were deemed to be actively used facilities, 26 were deemed to be no longer active and the team were unable to determine if the remaining 17 were in active use.

The two areas with the largest amounts of active dipping facilities were the Reelin_020 and the Finn_040 sub-catchments (7 and 17 active sites respectively). For the Reelin_020 site, the scoping report indicated that this area had recorded Poor WFD status during the 2015 and 2018 designations. The Finn_040 recorded Moderate WFD scores for both those years. Additionally, sampling for the scoping report revealed that macroinvertebrate scores at 1 out of 2 sites surveyed in the Reelin_020 were Poor and Fish EQR at both sites was Moderate. In the Finn_040 sub-catchment, 3 out of 4 sites sampled for macroinvertebrates recorded Poor results and two out of four sites recorded Moderate Fish EQR's.

The results of the sheep dip survey allowed Loughs Agency to identify sheep dipping activity as one of the key pressures impacting upon water quality in these two sub-catchments, along with pasture, forestry, peat and waste water discharge.

The data collected during the sheep dip survey highlighted the extent to which sheep dipping was taking place in the Catchment, and results from the site surveys as well as from the questionnaires revealed that there was not great knowledge amongst sheep farmers on how to dispose of spent dip and the impacts that it could have on the aquatic environment if introduced.

To help address this lack of knowledge, Loughs Agency and Donegal County Council produced an infographic with information on how to adequately dispose of spent sheep dip. This was distributed throughout the Catchment at all public CatchmentCARE events.

In addition to this, a demonstration day was held on a local farm in the Finn Catchment where the appropriate method of dipping sheep and disposing of the spent dip properly were displayed. As attendance of this event was hampered by Covid-19 restrictions in place at the time, a video was created featuring industry officials from Bimeda, Teagasc, The Hill Sheep Farmers Association and Loughs Agency which provided detailed descriptions of the proper method of dipping, treatment of dipped livestock, disposal of spent dip and the impacts that introduction of spent dip can have on the aquatic environment. This video was posted to CatchmentCARE social media feeds and was also shared on Teagasc's website and is now shown as part of their agricultural training courses.

Data gathered from the sheep dipping survey also identified three publicly used sheep dipping facilities that were likely to be impacting on the local watercourse by the improper disposal of spent dip. In order to address this issue, Loughs Agency and Donegal County Council installed three Integrated Constructed Wetlands at the outfall of these facilities that will remove spent dip from the effluent before allowing treated water to enter the river.

And finally, the data collected during the sheep dip survey allowed Loughs Agency to identify two sites where passive sampling devices were deployed to collect data on four chemicals of concern in the Catchment; Cypermrthrin, Acetamiprid, Diazinon and MCPA.

3.4. Discussion

The sheep dipping survey carried out in the Finn Catchment was very beneficial as it allowed the identification of an additional 60 dipping locations which were previously unknown. These data are now available to Loughs Agency staff who can use it to tailor their habitat protection measures as well as in the event of a pollution event where spent dip is suspected.

The efforts to distribute infographics containing information on how to dispose of spent dip, the demonstration day and resulting video, the questionnaire and the sheep dip survey itself all helped increase the awareness of sheep farmers in the Catchment to the negative impacts of spent dip entering the watercourse. They also provided farmers with knowledge on how to properly dip sheep and how to treat them after dipping as well as how to safely dispose of the spent dip. This knowledge and awareness will likely help reduce the introduction of spent dip into the watercourse and make farmers aware of the negative impacts it can have on a watercourse and the efforts that are being taken by local authorities to address the issue.

The data collected during the sheep dip survey and questionnaire allowed Loughs Agency to launch a 12 month passive sampling programme at 5 locations in the Catchment. Two of those sites were selected based on information from the surveys conducted and targeted areas where dipping activity was high. Data collected during this survey helped define the extent of introduction of chemicals to the aquatic environment in the Catchment, which chemicals were most prevalent and at what time of year that increases in chemical export occur.

Finally, the surveys conducted allowed three publicly used dipping facilities to be targeted for installation of Integrated Constructed Wetlands as measures to mitigate against the introduction of spent sheep dip into the local watercourse. These types of installations could be replicated at other facilities similar to the ones in the Finn nationwide and could be a simple, elegant solution to helping reduce the amount of chemical export into local rivers.

Overall, the investigations into dipping facilities in the Finn allowed Loughs Agency to target several key areas of concern by promoting awareness of the issues surrounding chemical export as well as increasing the knowledge of local sheep farmers in the proper disposal of spent dip. It also allowed Loughs Agency to tailor an innovative investigative survey into chemical export in the Catchment and allowed the issue to be addressed directly through mitigation measures at three publicly used dipping facilities.

FIGURE 2, SHEEP DIP SURVEY DASHBOARD.

4. FORESTRY SURVEY

4.1. Introduction

The chemical export literature review and the North Western River Basin Management Plan stated that commercial forestry plantations were a potential source of chemical export to waterbodies in the Finn and, along with agriculture, was one of the two biggest pressures in the Finn Catchment impacting on water quality.

There is very little information regarding commercial forestry or silviculture on the island of Ireland before the 20th century (O'Carroll, N. 2004). Records from 1766 exist which detail a scheme organised by the Dublin Society which encouraged the planting of a mix of commercially valuable timber species for which a grant was provided and this focused particularly on cultivation of broadleaf species (O'Carroll, N. 2004). The first state forest was located in Ballykelly, Co. Derry and was managed by Timothy Donovan from 1910 ((O'Carroll, N. 2004). In the proscribed first Irish parliament (Dail Eireann 1919-1922) Art O'Connor became Minister for Agriculture and was in charge of managing the nation's woodlands

(O'Carrol, N. 2004). In 1946 the Forestry Act was enacted which proposed planting of one million acres of land with trees and designated the Forestry Service as the entity responsible for managing Ireland's woodlands (O'Carroll, N. 2004). The Forestry Service was replaced by Coillte in 1989 as the Government Agency responsible for commercial Forestry and the million acre planting landmark was achieved by 1991 (O'Carroll, N. 2004). The year 1991 was also the year that Coillte began introducing measures that should be incorporated when planting commercial forestry that would help mitigate against the negative impacts that these plantations can potentially have on water quality.

Plantations, if not properly planted or harvested, can have negative impacts on river water quality in several ways. These can include excessive overshading of watercourses, changes to water flows within catchments, acidification of waters, soil erosion and discharges of silt during planting and harvesting operations.

As commercial forestry is such a long lived crop, taking on average between 30 or 40 years to grow to an appropriate size for harvest, there are still unharvested crops in existence today that, when initially planted, did not implement measures suitable for the protection of local watercourses.

To help inform any potential mitigation measures that could be implemented on forestry in the Finn Catchment, Loughs Agency carried out a survey of plantations in the area and assessed those that were deemed in need of mitigating measures.

The below report outlines the methodology, results and conclusions of this survey.

4.2. Methodology

A desktop review of already available information was initially carried out to determine the extent of commercial forestry plantations in the Finn Catchment.
Coillte provided GIS layers to Donegal County Councils GIS Officer who created an ArcGIS map of forestry locations in the Finn Catchment. The GIS Officer then added additional information to the map that would be beneficial in pinpointing areas of concern.

Data included in the map showed:

- Location and boundary shape of the forest;
- Whether a plantation was privately owned or in the management of Coillte;
- The size of the plantation;
- Ground slope;
- What tree species made up the crop;
- When the crop was planted (if data available);

- Proximity to a watercourse;
- Presence/ absence of a suitable buffer strip;
- Vulnerability to watercourse of run off;
- River WFD Status; and
- Loughs Agency & EPA Macroinvertebrate Q-Scores (where available).

This map allowed plantations in the Catchment to be targeted for ground surveys to determine if mitigation measures were needed and what those measures might be.

The team used features such as smaller than expected or non-existent buffer zones between the crop and the waterbody, drainage gullies that ran directly into the river and plantations on land with significant slope as indicators of forestry sites which were likely to impact on the aquatic environment to select sites for closer inspection.
An associated Survey123 Forestry Survey App was created and installed onto tablets that the ground survey team could use to gather further information.

Data that could be entered into this App included:

- Location of drainage gully/ watercourse on plantation including length and width;
- Flow path of drainage gully/ watercourse;
- Whether the drain/ watercourse was blocked or not;
- Observed rate of flow in drain/ watercourse;
- Distance of drain/ watercourse from crop;
- If watercourse, whether 1st, 2nd, 3rd etc. order;
- Was the drain/ watercourse vegetated as expected;
- Any indications of enrichment/ pollution;
- In situ pH reading of drain/ watercourse;
- In situ Conductivity reading of drain/ watercourse;
- In situ Dissolved Oxygen reading of drain/ watercourse;
- In situ Temperature reading of drain/ watercourse;
- In situ Turbidity reading of drain/ watercourse;
- If drain, did it discharge directly into local watercourse;
- Were there signs of sediment in the river;
- Weather conditions at the time of sampling;
- Photo attachments; and
- Additional comments section.

In addition to the above, a desktop review of mitigation measures that could be implemented on forestry crops was conducted that would be used when assessing sites of concern.

Finally, a forestry infographic was produced that highlighted best practice methodologies and considerations that should be made when planting a commercial forest to ensure that water quality in the vicinity is protected.

4.3. Results

The desktop survey identified that, overall, forestry covered 108.59km^2 of the Finn Catchment Area which is 494km^2 in size. This accounts for 21.98% of the total Catchment land use. 482 private forests covering 28.171km^2 were recorded and 115 Coillte forests covering 80.417km^2 of the Catchment were also recorded.

Six plantation areas were selected for ground surveys based on data collected as part of the desktop research phase of the survey. The ground based forestry survey was completed in early spring 2021 by the Loughs Agency and Donegal County Council CatchmentCARE Teams.

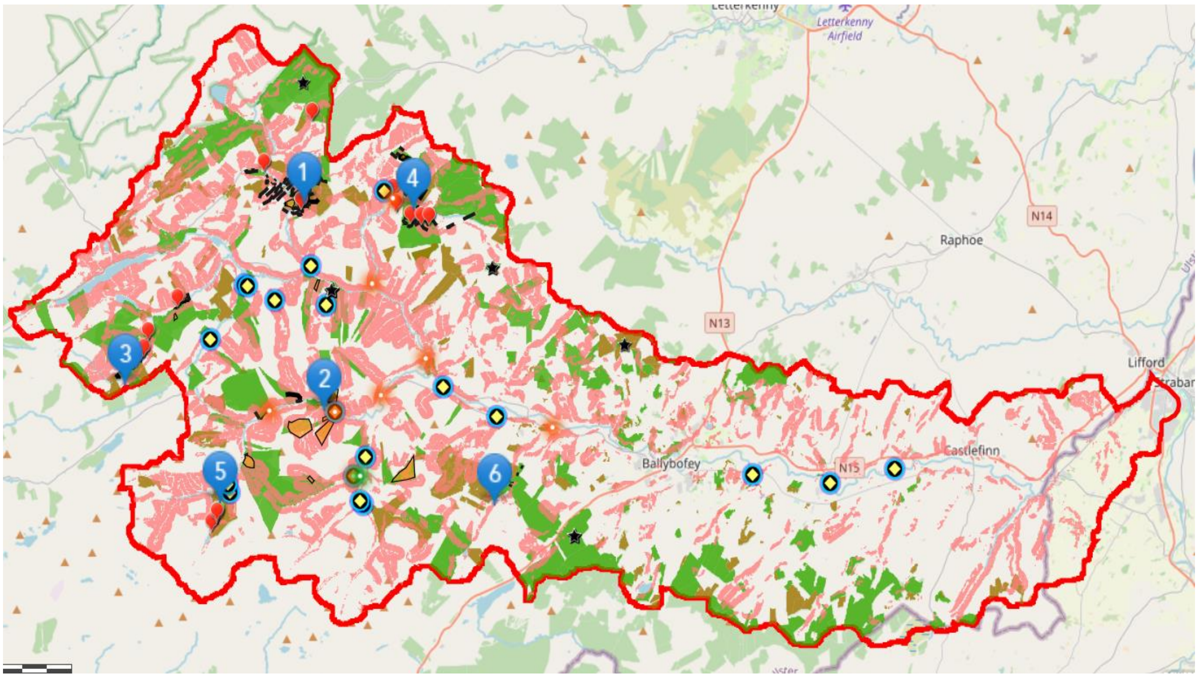


FIGURE 3, SHOWING LOCATIONS OF 6 AREAS SELECTED FOR GROUND SURVEY.

The six locations investigated in the ground survey exhibited several issues that were likely to pose a threat to the water quality of the water bodies in their immediate vicinity. Issues identified included insufficient or no buffer zone between the plantation and the river, drainage gullies flowing directly in to the local watercourse, high slope which increased the intensity of surface run-off and sediment transport, elevated pH levels in drainage gullies and extensive overshading of rivers in some areas.

The review of mitigation measures which could be implemented at forestry plantation sites was carried out and these mitigation measures included:

- introducing water setbacks;
- Implementation of riparian zones planted with native broadleaf trees and shrubs;
- Incorporation of leaky dams/ straw bales to slow flow and trap sediment;
- Introduction of sumps/swales in the riparian buffer zone to trap run-off and further reduce sediment;
- Placing limestone in gullies to help reduce pH levels of run-off; and
- Installation of artificial wetlands.

In order to determine the feasibility of the mitigation measures identified as potential solutions, the CatchmentCARE team met with representatives of Coillte and delivered a presentation laying out the Team's investigation and the mitigation measures it hoped to implement at the six selected locations in the Finn. Site visits to several plantations on the Finn were also carried out in the presence of Coillte representatives and implementation measures discussed for each site.

Preliminary research and desktop reviews of mitigation measures and forestry practices had already revealed that Coillte had begun adopting sufficient mitigation measures for protecting watercourses from impacts related to tree plantations and these had begun to be implemented on new crops since 1991. The main issue from forestry on water quality extant today is the impact that crops planted before this time have on the aquatic environment as they do not have the same measures implemented.

When detailed discussions and site visits to several Coillte owned forestry sites in the Finn Catchment were carried out, it became apparent that the mitigation measures suggested by Loughs Agency could not be implemented on any mature crops without risking significant crop and financial loss. This is mainly due to the boundary trees in a crop which have developed stronger rooting systems due to being on the outermost edge of the plantation. These deep roots protect the tree from being blown over in heavy wind. The trees inside this boundary do not possess the same root structure and, if the boundary trees were removed, would be impacted by wind blow and cause crop loss.

As the majority of measures suggested involved removal of a portion of the boundary trees to implement suitable mitigation measures, then this would have opened the crop up to significant losses.

It was decided that the only viable option was to allow mature crops to be harvested when ready and then, when re-planting, incorporate measures that would help protect the riverine environment.

To help promote this approach, especially with private forestry owners, Loughs Agency and Donegal County Council produced an infographic that gave an example of a forest crop that was implemented with all the required measures to ensure that its presence did not negatively impact upon the aquatic environment. Further details of this are provided in **AWARENESS RAISING**.

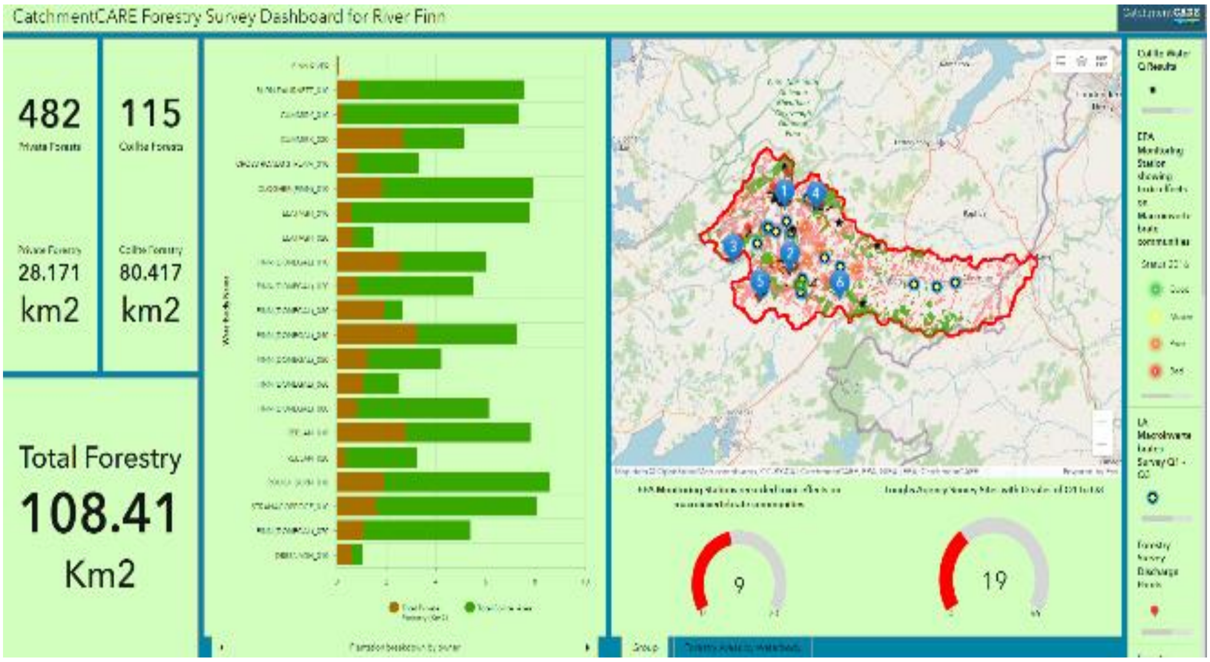


FIGURE 4, FORESTRY DASHBOARD.

4.4. Discussion

The survey into forestry in the Finn Catchment provided a lot of useful data and allowed the CatchmentCARE team to identify six plantations that were likely having a negative impact on the water quality of the rivers and tributaries adjacent to them.

Although measures were selected that could be implemented at these sites and would help alleviate pressures from forestry on the adjacent waterbodies, it quickly became clear following discussions with representatives from Coillte that implementation of any of these measures on the crops selected would cause unacceptable losses of crop and would make the plantation financially unviable.

It should be noted that all six of the areas selected for mitigation consisted of mature crops that had been planted prior to the year 1991, when Coillte implemented a suite of measures that must be employed on all new crop installations that will protect against any negative impacts of water quality. Any crops that have been planted after this date have been planted with considerations for the protection of water quality. Therefore it is only older “relic” crop stands that have the potential to impact on water quality. Due to the advanced age of these crops (which would have been planted at least 32 years ago at the time of writing) they will likely be felled in the near future (as crops are generally planted for 30 to 40 years) and, if the area is replanted, the new crop will take into account considerations for water quality.

As Coillte are also aware of these “relic” crops, they have the opportunity to fell them in a manner that will mitigate against negative impacts on water quality. This could be achieved in several ways but may include leaving boundary trees adjacent to water bodies in place and installing sediment traps during felling operations so that there is a buffer between the felling and the adjacent waterbody.

As Loughs Agency were unable to implement any mitigation measures on the six sites that they had surveyed and selected, an infographic was instead produced that aimed to promote the responsible planting and cultivation of forestry. More information on this infographic is given in Section **AWARENESS RAISING**.

5. PASSIVE SAMPLING SURVEY

5.1. Introduction

To help further investigate chemical export from land use and supplement the information gathered during the literature review, sheep dip and forestry surveys, Loughs Agency identified a need to carry out a direct survey on the presence of the four target chemicals (Cypermethrin, Acetamiprid, Diazinon & MCPA) in the waterbodies of the Finn.

In order to select the appropriate sampling methodology, Loughs Agency conducted a literature review into the most commonly used methods of sampling for pesticides and herbicides as well as other less commonly used methods. A brief summary of the findings of this review are given in this introduction however the complete review can be found **APPENDIX II**.

During Loughs Agency’s investigations, it was determined that the most commonly used sampling methods for detecting pesticides and herbicides generally relied on taking spot samples. These samples usually are water samples but can also be grab samples of sediments from the river bed.

There are several issues connected with these types of sampling methodologies. The key issues are that a sample will only give a snapshot of chemical concentrations at the target location at the time of sampling. This means that a chemical export event could be easily missed if it occurs just after sampling or if it occurred a long enough time before sampling that the target chemical has had time to break down to low levels of detectability.

Spot sampling of water samples is the most commonly used sampling method however this sampling requires the use of special sampling bottles made of borosilicate with teflon lids and, even when using these types of containers, loss of sample to the glass during transport can be significant and could give a false representation of the level of the target chemical present in the water column at the time of sampling. Proper storage at cool temperatures and prompt transport of the samples to the lab for timely analysis also add to the difficulty of using these sampling methodologies, particularly if time and personnel are not readily available resources.

Finally, in order to increase the likelihood that a spot sampling regime will detect a chemical export event, a high frequency of samples would need to be taken which, again, is not suitable if time and personnel are not readily available and can become prohibitively expensive in terms of equipment and lab analysis needed.

Loughs Agency investigated other sampling methods that would allow for more extensive temporal analysis to be carried out that would require such significant resource implications.

Initial consideration was given to an in situ monitoring device called the Guardian Blue system which was designed to detect pesticides and herbicides in real time at a certain location. When a spike in the target chemicals is detected by the device it immediately takes a water sample and sends an alert to the scientists conducting the monitoring.

Unfortunately, the device was not available outside the mainland USA and, even if it had been, to set up enough systems in enough areas to get reasonable coverage of the Finn Catchment would have not been fiscally feasible.

Ultimately the review by Loughs Agency highlighted the passive sampling methodology which was the one that was selected to progress as part of a sampling programme into Chemical Export.

Passive sampling devices are, as their name suggests, devices that can be deployed at a location and will passively collect the target chemical from the water column, if present.

Depending on the analyte being targeted, the devices can be deployed for between 2 weeks and 4 weeks and they will sample continuously during this time.

When collected and analysed, the laboratory can provide a time weighted average concentration of the target chemical within that 2/4 week time period. This allowed Loughs Agency to determine if a target chemical had been introduced to the water at a certain site within that time period and if the concentration of that chemical occurred above the threshold levels provided by the EPA's Parameters of Water Quality (EPA, 2001). The data collected is also able to highlight what months of the year are the most likely to see chemical export occur.
Once passive sampling was selected as the appropriate method for sampling of chemical export in the Finn, Loughs Agency began to make contact with laboratories on the island of Ireland that could provide the necessary equipment and associated analysis.

To facilitate Loughs Agency's needs, TE Labs of Co. Carlow set up a collaboration with E&H Services who are based in Czechoslovakia and have extensive training and experience in the use of passive sampling equipment for the detection of pesticides and herbicides in water.

With TE Labs and E&H Services advice, Loughs Agency selected 3 passive sampling devices which would target four chemicals; Cypermethrin, Acetamiprid, Diazinon and MCPA. This report details the methodology, results and conclusions of the passive sampling survey.

5.2. Methodology

Using data collected from the Sheep Dip Survey and the Forestry Survey, Loughs Agency selected 5 monitoring locations in the Finn Catchment where passive sampling devices would be deployed.

The 5 sites were selected for their land use characteristics which could have been potential sources of chemical export into the local watercourse, specifically relating to sheep dipping activity and forestry activity, with one site selected as a control. The site profiles were as follows:

Site One – Control Site (GPS Co-Ords: 54.8277302N, -8.1375901W)

Area was remote upland heath that had no known forestry or agricultural practice within the vicinity so detection of any target chemicals was unlikely.

Site Two (GPS Co-Ords: 54.821608N, -7.964592W)

Area selected due to density of active sheep dipping facilities upstream of the sampling point.

Site Three (GPS Co-ords: 54.8148797N, -7.8901034W)

Area selected due to density of active sheep dipping facilities upstream of the sampling point.

Site Four (GPS Co-Ords: 54.816317N, -8.035482W)

Area which had known forestry activity upstream which was privately owned.

Site Five (GPS Co-Ords: 54.906022N, -8.031282W)

Area which had known forestry activity upstream which was publicly owned.

The 5 sites selected were continuously surveyed for a period of 12 months between August 2021 and July 2022.

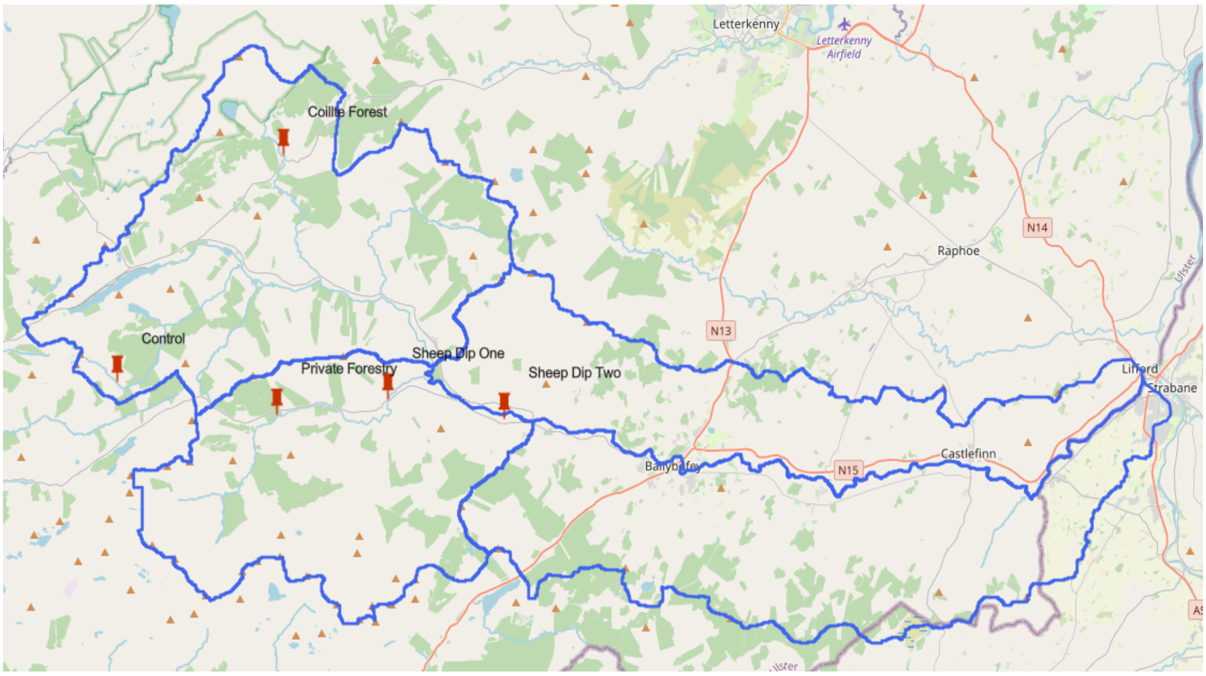


FIGURE 5, MAP SHOWING LOCATION OF PASSIVE SAMPLER DEPLOYMENTS.

Passive sampling containers containing a mixture of Chemcatchers, POCIS & Silicone Rubber (SR) Sampler passive sampling devices were deployed at each site. Different passive sampling membranes were installed on the different types of passive sampling devices listed above as each membrane targets different chemicals at each site. The details of which membrane was used to capture which chemical are given below:

Chemcatcher

Chemcatcher passive sampler equipped with anion SR/ SDB RPS receiving disk and diffusion limiting membrane for detection of Diazinon and MCPA.

Silicone Rubber (SR)

Silicone Rubber (SR) sampling spider (strip 2.7 x 92 cm with loops) used to detect Cypermethrin.

Polar Organic Chemical Integrative Sampler (POCIS)

Standard POCIS sampling disc used for sampling Acetamiprid

Samples were deployed on monthly cycles with Acetamiprid and MCPA collected after 14 days and Diazinon and Cypermethrin collected after 28 days.

On each deployment at a site, the passive sampling canister contained:

- 2 x Chemcatcher samplers to detect MCPA;
- 2 x Chemcatcher samplers to detect Diazinon;
- 2 x POCIS samplers for detection of Acetamiprid; and
- 2 x SR Spider samplers for detection of Cypermethrin.

As well as the above samplers, field blank samplers were used when deploying the samples at each site. This was a collection of 2 x Chemcatcher samplers for detection of MCPA & Diazinon, 1 x POCIS sampler for detection of Acetamiprid and 1 x SR Spider sampler for detection of Cypermethrin which were opened when a deployment was being prepared and then closed and stored in a cooler when deployment was complete.

A lab blank with the same compliment of passive samplers as the field blank was also used and these were stored, closed, in a fridge and were never taken to site.

5.3. Results

Note on Rounds

Please note that each Round (of which there are 12) used in the following description corresponds to a month when that data was collected. The Rounds and Corresponding Months are listed below:

- Round 1 = August 2021

- Round 2 = September 2021
- Round 3 = October 2021
- Round 4 = November 2021
- Round 5 = December 2021
- Round 6 = January 2022
- Round 7 = February 2022
- Round 8 = March 2022
- Round 9 = April 2022
- Round 10 = May 2022
- Round 11 = June 2022
- Round 12 = July 2022

Sampling Rates and $_{cw}$ Calculation

For Acetamiprid, Diazinon and MCPA the same sampling rates (R_s) were selected for all exposures, based on the literature sources from PaSOC (*2020 & 2022*). The adopted R_s are summarised in Table 1.

Table 1. Adopted sampling rates (L/d).

Round #	1	2	3	4	5	6	7	8	9	10	11	12
Acetamiprid	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Diazinon	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81
MCPA	0.062	0.062	0.062	0.062	0.062	0.062	0.062	0.062	0.062	0.062	0.062	0.062
Cypermethrin	5.7	5.7	5.7	5.7	30.9	17.8	5.7	5.7	5.7	5.7	5.7	5.7

A relatively strong flow-dependency can be expected for sampling Cypermethrin via silicone samplers. The in-situ calibration of uptake kinetics for compounds like Cypermethrin is usually done by measuring the dissipation rates of performance reference compounds (PRCs). Some uncertainty exists for present PRC data, because PRCs were not analysed for Rounds 1-5 and for rounds 6-11 the PRCs based R_s showed a relatively large scatter. For Round 12, Semi-Permeable Membrane Devices (SPMDs) were accidentally shipped and exposed instead of silicone samplers. The number of different PRCs in these SPMDs (3 instead of 7) turned out to be insufficient to estimate Cypermethrin R_s for Round 12. PRC based sampling rates for Round 5 (31±14L/d) and Round 6 (18±10 L/d) were larger than for Rounds 7-11 (6±4 L/d). It is assumed that the Cypermethrin Rs for Rounds 7-11 also apply to Rounds 1-4 and Round 12.

Aqueous Concentrations (C_w) were calculated from the accumulated amounts (N) using the following equation:

$$Cw = \frac{N}{Rs\,t}$$

Where *t* is the exposure time.

Detection Limits

E&H Services reported detection limits (LOD) for the chemical analysis as shown in Table 2. LODs of Acetamiprid and MCPA for Rounds 1 and 2 were higher than for Rounds 3-12, because new and more sensitive equipment was used in the latter rounds. LODs were converted from ng per sample to ng per litre using eq. 1 (See Table 3).

Table 2. Detection limits (ng per sample) for the chemical analysis as reported by E&H Services.

Round #	1	2	3	4	5	6	7	8	9	10	11	12
Acetamiprid	10	10	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
Diazinon	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
MCPA	10	10	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Cypermethrin	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001

Table 3. Detection limits (ng per litre) based on the amount LODs from Table 2 and the sampling rates from Table 1. For the calculation of detection limits typical exposure times of 14 d (Acetamiprid and MCPA) and 28 d (Diazinon and Cypermethrin) were adopted.

Round #	1	2	3	4	5	6	7	8	9	10	11	12
Acetamiprid	4.8	4.8	0.0024	0.0024	0.0024	0.0024	0.0024	0.0024	0.0024	0.0024	0.0024	0.0024
Diazinon	0.00044	0.00044	0.00044	0.00044	0.00044	0.00044	0.00044	0.00044	0.00044	0.00044	0.00044	0.00044
MCPA	12	12	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012
Cypermethrin	6.3E-06	6.3E-06	6.3E-06	6.3E-06	1.2E-06	2.0E-06	6.3E-06	6.3E-06	6.3E-06	6.3E-06	6.3E-06	6.3E-06

The sampler field blanks should be taken into account to determine if elevated aqueous concentrations occur at the exposure sites. Detected amounts in the field blanks were often larger than the LOD for chemical analysis. The field blanks are discussed in the compound-specific sections below.

Acetamiprid

Slightly elevated concentrations of Acetamiprid (relative to the field blanks) occurred at sites Two, Three and Five, but not at Site Four and the control site (Figure 6). For Rounds 1 and 2 it can only be concluded that C_w < 5 ng/L, due to the higher detection limits for Acetamiprid in these rounds.

Diazinon

Concentrations of Diazinon appear to be elevated for Rounds 1,2 and 12 at sites Two and Three (July-August-September). Elevated concentrations also occur for Round 7 at Site Four.

MCPA

Elevated MCPA concentrations possibly occurred for Site Two and Site Three during rounds 10 and 11. The highest concentrations (~250 ng/L) were observed for 2 samplers (Tellab codes 18373 and 18374) that were exposed at the control site during Round 2 (August-September), but the C_w that was estimated from a third sampler (18375) was much lower (~0.01 ng/L). This result is surprising, because sampler 18375 was exposed longer than the other two samplers (29 d vs. 14 d).

Cypermethrin

No elevated concentrations occurred for Cypermethrin in any of the sites. The Cw estimates for Round 4 may be an exception, but concentrations are not clearly above the blank levels that were observed for Round 8. In general, the blank levels are rather high (median = 3 ng/L), when compared with the detection limits that are based on the chemical analysis alone (~ 6 fg/L, Table 3). The blank levels are slightly higher than the EU maximum EQS for inland surface waters (0.6 ng/L). It is worth the effort to identify the origin of the high Cypermethrin blank levels before future monitoring studies are initiated.

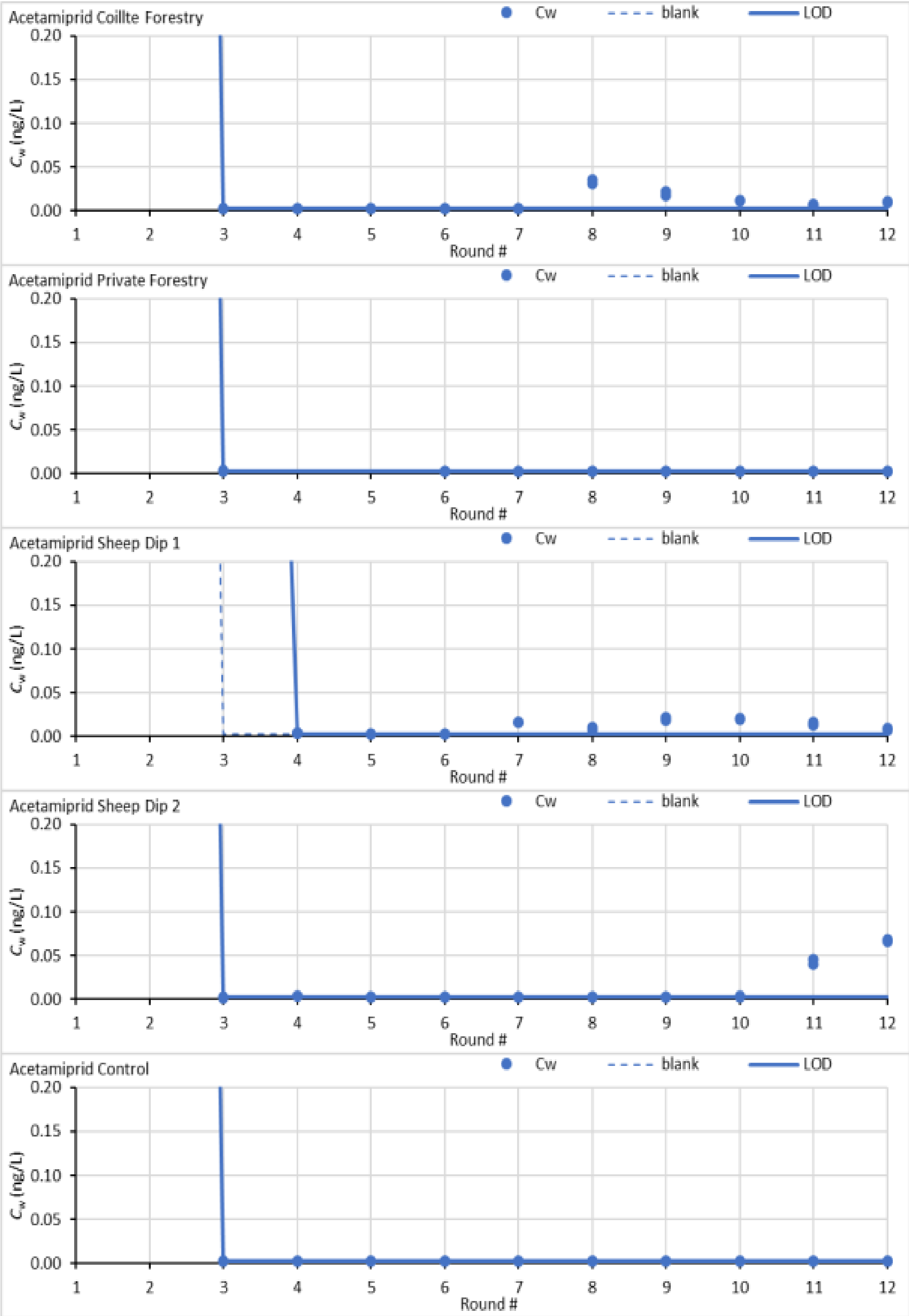


FIGURE 6, TIME WEIGHTED AVERAGE CONCENTRATIONS OF ACETAMPRID AT THE FIVE EXPOSURE SITES (BLUE CIRCLES).

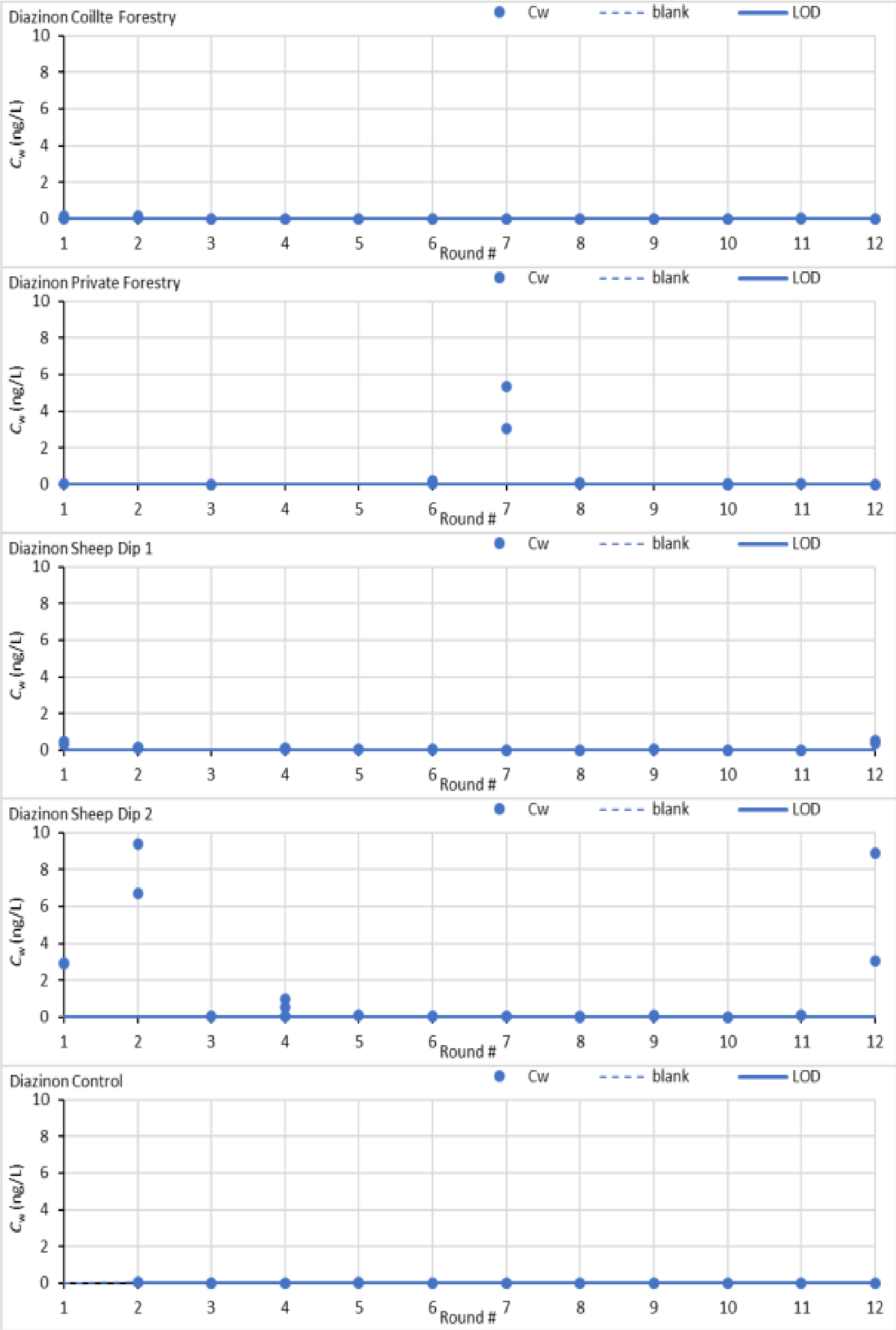


FIGURE 7, TIME WEIGHTED AVERAGE OF DIAZINON AT THE FIVE EXPOSURE SITES (BLUE CIRCLES)

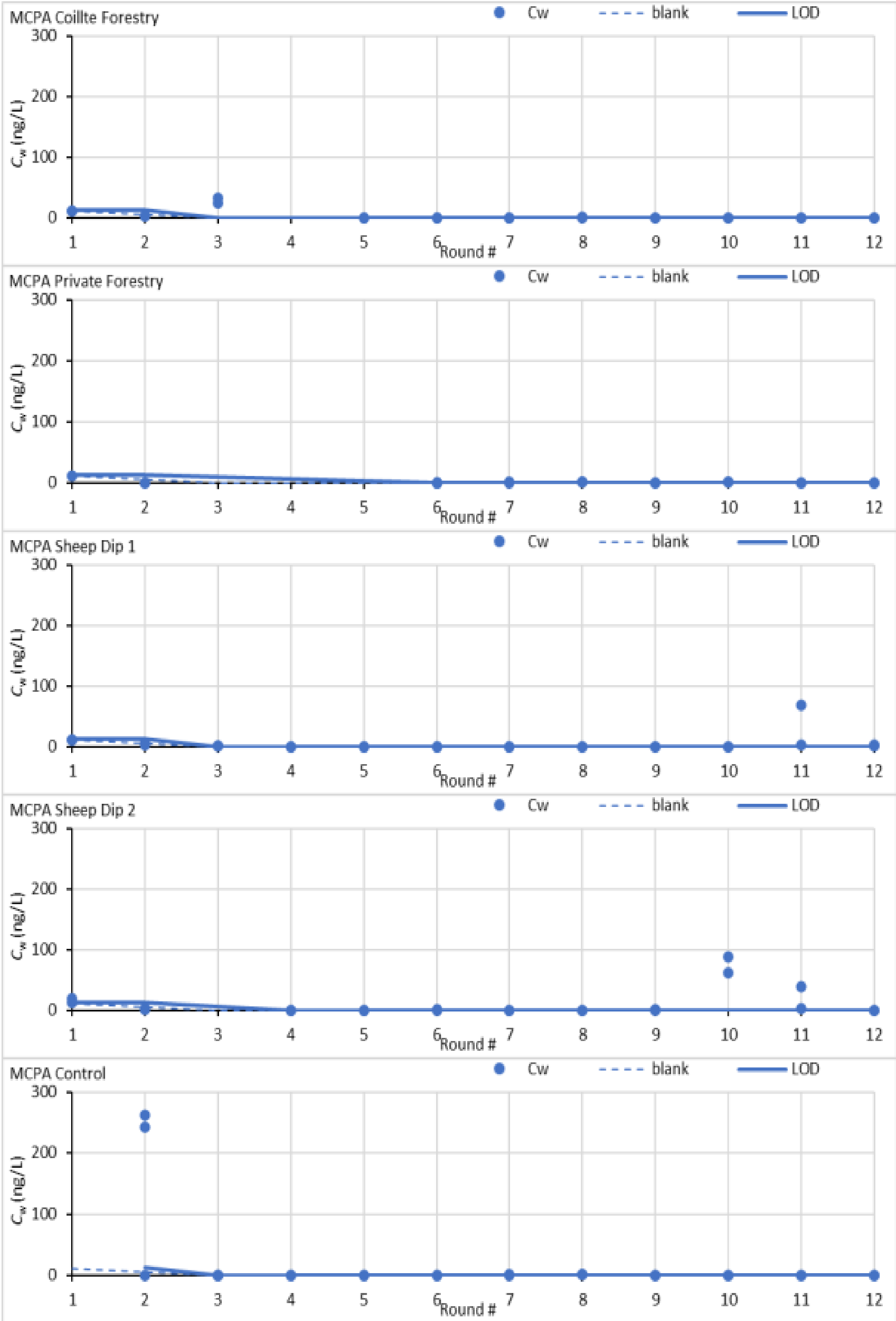


FIGURE 8, TIME WEIGHTED AVERAGE CONCENTRATIONS OF MCPA (BLUE CIRCLES)

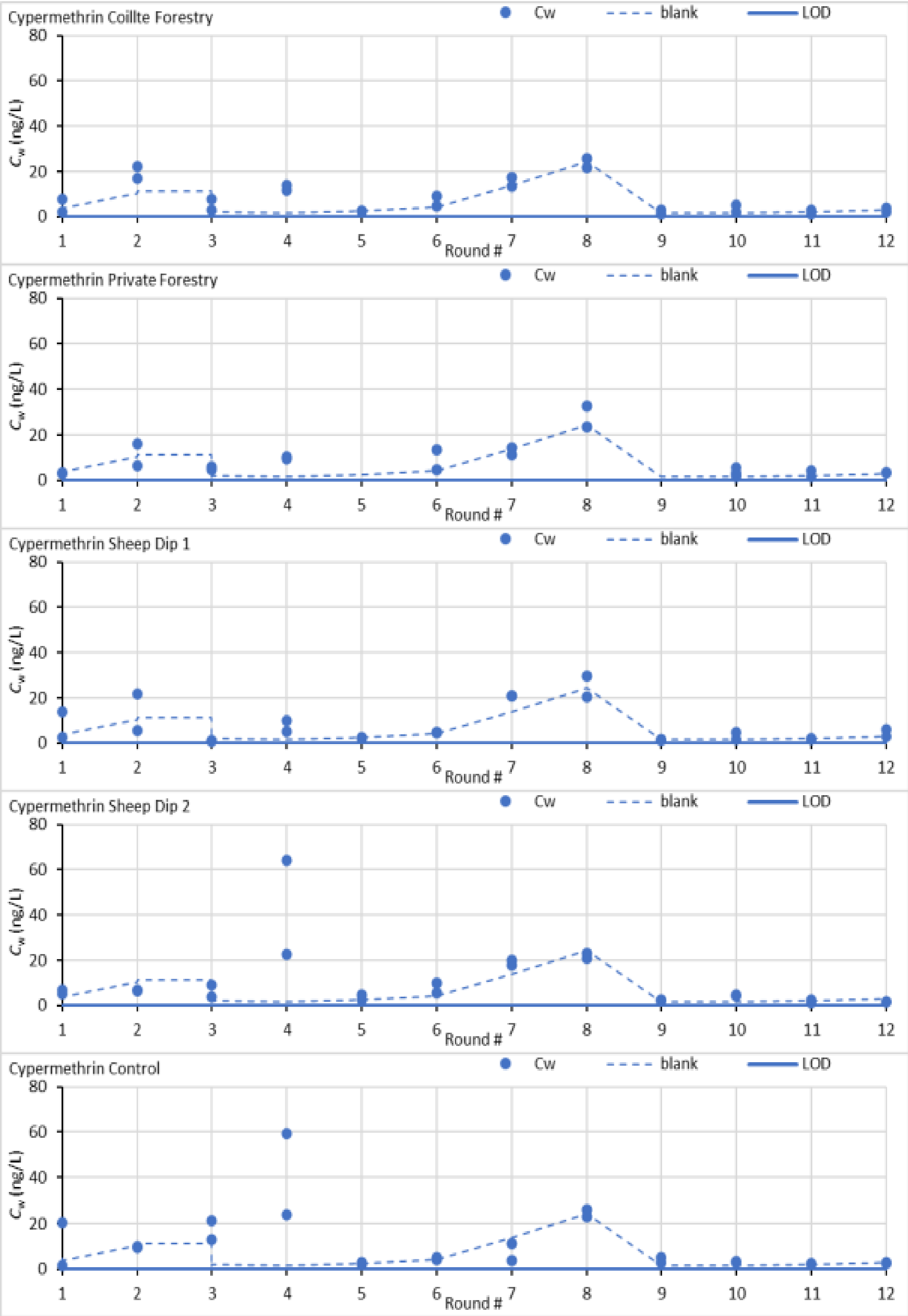


FIGURE 9, TIME WEIGHTED AVERAGE CONCENTRATIONS OF CYPERMETHRIN (BLUE CIRCLES)

FIGURE 10, SR PRE DEPLOYMENT.

FIGURE 11, SR POST DEPLOYMENT.

5.4. Discussion

The results collected from the passive sampling survey were very interesting.

The laboratory report stated that Acetamiprid had shown elevated concentrations between March and August 2022 at Site 5, which was placed in a location below extensive tracts of forestry plantations administered by Coillte.

Elevated concentrations of Acetamiprid were also recorded between February and August 2022 at Site 2 and between May and July 2022 at Site 3. Both these sites were selected as there were large concentrations of active sheep dips upstream from their locations.

It is possible that the elevated levels of Acetamiprid at Site 5 could have been exported from the Coillte owned forestry, however, given the time of year, it is unlikely as these months are generally drier than the remaining months of the year so wash off from land is less likely. It also cannot be said with any certainty that the Acetamiprid originated from the tree crops in these areas as there are pockets of agricultural land and rural housing along the river in these areas as well, so the source could be from these.

The presence of elevated levels of Acetamiprid below Sites 2 & 3 is unexpected as Acetamiprid is not an ingredient used in commercial dipping solutions so its presence is unlikely to be related to sheep dipping activities. The presence of Acetamiprid in the area where these samplers are located may indicate that Acetamiprid export in to the water column is extensive enough upstream from their locations that elevated concentrations of the chemical are still detectable at Site 2 & 3.

Acetamiprid is very water soluble, stable to hydrolysis at environmental temperatures and photodegrades relatively slowly in water. It is also not likely to persist in surface soils and can be easily washed off land if sprayed before a significant rainfall event. The half-life of Acetamiprid depends on whether there are aerobic or anaerobic conditions in a water body but can range from 45 days for the former to 365 days for the latter.

This could explain why elevated levels of Acetamiprid were detected at these three locations, particularly if anaerobic conditions were present, which is a possibility at the time of year when the detections were made, as less rainfall is associated with these months.

It should be noted that Coillte have moved from using Cypermethrin on their plantations to Acetamiprid so the potential for forestry operations in the area to be the source of these elevated levels of Acetamiprid is not negligible.

Elevated levels of Diazinon were recorded at Site 2 & 3 also although in the months August and September 2021 and July 2022.

Diazinon is an Organophosphate used in the production of sheep dipping products so detection of elevated levels at Site 2 & 3 was more likely than at the other sites due to the concentrations of active sheep dipping facilities upstream from their locations.

The time of year when the detections were made also corresponds to evidence gathered when speaking to sheep farmers in the catchment that sheep dipping occurs in the summer months.

Lower water levels are also generally observed in the Finn Catchment at this time of year so the detection of concentrated levels of Diazinon is more likely.

Although Diazinon is also used as a plant pesticide on crops, there is not a significant amount of cropland present in the Finn Catchment and particularly not in the area upstream of Site 2 & 3. Therefore it is more likely that these elevated levels of Diazinon originated from sheep dipping facilities upstream of these two locations.

Elevated MCPA concentrations were recorded at Site 2 & 3 during May and June 2022 also.
MCPA is a widely used herbicide and commonly used to eliminate the presence of Common Rush (*Juncus effusus*) which is readily found in the Finn Catchment, particularly in the Western, upland reaches of the Catchment. The seeds germinate in April-May time and so the detection of MCPA in May and June of 2022 would seem to coincide with a spraying effort to eliminate these unwanted plants as they appeared.

MCPA is prone to leaching directly into watercourses from land drains due to its inability to bind to soil particles. When released into water it is not expected to adsorb to suspended solids and sediment. The direct phytolysis half-life of MCPA in surface water in summer conditions is approx. 19-20 days however it does not break down readily in anaerobic conditions which means it could last for a long time in a watercourse under the right conditions.

Therefore detections of this chemical at Site 2 & 3 could be related to spraying activities much further upstream and the source cannot be accurately identified. However, the detection of MCPA in the passive sampling equipment confirms that export of this chemical from land spraying is an issue.

The results for Cypermethrin from the passive sampling survey, as interpreted by the lab using their corrective algorithm to calculate wet concentrations of the chemical, indicate that Cypermethrin was not in exceedance at any site over the entire 12 month sampling period.

However, it should be noted that the lab used the results from field blanks to create a baseline from which they then determined the amount of the chemical present in the water based samplers. Essentially, measurements from the field blank samplers were used to apply a correction to the water based samples by providing a theoretical baseline from which the wet samples would be measured.

The results from the lab stated that concentrations of Cypermethrin on the field blanks was exceptionally high, indeed slightly higher than the EU Maximum EQS for inland surface waters. The analysts suggested that measures should be taken in future to eliminate any possible sources of contamination of the blanks so that a lower theoretical threshold could be achieved.

This suggestion is definitely one that should be considered and implemented if future analysis of Cypermethrin in the area is to be carried out. However, as all passive sampling equipment, when being deployed, was treated using the same scientifically accepted aseptic technique, it is unusual that the Cypermethrin samplers alone exhibited such high levels of Cypermethrin on field blank samplers.

In any future deployments of passive sampling equipment targeting Cypermethrin in the area, consideration for the potential that Cypermethrin is in fact very prevalent in the Catchment, both in the water and on land, should be factored into the survey design. Implementing this as well as additional precautions against cross contamination would help provide a clearer picture of the prevalence of this chemical in the Finn Catchment.

The passive sampling survey was not designed to pinpoint the source of the target chemicals in the Finn Catchment but rather to determine their presence or absence in an area and at what time of year they are likely to be exported into the water column. In this regard, the survey has provided much useful information that will allow any future decisions on monitoring for pesticides or herbicides in the Catchment to be made.

The data have revealed that the period of year most likely to experience chemical export from land use is between May and September, although some instances have been recorded occurring outside this window. These records are of Acetamiprid export and, as stated in the literature review, Acetamiprid has the capacity to persist for extensive periods given the right conditions so detection of these samples outside of this window could potentially be from export events which occurred several months before.

The data confirm that all four chemicals are present in the Catchment and that Acetamiprid appears to be the most prevalent in elevated amounts, however further investigation into the presence of Cypermethrin in the Catchment is recommended.

Overall, this data set provides a good baseline on which to base future surveys into chemical export in the Finn Catchment.

6. AWARENESS RAISING

The Catchment Care team aimed to raise awareness on chemical export from land use throughout the course of the project via various media forums such as social media pieces, infographics, storyboards and demonstration videos as well as an in person demonstration day, presentations and discussions at Water Framework Directive Sub Committee meetings and conference events.

6.1. Sheep Dip Awareness

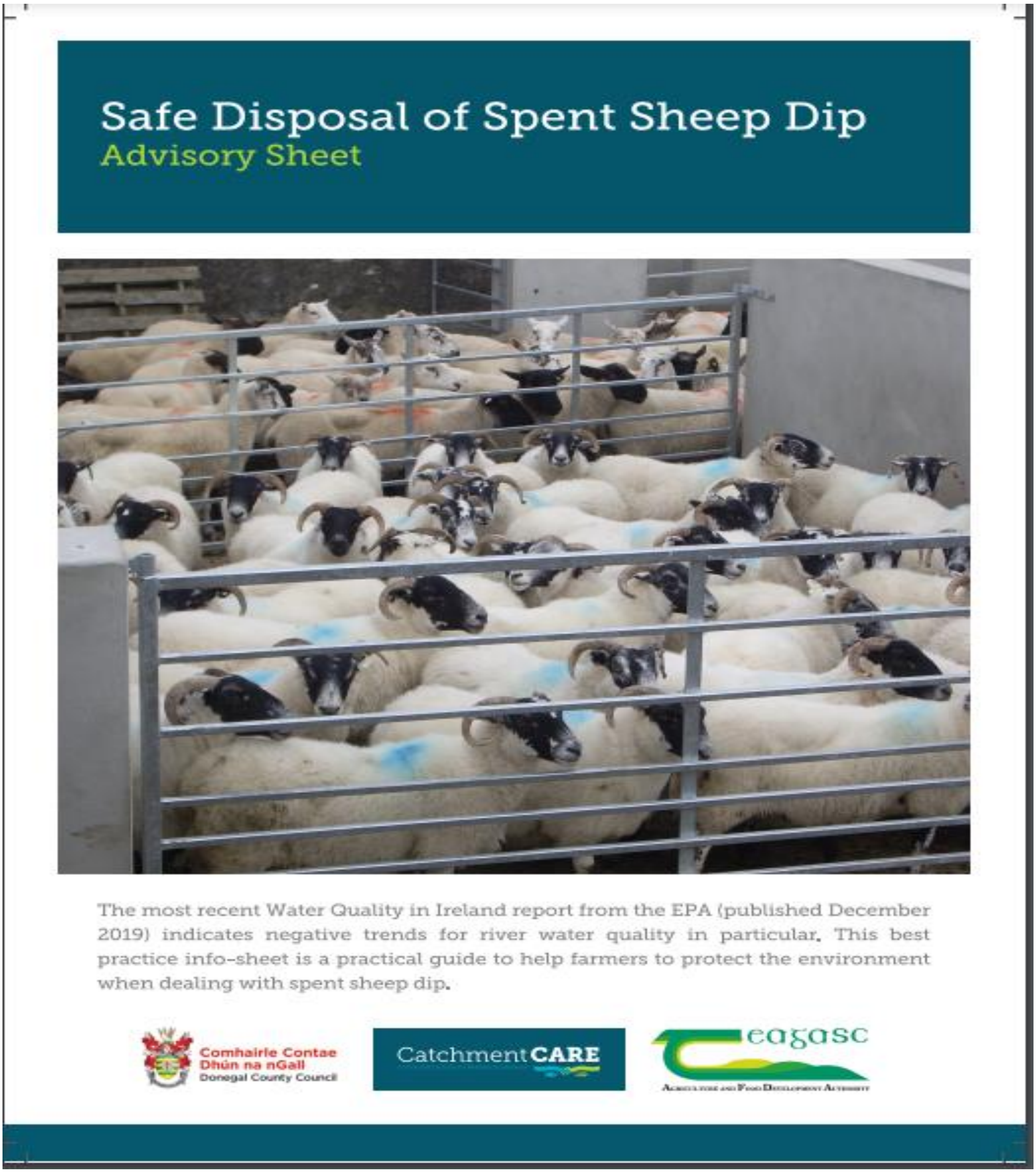
Loughs Agency and Donegal County Council initially planned to hold a sheep dipping demonstration day in the Finn Catchment in partnership with the local sheep farming community, represented by the Irish Hill Farmers Association, Teagasc and Bimeda however, due to covid restrictions at the time, the event had to be modified into the creation of a demonstration video to be shared online and amongst the farming community. The video highlights the correct procedure for sheep dipping and also displays the disposal method for used sheep dip as per Teagasc guidelines. Loughs Agency personnel also explain how introduction of spent dip into the River can negatively impact on the aquatic ecosystem.

The Video can be found here - https://www.youtube.com/watch?v=AGLOgeMmA5g or in Irish narration here: https://www.youtube.com/watch?v=_LEQzJVWIxc

The demonstration video was well received and it was shared on the CatchmentCARE website, social media channels and is also shared on Teagasc's website. Teagasc now also use the video in their agricultural training courses to make young farmers aware of the proper procedures and the risks to the environment from unspent dip.

In addition to the demonstration day, a Sheep Dip Advisory Leaflet was developed in partnership with Teagasc and Donegal County Council to raise awareness on the correct disposal method for spent sheep dip. The advisory leaflet highlighted the Teagasc advice on the safe disposal of sheep dip and also added the additional precautions which should be followed during sheep dipping procedures. This piece was also shared by the Irish Hill Farm Association to its members pre dipping season to encourage farmers to follow the correct guidelines. The leaflet was distributed at all major public CacthmentCARE events held in the Finn Catchment.

Loughs Agency also visited sheep mart events in the Finn Catchment on multiple occassions to ask local sheep farmers to fill out a questionnaire on their sheep dipping practices and highlight the issues that improper disposal of spent dip could cause in the aquatic environment. This activity, along with visits performed by CatchmentCARE staff during the sheep dip survey, helped create a greater awareness of the issue in the Catchment and allowed the team to interact directly, and widely, through the sheep farming community and raise awareness. The impact that these direct interactions had is not easily measurable but much information in the farming community on the Finn is distributed by word of mouth so it is likely that these activities helped raise awareness among the community.



Safe Disposal of Spent Sheep Dip

Advisory Sheet

The most recent Water Quality in Ireland report from the EPA (published December 2019) indicates negative trends for river water quality in particular. This best practice info-sheet is a practical guide to help farmers to protect the environment when dealing with spent sheep dip.

Comhairle Contae Dhún na nGall
Donegal County Council

CatchmentCARE

Teagasc
Agriculture and Food Development Authority

FIGURE 12, SHEEP DIP ADVISORY LEAFLET FRONT PAGE.

Teagasc Advice on the Safe Disposal of spent Sheep Dip

Spent Sheep Dip is a serious pollutant. The chemicals involved are highly toxic insecticides. It must never be allowed to enter a watercourse or the groundwater. It must never be disposed of to a soak pit or dumped on "waste ground".

The proper procedure is to land spread by slurry tanker at a dilution rate of one part spent sheep dip to three parts water or slurry at a rate not exceeding 20m³ per hectare (1760 gallons per acre) of diluted dip.

Spent Sheep Dip must be land spread as soon as practicable after use. Farm animals should be excluded from the disposal area for at least 28 days.

Empty dip containers should be triple rinsed when the dip is being prepared, and the rinsing liquid added to form part of the diluted dip. Empty rinsed containers should then be recycled through a permitted waste collector.

Sheep dipping tanks should not have a stopper or bung for emptying purposes.

In addition, the following precautions should be followed:

- Never dispose of spent sheep dip on frozen or waterlogged soils.
- Do not land spread between 1st November and 31st January (Closed Period for land - spreading). If necessary store in a slurry or effluent tank.
- Do not spread adjacent to an open stream, lake or watercourse – maintain a buffer zone of at least 5m, but 200m in the case of extraction points for drinking water.
- For safety, all sheep dipping baths should have a suitable cover in place when not in use.

www.catchmentcare.eu

A project supported by the European Union's INTERREG VA Programme, managed by the Special EU Programmes Body (SEUPB)

FIGURE 13, SHEEP DIP ADVISORY LEAFLET PAGE 2.

6.2. Forestry Awareness

As no direct mitigation works on forestry crops in the Finn Catchment were feasible, a Forestry Infographic (Figure 14 and Figure 15) was developed as a guidance piece from the project to be shared publicly via social media and the CatchmentCARE website whilst also being directly shared within the Private and Public forestry sectors. The infographic highlights how Forestry Operations in Ireland are regulated under the Forestry Act 2014 and are subject to licence and explains features such as set back/buffer zones, interceptor drains, and brash mats etc. which are features found within forestry as outlined in the Forestry Act 2014 Regulations.

FIGURE 14, FORESTRY REGULATIONS AND WATER GUIDANCE INFOGRAPHIC FRONT COVER.

FIGURE 15, FORESTRY INFOGRAPHIC INFORMATION ON BACK PAGE.

The CatchmentCARE Team also met with representatives from both the private and public forestry sector to discuss the impacts of the chemicals commonly used within forestry practices and the potential negative impact they can have on the aquatic environment. The team recommended alternative procedures and advocated for the implementation of mitigation measures to be incorporated within any planned crop planting such as the set back/buffer zone planted with native trees to reduce run off from the forestry or stepped drains with limestone rock to trap sediment and also to raise the pH of the runoff before entering a watercourse. The details of measures recommended are included in the forestry infographic.

7. INTEGRATED CONSTRUCTED WETLANDS

7.1. Introduction

As sheep dipping activity was highlighted as one of the main activities that was likely responsible for chemical export to water, Loughs Agency along with Donegal County Council, used the information collected from the Sheep Dip Survey to identify three facilities where mitigation measures might be implemented that would help eliminate the introduction of spent dip into the local watercourse.

The data collected allowed us to identify three publicly and regularly used dipping facilities that did not have adequate protections against discharge to the aquatic environment and showed signs that spent dip was being regularly introduced to the local watercourse. Publicly used dips are not owned by a single person and, as their name suggests, are available to all the public for use. Due to this aspect however, determining who is responsible for releasing spent dip into the river is very difficult as the person responsible must essentially be caught in the act to ensure that the activity is stopped.

To help remedy this issue, Loughs Agency and Donegal County Council decided that a passive treatment system should be put in place that would be able to remove any spent dip from effluents released from the facility. This would allow the elimination of spent dip from entering the watercourse more effectively than attempting to cease the activity which, to date, could not be achieved.

A brief desktop review of available literature was carried out and it was determined that installation of an Integrated Constructed Wetland (ICW), planted with a specific array of plants capable of removing the active chemicals in spent dip, could be installed that would allow any effluent from the facility to be cleaned so that, when it reached the watercourse, there would no longer be any chemicals present which could harm the aquatic environment.

Integrated Constructed Wetlands are a series of artificially created ponds, several of which are planted with specific assemblages of wetland plants. Generally, there is an initial receiving pond which is deep, unplanted and exists to collect the effluent of the target facility and hold it so that any suspended material can settle out and a portion of the effluent can evaporate. This pond is connected to a second shallower pond that is planted and then the second pond is connected to a third pond, similarly planted and shallow like the second. The ICW is designed to retain the effluent and slow the flow of it through the complex of ponds so that it remains in the treatment area for as long as possible for the target chemicals to be removed. Once the effluent has passed completely through the second planted pond, all harmful pesticides that were contained in the sheep dip will have been removed and only clean water is discharged into the local watercourse.

ICW's are able to remove pesticides such as Diazinon and Cypermethrin from sheep dip effluent by several natural processes. For example, in the first receiving pond the pesticides that are collected and stored there are broken down by photolysis, which occurs when sunlight interacts with and breaks the molecules of the pesticides apart causing them to be inert. This action works on both Diazinon and Cypermethrin, the two chemicals being targeted. In addition to photolysis, pesticides in the effluent will adsorb to sediment molecules and these will settle out of the effluent and become trapped in the pond leachate. This will actively remove Cypermethrin as it readily binds to soil but will have little effect on Diazinon which doesn't adsorb readily.

As water and effluent slowly collect in the first pond, the volume of liquid in it will increase so that any excess will overflow into the first planted pond. In this pond the same actions of photolysis and adsorption to sediment are continued, however an additional process is also introduced, and that is breakdown by microorganisms.

These microorganisms occur naturally in the root structure of the wetland plants in a micro-ecosystem called a Rhizosphere. The Rhizosphere is a region of the soil in the vicinity of plant roots which influences the chemistry and microbiology through the roots growth, respiration and nutrient exchange.

The microorganisms present in the Rhizosphere will readily breakdown any remaining pesticide chemicals present in the effluent as Photolysis and breakdown by Microbial Action are the two key ways in which Cypermethrin and Diazinon are broken down, making them inert and no longer a danger to the aquatic environment.

The flow through the 1st planted pond is also designed to be slow to ensure that the effluents received can be retained for as long as possible to allow for the breakdown of the target chemicals. However, when it eventually fills and overflows, it will transfer the remaining effluent to the 2nd planted pond, which is the final in the ICW system.

Like the 1st planted cell, the 2nd cell will remove the target chemicals through photolysis, adsorption to sediment and microbial action and will be sufficient in removing any remaining pesticide chemicals as the ICW is always designed to take into account the level of effluent that it must process in order to discharge clean water.

Finally, once the 2nd planted cell, and the final cell in the ICW system, overflows, it will discharge clean water to the local watercourse.

An agreement between Loughs Agency and Donegal County Council decided that three public sheep dipping facilities, with high likelihood of introduction of spent sheep dip in to the river, would have Integrated Constructed Wetlands installed at the outflow pipe of the dipping facility to capture and treat the pesticide containing effluent.

This project targets a key deliverable for the CatchmentCARE project, notably: Activity A.T2.4 Control of Chemical Escape from Land Use of which the key deliverables are: Investigative monitoring as directed by WP3; Implement recommendations from WP3; and develop best practice solutions.

This report gives details on the installation of the three ICW's at the three locations selected in the Finn Catchment.

7.2. Delivery

The Integrated Constructed Wetlands were implemented at three sites within the Finn Catchment; Ballykerrigan, Lough Muck and Montymeane.

The Ballykerrigan site is situated at coordinates 54.795231N, -7.989369W (Irish Grid Ref: 00733E 94133N) and the planned ICW installation covers an area of approximately 640m^2.

FIGURE 16, BALLYKERRIGAN PROPOSED SITE LAYOUT.

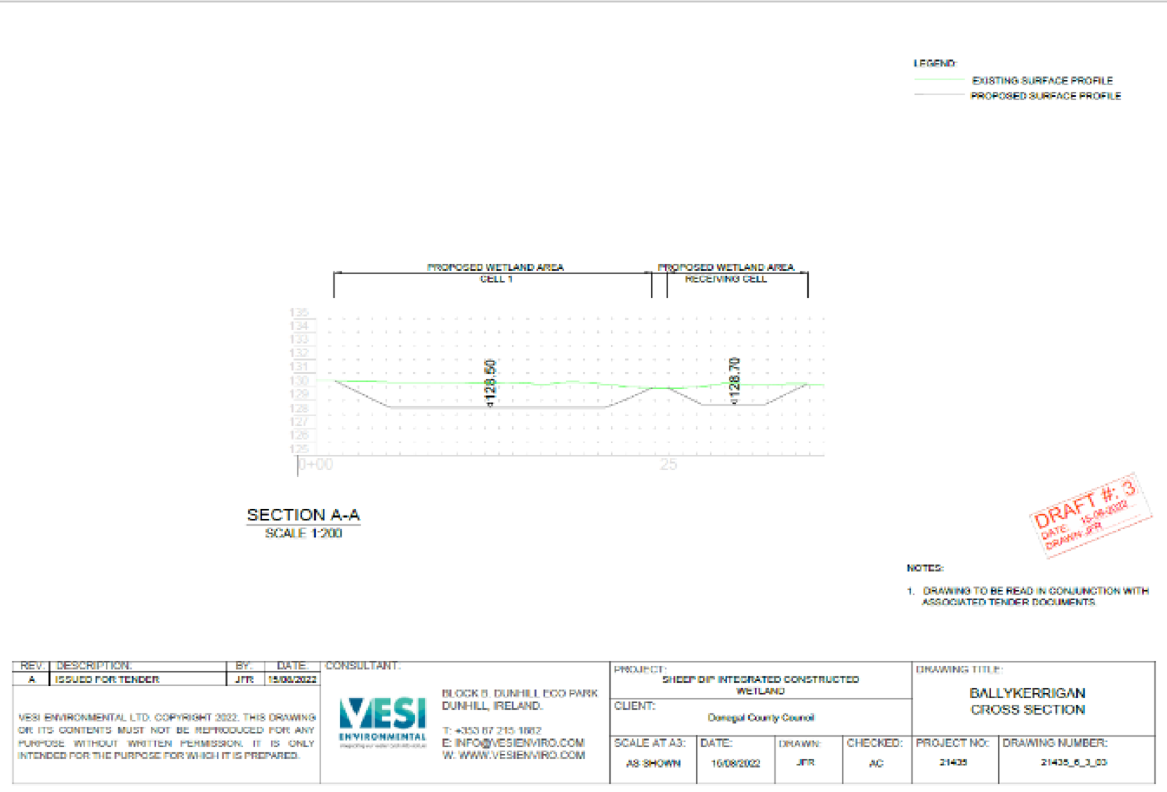


FIGURE 17, BALLYKERRIGAN ICW CROSS SECTION.

The Lough Muck site is situated at the coordinates 54.852739N, -8.1116666W (Irish Grid Ref: 192878E 400540N) and the proposed ICW installation area is approximately 1130m^2.

FIGURE 18, LOUGH MUCK PROPOSED SITE LAYOUT.

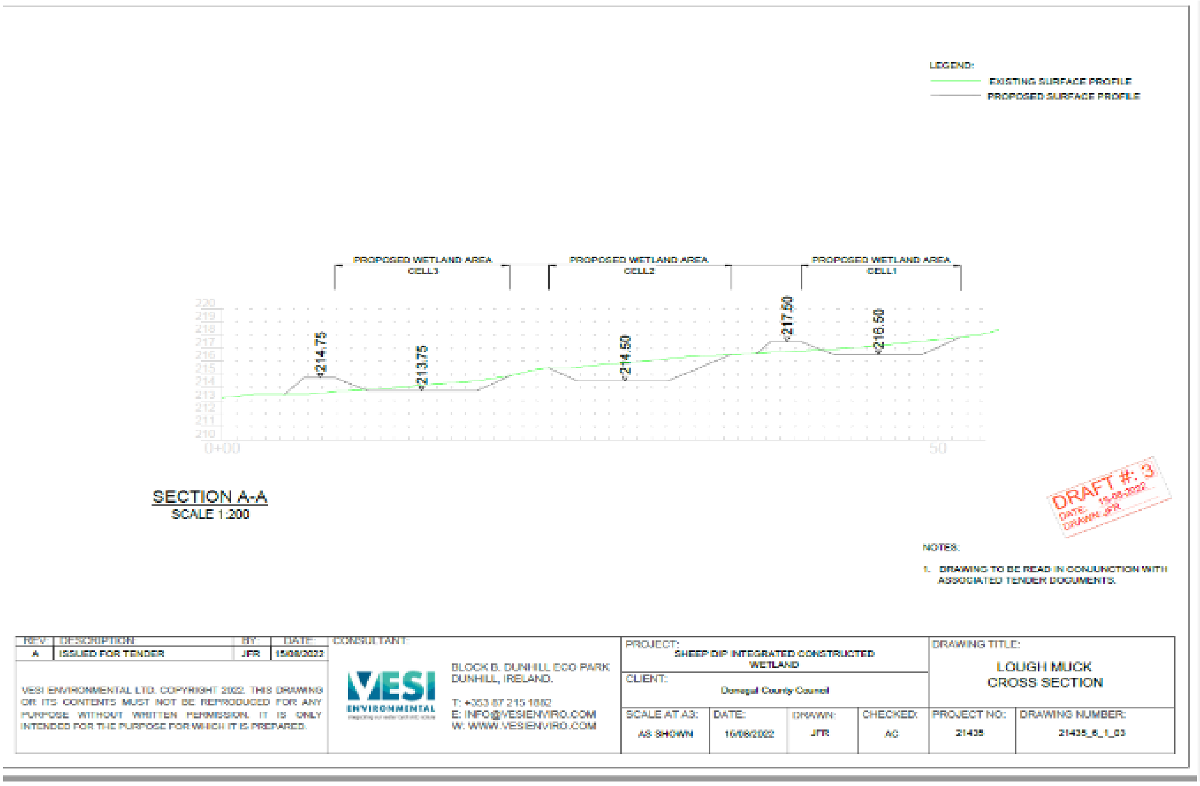


FIGURE 19, LOUGH MUCK ICW CROSS SECTION.

The Montymeane Site is situated at coordinates 54.858266N -8.0689672W (Irish Grid Ref: 195620E 401152N). The site for the Integrated Constructed Wetland is 3.1 km east of Lough Muck, Co Donegal on the L2023 road. The site lies within a freehold folio of approximately 2.63 ha.

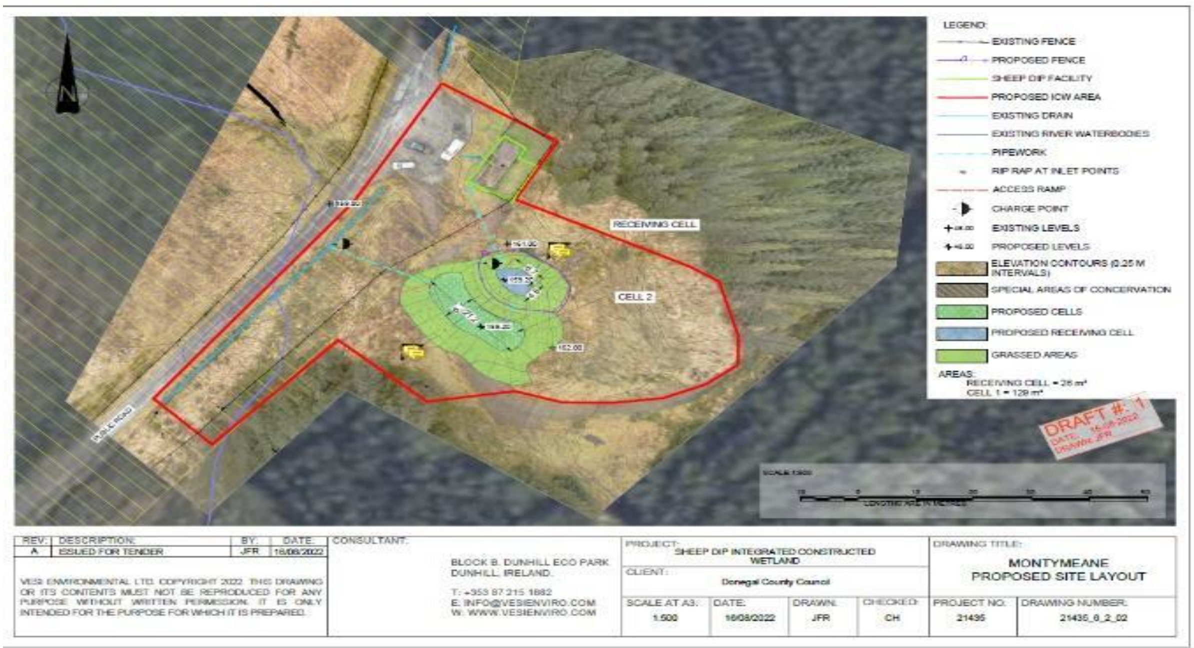


FIGURE 20, MONTYMEANE ICW SITE LAYOUT.

Once the three sites were selected, Loughs Agency and Donegal County Council contracted an environmental consulting firm, named Vesi, specialising in designing Artificial Wetlands to visit the sites and make up site plans for each.

Vesi, using information collected during the Sheep Dip Survey, calculated the anticipated volume of sheep dip effluent that would be issued from each site and based their designs on the amount of surface area and retention that would be needed to successfully remove all pesticides before the effluent was introduced into the river.

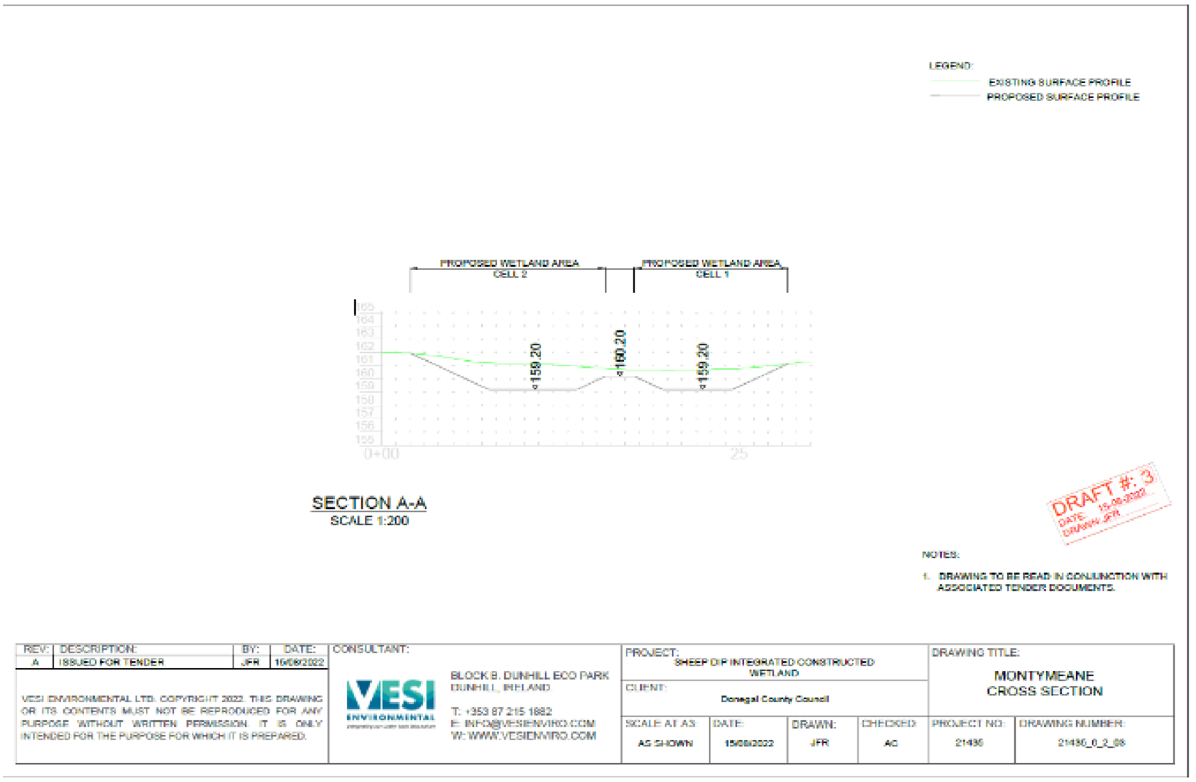


FIGURE 21, MONTYMEANE ICW CROSS SECTION.

Vesi created detailed blueprints for the three sites and incorporated these into a specification of works document.

Loughs Agency used the specification of works, as well as visits to the site, to create three screening for appropriate assessment documents for the work and sought peer review from National Parks and Wildlife Service (NPWS) on the proposed project, to which NPWS responded positively.

Once all documentation relating to the three projects, Loughs Agency carried out a tender competition via the eTenders website and appointed a suitable contractor.

Works commenced in February 2023 and were completed by April 2023.

7.3. Discussion

When investigating the feasibility of using Integrated Constructed Wetlands as a mechanism for treating pesticide effluent from sheep dips, it became apparent that there were significant amounts of scientific data contained in numerous papers that supported the use of these installations for this purpose.

Indeed, several of the papers reviewed suggested that ICW's are particularly effective at removing Cypermethrin and Diazinon, which were the two main target chemicals of concern for the CatchmentCARE project relating to sheep dip effluent.

In mainland Europe, a project called the LIFE Project has been investigating the use of wetlands for the removal of pesticides since January 2020 and is set to complete in December 2023 so the concept is starting to gain traction as a viable option for treatment of these chemicals.

Although there is significant scientific data and there are projects that are investigating the use of ICW's for treatment of pesticides, there are very few real life examples of these installations that have been installed for the specific purpose of treating sheep dip effluent. In Ireland, at the time of writing, Loughs Agency were unable to find any evidence of ICW's being used to treat sheep dip specifically.

It is the hope that the three installations on the Finn will act as a pilot project and promote the use of ICW's in treatment of spent sheep dip.

ICW's are an ideal choice for this as they are a low maintenance, low cost and passive solution to preventing chemical export from sheep dipping activities to the aquatic environment.

Installing ICW's in areas that have been traditionally difficult to effectively monitor (i.e. in remote areas) but where water quality is known to be impacted from their activities will address issues relating to improper disposal of spent dip when export events are not witnessed by protection officers also.

Loughs Agency have agreed to conduct routine monitoring of the ICW effluent to determine their effectiveness going forward and Donegal County Council have committed to maintaining the sites to ensure their effectiveness in treating effluent.

The installations were completed in April 2023 so no data is yet available that illustrates their effectiveness in treating the effluent from the dipping facilities however this data will be collected going forward and recorded by Loughs Agency.

It is hoped that the three facilities installed will be an effective working example that can be replicated by competent authorities in other areas on the island of Ireland, where there is a need to address the issue of spent sheep dip entering the local river.

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9. APPENDIX I

9.1. Literature Review

The introduction of pesticides into the aquatic environment is of great concern both for ecosystem conservation and human health. Poorly managed agricultural & forestry operations can lead to the contamination of surface and groundwater by nutrients and pesticides (Spalding & Exner 1993*,* Kolpin *et al,* 1998, Pereira *et al,* 1996*,* Novotney 2005*,* Gunningham & Sinclair, 2005*)*. Due to the potential for harm to the aquatic environment and associated biota, there is an increasing need for monitoring of these chemicals to ensure the protection of aquatic ecosystems.

The impacts of pesticide introduction to the aquatic environment can be severely detrimental and can include; macroinvertebrate and fish mortality, species behaviour change as well as impacting the fauna of the adjacent riparian zone.

As part of the CatchmentCARE Activity A.T1.7, 'Control of Chemical Export from Land Use Activities', a desktop chemical export literature review was carried out on commonly used agricultural & forestry pesticide and herbicide chemicals and these included; Cypermethrin, Acetamiprid, Organophosphates and MCPA.

Cypermethrin was historically used in treatment of forestry crops however this chemical is being replaced with Acetamiprid by Coillte and the changeover began in 2018.

This literature review aims to help identify the potential impacts of these chemicals on the aquatic environment with focus on, among other aspects; potential pathways of introduction to the environment, persistence within the environment and effects on macroinvertebrates and fish. The literature review is intended to aid in the selection of the most appropriate measures to help eliminate or, at the very least, reduce the potential for the introduction of these chemicals to the aquatic environment.

Cypermethrin is a widely used insecticide within the agricultural sector, primarily as a component of sheep dip. It is a lithospheric neuropoison which works by terminating the functions of the nervous system in parasites by interacting with the sodium channels of the target organism (WHO 1989). This has long-lasting effects on the permeability of the nerve membrane in target parasitic groups causing problems within the sense organs and nerve impulses of tissue fibre. It has the same effect on non-target macroinvertebrate species.

Acetamiprid is an insecticide and part of the neonicotinoid substance group. It is ideally used to control Hemiptera *spp*. (True Bugs) particularly aphids. The chemical formula is $C_{10}H_{11}ClN_4$. It is extremely soluble in water and can be volatile. It does not show great penetration when absorbing in to soils (Smith *et al* 2008) although studies have found that it may pose a risk of transference to surface and ground water (*Dujaković et al., 2010*) .

Organophosphates are commonly used pesticides within the agricultural sector, particularly sheep dips. Organophosphates are a cholinesterase-inhibiting pesticide which work by terminating the functions of the acetylcholine neurotransmitter within the nervous system of the target parasite, however the chemical is not target specific and affects non-target macroinvertebrate species in the same way. This is an irreversible reaction due to this target area inhibition. Organophosphates have very toxic effects on both animals and humans. Organophosphate exposure pathways overlap for many wildlife species and humans and contamination of well water can harm humans, long after the adverse impact of spraying on wildlife has occurred. (Vermeire *et al* 2003). Organophosphates are relatively non-persistent in the environment, particularly in dry conditions, however introduction to the aquatic environment can greatly increase the half-life of these chemicals, causing them to persist for longer. They generally show very little adsorption to soils but if they do they can persist bonded to soil particles years after their initial application (Ragsnardottir, Vala K., 2000).

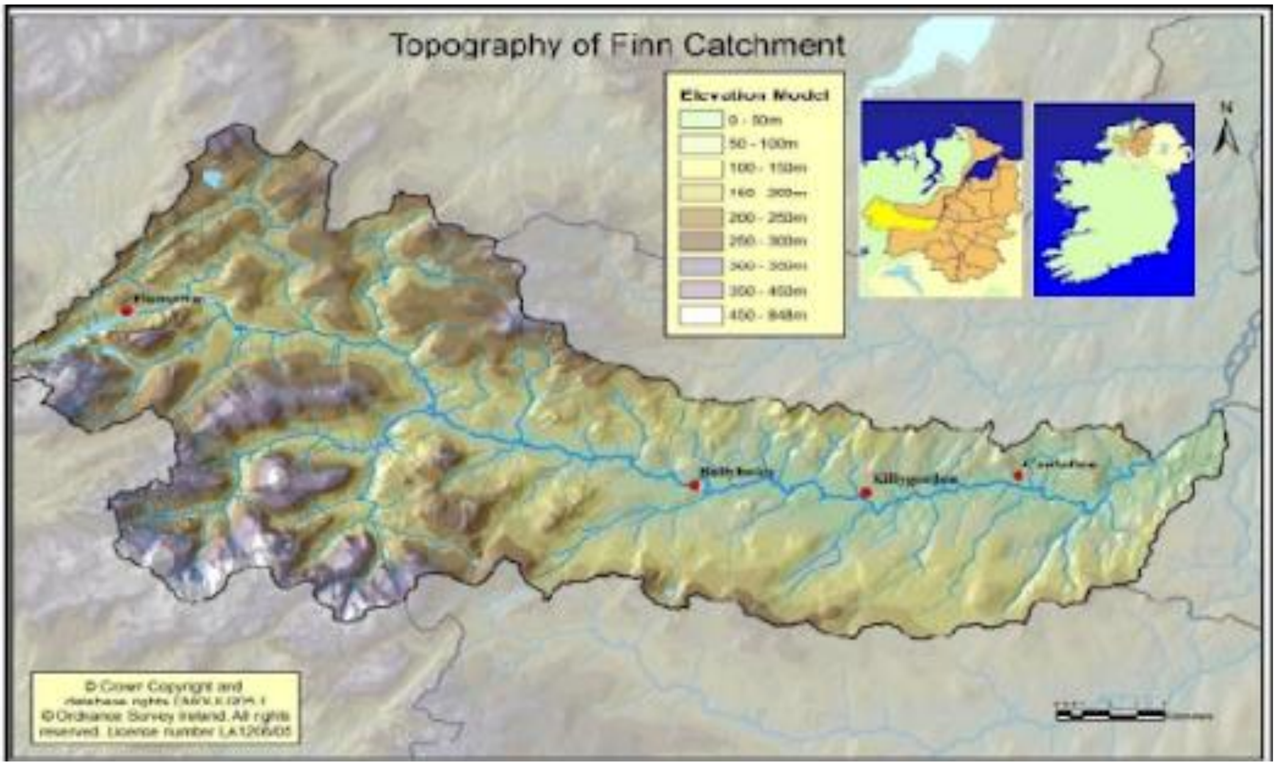


FIGURE 1, FINN CATCHMENT WAS THE STUDY AREA.

The River Finn begins in the Blue Stack Mountain range and drains easterly towards the Lifford/Strabane area where it meets the confluence of the tidal River Foyle. The River Finn and its tributaries have a channel length of approximately 101km with a catchment area of 494km^2 (*See figure 1*). The dominant land uses include commercial forestry plantations and upland grazing changing to lowland grazing with arable farmland in the lower reaches.

The following literature review outlines the molecular mechanics and life cycles of the above named pesticide chemicals. The consolidated review of the chemicals considered in this report will help inform successful mitigation solutions and recommendations for the reduction and prevention of chemical pollutants entering the watercourses within the Finn Catchment area.

9.2. Cypermethrin

Cypermethrin is a Pyrethroid insecticide and was first synthesised in 1974 (NPIC 1998). It is commonly used to control the growth and spread of the large pine weevil (*Hylobius abietis*) in certified forest plantations in Ireland (FSC 2016) as well as the UK and Europe. Cypermethrin is also an active ingredient in certain sheep dips.

Cypermethrin is a synthetic chemical similar to the pyrethrins in pyrethrum extract found in the Chrysanthemum plant, however, pyrethroids, including cypermethrin, were designed to be effective longer than pyrethrins (*NPIC 1998*). Cypermethrin is mainly found as an emulsifiable concentrate but also exists as a wettable powder and in combined formulations with other pesticides (WHO 1989). The molecular
formula is $C_{22}H_{19}Cl_2NO_3$. Cypermethrin is currently included in Annex I of Council Regulation (EEC) No. 2377/90 (*EMEA 2004*).

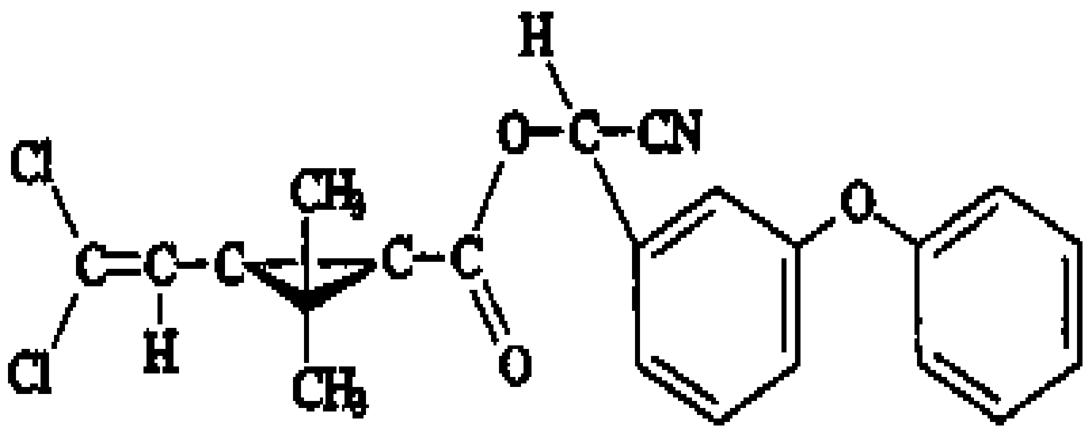


FIGURE 2: DIAGRAM SHOWING CHEMICAL MAKEUP OF CYPERMETHRIN

Synthetic pyrethroids are lithophilic neuropoisons acting on the axons in the peripheral and central nervous systems by interacting with sodium channels in mammals and/or insects (WHO 1989). The sodium channel in the nerve membrane of the nervous system is the primary target site of Cypermethrin. *(*WHO 1989). It causes a long lasting prolongation of the normally transient increase in sodium permeability of the nerve membrane, resulting in long lasting trains of repetitive impulses in sense organs and frequency dependent depression of the nerve impulse in fibres (WHO 1989). When this happens in insect populations it results in an effective paralysis which inhibits the ability to feed and so insects essentially die of starvation.

Chemically, Cypermethrin is the alpha-cyano-3-phenoxybenzyl ester of the dichloro analogue of chrysanthemic acid, 2, 2-dimethyl-3-(2,2-dichlorovinyl) cyclopropanecarboxylic acid. The molecule embodies three chiral centres, two in the cyclopropane ring and one on the alpha cyano carbon. These isomers are commonly grouped into four cis- and four trans-isomers, the cis-group being the more powerful insecticide (WHO 1989).
Cypermethrin was initially synthesised in 1974 as a highly active synthetic pyrethroid insecticide effective against a wide range of pests in agriculture, public health and animal husbandry. In agriculture, its main use is against foliage pests and certain soil pests (e.g. *cutworms*) (WHO 1989). In addition to its agricultural uses, Cypermethrin is used in certified forest plantations in Ireland to control the large pine weevil *(*FSC 2016) as well as an active ingredient in sheep dip (NRA 1994).

Applications in forestry are generally made in two stages. The first application involves the dipping of bundles of plants in a Cypermethrin insecticide solution before planting, and the second application occurs via spraying after planting (WRBD 2006). Spraying of planted trees usually takes place approximately twice a year although this can vary depending on the risk of infestation by large pine weevil. It should be noted that Coillte are moving away from using Cypermethrin based insecticides soon and will instead be using products containing a chemical called Acetamiprid.

Cypermethrin is an active ingredient in sheep dips such as Cyperguard which protects the livestock against sheep scab (caused by the mites *Psoroptes ovis* and *Sarcoptes scabiei*), blowfly, headfly, ticks, lice and keds (NRA 1994). Cypermethrin is also applied topically to cattle and poultry (NPIC 1998). In addition to Cypermethrin sheep dips there are also Organophosphate and Formamidine sheep dips. *(*URL 1*)*

The most widely adopted procedures for the determination of Cypermethrin residues in crops, soil, animal tissues and products, and environmental samples are based on extraction of the residue with organic solvent. Post detection, clean-up of the extract, is done by means of solvent-solvent partition and adsorption column chromatography, followed by determination of the residue using gas chromatography with electron capture detector (GC/ECD). The identity of residues can be confirmed by GC with mass selective detection (~C-MSD) or by thin-layer chromatography (TLC) followed by GC/ECD (WHO 1989). Crossland (1982) used redistilled hexane to separate

Cypermethrin from water samples and then analysed them by gas-liquid chromatography using an electron capture detector.

The physical and chemical characteristics of Cypermethrin mean that it is comparatively immobile in the outdoor environment and transport between media is restricted (WHO 1989). It has very low vapour pressure and water solubility and is strongly absorbed from aqueous solutions by solid surfaces (WHO 1989). This drastically restricts its movement in air and water, and particularly in soils (WHO 1989).

However, in previous studies, under field conditions, run-off Cypermethrin has been shown to occur to some degree. Run-off of Cypermethrin was probably due to physical transport of solid particles during erosion or during clear felling of trees increasing sediment levels reaching water courses which could have Cypermethrin bound to them. Run-off of Cypermethrin bound sediment could cause a potential flush of Cypermethrin which could kill macroinvertebrate populations (USEPA 1989). The physico-chemical properties of Cypermethrin result in strong sorption to sediment and suspended matter (SCHER 2011). This leads to low mobility through sediment, reducing the likelihood of introduction to the water course, if sufficient space exists between the water's edge and the area that is being treated with the insecticide. Type of soil plays a large part in the binding of Cypermethrin, with soils containing large amounts of clay and organic matter showing strong absorption of the chemical (WHO 1989).

According to detailed soil maps from Teagasc, the dominant soil type in the upper reaches of the Finn catchment is peat. It is also stated in the River Finn SAC site synopsis that much of the area is covered in upland blanket bog (DAHG 2014).
Cypermethrin is also relatively immobile in surface waters and is typically confined to the surface film (WHO 1989). This implies that introduction to any drainage gullies around areas of application, if contaminated by overspray, could convey the pesticide to main water bodies on the surface film.

If Cypermethrin is accidentally introduced to the waterbody and if it has a significant level of suspended sediment or organic material then the tendency of the chemical to bind to these will result in its removal from the water column and binding in the sediment (Muir 1985).

There are guidelines (DAFM 2019) in place to ensure that Cypermethrin related pesticides used in agricultural practices such as sheep dipping and forestry plantations are not introduced to the aquatic environment. If followed properly the guidelines should be sufficient to avoid this but there are no specific regulations in place which may act as further incentive to follow these guidelines as prosecutions could be brought against offenders. The Irish National Action Plan for the Sustainable Use of Pesticides (Plant Protection Products) provides advice on how to responsibly conduct application of pesticides (DAFM 2019).

Studies in England and Wales found that poor operational practices are widespread, including sheep having access to water courses shortly after treatment and improper disposal of spent dip (EA 2007).

Cypermethrin is very highly toxic to water insects and highly toxic to fish (NPIC 1998). The 96-hour LC50 for cypermethrin in rainbow trout is 0.82 ppb and 0.2 ppb for *Daphnia magna*, a small freshwater crustacean (USEPA 1989). Fish sensitivity to the pyrethroids may be explained by their relatively slow metabolism and elimination of these compounds. The half-lives for elimination of several pyrethroids by trout are all greater than 48 hours (Bradbury 1989*)*. The presence of suspended solids decreases the toxicity of Cypermethrin by at least a factor of 2 due to the chemicals adsorption to solids (WHO 1989). Aquatic invertebrates show a wide range of susceptibility to Cypermethrin. It can be concluded that effects can be expected when concentrations of Cypermethrin of the order of 0.01 µg/litre are maintained in the water phase for more than 96 h (WHO 1989).

Two studies were conducted by Crossland & Bennett (1976*)* and Crossland *et al* (1978) involving deliberate over spraying of experimental ponds under field conditions. Observations on invertebrates were included in these two pond studies. In the first study, which lasted 2 weeks, populations of Crustacea, mites, and insects were severely reduced. Surface breathing insects were affected most rapidly, within hours of treatment. Free-swimming dipterous larvae were not noticeably affected for 24 h, while zooplankton were killed between 1 and 2 days after treatment. Bottom dwelling invertebrates, including chironomid larvae, snails, leaches, and flatworms, did not appear to be affected, though the numbers in the last 2 groups were low in pre-treatment samples.

The second study was continued for 15 weeks after treatment. Initial results were similar to those reported above. Macro-invertebrates were markedly reduced in numbers, two weeks after treatment. However, both numbers and diversity returned to normal levels after 15 weeks. Snails and flat worms (again numbers low in this group in pre-treatment counts) were unaffected, but no arthropods were present in the samples taken at two weeks.

Recolonization by flying insects (beetles and chironomids) commenced four weeks after treatment. The Crustacean *Asellus* had not reappeared by the end of the study. No Daphnids or copepods were found in the zooplankton samples, one week after treatment, and they only reappeared in the 8-week post-treatment sample. Populations returned to normal levels in 10-12 weeks. Some two weeks after treatment, an increase in filamentous algae was noted, and this persisted until the end of the study. It was inferred that this was a secondary effect following from the elimination of known feeders on algae, for instance, the mayfly, *Cloeon dipterum*, and the daphnid, *Simocephalus* sp. (Crossland & Bennett 1976; Crossland *et al.* 1978). Siegfried (1993), suggests that aquatic insects show higher susceptibility to Cypermethrin than terrestrial insects because of lower levels of exposure to lipophilic compounds in an aquatic environment which leads to lower potential to detoxify lipophilic xenobiotics such as insecticides.

The typical half-life of Cypermethrin in the soil is 30 days, although it can range from two to eight weeks. Soil microbes rapidly break down Cypermethrin (NPIC 1998). Cypermethrin is not soluble in water and has a strong tendency to adsorb to soil particles. It is therefore unlikely to cause groundwater contamination (USEPA 1989).

Under laboratory conditions, Cypermethrin degrades more rapidly on sandy clay and sandy loam soils than on clay soils and more rapidly in soils low in organic material. In aerobic conditions, its soil half-life is 2 to 8 weeks. Cypermethrin is more persistent under anaerobic conditions (USEPA 1989).

Muir *et al* (1985) found that when 125g of concentrated Cypermethrin was applied to open water the concentrations of the chemical dropped by 95% within 24 hours. It was assumed that the rapid loss was due to adsorption of Cypermethrin to sediment and suspended soil particles.

Cypermethrin hydrolyses and photolyzes more quickly in a basic environment, where the chemical degrades much faster in river water versus distilled water. This suggests that naturally occurring substances enhance the breakdown of Cypermethrin, and because of its high affinity for organic matter, Cypermethrin readily adsorbs to suspended matter in natural waters (USDPR 1998).

Kidd and James, (1991), reported that in river water, rapid degradation occurred with a half-life of about 5 days, which is three to four times faster than degradation in distilled water. They surmised that this suggested indirect photolysis involving naturally occurring substances that result in enhanced photo degradation. The main route of degradation of Cypermethrin is cleavage of the ester linkage to give two main degradation products containing the cyclopropane, and the phenoxybenzyl moiety (*WHO 1989*).

According to Agnihorti *et al*. (1986), the reduction in Cypermethrin aqueous concentrate was rapid, with about 95% lost within 24 hours after application to water and sediment contained in open trenches. In that study the reduction in concentration was primarily due to rapid sorption to sediment and suspended particles and not degradation.
Because of its strong affinity for soil, Cypermethrin may be carried away to nearby water bodies in suspended sediment by rain and irrigation. Yet, once the pesticide is adsorbed to soil particles, bioavailability is reduced, diminishing the toxicological risk to aquatic animals (Agnihorti *et al.* 1986).

In pond experiments, fish have survived in pond water that contained apparently lethal concentrations of Cypermethrin (5 ppb) because the chemical was absorbed onto suspended solids (Crossland 1982).

Upon conducting this literature review on cypermethrin it is evident that it poses a risk to aquatic fauna and, in particular, aquatic macroinvertebrates. This is unsurprising as the main purpose for the synthesis of Cypermethrin was for use as an insecticide to control unwanted pests in agriculture, animal husbandry and forest plantations.

Studies have shown that direct introduction of Cypermethrin to the aquatic environment results in rapid initial loss of aquatic macroinvertebrate communities. However, as the chemical readily binds with organic material and suspended sediments in the natural environment it does not remain bioavailable for long. This is particularly true of natural waters which are more likely to have suspended sediments and organic material for the substance to bind to. In addition, Cypermethrin is relatively quickly broken down by photo-degradation and organic microorganisms in sediment and organic material.

Cypermethrin's tendency to readily bind to soil, and the short time it remains bioavailable in the environment are likely the best attributes to exploit when attempting to avoid any negative consequences to the aquatic environment. According to Kaufman *et al*. (1981), very little Cypermethrin insecticide moves through the soil with the carbon content of the soil greatly affecting the amount of chemical that is absorbed. Cypermethrin was found to have an average Koc of 6.1x104 cm^3 /g for five different soil types indicating that Cypermethrin is relatively immobile in soil (USDPR approx.. 1998 – cyperm).

The above information suggests that implementation of buffer zones for forestry plantations would be sufficient to avoid accidental introduction of Cypermethrin to surrounding waterbodies. These buffer zones would have to take in to account drainage ditches and gullies as these could facilitate the introduction of Cypermethrin in to the main water body.

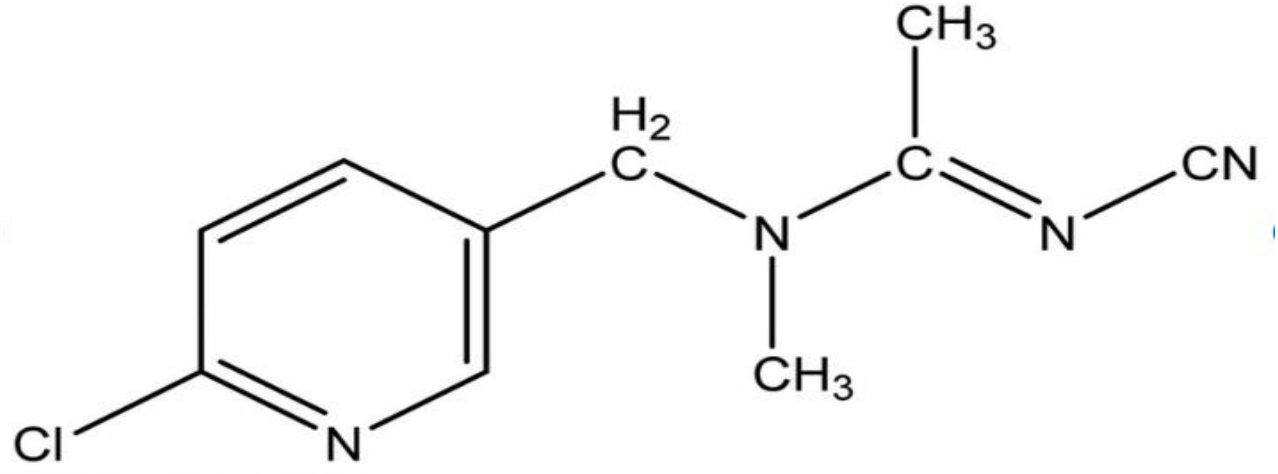
If proper buffer zones are implemented then the aquatic environment should recover from any Cypermethrin related effects on aquatic fauna as it has such a short half-life in the natural environment. Regulations already exist within Coillte to ensure that proper buffer zones are implemented during forestry plantation (FSC 2016) however numerous plantations in existence today may have been planted before such regulations were in place. Creation of buffer zones in well-established forestry plantations is unlikely to be welcomed by Coillte as the loss of boundary stands of trees would risk the felling of trees further within the plantation due to heavy winds. As these inner trees have been protected by trees along the boundary from wind throughout their growth they have not had the need to develop as deep a rooting system to ensure they are better anchored to the ground.

A better method would be to allow these stands to be clear felled when they are ready for harvest and ensure that a new plantation in their place is planted with sufficient buffer zones in mind.

There is also the danger of Cypermethrin introduction to the environment via the use of certain kinds of sheep dip. Guidelines are in place to guide farmers (DAFM 2019) in the proper application and disposal of the insecticide which should be sufficient to control the introduction of Cypermethrin to waterways. However, studies in England and Wales (*EA 2007*) suggested that poor operational practices were responsible for water quality in numerous waterways being negatively affected by the introduction of Cypermethrin. It is possible that similar poor operational procedures in the Finn catchment may also be an issue therefore it would be prudent to formulate regulations to manage proper sheep dip disposal.
Ensuring that proper disposal of spent dip is carried out as well as ensuring that proper fencing along rivers is in place to stop recently treated sheep from entering waterways would be a priority to stop any negative impacts to the aquatic environment. This would likely involve installing more fencing along waterways to ensure animals could not access the water as well as a community education campaign, for sheep farmers in particular, to show the negative consequences of spent dip entering waterways, and to reinforce the knowledge of how to dispose of spent dip properly.

9.3. Acetamiprid

Acetamiprid is an insecticide and part of the neonicotinoid substance group. It is ideally used to control *Hemiptera spp*. (True Bugs), particularly aphids. The chemical formula is $C_{10}H_{11}ClN_4$. It is extremely soluble in water and can be volatile. It does not show great penetration when absorbing into soils (Smith *et al* 2008) although studies have found that it may pose a risk of transference to surface and groundwater (Dujaković *et al.,* 2010). (URL 10).



Chemical structure of acetamiprid.

FIGURE 3, ACETAMIPRID CHEMICAL STRUCTURE

Acetamiprid is a carboxamidine that is acetamidine in which the amino hydrogens are substituted by a (6-chloropyridin-3-yl) methyl and a methyl group while the hydrogen attached to the imino nitrogen is replaced by a cyano group. Acetamiprid derives from a 2-chloropyridine. Acetamiprid is very soluble in water. It is a member of a class of pesticides known as neonicotinoids which are toxic to plant pollinators such as honey bees. It is mainly used as a pesticide on various fruit, vegetable and cotton plants as well as ornamental plants and flowers. (National Centre for Biotechnology Information, 2019). There is no regulation regarding its use in the EU. *(*Mateu-Sanchez *et al*., 2003*)*

Acetamiprid reacts like nicotine within the body, it is a natural insecticide which reacts with the nicotinic acetylcholine receptors (nACh-R) which are located in the postsynaptic dendrites of all neurons in the brain, ganglia, spinal cord and muscular junctions. This then causes hyperactivity within the neurons, muscles spasms and eventually death (Mateu-Sanchez *et al.*, 2003)

Neonicotinoids have active compounds and basic by-products that exhibit high water solubility and polarity, increased photo-stability as well as persistence in water and soil matrices. This enables their transference in both surface and groundwater (Dujaković *et al.,* 2010). It absorbs to less than 290 nm and therefore is stable to the influence of solar radiation (Kagabu & Medej*,* 1995).

Yao *et al.* (2010) noted that soil enzymes have markedly different responses to acetamiprid. Some enzyme activity may be stimulated by the pesticide, whilst others may be inhibited. Soil adsorption might reduce the concentration of acetamiprid contact with microorganisms, however, acetamiprid is stable to hydrolysis at environmental temperatures and biodegradation is reported to be the most significant mechanism for its dissipation from soil (Yao *et al.,* 2010).

In insects, these neonicotinoid insecticides are known to act on acetylcholine nicotinic receptors. After oral consumption acetamiprid increased sensitivity to antennal stimulation by sucrose solutions at doses of 1 lg/bee and impaired long-term retention of olfactory learning at the dose of 0.1 lg/bee. Acetamiprid thoracic application induced no effect in these behavioural assays but increased locomotor activity (0.1 and 0.5 lg/bee) and water-induced proboscis extension reflex (0.1, 0.5, and 1 lg/bee). (El Hassani *et al.,* 2008). Acetamiprid is a very efficient insecticide able to bind and interact with acetylcholine receptors located in neurons of the central nervous system in target insects causing paralysis leading to death (Bowník *et al.,* 2017*).*

Acetamiprid is commonly used as an insecticide to control *Hemiptera Spp*. (True Bugs), particularly *aphids.* It is normally used on produce such as leafy vegetables, citrus fruits, grapes, fruiting vegetables, ornamental plants and flowers to protect against sucking-type insects. It is also described as having relatively acute mammalian toxicity. (Yao *et al.,* 2010). Acetamiprid is also used for defence against pine weevil (*Hylobius abietis*) damage to conifer seedlings (Olenici *et al.,* 2014). Acetamiprid is now a common insecticide used in place of Cypermethrin pesticides and Coillte are planning to use it as a replacement for Cypermethrin in their forestry plantations. Acetamiprid is also commonly used for pest control of bed bugs.
Detection of Acetamiprid in the water body is usually carried out through water sampling or grab sampling of sediments. Main *et al*., *(*2014) took one litre samples of water using a subsurface grab at a depth of 10 cm in chemically cleaned (acetone: hexane washed) amber glass jars. Bottles were sealed with Teflon-lined caps and then stored in the dark during transport and refrigerated at 4°C until analysis. Water samples were passed through Oasis HLB cartridges which had been sequentially conditioned with methanol (10 mL) and water (10 mL).
After sample loading, the cartridges were washed with de-ionized water (5 mL) to remove salts and the cartridges were dried under vacuum for 5 min. The retained analytes were eluted with methanol (10 mL), the eluates were evaporated to dryness and the extract residues reconstituted in 500 µL of water followed by addition of the internal standard.

A Waters 2695 Alliance HPLC (High Performance Liquid Chromatography) system, consisting of a solvent degassing unit, pump and autosampler, was used with a Waters XTerra MS-C8 (3.5-mm dia. particle size) column (2.1-6100-mm) at 30°C. Isocratic elution of the analytes was achieved with an 80/20 mix of solvent A (100% water and 0.1% formic acid) and solvent B (90% acetonitrile, 10% water and 0.1% formic acid). The run time was 10 min and the injection volume was 20 µL.
The neonicotinoid insecticides were quantitated (internal standard method) and their presence confirmed using a Micromass Quattro Premier triple quadrupole mass spectrometer equipped with an electrospray ionisation interface set to positive ion mode. Ionisation and MS/ MS conditions were optimised by infusing a 0.5 mg/L solution of each insecticide into the ion source in a 50:50 (v/v) acetonitrile water solution with a syringe pump.

Studies by Bownik *et al.,* (2017) have shown that parameters such as swimming velocity, heart rate and thoracic limb activity may be treated as sensitive, early biomarkers of neurotoxicity in *cladocerans*. Current standard experimental equipment typically consists of one observation container or flat vessel or a set of containers in which the exposed daphnids are kept and monitored by one or two video cameras connected to a computer with software for movement analysis. Various parameters of swimming behaviour may be considered as a sensitive method recommended for assessment of chronic toxicity and also as a promising approach for monitoring of water quality.

Acetamiprid is mobile and is not likely to persist in surface soils, however, it can move to surface water through spray drift and through run off if it rains soon after application (EPA 2002). It is moderately persistent in aquatic environments and is stable to hydrolysis at environmental temperatures. It photodegrades relatively slowly in water. Degradation occurs faster in aerobic water conditions compared to anaerobic conditions (EPA 2002). The half life of acetamiprid in aerobic water conditions is 45 days (Loamy sand sediment) compared to 365 days in anaerobic conditions. The primary route of degradation is through aerobic soil metabolism where there are four major degradates (EPA 2002). It is not expected to bind readily to most soils or to aquatic sediments.

If acetamiprid is released to the environment as a vapour, it will be broken down in air. Acetamiprid released to air will also be in or on particles that eventually fall to the ground. It will not move into air from moist soil and water surfaces. It is expected to move through soil. It is not expected to build up in fish. *(National Centre for Biotechnology Information, 2019*)

Kim *et al* (2012) found that acetamiprid deposits on plants washed off by rainfall and reaching the soil surface was *circa*. 17% of the application rate. All acetamiprid on the ground resided in the forest floor covering the soil surface, where acetamiprid residues were decreased to a quarter 48 days after the second application, but they were not detected in soil beneath it. Only low level acetamiprid residues (0.0003 mg/L), were detected in the reservoir nearby the experimental forest on the day of aerial application. The acetamiprid detection was presumably due to spray drift. (*Kim et al., 2012*)

Acetamiprid is persistent in water and may reach concentrations up to 41 µg/l (PPDB 2017). A number of studies indicate that *Cladocera* seem to be one of the most resistant invertebrates to neonicotinoids, however they present a wide range of sensitivity with LC50 (Lethal Concentration) from 4100 to >1000 000 µg l–1 (Bownik *et al.,* 2017). Studies found that acetamiprid is very highly toxic to the amphipod *Gammarus fasciatus* and the midge *Chironomus riparius*. This indicates a wide range of acute and chronic sensitivities among freshwater invertebrates (EPA 2002)

If released into water, acetamiprid is not expected to adsorb to suspended solids and sediment based upon the Koc values. Volatilization from water surfaces is not expected to be an important fate process based upon this compound's estimated Henry's Law constant. (URL 2)

Studies by Bownik *et al* (2017) found that acetamiprid induces concentration-dependent inhibition of swimming velocity and thoracic limb activity in *Daphnia magna* after exposure. It also depressed the heart rate after 24 hours of exposure. The study suggests that neonicotinoids may alter behavioural and physiological parameters in *Daphnia magna* thereby increasing susceptibility of these invertebrates to higher predator pressure. High persistence in water and the ability to induce cumulative toxicity suggests that this neonicotinoid may interact with nicotinic receptors and thereby affect the nervous system of sensitive species of Cladocerans which may result in behavioural and physiological changes. (Bownik *et al.,* 2017)

Studies have shown that acetamiprid can initiate drift of stream dwelling macroinvertebrates at concentrations that cause no significant mortality (Beketov & Liess, 2008). Chemical pollution and abrupt changes in water quality have also been shown to precipitate catastrophic drift (Baxter *et al.,* 2017).

Studies to show the lethal and transcriptional effects of pesticides on aquatic systems (zebrafish) show acetamiprid as the chemical that has the lowest toxicity to organisms. The synergistic response of binary and ternary mixtures that include acetamiprids demonstrated some effects of toxicity.
The expressions of 16 genes related to cell apoptosis pathway, oxidative stress response, innate immunity and endocrine disruption at the mRNA level showed that zebrafish embryos were affected by the individual or combined pesticides. Taken together, increased toxicity might be triggered by the simultaneous presence of several pesticides in the aquatic environment, which seriously damages the non-target organisms. (Wang *et al.,* 2018)

Zebrafish embryos exhibited significant mortality and teratogenic effects at concentrations greater than 263 mg/L, with bent spine being the main malformation. *(Ma et al., 2019).*

Changes in metabolites of zebrafish showed that acetamiprid disturbed amino acid metabolism, the TCA cycle and the balance of neurotransmitters. The change in metabolites in the liver, head, and blood indicated that metabolites in the liver were more sensitive than those in the head and blood *(*Zhang & Zhao*,* 2017*).* Although these studies were carried out on tropical fish species, it is reasonable to expect that a similar impact could be felt on native fish species in Ireland.

Exposure to acetamiprid caused a decrease in lysosomal membrane stability of gonad tissue in the Marine species *Mytilus galloprovincialis* (Mediterranean Mussel). Exposure to neonicotinoids may have subtle cellular-level chronic effects in mussels that could result in adverse effects at the organismal level. However, it is important to consider that the magnitude of the effect concentrations suggest that freshwater mussels are not likely to be chronically exposed to concentrations of this order of magnitude in the environment *(*Prosser *et al*., 2016*).*

Acetamiprid has a moderate persistence in soil under field capacity and submerged moisture regimes, under laboratory conditions. *(Gupta, S. & Gajbhiye, V. 2007).*

Soil enzymes have markedly different responses to acetamiprid,. On one hand, soil adsorption might reduce the concentration of acetamiprid contact with microorganisms, however, acetamiprid is stable to hydrolysis at environmental temperatures and biodegradation is reported to be the most significant mechanism for its dissipation from soil (Yao *et al.,* 2010)

Acetamiprid is mobile and unlikely to persist on the soil surface although, if applied before a significant rain event it has the potential for surface run off (EPA 2002). The chemical is moderately persistent in aquatic environments but is broken down by photodegradation, although it is stable to hydrolysis at environmental temperatures (EPA 2002). The primary route of degradation of acetamiprid is through aerobic soil metabolism (EPA 2002).

Studies carried out by the European Food Safety Authority *(EFSA, 2016)* found that Acetamiprid was stable under the conditions of aqueous hydrolysis investigations at pH 4, 7 and 9 at 20^{0}C.

Following good agricultural practices when applying this pesticide would be extremely beneficial to the surrounding environment. As acetamiprid does not bind readily to soil and is water soluble, any applications should keep in mind the proximity of the aquatic environment and the prevailing weather conditions. A significant buffer zone should be employed for any agricultural land and/or forestry plantation spreading (at least 5m distance depending on intended use of adjacent water body). In addition, no pesticide application should be carried out if there is a chance of rainfall which could lead to the washing of the chemicals into the watercourse.

Also, consideration should be given to an increase in the use of selective insecticides, Lower dosage of insecticides, improved timing of insecticide applications, special insecticide formulations, site-specific applications and special application methods.

Studies by Wang *et al*., (2013) looked at using bacterial strains to reduce levels of acetamiprid in soil. Two strains were identified which showed the potential to reduce acetamiprid levels. These included the addition of the *Pigmentiphaga sp*. strain AAP-1 into soils treated with acetamiprid which gained a higher degradation rate, and the bacteria community analysis by T-RFLP in contaminated soil recovered after inoculation of the AAP-1 strain. On the basis of these results, strain AAP-1 has the potential to be used in the bioremediation of acetamiprid-contaminated environments. This is the first report of acetamiprid-degrading isolate from the genus of *Pigmentiphaga*.

9.4. Organophosphates

OrganoPhosphates (OP) are produced by the process of esterification between phosphoric acid and alcohol. The OP compounds can be classified as aliphatics, aromatics, heterocyclics etc.

The overall structure of OP insecticides: four atoms are connected to the phosphorus atom by single bonds and one by a coordinate covalent bond or commonly known as a double bond. All four of these surrounding atoms are oxygen. OP insecticides are commonly derived from phosphoric acid. These OP compounds are often highly reactive materials and are useful in the requirement for short residual activity for example, on dairy cattle or on vegetables nearer to harvest. Several types of OP's include Parathion, Diazinon, Dursban, Coumanphos, Sarin and Soman.

The inhibition of acetylcholinesterase activity adversely affects animals because this enzyme normally regulates the proper levels of the neurotransmitter acetylcholine in the central nervous system, the neuromuscular junction, the parasympathetic nervous system, and the sympathetic synapses. If acetylcholinesterase activity is depressed due to exposure to a cholinesterase inhibitor, then the ordinarily rapid breakdown of released acetylcholine is slowed, resulting in overstimulation of the target cells, which can be fatal (Padilla, 1995). As a rule, recovery is much slower in fish than in mammals (Wallace & Herberz, 1988). Required time to recover (days to weeks) is a function of both concentration and exposure.

Organophosphate insecticides have been used extensively for more than 40 years for agricultural purposes (Lambropoulou & Albanis 2001). Due to the increased need of produce globally the use of agricultural pesticides have also increased to insure high quality produce. Pesticides normally have a targeted species however also have adverse effects on the surrounding environment. Organophosphates are used more commonly than their Organochlorine counterparts due to their ability to degrade more readily in the environment *(*Lambropoulou & Albanis 2001*;* Schellin *et al.* 2004*).*

Chlorinated and brominated organophosphates are commonly used in flame retardants in polyurethane foam. Organophosphates are often used in the medical treatment of Myasthenia gravis, glaucoma, paroxysmal atrial tachycardia and anticholinergic poisoning. *(*Ballantyne & Marrs, 2017*).*

Organophosphates are commonly used in the removal of parasites from pets and livestock. OP's are also used for sheep dips against sheep scab, ticks and blow fly strike. Also used in flea powders

and collars for household pets such as cats or dogs. OP chemical Coumaphos is used in wound dressings for horses. Also used for human medication against head lice. *(*URL 7*).* The AchE in the medication terminates the transmission of nervous signals where acetylcholine is the neurotransmitter. By doing this the OP's prevent the termination of the nerve signals which disturbs the normal movements of the parasites which leads to paralysis and eventually mortality.
Wee *et al* (2016) collected direct samples by inserting a sterilised amber glass bottle into the target water body at the target depth whilst indirect sampling was carried out using a purging pump (usually groundwater). Surface water samples were obtained in amber glass bottles whilst ensuring no air pockets. All samples were stored in a refrigerated container ± 4^{o}C to be analysed in the laboratory. At each of the sampling sites parameters such as pH, temperature, salinity, conductivity, dissolved oxygen and turbidity were also measured *(Wee et al, 2016).*

Several sampling methods for Organophosphates are given below:

Liquid-Liquid Extraction (LLE)

An effective method for pesticide extraction in water samples which involves creating a partition of different substrates between the aqueous sample and an immiscible organic solvent. The LLE method is dependent on the solvent used and the nature of the water matrix. Other parameters such as pH, ionic strength, and water to solvent ratio, number of extractions, type, and concentration of analyte must also be measured using this technique (Barcelo, D. 1991*).*

Solid-Phase Extraction SPE

This method involves a column containing a suitable sorbent to trap the analyte. The sample solvent flow through the column by gravity or by positive (syringe)/negative (vacuum) pressure. The method process involves, the activation of sorbent, removal of activating solvent, sample application, removal of interferences, and elution of concentrated analytes and the regeneration of the column (Barcelo, D., 1991).
In a study carried out by Schäfer *et al* (2012) water samples were collected in 1L bottles and kept cool or frozen within 24 hours of collection. These samples were then filtered (Whatman GF/C) and suspended solids were measured based on weight of filtered material. Soluble reactive phosphorus was determined by colorimetry. Atomic absorption uncovered the presence of calcium and magnesium, sulphates were determined by turbidimetry whilst chlorides were determined using silver nitrate titration. Gran titration uncovered bicarbonates whilst photometry identified sodium and potassium. At each site the maximum stream width (m),depth (m), velocity (m/s) and percentage of area covered by emergent, submerged and floating vegetation (%). Composite sediment samples were also collected from 3 to 5 locations at each site, using sonication, insecticides were extracted from sediments. These samples were then analysed for cypermethrin, lambda-cyhalothrin, endosulfan and chlorifos by gas chromatography-electron capture detection (GC-ECD), using gas chromatography- mass spectrometry- negative chemical ionisation (GC-MS-NCI) also analysed for pyrethroids and organochlorine.

There are 3 different elements to vulnerability of fauna, they are susceptibility to exposure, direct sensitivity and recovery capability (Ippolito *et al,* 2010*,* De Lange *et al,* 2010*,* Turner *et al,* 2003). Leiss & Von der Ohe (2005) and Schafer *et al* (2012) found that increased concentrations of Organophosphates are often correlated with several other stressors such as nutrients, particle transport and habitat degradation. The loss of functional performance may have cascading effects reducing the amount of available energy for growth and reproduction and therefore also the chances for an organism to successfully reproduce and compete for space and food. *(Rasmussen et al, 2013*).

In the study by Ippolito *et al* (2011), it was found that factors such as behavioural complexity, body shape and body length were important macroinvertebrate traits for the prediction of sensitivity to Organophosphate pesticides. It was found that the length and shape of the body influenced chemical intake as it determines the surface to volume ratio. Due to this filter feeders are more sensitive to OP's. Macroinvertebrates are ideal indicators to toxic stress due to their processing of organic matter and cycling of nutrients. Within Ippolito's (2011) study the macroinvertebrate taxa had variable responses, mostly negative resulting in mortality. Within fish species it was found that OP's decreased growth rates, reproductive behaviour, whilst also directly causing neurological disorders and deformities within the spinal structure, gills, tissue, kidney and liver (Dieter *et al,* 1996). Kamanyire & Kamalliedde (2014) also found that after a period of 1 to 4 days post introduction of OP's to the aquatic environment fish behaviour changed, species became restless, agitated, lost equilibrium and coordination whilst suffering from suffocation which then lead to mortality.

Uddin *et al* (2016) found that organophosphates decrease habitat suitability, therefore, making fish more susceptible to predators. It was also found that organophosphates can indirectly impact the aquatic ecosystem by interrupting the food chain and therefore resulting in the loss or shift in the abundance of natural species.

Organophosphate can be introduced into the aquatic environment through various inputs such as sheep dipping, grazing, agricultural sprays and agricultural runoff. During sheep dipping procedures OP vapour can travel through the air after being released when diluting dip wash and during dipping. After dipping can also cause introduction to the environment through sheep grazing near watercourses. Dip in the fleece has a half live ranging from 12 to 53 days. Therefore sheep grazing can transfer OP's from fleece to land causing leaching through soil and if drinking from a water source there is a direct introduction. Agricultural spraying near watercourses with no buffer zone implementation defence allows watercourses to be directly impacted by Organophosphates within the aquatic environment (M.F.Woods, DoH, URL 7)

Persistence of OP's in the environment is determined by abiotic and biotic processes such as biodegradation, metabolism, hydrolysis, photolysis and oxidation. (FAO, URL 5)

It was found that it takes up to three weeks for fauna to recover from Organophosphate introduction to their systems. Deer, H (*1999*) found that the half-life of Diazinon in animals was up to 12 hours, in soil was 40 days and in water can last between 12 to 138 days depending on hardness, temperature and salinity. Sanders and Sieber (*1984*) found that Parathion had a half-life of 130 days in soil and 9.6 days in water. Whilst Carbofuran degraded with a half-life of 2 to 12 hours within natural and sterilised water. *(*Sharom *et al,* 1980*).* Bondarenko *et al* (2009) stated that OP compounds are known to use abiotic and biotic pathways for degradation within water. These abiotic transformations may include chemical hydrolysis and photocatalytic reactions.

Eyhorn *et al* (*2015*), recommended the following solutions to prevent or reduce the effects of Organophosphates in rivers.

- Reduce the reliance of these pesticides within agriculture
- Phase out of highly hazardous pesticides/introduce resistant varieties into the market and also support the development of alternative methods. This involves using less harsh pesticides more often than the higher hazardous pesticides.
- Redesigning of farming systems based on agroecology
- Advancing alternative crop protection methods.
- Provide education, training and information for better pest management.
- Promoting sustainable farming systems.

Integrated Pest Management (IPM)

IPM and biological control programs are increasingly recognized and promoted as viable alternatives. For example, Denmark in 1986 introduced the first pesticide reduction plan to protect groundwater that is consumed directly without any purification treatment. This was a 3 pronged strategy, including designating spray free zones, organic farming development and general use reduction through technology and better farming practices.

Stockholm Convention

The Stockholm Convention aims to eliminate or restrict the use of some pesticides based on a specific review process, the pesticides that fulfil the criteria can then be listed for restriction or elimination. They are primarily concerned with Persistent Organic Pesticides which persist in the environment, have the ability to bioaccumulate in the tissue of aquatic fauna and represent a threat to human health and the environment.

Degradation

Dowling and Lemley, (1995) conducted an investigation on the degradation of Methyl parathion and malathion using a combination of ferrous ion plus Hydrogen Peroxide (Fenton's Reagent). Methyl parathion, Malathion and their degradation products were analysed with a Hewlett Packard

5890 Series II Gas Chromatograph/5971A Mass Selective Detector equipped with a Supelco SPB-608 fused silica capillary column (0.25 mm film, 0.25 mm ID x 30 m). Following this, Solid Phase Extraction (SPE) was used with Baker bond cyclohexyl which transferred Methyl Parathion and the Malathion from an aqueous solution to methanol. Each single compound was analysed by GC/MSD in the scan mode to confirm if purities are present. Insecticide disappearance was quantified against a set of standard solutions. Detection, by single-ion monitoring of the most abundant ion of each compound, maximised quantification. Formation and disappearance of methyl parathion's breakdown products were tracked qualitatively; Malathion degradation product identities were confirmed by GC/MSD in the scan mode. The high water solubility of methamidophos made its solid phase extraction for GC/MSD; thus it was analysed using a Hewlett Packard 1090A HPLC with diode array detection (212 run). Aqueous samples of 200 µL were injected onto a Supelco LC-8-DB column (3 mm particle size, 4.6 mm ID x 15 cm) equipped with a Supelguard LC-8-DB guard column. The oven temperature was 50°C, and the mobile phase was 10%/90% methanol/water at 1 mL min^{1}. No methamidophos breakdown products were detected by HPLC, but the pungent mercapturic odour released during methamidophos experiments points to methyl mercaptan evolution.

<u>Detoxification</u>

This process involves using a nylon based immobilised phosphotriesterase from *Pseudomanas diminuta*. This involves the partial purification of phosphotriesterase and catalyses the hydrolysis of organophosphotriesters. The enzyme immobilises the phosphotriesterase onto a solid support. Covalent immobilisation of the enzyme may also be needed. This then goes through acid hydrolysis to generate additional free amino groups. *(*Caldwell. S.R., Raushel, F.M., 1991*).*

As a result of conducting this literature review it has become evident that all three pesticide chemicals investigated have the potential to affect the aquatic environment and associated fauna if not responsibly used.

Cypermethrin is used for sheep dips and as a pest control on forestry plantations. Acetamiprid is set to replace Cypermethrin on forestry plantations by Coillte and introduction of this pesticide began in 2018 as the potential impacts of Cypermethrin on the environment have caused concern among the public.

Organophosphates are a commonly used pesticide and have been for over 40 years. They have the potential to bioaccumulate in aquatic fauna and have the capacity to persist in the environment for years under the right conditions.

The impacts of these chemicals on the aquatic ecosystem vary from mortality of sensitive species to behavioural and physiological complications such as decreased/stunted growth and reproduction rates in less sensitive species. Increases in predation due to a decrease in habitat suitability *(*Uddin *et al*, 2016*)* is also a potential impact caused by pesticide introduction to the aquatic environment*.*

These potential impacts are of concern for the aquatic ecosystem, especially within the River Finn, as historical data shows that macroinvertebrate communities have been returning consistently low ecological scores. In addition, recent findings by Loughs Agency show a declining trend in salmon and trout populations in the Finn River and its tributaries. This could be a knock on effect of the poor performance of macroinvertebrate populations.

There are various methods to detect these chemicals within the water course. For example, Main *et al* (2014)*,* detected Acetamiprid using a Micromass Quattro premier triple quadrupole mass spectrometer with an electrospray ionisation interface set to positive ion mode. Cypermethrin can be identified using solvent-solvent partition and adsorption column chromatography with confirmation using gas chromatography with electron capture detector (GC/ECD*) (*WHO 1989*).* Barcelo, D, (1991) found that Organophosphates can be detected through the use of liquid-liquid extraction (LLE) and solid-phase extraction (SPE).

Although these chemicals have varied impacts and detection strategies there are several possible solutions that the agriculture community can take into account to prevent these impacts such as the approach suggested by Eyhorn *et al,* (2015) to redesign farming systems based on agroecology, with the phasing out of highly hazardous pesticides whilst supporting the development of alternative methods.

Yang *et al* (2013) suggested bioremediation as a degradation of acetamiprid. Similarly, Caldwell & Raushel (1991) carried out studies in which nylon based immobilised phosphotriesterase from *Pseudomanas diminuta* was used to detoxify sediments containing Organophosphates. Although innovative, these methods may be too complex to implement on such a large scale in the Finn Catchment, although further investigation into their viability is certainly warranted.

9.5. MCPA (2-Methyl-4-Chlorophenoxyacetic Acid)

MCPA is one of the main phenoxy herbicides used on permanent grassland. It has no effect on grass yield and is an effective treatment of broadleaf weeds and rushes. It is used as an herbicide for control of annual and perennial weeds in crops (URL 2). Phenoxy herbicides were first identified in the 1940s (Moran, 2015).

MCPA acid is a white to light brown solid, flake, or microcrystalline powder with a melting point of 114-119 C, density of 1.18-1.21 g/ml at 20°C, octanol/water partition coefficient (log KOW) of 2.73, and vapour pressure of 7.7 x 10-6 mbar at 20°C. MCPA is practically insoluble in water (0.03 g/100 g at 20°C) (US EPA, 2004).

Its properties as an herbicide were first discovered in 1945 and it has been sold in various forms commercially since the 1950's. MCPA is also used in combination with many other products as it offers a wider spectrum of control. MCPA is available as technical acid flake, technical ester and as dimethylamine and potassium solutions and can be purchased in various combinations including 750 Kg bags to 25 Kg bags (flake), tankers, IBC's, drums or filled on site (URL 11).

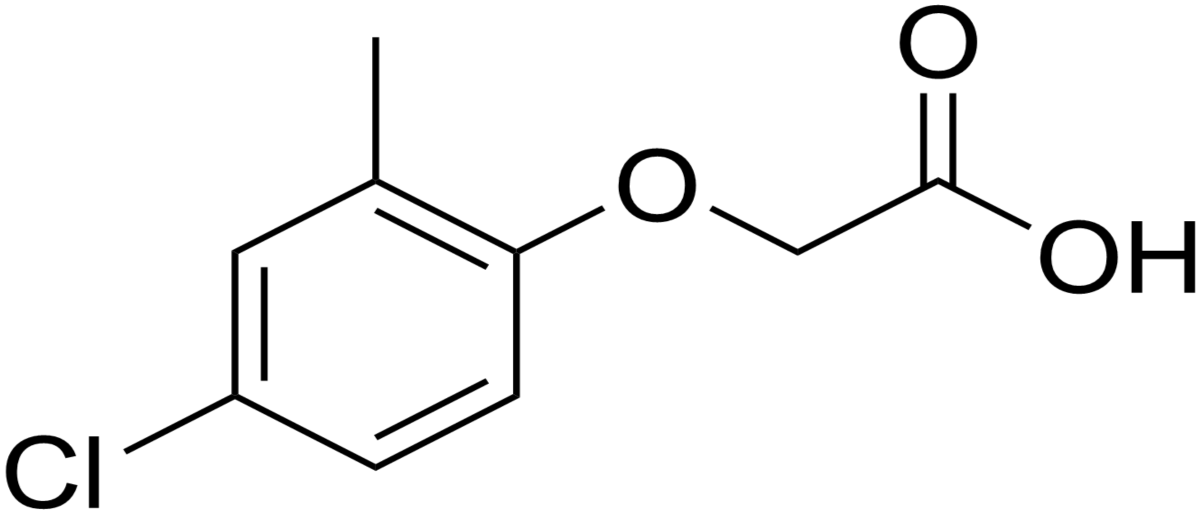


FIGURE 4: MOLECULAR COMPOSITION OF MCPA

MCPA is widely used in agriculture across the island of Ireland for controlling the growth of many broad-leaved weeds e.g. Thistles, Buttercup, Ragwort and in particular soft Rush in agricultural grassland, which has flourished following wet weather periods in recent years (URL 3) & (URL 8).

In Europe, MCPA has been extensively used in forest management. It is also used for control of broadleaf weeds on residential lawns (URL 11).

MCPA is a Phenoxy herbicide which mimics the natural plant hormone Auxin. This hormone regulates the growth of the plant and one of their functions is to cause the plant to grow towards sunlight. When the Phenoxy herbicide is applied it travels throughout the plant causing an overdosing impact through uncontrolled growth with severe thickening and twisting which in turn causes the plant to overgrow itself to death (Moran, 2015).

Phenoxies are truly systematic and travel throughout the plant (Moran, 2015).

Due to this unique mode of action replicating a plant's natural growth system, phenoxies aren't as affected by resistance issues in broad-leaf weeds. Products containing previously mentioned phenoxies such as MCPA are selective in grass and cereals in addition to a range of additional crops (URL 7).

MCPA is prone to leaching directly into watercourses or through land drains due to its inability to bind to soil particles. When introduced to watercourses it can take between 3 to 4 weeks to be broken down in untreated areas. The half-life of MCPA within soil ranges from <7 to 41 days (URL 3).

In a previous study, MCPA did not volatilize from an aqueous solution (pH 7.0) heated for 13 days at 34–35 °C, nor was it hydrolysed at neutral pH (5). In aqueous solution at pH 8.3, MCPA had a photolytic half-life of 20–24 days in sunlight. MCPA can be expected to leach readily in most soils. Mobility increases as organic matter content decreases. Its half-life in soil was 15–50 days. It degrades twice as quickly (6– 12 days) when applied a second time to soil than after one application (15–28 days) (WHO, 2003).

Biodegradation appears to be slower in drier soils and in flooded (anaerobic) soils. If released into water, MCPA is not expected to adsorb to suspended solids and sediment based upon its KoC. The direct photolysis half-life of MCPA in water (at surface conditions under summer sunlight) is about 19-20 days (URL 18).

MCPA does not break down in anaerobic conditions, which means it may last in soils or in sediment for a long time. Mobilisation of this stored legacy MCPA in anaerobic zones is difficult to quantify but produces a risk for the future (Morton *et al*, 2019).

Herbicides are typically applied by either a boom sprayer, knapsack or a weed-wiper. In Ireland, Weed-wipers and knapsacks are not a legal method for applying MCPA. (URL 5 & 26). Therefore MCPA is almost exclusively applied via tractor mounted boom-sprayer.
It is recommended to apply MCPA in the spring when rushes are 15–25 cm tall and actively growing. If the ground is very wet then you should delay application.(URL 8).

The Sustainable Use of Pesticides Directive (SUD) establishes a framework for European Community action to achieve the sustainable use of pesticides by setting minimum rules to reduce the risks to human health and the environment that are associated with pesticide use. Implementation of the SUD relies heavily on the training and registration of the various people involved at all levels of the industry, including Pesticide Advisors, Pesticide Distributors, Professional Users/Sprayer Operators, and Inspectors of Pesticide Application Equipment (URL 9).

In Ireland farmers who spray grassland/arable crops with a sprayer must register with DAFM and obtain certified training. If a contractor is employed the farmer does not need to register but the contractor does. In addition, all boom sprayers greater than 3m and all blast and orchard sprayers must be tested. The interval for testing between inspections must not exceed 5 years until 2020 and must not exceed 3 years thereafter (URL 10).

Similarly, in Northern Ireland all professional users of pesticides must have a sprayer licence. In the past farmers who were born before 31 December 1964 could spray their own land under an exemption called "Grandfather Rights", however that is no longer the case. All professional users of pesticides must now have a licence, irrespective of age (URL 6).
The transport and fate of MCPA residues is a process that requires the knowledge of many parameters, such as soil physical, (bio)chemical and hydrogeological properties as well as climatic conditions and agricultural practices (Petitta, 2010).

MCPA may enter a waterbody from point sources (normally a farmyard) by leaks from storage areas, or spills from handling operations like mixing, filling and washing. It may also enter a waterbody through diffuse sources (normally in the field) during or after application, by spray drift, runoff, and drainage (Moran, 2015).

Spray drift is the downwind movement of airborne spray droplets beyond the intended area of application. Run-off is the transport of pesticide-contaminated water and sediment from the surface of a field by overland flow to a non-target area due to a precipitation event. Seepage through soil into groundwater and leaching (the process via which water-soluble chemicals are dissolved and pass through the soil into the groundwater) may also lead to MCPA reaching a waterbody. Source point routes include pesticide handling/ storage areas: Mixing, Tank filling, Spillages, Washings and waste disposal (EPA, 2019b).

A combination of factors may contribute to spray drift, including: the speed of the wind; the height of the spray nozzles, the design of the equipment and ground conditions; the spray quality (which will depend on the choice of nozzles and the spray pressure); the type of crop or other vegetation, if any; the speed of the vehicle the spray is being applied from; local atmospheric conditions; the condition of the equipment used to apply the pesticide; and the equipment settings. (DAERA, 2015).

Rushes grow where there is an abundance of water therefore increasing the risk of MCPA getting into a waterbody (Moran, 2015). MCPA use is prevalent in areas of marginal and upland agriculture land but here it is also most vulnerable to run-off due to soil and drainage characteristics. In these areas grass swards are in competition with rushes due to high rainfall and low soil permeability (Morton *et al*, 2019). The western half of the Finn Catchment is dominated by this type of land.

MCPA in water can be determined by a gas chromatographic method, after extraction with dichloromethane and esterification with diazomethane. The method sensitivity is about 0.1 µg/litre. (Frank *et al*, 2003). The quantitative determination of residues of MCPA in water can be achieved by capillary gas chromatography with mass selective detection (URL 17).

Methods for the routine analysis of MCPA are available to measure it at concentrations well below the HBV. For example, Method 555 (Rev. 1.0) of the United States Environmental Protection Agency (USEPA), which employs high-performance liquid chromatography with a photodiode array ultraviolet detector, has a method detection limit of 0.8 µg/L (USEPA, 1992). If even greater sensitivity is desired and/or in more complex matrices, USEPA Method 1658 provides an estimated detection limit of 0.09 µg/L using derivatization and gas chromatography with electron capture detection (USEPA, undated); similar methods with mass spectrometry detection are also available. A recent monitoring paper from the European Union utilised liquid chromatography with tandem mass spectrometry to achieve a limit of quantification of MCPA in water of 0.0005 µg/L (Loos *et al*., 2013, WHO, 2016).

In 2016, Irish Water began a standardised pesticide monitoring programme for all public supplies. They monitor for 21 pesticides most likely to be found in Irish waters. The programme highlighted an issue of widespread and, in a small number of supplies, persistent failures to meet the pesticide standards. At the end of 2018, the EPA was investigating 42 supplies serving almost 283,500 people,

due to failures to meet the pesticide standard. 75% of all failures detected were of the herbicide MCPA (EPA, 2019).
Drinking water monitoring results for Ireland show that a number of pesticides commonly used on grassland, such as MCPA, are being detected more frequently. A single drop of pesticide can breach the drinking water limit in a small stream for up to 30 kilometres. This clearly highlights the potential risk facing many of Ireland's drinking water sources (URL 8).

In Northern Ireland, MCPA was the most commonly detected herbicide in 2018. In 2018 two samples contravened the standard for MCPA at the Derg WTW (DAERA, 2018).

The EU legal limit for MCPA (0.10 microgram/litre) in drinking water is set low to keep pesticides out of drinking water. 0.1 microgram/litre of the pesticide MCPA is about the same as one drop of pesticide in an Olympic sized swimming pool. The WHO set two health-based limits for MCPA in 2017. Both WHO limits are set at a higher level than the EU legal drinking water limit (URL 16).

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 (Morton *et al*, 2019).

Herbicides pose a risk to aquatic life and increase costs of treating drinking water (Water Catchment Partnership, 2019, URL 4).

MCPA is only slightly toxic to freshwater fish, with reported LC_{50} values ranging from 117 to 232 mg/L in rainbow trout. MCPA is practically non toxic to freshwater invertebrates, and estuarine and marine organisms (URL 13). MCPA is classed as slightly toxic to fish (but does not particularly affect other aquatic organisms), moderately toxic to birds and non-toxic to insects (URL 14).

These differences (in toxicology) are most likely due to use of different ecotoxicology classification systems (e.g., UN, 2015). The EC_{50} (half maximal effective concentration, that is, reduces cell growth or density by half) for aquatic algae is between 32.9 and 392mg MCPA/L, depending on the species, and is just 152ug/L *for Lemna gibba*, a common aquatic plant species (AERU, 2016; EC, 2008). Acute toxicity (LC_{50}; lethal concentration required to kill 50% of the population) for fish is 50-72 mg/L, although is over 190 mg/L for aquatic invertebrates, with a long term NOEC (no observable effect concentration) of 15 mg/L for fish and 50 mg/L for aquatic invertebrates (AERU, 2016; EC, 2008). For comparison, the maximum concentration at which MCPA can legally be applied to fields is 6.75g/L (Nufarm UK Limited, 2016) (Morton *et al*, 2019).

The interaction between herbivores and producers in aquatic systems is directly affected by the presence of agrochemicals. Substances like fertilizers can increase nutrient availability, thereby stimulating biomass of primary producers, and consequently, favouring the primary and secondary consumers due to bottom-up control effects. On the other hand, when herbicides such as MCPA are present, these substances can limit primary production, decreasing the abundance of algae and macrophytes, and subsequently negatively affecting consumers (Mello *et al*, 2018).

Conventional treatment (coagulation, flocculation, filtration, disinfection) of water in drinking water treatment plants in Ireland does not remove pesticides or herbicides. As a result, any of these chemicals present in raw water sources are likely to pass through the treatment plant and into the drinking water distribution network. A number of non-conventional treatment processes can reduce pesticide and herbicide levels in water. Use of granular or powdered activated carbon is the most commonly employed process for this purpose. Ultraviolet, reverse osmosis and nanofiltration have been shown to provide some degree of pesticide and herbicide removal. Some compounds have proven difficult to remove, even with dedicated treatment. While treatment for the removal of pesticides & herbicides is an option available to drinking water providers towards achieving compliance, this should only be considered when efforts to prevent contamination of source waters fail (EPA, 2019b, p.3&12).

9.6. Discussion

The findings of this literature review conclude that all three pesticide chemicals and the one herbicide chemical investigated, namely; Cypermethrin, Acetamiprid & Organophosphates (pesticides) and MCPA (herbicide) have the potential to affect the aquatic environment and associated fauna if not responsibly used.

Cypermethrin is used for sheep dips and as a pest control on forestry plantations. Acetamiprid is set to replace Cypermethrin on forestry plantations by Coillte and introduction of this pesticide began in 2018 as the potential impacts of Cypermethrin on the environment have caused concern among the public.

Organophosphates are a commonly used pesticide and have been for over 40 years. They have the potential to bioaccumulate in aquatic fauna and have the capacity to persist in the environment for years under the right conditions.

MCPA is commonly used to control the growth of rushes in rough upland pasture land which is prevalent in the western Finn Catchment. Although it doesn't really have any direct impact on fish and macroinvertebrate populations due to toxicity, it can have indirect effects by reducing the amount of aquatic plants and algae that sustain numerous macroinvertebrates. Additionally, it is very difficult to remove during water treatment and has the potential to negatively impact human health. Due to its solubility in water and high mobility through soil, it is of particular risk of being introduced to the river environment if not properly managed.

The impacts of these chemicals on the aquatic ecosystem vary from mortality of sensitive species to behavioural and physiological complications such as decreased/stunted growth and reproduction rates in less sensitive species. Increases in predation due to a decrease in habitat suitability *(*Uddin *et al*, 2016*)* is also a potential impact caused by pesticide introduction to the aquatic environment.

These potential impacts are of concern for the aquatic ecosystem, especially within the River Finn, as historical data shows that macroinvertebrate communities have been returning consistently low ecological scores. In addition, recent findings by Loughs Agency show a declining trend in salmon and trout populations in the Finn River and its tributaries. This could be a knock on effect of the poor performance of macroinvertebrate populations.

There are various methods to detect these chemicals within the water course. For example, Main *et al* (2014), detected Acetamiprid using a Micromass Quattro premier triple quadrupole mass spectrometer with an electrospray ionisation interface set to positive ion mode. Cypermethrin can be identified using solvent-solvent partition and adsorption column chromatography with confirmation using gas chromatography with electron capture detector (GC/ECD) (WHO 1989). Barcelo, D, (1991) found that Organophosphates can be detected through the use of liquid-liquid extraction (LLE) and solid-phase extraction (SPE).

Although these chemicals have varied impacts and detection strategies there are several possible solutions that the agriculture community can take into account to prevent these impacts such as the approach suggested by Eyhorn *et al,* (2015) to redesign farming systems based on agroecology, with the phasing out of highly hazardous pesticides whilst supporting the development of alternative methods.

Yang *et al* (2013) suggested bioremediation as a degradation of acetamiprid. Similarly, Caldwell & Raushel (1991) carried out studies in which nylon based immobilised phosphotriesterase from *Pseudomanas diminuta* was used to detoxify sediments containing Organophosphates. Although innovative, these methods may be too complex to implement on such a large scale in the Finn Catchment, although further investigation into their viability is certainly warranted.

Buffer zones are a viable and elegant potential solution to mitigate the introduction of pesticides & herbicides to the aquatic environment. They provide a space between targeted crops and the aquatic environment which gives the intervening soil the potential to bind any pesticides to it before coming in contact with a water body. Although their effectiveness is reduced if chemicals are applied during or shortly before a significant rainfall event.

In addition to allowing certain pesticides to bind the soil, buffer zones also provide a surface area for microbial and photo degradation of pesticides which helps reduce their persistence in the environment. Buffer zones should be implemented in any areas where a standing crop/ plantation which is set to be treated with pesticide is located adjacent to a water body. Similarly, buffer zones should be maintained by farmers disposing of spent sheep dip on land surfaces which are large enough to ensure that these pesticides are not inadvertently introduced to the aquatic environment by rainfall or other factors (e.g. slope of terrain). Buffer zones also introduce a barrier between the field and the river which can eliminate spray drift of pesticides or herbicides.

Directive 2009/128/EC (European Parliament and of the Council 2009) Article 15 of the Official Journal of the European Union states:

"*The aquatic environment is especially sensitive to pesticides. It is therefore necessary for particular attention to be paid to avoiding pollution of surface water and groundwater by taking appropriate measures, such as the establishment of buffer and safeguard zones or planting hedges along surface waters to reduce exposure of water bodies to spray drift, drain flow and run-off. The dimensions of buffer zones should depend in particular on soil characteristics and pesticide properties, as well as agricultural characteristics of the areas concerned. Use of pesticides in areas for the abstraction of drinking water, on or along transport routes, such as railway lines, or on sealed or very permeable surfaces can lead to higher risks of pollution of the aquatic environment. In such areas the pesticide use should, therefore, be reduced as far as possible, or eliminated, if appropriate*".

Therefore, protection of surface water bodies is a requirement of existing EU Legislation. Furthermore, the above mentioned Directive addresses the regulation of pesticide use in areas of Special Areas of Conservation (SAC's), such as the Finn River Catchment, further in Article 16 of the same document:

"*Use of pesticides can be particularly dangerous in very sensitive areas, such as Natura 2000 sites protected in accordance with Directives 79/409/EEC and 92/43/EEC. In other places such as public parks and gardens, sports and recreation grounds, school grounds and children's playgrounds, and in the close vicinity of healthcare facilities, the risks from exposure to pesticides are high. In these areas, the use of pesticides should be minimised or prohibited. When pesticides are used, appropriate risk management measures should be established and lowrisk pesticides as well as biological control measures should be considered in the first place*".

Directive 2009/128/EC outlines the need for a National Action Plan (Dept. of Agriculture, Food & the Marine 2013) to be devised by each member state to deal with the various concerns outlined in the document. This document lays out specific processes for satisfying the requirements of the EU Directive and covers aspects such as; use near watercourses, in Natura 2000 sites and education programmes designed to inform professional and amateur users of pesticides about the health risks of use to humans and the environment. The education portion of the document for Professional Users indicates that training on proper disposal of pesticides after use is provided but does not detail what these processes are. However guidelines on proper disposal of sheep dip and application of pesticides on farm land can be found online [URL 11] and they follow best practice as stipulated in Directive 2009/128/EC.

One aspect that is not addressed in the National Action Plan but which is raised in Directive 2009/128/EC Article 21 is the issues of penalties for failure to properly implement the recommended procedures for pesticide use:

"*Member States should determine penalties applicable to infringements of national provisions adopted pursuant to this Directive and ensure that they are implemented. The penalties should be effective, proportionate and dissuasive*".

At the time of this literature review it was unclear if any penalties have been formulated to help dissuade the inappropriate use and disposal of pesticides. It would be prudent to investigate further if this is indeed the case and, if so, the formulation of a sufficient penalty system would be recommended.

A review of historically mapped sheep dipping locations was carried out by the Donegal County Council which helped identify structures which could pose a likely threat to the integrity of the water bodies in the River Finn Catchment. Although great effort was expended visiting all sites mapped, it cannot be confidently concluded that all sites which dipping is carried out were identified and surveyed. Anecdotal reports from residents in the Finn River Catchment indicate that sheep dipping facilities may exist which are not included on the currently available maps.

If this is indeed the case, then it would be prudent to attempt further identification of undocumented dipping sites to give a better understanding of how many of these exist in the catchment. This effort could highlight sites that have the potential to be point source impacts of pesticide pollution. It is envisioned that this survey could be carried out with a combination of GIS, planning maps and aerial surveys using modern technology.

In conclusion, the prospective impacts of pesticide and herbicide use within the Finn Catchment area have the potential to be detrimental to the aquatic environment. The chemicals outlined in this literature review have differing levels of persistence in the environment ranging from hours to weeks (and potentially years in unique cases) which is likely to have potential impacts for aquatic fauna in the longer term.

The main avenues of potential pesticide & herbicide introduction to the aquatic environment in the catchment are likely to come from diffuse sheep dipping facilities, inappropriate disposal of spent dips, application of herbicides in wet conditions or close to a waterbody and forestry plantations that do not have adequate buffer zones in place.

Changing farming practices could lead to the prevention of agricultural runoff. Farming practices could be improved in a multitude of ways ranging from simple housekeeping practices to completing qualified training. Stricter adherence to existing guidelines or changing common practices (such as ensuring sprayer operators are fully trained and hold the certificate of competence, ensuring equipment is properly maintained and tested regularly) could have a significant impact on the quantities of pesticides reaching watercourses. These measures are already stipulated in the National Action Plan (DAFM) as requirements that need to be met but an effort to identify adherence to these requirements would be beneficial.

These steps not only have the potential to reduce the chances of agricultural runoff but also reduce financial loss for the farming communities. By following regulations such as maintaining a suitable distance from any watercourse including ditches or drinking water supplies especially when applying or handling fertilisers, herbicides or pesticides. The adoption of crop protection management plans (CPMPs) or precision farming can assist in minimising risks of pesticide & herbicide pollution. There are a few guidelines suggested by the voluntary initiative *(*URL 8, 2016*)* ranging from not spraying areas due to weather conditions to ensuring that the tyres are clean from mud before leaving the field as mud on tyres can carry chemicals out of the field.

The designation of adequate buffer zones, as well as identification of point source pollution sites to mitigate entry of pesticides & herbicides to the water course, is considered the method most likely to produce positive changes to water quality and also fulfils recommendations laid out in Directive 2009/128/EC.

The prevention of basin erosion within agricultural areas aids in the control of the overall concentration of different pesticides & herbicides in river water and sediments. Conservation buffers are areas or strips of land maintained in permanent vegetation. These buffers are used in the management systems of soil, pesticides, water and nutrients. Some pesticides are highly absorbed into soil particles (USDA, 2000). Several different types of buffer zone exist and are detailed below:

<u>Water Buffers</u>
Grassed waterways: Constructed or natural vegetated channel which is shaped and graded to ensure that surface water can be carried to a stable outlet at a non-erosive velocity. Waterways are most effective in the trapping of sediment and dissolved chemicals if designed to spread concentrated water flow over a vegetated filter adjacent to a watercourse.

Contour buffer strips: Buffer strip of vegetation in alteration with wider cultivated strips that are farmed on the contour. Contour buffer strips are most effective to trap pesticides as there is less chance for concentrated flow and smaller areas of cultivated field to deliver runoff directly to each strip within a relatively short distance compared to some edge-of-field buffers.

Vegetative barriers: These are permanent narrow strips of tall, dense, stiff stemmed perennial vegetation structured in parallel rows perpendicular to the slope of the field. These function similarly to the contour buffer strips and are effective in dispersing concentrated flow therefore increasing sediment trapping and water infiltration.

Edge-of-Field water buffers

Field Borders: These borders are strips of perennial vegetation on the edge of a cropland field. These borders reduce pesticide runoff only when the runoff flows over the strip. Even when there is no water flow over the strip these borders may benefit water quality as spraying operations are physically separated therefore reducing drift and direct application to watercourses and riparian areas.

Filter strips: These are strips of grass or permanent vegetation located between crop fields and water bodies and are used to reduce contaminants such as sediment, pesticides and nutrients to help maintain or improve water quality. By encouraging sheet-flow across the strip and minimising concentrated flow more pesticides can be removed.

Setbacks: By seeding areas where surface runoff enters watercourses with perennial grass improves the trapping of herbicides.

Riparian forest buffer

These buffers are areas of shrubs and trees often combined with perennial grass buffers located adjacent to watercourses such as streams, ponds or wetlands. The woody vegetation provides ideal shelter and food sources for wildlife whilst shading the waterbody and therefore aiding lower water temperatures. The other benefits of this buffer include protection of stream banks, contribution of energy sources to aquatic communities. Deep tree roots may also aid in the interception of nitrate from entering streams in shallow subsurface flow whilst also providing carbon for microbial energy within soil. Therefore increasing the degradation of pesticides and denitrification of nitrate.

Sediment Ponds

These sediment ponds can play an effective role in reducing sediment load and pesticide runoff from agricultural runoff. (California Storm water Quality Association, 2003). A study found that the outlet water concentrations were lower than inlet concentrations therefore, indicating the effectiveness of sediment ponds in reducing non-point source pollution.

Vegetated Ditches

Reduces pollutants by increasing the channel roughness, sedimentation and pollutant adsorption to plant surfaces. Moore *et al*, (2001), found that vegetated ditches aided in the trapping of many common pesticides. The results of this study suggested that this method would be best put into practice in conjunction with other pest management strategies to be optimally effective in pesticide reduction.

In addition to the above buffer zone solutions, a program of public education, with a specific focus on farmers in the catchment to inform about the negative consequences of inappropriate pesticide use and disposal would be of great benefit. This is a major issue within the agricultural community.

The willingness of farmers to carry out these recommendations may be influenced through common beliefs, cost awareness, administration worries etc. An increase in the education of these chemicals, their impacts and the recommendations made to reduce these impacts may increase the willingness of farmers to participate as well as scheme incentives. (URL 9, GOV).

If specific penalties could also be implemented, at a national legislative level, then the education program could be used as an information platform to educate farmers about proper pesticide & herbicide use and also inform them of the potential consequences of infringement which could affect them personally. This would hopefully act as a good dissuasion from improper use and disposal of harmful chemicals and increase adherence to existing guidelines.
The regulations of sheep dip disposal involves the disposal of dip wash which must be emptied from the dip bath as soon as practical and never into or near watercourses. Empty containers must be rinsed at least three times and then crushed or punctured to avoid reuse, these containers are then disposed of at a local waste disposal site. PPE/Contaminated clothes must be placed in sealed containers and also disposed of at a local waste disposal site. If a spillage of sheep dip occurs absorbent materials such as earth, sand and sawdust must be laid on and then placed into a sealed container and labelled for disposal at a local waste disposal site. For health and safety concerns, COSHH requires that a record is kept whenever health surveillance is undertaken (HSE, 2013).

The detection process for these chemicals through water sampling can be quite complex, costly to provide and also time consuming. Biological indicators such as macroinvertebrates and fish populations should provide adequate indications of the effectiveness of proposed mitigation measures to avoid chemical export to local water bodies Additionally, in situ monitoring stations may be able to provide an early warning system for pesticide influx if an appropriate metric can be identified which correlates with such a flux (for example increase in turbidity, pH spike etc).
It is also recommended that further investigation into innovative measures to reduce the impacts of pesticide use be carried out to determine if there is a viable option that could be implemented on a catchment wide basis.

The most effective and straightforward way to reduce pesticide application is to minimise pesticide application. Various approaches can be made to reduce the use of pesticides. The Integrated Pest Management (IPM) practices provide various alternative management practices, for example, pest pressure monitoring to avoid application during dormant season and increase the biological control and reduce the risk of pesticides. Smart sprayer technologies can also be used to increase the spray precision and reduce total pesticide use.

It is recommended that further surveys of the area to identify as yet unknown sites of potential point source pollution should be carried out so that better decision making on preventative measures can be made.

10. APPENDIX II

10.1. Feasibility study of Chemcatcher passive sampling equipment

This literature review was carried out to assess the suitability of the 'Chemcatcher' system for use in monitoring pesticide and herbicide residues within the Finn River Catchment. As part of the CatchmentCARE Project, Loughs Agency has been tasked with investigating Chemical Export in the Finn Catchment from use on land into the Finn and its tributaries.

This is a requisite of Activities A.T1.7 & A.T2.4 of the CatchmentCARE Project which have the following deliverables:

Activity A.T1.7

- A.T1.7.1 – Report on areas that are most likely to be impacted by chemical export; and
- A.T1.7.2 – Report outlining possible actions to prevent chemical export from land use in the identified areas.

Activity A.T2.4

- A.T2.4.1 – Investigative monitoring as designated by WP3;
- A.T2.4.2 – Implement Recommendations from WP3; and
- A.T2.4.3 – Develop best practice solutions.

In the process of investigating Chemical Export in the River Finn Catchment to address the above deliverables for the CatchmentCARE Project several potential methods of data collection were discovered and assessed. Of those methods, Chemcatcher is believed to be the method most suitable for monitoring Chemical Export in the Finn.

Investigations into Chemical Export in the Finn Catchment were initiated by the compilation of a detailed literature review on pesticides associated with the main industries in the Finn River Valley. Namely, agricultural practices such as sheep breeding and associated dipping practices and public and private forestry plantations which are routinely sprayed with pesticide to eliminate the spread of pests such as Pine Weevil (*Hylobius abietis*). Agriculture and Forestry make up for the majority of land use in the Finn Catchment (Donegal County Council 2015, EPA 2012).

During this review several chemicals were identified which were seen to warrant further consideration and analysis. These included Cypermethrin (a pesticide used historically in spraying of forestry plantations as well as a component in sheep dipping products), Organophosphates (used as a component in sheep dipping products) and Acetamiprid (a pesticide which is in the process of replacing Cypermethrin use in forestry spraying practices) (Loughs Agency 2019).
In order to quantify the threat from pesticide use for sheep dipping practices, several strategies were employed and they included:

- On the ground assessments of known sheep dipping locations to ascertain if they were in use, what chemicals were used in them, the practices employed by the shepherds, and their connectivity to the local watercourse;
- Loughs Agency inspectors for the Finn were tasked with locating existing sheep dipping locations that were not recorded in any official way so that they could be surveyed for the same parameters as above;
- Conducting surveys of shepherds at sheep marts in the Finn Valley to ascertain the types of chemicals used and adherence to recommended disposal practices;
- Attendance of conferences on sheep farming to create visibility for the CatchmentCARE project and its efforts to mitigate against the negative effects of pesticides;

To quantify the potential threat from forestry related activities the following strategies were employed:

- A desk study was carried out to identify and map known plantations in the Finn Catchment and whether they are publicly or privately owned;
- Maps indicating slope of the terrain and areas where water bodies are at increased risk of run off from adjacent forestry;
- Ground surveys were conducted on the publicly owned plantations that were adjacent to significant water bodies. These studies recorded information on:
    - The age of the forest;
    - If any clear felling had taken place there;
    - The existence of drainage gullies (if any);
    - The pathways of connectivity of the drainage to the local watercourse;
    - The existence of buffer zones (if any); and
    - In situ water chemistry analysis of pH, Conductivity, Dissolved Oxygen and Temperature.

- Compilation of a decision matrix to aid the selection of a site for 'Best Practice' mitigation measures implementation;
- Considerations are also being given to the purchase of UAV Drone equipment to help survey areas that are difficult to access on foot. It is hoped that a combination of photography and LiDAR will allow the identification of likely pathways for surface water run-off from forested areas in to local water courses;
- Once a site is selected for the implementation of 'Best Practice' mitigation measures, a macroinvertebrate survey will be designed to establish a baseline and ongoing monitoring. This will highlight the success of the mitigation measures introduced.

These above strategies contributed to the delivery of Activity A.T2.4.1, however additional measures were needed that provided a statistically reliable and replicable type of analysis so that a trend in pesticide levels in the watercourse could be determined.

Initially it was hoped that this could be achieved using an in situ sonde device with appropriate sensors that could detect spikes in different types of pesticides and herbicides simultaneously. Once detected, the sensor would trigger an automatic water sampling device to retrieve a sample which could be taken to the laboratory for analysis.

However, when this avenue was investigated further it became apparent that these types of sensors are not readily available for use in environmental monitoring. Biosensors that are suitable for pesticide and herbicide monitoring utilise nanotechnology to create nanomaterials such as nanoparticles and nanotubes (Sassolas *et al* 2012). These allow for more efficient detection of the target analytes, however different types of nanomaterials are needed for different analyte detection (Sassolas *et al* 2012, Zamora-Sequeira *et al* 2019). These types of materials are prohibitively expensive, not readily available and are still subject to ongoing research as the Limit of Detection of the sensors for most analytes is not yet sensitive enough for field use (Sassolas *et al* 2012, Zamora-Sequeira *et al* 2019, Xiang *et al* 2020, Obare *et al* 2010).

To date, the main method of analysing pesticide concentrations in water samples is conducted by collecting large samples (between 1L and 2.5L) and analysing them through a variety of means in the laboratory (Hladik *et al* 2009). These methods have a high selectivity and detectability and include: Gas Chromatography-Mass Spectrometry (GC-MS), Liquid Chromatography-tandem Mass Spectrometry (LC-MS/MS), Ultra-High-Performance Liquid Chromatography-tandem Mass Spectrometry (UHPLC-MS/MS), Gas Chromatography – Negative ion Chemical Ionization Mass Spectrometry (GC-NCI-MS), (Zamora-Sequiera *et al* 2019, Feo *et al* 2010, Hassan *et al* 2017, Hladik *et al* 2009).

However, not only does the above type of analysis require sophisticated lab equipment to process the samples, it also requires special considerations during collection. Sampling methods vary depending on what analyte is being targeted. For example, Cypermethrin and Organophosphates can be collected in amber borosilicate glass bottles with screw top, teflon lined lids however Cypermethrin must be analysed within three days of collection whilst Organophosphates need to be analysed within 7 days (Hladik *et al* 2009). A volume of 1L of water must be collected to effectively test for Cypermethrin whereas 2.5L is needed to effectively test for Organophosphates (Hladik *et al* 2009). Additionally, sample bottles for Organophosphates must be specially prepared by pre-washing with phosphate free detergent and then rinsing with deionized water and methanol (Hladik *et al* 2009). From collection to analysis, both Cypermethrin and Organophosphate must be kept refrigerated at 4°C to maintain sample integrity (Hladik *et al* 2009).

Even with all the above measures taken, sample loss due to chemical interactions between the target analyte and the sampling bottle can occur which can result in a lower concentration of the target analyte being detected than is present in the sampled water course (Hladik *et al* 2009, Sharom & Solomon 1981, Lee *et al* 2002). Studies by Lee *et al* (2002) indicated that permethrin loss in a 1L sample bottle could be as high as 36%. Sharom & Solomon (1981) concluded that an increase in volume to contact area ratio increased loss of permethrins to the surface of the sample bottle and recorded losses between 42% and 70% of the target analyte depending on the size of sample taken.

During the search for an accurate, reliable and cost effective system for monitoring pesticide levels in the Finn, Loughs Agency staff came across a system developed in a partnership between Hach and the U.S Department of Homeland Security. The system was called the Guardian Blue Early Warning System. The Hach website describes the Guardian Blue System as being able to detect “Fluoride overfeed, pesticide contamination, cyanide and warfare agents” (URL 1).

The system does this through the use of sensors that monitor pH, Conductivity, Turbidity, Chlorine and Total Organic Carbon (TOC) in the target waterbody (URL 2). A known baseline is programmed into the system for all these parameters so that, if a deviation in the baselines occurs, the system will identify it (URL 2). Once a deviation from the baseline has been identified, the Guardian Blue System compares the fingerprint of the detected analyte to its ‘Agent Library’ database containing fingerprints of numerous chemicals that pose a threat to water quality and human health. Whilst identifying the analyte, the system triggers an alarm alerting the responsible agency to the spike and also activates an automatic sampling device that takes a sample of the contaminated water (URL 2).

The Guardian Blue Early Warning System initially seemed like an ideal option for use in monitoring pesticides in the Finn. However, on further investigation it was revealed that the system was incredibly expensive and also not available outside of the United States (Michael Deeney – Lab and Process Instrumentation – *Pers Comm.*). Additionally, the ‘Agent Library’ is also not available outside of the U.S. which is the crucial database of fingerprints for target chemicals (URL 2). Also, due to the prohibitively high cost of the system, there would only be scope for purchasing one and analysing a single location in the Finn Catchment.

During the AFBI seminar on the use of Willow in the protection of water quality, held on the 5th of March 2020, a lecture was given by Dr. Eddie Burgess on catchment potentials and opportunities in which he described using a monitoring system similar to that of the Guardian Blue System. However, when Loughs Agency staff investigated this, it was made apparent that the system used in Dr Burgess’ work was for analysing spikes in Phosphorus levels in water samples, and could not be used for pesticide and herbicide detection. This investigation led to discussions with Dr. Sara Vero and Dr. Phoebe Morton of AFBI who highlighted their use of the Chemcatcher system and its potential for use in monitoring pesticides and herbicides.

Chemcatcher is manufactured and distributed by TelLab through T.E. Laboratories in Carlow and Natural Resources Wales which has three locations in Wales including Cardiff and Llanelli.

The system was developed in a collaboration between the University of Plymouth and Chalmers University of Technology, Sweden (Kingston *et al* 2000, Persson *et al* 2001)

Chemcatcher is a cost effective passive sampling device that allows for monitoring of a variety of pollutants including; metaldehyde (Castle *et al* 2019, Castle *et al* 2018 (b)), herbicides & pesticides (Mutzner *et al* 2019, Mutzner *et al* 2018, Endo *et al* 2019, Townsend *et al* 2018), Polycyclic Aromatic Hydrocarbons (PAHs) & PolyChlorinated Biphenyls (PCBs) (Mutzner *et al* 2019, Mutzner *et al* 2018, Endo *et al* 2019), pharmaceuticals, personal care products, illicit drugs, radionuclides, Per and Poly-Fluoroalkyl substances (such as Perfluorooctane sulfonate (PFOS) and Perfluorooctanoic acid (PFOA), heavy metals and organic nutrients (e.g. Nitrogen & Phosphorus) (Mutzner *et al* 2019) (URL 3, URL 4).

The Chemcatcher System is made up of either a 47mm or 52mm PTFE (Polytetrafluoroethylene) housing unit (the 52mm housing is to accommodate a HLB-L receiving disk which analyses for pharmaceuticals, personal care products and illicit drugs), a receiving disk (which is specific to the target analyte and non-reusable – this is what is sent to the lab for analysis), a retaining ring and a diffusion limiting membrane (cannot be reused) (Sandra Lacey of TelLab – *Pers. Comm.*) (See Figure 5).

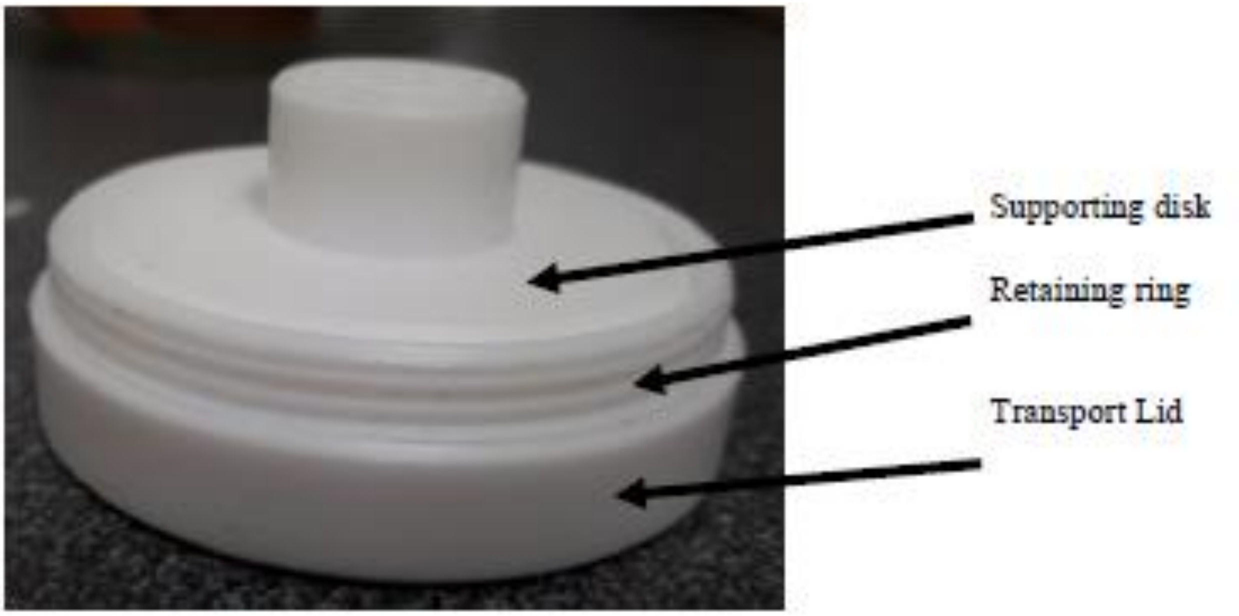


FIGURE 5: PHOTOGRAPH OF 47 MM CHEMCATCHER WITH LABELLED COMPONENTS

Chem Catchers are deployed within either a steel or plastic cage to protect them from debris in the river (plastic used for metal analysis as steel cage will affect results) (See Figures 6, 7 & 8). There are two layers within the cage, each of which can house 3 Chemcatcher units meaning 6 can be deployed at any one time (Sandra Lacey – TelLab – *Pers. Comm.*). Different combinations of receiving disks and membranes can be used in a single cage unit to target a variety of pollutants simultaneously. The target compound is concentrated on to the receiving disk during the systems deployment which can be anywhere from one week to three months, however the average time is two weeks (Sandra Lacey – TelLab – *Pers. Comm.*). This allows the target compound to be sequestered continually from the environment and allows Chemcatcher to capture sporadic, transient, inputs of pollutants and fluctuations in levels over time. A time weighted average can be calculated for the deployment period (Sandra Lacey – TelLab – *Pers Comm.*).

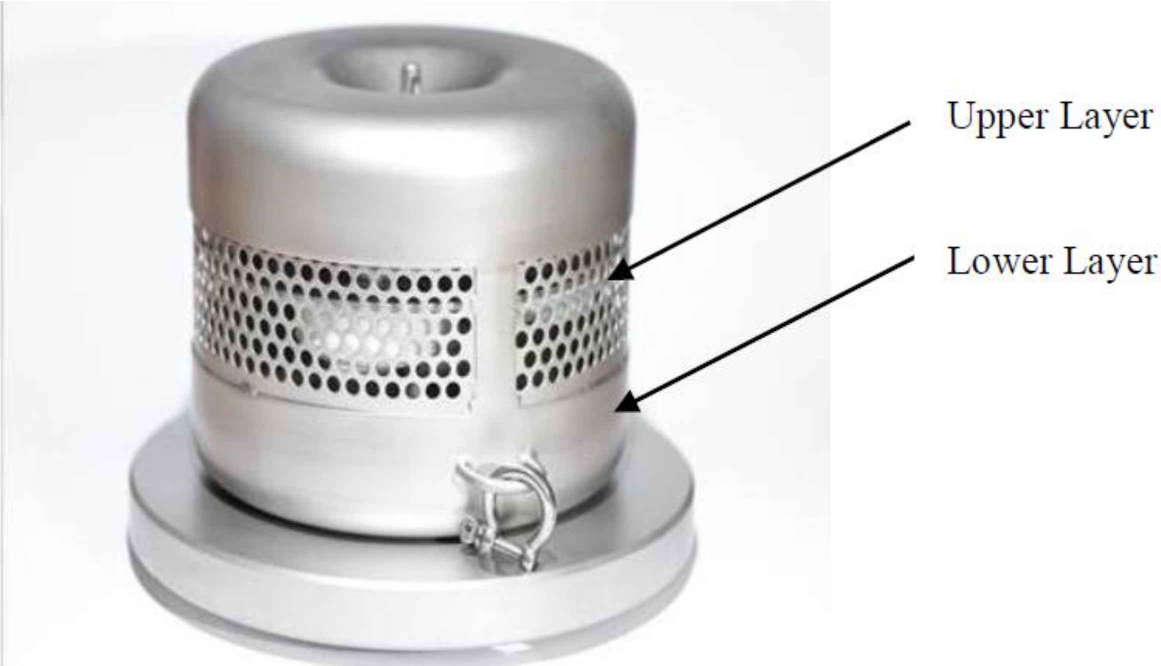


FIGURE 6: PHOTOGRAPH OF STEEL CAGE HOUSING FOR CHEMCATCHER DISKS SHOWING UPPER AND LOWER LAYERS

FIGURE 7: PHOTOGRAPH SHOWING INTERNAL PLACEMENT OF CHEMCATCHER RECEIVING DISKS ON A LAYER

FIGURE 8: PLASTIC CAGING HOUSING CHEMCATCHER AND USED IN METAL ANALYSIS

Chemcatcher has been used successfully in numerous studies to quantify the effect of pesticides and herbicides on the aquatic environment (Castle *et al* 2019, Mutzner *et al* 2019, Mutzner *et al* 2018, Endo *et al* 2019, Castle *et al* 2018 (a), Castle *et al* 2018 (b), Townsend *et al* 2018).

The system is considered a ‘passive sampling device’ meaning that it utilises a selective collecting medium over a period of deployment to determine concentrations of chemicals in the aquatic environment (Salter 2005). This is in contrast to an ‘active sampling device’ (also known as ‘Spot sampling’) which involves a targeted action at a set time to detect chemicals (e.g. a grab sampler/ ISCO sampler). Active sampling devices generally have moving parts such as an air pump or trigger mechanism whereas passive sampling devices rely solely on molecular diffusion to a collecting membrane (Salter 2005). The Chemcatcher System is based on the diffusion of targeted organic compounds through a rate-limiting membrane and the subsequent accumulation of these species in a bound, hydrophobic and solid-phase material (Kingston *et al* 2000).

Several studies have examined the comparability of passive sampling devices to traditional active sampling devices and have concluded that results obtained are at least as accurate as traditionally used methods (Regan *et al* 2018). Ahrens *et al* (2015) concluded that overall, the comparison between passive samplers and traditional active samplers showed a good agreement and that passive samplers were suitable for capturing compounds with a wide range of KOW's in water. KOW refers to the octanol/ water partition coefficient which is defined as the ratio of a chemical's concentration in the octanol phase compared to the aqueous phase of a two phase octanol/ water system (Ahrens *et al* 2015). Indeed, passive sampling techniques have an advantage of active sampling techniques as the latter may not fully account for temporal variations in concentrations due to fluctuations in flow, precipitation or episodic inputs (Ahrens *et al* 2015). Additionally, due to their easy handling during deployment and extraction, they serve as a cost effective and robust alternative to traditional active sampling approaches (Moschet *et al* 2015).

Although studies are ongoing on the use of passive sampling devices for monitoring of chemicals in the aquatic environment, research into this type of monitoring system is still relatively new. As such, this type of sampling has not yet been incorporated in to the Water Framework Directive (2000/60/ EC) regulations which stipulate that spot sampling (e.g. water, sediment & biota sampling) must be carried out when quantifying pesticide levels in the aquatic environment (Regan *et al* 2018). However, this does not eliminate the use of this sampling system in baseline monitoring and it is still very reliable tool when being used to identify areas of concern for chemical export (Regan *et al* 2018, Ahrens *et al* 2015, Gong *et al* 2018, Kingston *et al* 2000, Moschet *et al* 2015).

10.2. Conclusion and Discussion

Studies by Mochet *et al* (2015) concluded that Chemcatcher was capable of detecting over 200 different chemicals in the aquatic environment at extremely low concentrations which illustrates the broad range of analytes that could be targeted. Additionally, Chemcatcher is particularly useful for deployment in rural areas as no external power input is required (Regan *et al* 2018) which is particularly relevant for the Finn catchment, the majority of which is rural.

An additional benefit of using passive samplers (such as the Chemcatcher with the appropriate collecting phase) is their ability to preconcentrate target substances in-situ and, if a diffusion-limiting membrane is employed, over longer time periods. This feature enables the achievement of much lower limits of detection/quantification for many target analytes compared to conventional grab samples (Munze *et al* 2015).

In conclusion, it seems that the Chemcatcher system would be of extreme benefit for chemical export analysis in the Finn Catchment. The system has a proven track record in successful monitoring of numerous chemicals and has been shown to be just as accurate as traditional active sampling techniques. Additionally, set up of the system and associated analyses can be performed at much lower costs than traditional techniques, which allows more areas to be surveyed during the lifetime of the CatchmentCARE project.

Due to the diffuse nature of chemical export in the catchment, it is important that as large an area as possible be surveyed so as to isolate potential areas of high chemical dosing. This will allow more targeted measures to be implemented in areas considered high risk. In addition to this, the diversity of chemicals that can be sampled by Chemcatcher will allow a further definition of the most problematic chemicals affecting the receiving waters and will allow the Loughs Agency to tailor their response accordingly.

Upon completion of the above feasibility study into the use of Chemcatcher as the project's passive sampling equipment, discussions began with T.E. Labs in Co. Carlow on how analysis of Cypermethrin, Acetamiprid, Diazinon and MCPA could be achieved. This discussion led to a partnership being formed between T.E. Labs and E&H Services who had extensive experience in the use of passive sampling for the detection of pesticides on mainland Europe.
T.E. Labs and E&H Services advised that Loughs Agency use three different types of passive sampling devices to collect the information needed about the target chemicals.
They suggested using Chemcatcher devices for collection of MCPA and Diazinon but recommended a POCIS sampler be used for collection of Acetamiprid and a Silicone Rubber (SR) sampling spider be used for collection of Cypermethrin. The reason for this is that different sampling membranes have different efficacy in collecting and retaining specific chemicals depending on what’s being targeted as they are made from different, more selective materials.

The use of passive sampling equipment for detection of pesticides in rivers is relatively new on the island of Ireland. At the time of writing, Loughs Agency were only aware of one study conducted by Dr. Fiona Regan of Dublin City University into Cypermethrin in the Finn Catchment using passive sampling equipment.

The collaboration between T.E. Labs and E&H Services allowed for this passive sampling survey in the Finn Catchment to take place and they developed a special algorithm to allow for calculation of the wet concentration of these chemicals in the target rivers.
The results of this survey are presented in this document.