



Feasibility of Lake Remediation via Phosphorus-fixing Chemicals

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Executive Summary

This report by the School of Geography and Environmental Sciences, Ulster University for the SEUPB funded CatchmentCARE project consists of:

First, part of T1 "Scoping and Action Targeting" and specifically part of Activity A.T1.1 "Feasibility of lake remediation via Phosphorus-fixing". The specific deliverables were D.T1.1.1 "Establish the ecological status of those lakes where status is unknown or uncertain", D.T1.1.2 "Report on phosphorus fixing chemicals" and D.T1.1.3 "Negotiations with regulatory authorities for the use of phosphorus fixing chemicals in lakes".

Second, part of T2 "Implementation" and specifically part of Activity A.T2.1 "Improve the Ecological Status of Lakes". The specific deliverables were D.T2.1.1, D.T2.1.2 "Report on the remediation of up to six lakes by the addition of phosphorus fixing chemicals by end of 2021, including improvement in phosphorus concentration, initial ecological response" and D.T2.1.3 "Final report on the remediation of lakes by the addition of phosphorus fixing chemicals including and assessment of long-term (18 months) ecological effects".

The report presents:

- 1. The scoping to decide on the five lakes chosen for remediation. These were Corcaghan, Greagh, Grove and Lambs in the Blackwater Catchment and Coolyermer in the Arney Catchment.
- The potential ecotoxicological impact and risks associated with the addition of metal salts to lake waters for remediation. Although the doses used in this project, maximum dose 1.35 mg Al/L calculated for Corcaghan, is well below the 3 mg Al/L protective threshold, so minimum risk was assumed.
- 3. The dosing calculations for aluminium and iron salts and the methods used to calculate these. The aluminium salt dose was calculated by two methods, one using the lake water TP concentrations and the other using the available BD-P in the top 4 cm of the lake sediment. The lake water method was chosen as it was a lower dose and so minimised risk and cost.
- 4. The negotiations and delays encountered with Covid 19 and in receiving permissions to dose and monitor lakes before and after remediation are also contained herein.
- 5. The lake monitoring conducted pre and post dosing, including fish removal by Dr David Kelly and more intense sampling immediately before and after remediation.
- 6. The results of the remediation on the lake water chemistry.
- 7. A discussion on the results and improvements that could have been made to the method in hindsight.
- 8. The legacy of the project for lakes in Ireland.

While the focus is the lakes in the CatchmentCARE Project, the evidence gathered here pertains to any small lake and so the findings can be applied generally.



1. Introduction

The most important and widely used way to improve the quality of lakes that suffer from eutrophication, and don't achieve Water Framework Directive Good Status, is a reduction in the loading of nutrients, in most cases, phosphorus (P) (DAERA 2021; EPA 2021). River Basin Management Plans identify the water bodies that need action to meet Good Status or Good Ecological Potential and what action is needed. Within this framework, occasionally, a longer timescale or an alternative objective to Good Status is allowed. Some eutrophic lakes have a substantial store of phosphorus in their sediment (legacy phosphorus), due to nutrient loading from the catchment over some years, and do not improve or only improve slowly after a reduction in loading occurs. Classic examples that demonstrate this behaviour are Lake Sodra Bergundasjon (Bengtsson 1975), Lake Norrviken (Ahlgren 1970) and Shagawa lake (Larsen et al. 1979), but the compilation by Jeppesen et al. (1997) is probably the best evidence for summer release from the sediment of relatively shallow eutrophic lakes. This showed that when the annual mean total phosphorus concentration was greater than 50- 100 μ g/L in lakes with a mean depth less than 5 m, then the concentration in summer was greater than in winter due to release of phosphorus from the sediment, called the internal load. Perhaps, the best observations on the long-term change in concentration after loading reduction in a wide range of lakes, many of which had delayed recovery due to internal load, is the compilation by Jeppesen et al. (2005) which provided evidence of a delay of up to 10 years after reduction in the loading in shallow lakes.

Several techniques have been used to reduce or remove the internal phosphorus load to speed-up recovery of the lakes that have legacy phosphorus in their sediment. These include removal of sediment by dredging, aeration of the hypolimnion (if present) and biomanipulation by encouraging piscivorous fish, however treating the lake with chemicals to immobilize (chemically fix) phosphorus has been the main method. The inactivation of recycled P in lake sediments using the addition of metal salts, (aluminium or iron) (Kennedy and Cook 1982), or lanthanum-modified clays (Phoslock) is an in-lake technique that has been used in Europe and N. America for decades.

The reduction of phosphorus (P) concentrations in lakes to improve water quality, and reduce potentially toxic algal blooms, is a major problem for recreational and drinking water management in Ireland. The 2015 lake water quality report by the Irish EPA (Bradley et al. 2015) showed that, of the 213 lakes monitored using WFD criteria, only 33 had improved status while 53 had declined compared to 2010 (McGarrigle et al. 2009). Reduction of P and nutrient loading into the lakes from the catchment has traditionally been the primary focus of any management regime. However, as stated this may not be sufficient to reduce eutrophication if water quality remains impacted due to internal nutrient cycling from enriched sediments.

The addition of aluminium, or iron, salts to the lake water causes the formation of a floc, which binds P from the water column as it settles. This treatment also reduces cycling of P by actively capping the P in the sediment, thereby controlling the internal nutrient load and potentially improving water quality for the long term (Gibbs et al. 2011). DAERA (2021) data shows that 88%



and 57% of surface water in the Blackwater and Arney catchments, respectively, have less than good water status. If chemical remediation by metal salts is successful within the CatchmentCARE project then there is potential for further improvements throughout the catchments and beyond.



2. Lake selection

This section describes how the five CatchmentCARE lakes were chosen, starting with the initial candidates, then widening of the search and the final selection to Coolyermer Lough in the Arney catchment and Lambs Lough, Grove Lough, Corcaghan Lough and Greagh Lough in the Blackwater catchment. Table 1 summarizes the basic characteristics of the selected lakes.

Table 1 - Key characteristics of the five lakes. The total phosphorus (TP) concentration and alkalinity are the mean for 12 samples collected monthly between December 2018 and November 2019 and 9 samples for chlorophyll-a between March 2019 and December 2019. * indicates the mean depth was measured using bathymetric survey, with the other lakes estimated using spot depths.

Lough	Coolyermer (Arney)	Corcaghan (Blackwater)	Greagh (Blackwater)	Grove (Blackwater)	Lambs (Blackwater)
Easting	218100	264912	264151	276107	267107
Northing	342400	327349	326925	342753	335880
Area, ha	13	4	3	1	7
Mean depth, m	*5.4	*3.0	3.5	3	*13.5
TP, mg P/L	0.053	0.119	0.077	0.058	0.067
Alkalinity, meq/L	2.17	1.34	1.40	3.35	2.66
Chlorophyll-a, ug/L	11.4	30.9	57.0	22.3	25.8

2.1. Selection criteria

Five selection criteria were used to isolate lakes suitable for remediation through immobilization of phosphorus by metal salts:

1. Total phosphorus concentration

A lake water total phosphorus concentration greater than 0.05 mg P/L was used so that the lake is eutrophic enough to require nutrient reduction.

2. Alkalinity

The addition of aluminium or iron salts lowers the pH of the water during hydrolysis of the metal ions, but this is buffered if the alkalinity is high enough. A widely used rule is that the pH is, practically, unaffected if the alkalinity is greater than 1 meq/L and this criterion was used. This is particularly relevant for aluminium, as its toxicity increases at pH<5.0-5.5. If alkalinity results were not available, the nature of the catchment was used: lakes in the upland with low weathering rate rocks have low alkalinity waters, whereas lowland, high weathering rate rocks would have high.

3. Lake size

This is mainly a cost criterion as larger lakes require more metal salts for immobilization compared to smaller ones. In addition, larger lakes are likely to be more widely used, for example, for water abstraction, leisure, or fishing, and obtaining permission for the remediation work could be more difficult. A criterion of 10 ha or less was used.

4. Boat access

The lake must be accessible to a boat. A boat needs to be launched to sample the lake and treat it with metal salts. Sampling would include taking water samples, retrieving sediment cores, sampling zooplankton using nets and completing a fish survey.

Catchment

5. Lake use

Lakes in constant use for water abstraction or leisure pursuits would be less suitable for this type of remediation.

2.2. Initial candidates

The initial candidates were provided at the pre-application stage of the CatchmentCARE Project. Application of the selection criteria was less strict at that stage. The following lakes were initially selected:

Shivnagh, Coolyermer, Emy, Grove, Greagh, Corcaghan, Glaslough, White, Lambs, Ballagh

2.3. Widening search

After the project started, the search was widened to improve the selection and include lakes in the Finn and Arney catchments. Information was sought from GIS maps of the river catchments, the EDEN database, the Northern Ireland Lake Survey and OS maps.

2.3.1. Finn catchment

In this catchment, the following lakes were the most suitable candidates; Lough Finn, Muck and Shivnagh. Lough Finn was not suitable as it is Good Status and is too large (115 ha). Lough Muck is not currently monitored but is in the uplands and so is not likely to be eutrophic. Shivnagh was included in the DOLMANT Project and had Moderate Status, but it is not suitable due to its low alkalinity (0.24 meq/L).

2.3.2. Blackwater catchment

In this catchment, the EDEN database was used to identify candidate lakes and Table 2 summarizes the information.

Lake	Size	EDEN WFD status	Input/ receiving	WFD Status of
	ha		waters	input/rec waters
Ballagh	5	Not monitored P/B?	Magherarney	Poor
Corcaghan	4	Not monitored P/B?	None	n/a
Emy	52	Moderate	Blackwater	Unassigned
Glaslough	21	Not monitored P/B?	Mountain water	Poor
Greagh	3	Not monitored P/B?	Magherarney	Poor
Grove	1	Not monitored P/B?	Mountain water	Poor
Lambs	7	Not monitored P/B?	Blackwater	Good

Table 2 - The candidate lakes in the Blackwater catchment.

Site visits were made to Ballagh, Corcaghan, Emy, Glaslough, Grove, Greagh and Lambs in September 2018, to check for vehicle access and to plan for future sampling. Following on from



these visits, more detailed maps and images of each of the lakes were generated using Google maps and ARC GIS. In December 2018 all the lakes were revisited with a view to eliminating those not suitable either because of access or reasons stated below.

Emy was eliminated as it is too large, improving in status, and the TP concentration is consistently below 0.05 mg P/L criterion (mean value 0.026 mg P/L in 2018). Although lake TP was suitable in Ballagh and Glaslough, neither of these were selected due to lack of boat access. The final lakes selected for the Blackwater catchment were Corcaghan, Greagh, Grove and Lambs.

2.3.3. Arney catchment

In this catchment, maps and Google Earth satellite imagery showed no small lakes in Leitrim or Cavan within the catchment boundary and so data from the Northern Ireland Lake Survey (NILS) was used to select suitable lakes from the Arney catchment area. NILS, a database of 614 lakes in Northern Ireland with spot sample water chemistry results, found 212 small lakes (<50 ha) in Fermanagh, although most of these lay outside the Arney catchment boundary. The Arney catchment has two main lake types: two large, eutrophic lowland lakes with limestone geology (Upper and Lower Lough Macnean, total area of 1439 hectares) and several small upland lakes on sandstone. Table 3 shows all the lakes in the catchment with an area less than 10 hectares.

Table 3 - Northern Ireland Lake Survey data for all lakes less than 10 hectares in the River Arney catchment along with spot sample results for total phosphorus (TP) and alkalinity from the Norther Ireland Lake Survey.

Lake	Area ha	TP μg/L	Alkalinity meq/L
Ora	7.25	96	0.34
Narrickboy	1	49	0.40
Acrottan	1.5	35	0.10
Nacloyduff	1.5	88	0.50
Namanfinn	4	44	0.15
Hamul	3	26	0.10
Martincrossagh	1	47	0.21
Anlaban	1.5	35	0.15
Nagor	1	96	0
Atona	2.5	18	0.10

All the Table 3 lakes are at an altitude above 200 m, where the geology is sandstone and which leads to the low alkalinities, less than the 1 meq/L criterion. Therefore, the lakes are not suitable for remediation by the addition of metal salts.

As there were no suitable small lakes in this catchment, the selection was extended to slightly larger lakes. This identified Lake Coolyermer (13.5 ha) and its characteristics meet the other selection criteria.



2.4. Final selection

The final selection of lakes was Coolyermer Lough in the Arney catchment and Lambs Lough, Grove Lough, Corcaghan Lough and Greagh Lough in the Blackwater catchment and some of their characteristics are now described. Monitoring their key properties began in December 2018 and this is described in the dosage section of this report, a basic characterization of them is presented in Table 1. Each selected lake is described in more detail below.

2.4.1. Corcaghan Lough

Corcaghan is a 4 ha lough in County Monaghan, mean depth 3 m and maximum depth 5 m. It has no inflow or outflow but is used for water abstraction by Irish Water. It is surrounded by pastoral agricultural land with fringing vegetation of alder and thorn and has easy vehicle and boat access. Inland Fisheries Ireland information signs state that the lake contains rudd, roach and pike and there was some evidence of fishing activity during summer sampling. Monthly sampling produced a mean concentration of 0.119 mg TP/L, the highest of the five lakes, and 1.34 meq/L alkalinity, above the 1 meq/L criterion (Figure 1).

2.4.2. Greagh Lough

Greagh is a 3 ha lough which lies adjacent to Corcaghan, mean depth 3.5 m and maximum depth 7 m. Although not currently used for abstraction, water from the lake can be pumped to Corcaghan in times of drought. The level of the lake is maintained by a weir, the outflow from which discharges into the Magherarney River when the lake is at capacity. It is surrounded by pastoral agricultural land with fringing vegetation of willow and alder and with easy vehicle and boat access. Inland Fisheries Ireland information signs state that the lake contains rudd, roach and pike but no evidence of fishing activity was observed during sampling visits. Monthly sampling produced mean concentration of 0.077 mg TP/L and 1.40 meq/L alkalinity, above the 1 meq/L criterion (Figure 1).

2.4.3. Grove Lough

Grove is a 1 ha lough which lies just west of Emyvale in County Monaghan, mean depth 3 m and maximum depth 6.5 m. There is no inflow but a small outflow to the Mountain Water. It has fringing willow and alder on three sides and a pastoral, unfenced field on the fourth; cattle are regularly seen drinking directly from lake. There is vehicle and boat access to the lake shore from the main road. Inland Fisheries Ireland information signs state that the lake contains rudd, roach and pike and there was some evidence of fishing activity during summer sampling. Monthly sampling produced a mean concentration of 0.059 mg TP/L and 3.35 meq/L alkalinity, the highest of the five lakes and well above the 1 meq/L criterion (Figure 1).

2.4.4. Lambs Lough

Lambs is a 7 ha lough just north of Monaghan Town, mean depth 13.5 m and maximum depth 31 m. There is a small inflow from a Blackwater River tributary but no outflow. There is vehicle and



boat access from a farm lane on the southern shore of the lake. Inland Fisheries Ireland information signs state that the lake contains rudd, roach and pike and, although there was no evidence of fishing, people swim there regularly during the summer months. This is the deepest and clearest water of the five lakes, although there were some algal blooms near the shore during early summer. Monthly sampling produced a mean concentration of 0.067 mg TP/L and 2.66 meq/L alkalinity, well above the 1 meq/L criterion (Figure 1).

2.4.5. Coolyermer Lough

Coolyermer is a 13 ha lough near Letterbreen in County Fermanagh, mean depth 5.4 m and maximum depth 13 m, with no inflow or outflow. Access is very good as there had been a fishing club at the lake and there is a concrete lane and slipway. It has fringing alder and willow on all sides with a significant willow plantation of several hectares on the north shore; phragmites and waterlily dominate the littoral zone. Monthly sampling produced a mean concentration of 0.053 mg TP/L and 2.17 meq/L alkalinity, above the 1 meq/L criterion (Figure 1).



Figure 1 - Alkalinity (meq/L) concentrations for the 5 chosen lakes from 07/12/2018 - 21/11/2019.



3. Ecological effects of aluminium and iron salts in lakes

This section reviews the results of case studies into the ecological effects of remediating lakes using the phosphorus-fixing chemicals aluminium and iron salts to improve the risk assessment.

3.1. Background

We focus on whole-lake case studies as these provide the most relevant evidence of what is most likely to happen, as their findings can be relatively easily applied, in contrast to results from laboratory or mesocosm experiments. Applying those findings needs considerable judgement, as laboratory and mesocosm experiments are very simple representations of the complexity of lake ecosystems. They do, however, give an indication of possible effects and so some of the most useful mesocosm studies are included.

The section on ecological effects improves the risk assessment based on the results of ecotoxicity tests. The use of LC/EC50 results to assess risks is based on the effect of a toxicant on a single species, although it must be noted that rules that use results from a range of species are often used to seek to protect the whole ecosystem. Nevertheless, this approach/methodology cannot account for the various ecological effects in an open ecosystem such as a lake, with trophic interactions (food web), predator-prey interactions and redundancy.

The value of field compared to laboratory/mesocosm studies and ecotoxicity test results is shown by the review of iron toxicity by Bakker et al. (2016). The bulk of the review brings together material on laboratory, mesocosm and toxicity tests that lead to findings that are presented as "could", "can have" or "been shown" to have an effect, but, after reviewing ten whole-lake and reservoir case studies, the overall conclusion was that "these effects remained absent during the restoration projects that also monitored biological effects".

Evidence can be produced that a particular effect could happen, and much of the literature is composed of this type of publication, but what is needed is an indication of the most likely effect. This should come, in our case, from whole-lake investigations; the eminent limnologist, Schindler (2012), advises that long term monitoring results and whole ecosystem experiments provide the only dependable evidence for policies to reduce eutrophication.

3.2. Ecological effects of aluminium salts

Although the focus of the major review by Sparling and Lowe (1996) was acid waters including the effects of aluminium, they found that fish were the most affected amongst invertebrates, fish, amphibians and reptiles, birds, and mammals. Almost all the evidence was based on laboratory ecotoxicity tests and experiments and not on field results.

However, their results on the accumulation of aluminium in fish tissue, mainly gills, is relevant, although gained through laboratory exposures. Concentrations up to a few hundred and



occasionally to over one thousand ug Al/g have been found, with the values generally increasing at lower pHs.

A summary of the findings from the whole lake case studies of the ecological effects of exposure to aluminium during the immobilization of phosphorus using aluminium salts in ten lakes is provided in Table 4, along with two field surveys, which included the effect of naturally occurring aluminium on fish. Most of the lakes have low alkalinities, less than 1 meq/L, which increases the risk of toxicity, and the exposure varies from 0.6 to 14 mg Al/L in the case studies and up to 0.5 mg Al/L in the field surveys.

The weight of the evidence from the whole lake case studies is that there are almost no ecological effects, at least based on the response of a range of fish species and benthic macroinvertebrates. The only effects found were a reduction in a fish condition index for yellow perch in Lake Morey and the temporary accumulation of aluminium in the tissue of perch and ruffle in Lake Tiefwarensee. These overall findings are supported by the three investigations that used mesocosms.

Table 4 - The ecological effects on biological groups exposed to aluminium salts in whole-lake case studies. The alkalinity of the lake water and the dose of aluminium are also given. The effects of low exposure to aluminium in acid lakes is also included.

Lake	Alkalinity meq/L	Exposure mg Al/L	Groups	Effects
Five lakes in Wisconsin	0.14, 1.5, 2.2, 2.4, 4.5	7 to 14	Benthic fauna	None
Lake Morey	0.9	5.2	Fish (yellow perch) and benthic fauna	Some; fish condition index decreased (77- 81 to 66)
Lake Tiefwarensee	2.52	2.4	Roach, bream, ruffle, perch, silver carp	Aluminium concentration in gills unchanged in three fish species, increased temporarily in two (perch and ruffle)
Lake Nordborg	3.5	8.8	Fish (perch and roach) and zooplankton	None
Spring Lake	Slightly alkaline	6.7	Benthic fauna	Favourable; decreased in oligochaetes and chaoborids and



				increased in chironomids
Okaro, Rotorua	0.65, 0.17	0.6, salt added to three inflows	Fish, amphibians, invertebrates, birds and plants	Little identifiable impact of local biota, through toxicity or bioaccumulation
Twenty-two lakes in Maine	<0.12	0.39	Fish	Almost no influence on the number of fish species in the lakes
Nine hundred lakes in Ontario	0 to 5	0.5	Fish	None

3.3. Ecological effects of iron salts

Peters et al. (2011), in deriving an EQS for iron in freshwaters in support of the Water Framework Directive and to improve on the current chronic EQS of 1 mg Fe/L as dissolved iron, used field results from streams and so this work contains much relevant information on the ecological effects of iron.

They used 90th quantile regression and field macroinvertebrate results from streams in the UK to derive effect thresholds for the Good/Moderate boundary based on an Observed/Expected ratio of the 10 and 20 % most sensitive taxa and of the whole community as represented by the EQI BMWP score, EQR N-Taxa and EQR-ASPT. Analyses from Spring and Summer were combined. Investigation of the effects of water colour (dissolved organic carbon) and hardness were completed but the findings were considered uncertain.

A chronic EQS of 0.73 mg Fe/L total iron was derived based on the most sensitive taxa and 1.84 for the whole macroinvertebrate community. The ten most sensitive taxa were Goeridae (Caddisfly), Gyrinidae (Beetle), Polycentropodidae (Caddisfly), Perlodidae (Stonefly), Rhyacophilidae (Caddisfly), Ephemeridae (Mayfly), Caenidae (Mayfly), Elmidae (Beetle), Ephemerellidae (Mayfly) and Heptageniidae (Mayfly), indicating that mayflies are the most sensitive group to iron, followed by caddisflies.

In addition, although based on less extensive results, they found that there were no declines in EQRs of fish, macrophytes and diatoms. This indicates that fish, macrophytes and diatoms are less sensitive to iron than macroinvertebrates.

It should be noted that these ecological effects and EQSs apply strictly to streams but there may be some relevance to the littoral zone of lakes.



Bakker et al. (2016) reviewed and synthesised the toxicity of iron to biota and the effectiveness of lake restoration using iron salt. They compiled the evidence from 10 case studies in lakes or reservoirs that included assessment of the ecological effects, although only five included macrophytes, zooplankton or fish. Their conclusion was that "toxic effects on both primary and secondary producers...remained absent during the restoration projects that also monitored biological effects".

There is less evidence from whole lake case studies of the ecological effects of exposure to iron during the immobilization of phosphorus using iron salts, and one of them concerns rivers rather than lakes, but this is usefully supplemented by two general reviews and syntheses.

The evidence is less consistent than with the aluminium case studies. With the three studies in lakes, there were no ecological effects based on fish, zooplankton, macrophytes at exposures of 3.5 to 5 mg Fe/L. Indeed, the ecological changes were of an improvement in the lakes. With the case study of naturally high and sustained iron concentrations in streams, ecological effects, reduction on abundance and diversity of macroinvertebrates, were observed at a total iron concentration of 2 mg Fe/L. It should be noted, however, that in this context the exposure was sustained (chronic) to iron rather than short term (days to a few tens of days).

The general review of iron toxicity during the immobilization of phosphorus by iron salts of Bakker et al. (2016), which includes case studies in 3.2 to 3.4 mg Fe/L concentrations and a range of other evidence concludes that there have been no toxic effects during restoration projects.

3.4. Overall findings

The weight of evidence of this review of the ecological effects of immobilizing phosphorus in lakes using aluminium and iron salts, based on whole lake case studies supplemented by major general work, found that there were almost none, based on zooplankton, benthic macroinvertebrates, fish and macrophytes.

The only effects observed were, for aluminium, and were a reduction in a fish condition index for one species in one lake and the temporary accumulation of aluminium in the tissue of two fish in another lake.



4. Lake Metal Salts Dose Determination and Costings

4.1. Introduction

This section details the dosage calculation and costings for phosphorus (P) fixing chemicals for inlake chemical remediation of five enriched lakes selected mostly from the Blackwater catchment, and one from the Arney. Lake selection and the dosage calculations are based on the results from the monthly monitoring of lake water TP, alkalinity and chlorophyl a in the lakes for a year prior to dosing. Two dosage calculations for aluminium salts are given; one based on lake water TP concentration (Figure 2) and the other using the mobile inorganic P concentration in the lake sediment cores. The iron dosage method is based on the Iron:Total Phosphorus (TP) molar ratio in the sediment cores. Although iron was not selected as a suitable method for these lakes, all of these methods are well established and have been used previously in other lake remediation projects worldwide. This section addresses the dosage rate, and costs, for remediation of candidate lakes for Work Package AT1.1.



Figure 2 - TP concentrations for the 5 chosen lakes from 7/12/2018 - 21/11/2019.

When alum was initially used there was no established method for dose calculation as shown in Cooke and Kennedy (1981) which reported on 28 uses of alum with a range of doses from 0.4 mg Al/L to 22.6 mg Al/L with varying degrees of success. Since then, based on laboratory and mesocosm studies, three methods of calculating the dose of aluminium salts needed to immobilize a given amount of phosphorus in lakes have been established (Cooke et al. 2005; Huser et al. 2016). These are based on (1) the total phosphorus concentration in lake water, (2) the concentration of available phosphorus in the sediment and (3) the size of the internal load of phosphorus (Cooke et al. 2005). There is no established method for dose calculations for iron salts as it is a less commonly used, but it has also successfully been used in both mesocosm experiments and field applications to combat

internal P loading by either adding the iron to the lake sediment (Smolders et al. 2001) or to the surface water (Hansen et al. 2003).

4.2. Aluminium salts dose determination

- For the purposes of this project the dose calculations are based on:
- (1) lake water total phosphorus concentration and
- (2) the concentration of the available P in the sediment.

4.2.1. Lake water TP concentration dosage calculation

The first method using lake water Total Phosphorus concentration and an 11:1 weight ratio Al/TP (Rydin et al. 2000) produces the following (Table 5). The lakes had been monitored monthly for one year from December 2018 and using mean annual TP concentration and an aluminium to TP ratio of 11:1 a calculation of the dose required (mg/L) aluminium was calculated. A bathymetric survey of the lake had been conducted which produced lake volume estimates. A combination of the lake volume and the required dose were used to calculate the amount of alum of a known concentration required for each lake.

Lake	TP mg/L	Al dose mg/L 11:1 weight ratio	Alum (T) required @ 42.35g Al/kg
Coolyermer	0.053	0.62	10.2
Corcaghan	0.119	1.35	2.6
Greagh	0.077	0.86	1.8
Grove	0.057	0.65	0.3
Lambs	0.067	0.69	16

Table 5 - Aluminium dose required based on lake water annual mean TP concentration.

4.2.2. Sediment available P concentration calculation

For the second method, the available phosphorus (mobile inorganic P) is determined in sediment cores (Rydin & Welch 1999). The analytical fraction is BD-P in the Psenner fraction scheme (Psenner and Pucsko, 1988), which extracts reduced metals, mainly Fe(II). Kajak-Brinkhurst cores were taken from each lake and sliced into 1 cm sections. The SRP in the top 4cm was determined by extraction for 1 hour with 0.11M sodium dithionite, 0.11M sodium bicarbonate. The dose of aluminium required to fix the available P in the sediment is calculated at an AL/SRP mass ratio of 100:1 (Table 6).



Table 6 - Aluminium dose required based on available P concentration in top 4cm of lake sediment
and 100:1 Al:BD-P ratio.

Lake	Mean BD-P (mg/g) top 4cm	Total lake BD- P (kg) in top 4cm	Al dose (kg) 100:1 ratio	Al dose required (mg/L)	Alum (T) required
Coolyermer	0.207	74	7400	14.79	175
Corcaghan	0.17	25	2500	12.17	57
Greagh	0.19	20	2000	21.70	46
Grove	0.056	1.2	120	2.24	2.6
Lambs	0.078	25	2500	2.57	57

As can be seen from the Tables 5 and 6, much more Alum is required for lake remediation based on the sediment method estimate than the lake water estimate e.g. Coolyermer 10.2T /175T respectively. This is also reflected when it comes to the difference in cost as can be seen in Table 7.

Table 7 - Cost for Alum based on Lake Water TP concentration calculations and sedimentAvailable P concentrations.

Lake	Sediment 100:1 Al :BD-P Alum Cost £	Lake Water 11:1 Al:TP Alum Cost £
Coolyermer	16778	1286
Corcaghan	5519	322
Greagh	4429	230
Grove	254	39
Lambs	5476	2020

4.3. Iron salts dose determination

As stated previously, there is no established method for determining the dose of iron salts, required to immobilise a given amount of phosphorus, in any lake. Jensen at al. (1992) calculated sediments with a molar ratio of Fe/TP greater than 8.3 would be capable of retaining phosphate in the oxidised surface layer. The molar Fe/TP ratios for each lake are shown (Table 8.) which shows that all lakes have a ratio greater than this threshold. None of the lakes therefore require the addition of any iron salts as the P in the surface sediment layer should be retained so long as the sediment surface remains oxidised. For this reason, it was determined that iron salts were unsuitable for use in these lakes.



Lake	TP mg/g	Fe mg/g	BD-P mmol/g	Fe mmol/g	Fe/TP mol ratio
Coolyermer	3.65	71.72	0.12	1.28	10.90
Corcaghan	3.89	62.33	0.13	1.13	8.66
Greagh	3.89	96.13	0.13	1.64	13.12
Grove	4.88	100.25	0.16	1.80	11.39
Lambs	0.77	13.11	0.03	0.26	10.33

Table 8 - Mean TP, Total Fe, BD-P mmol/g , Fe mmol/g and Fe/TP molar ratio of top 4cm of sediment from 3 cores in each lake.

4.4. Establishing presence of internal load in selected lakes

The most suitable dose and metal salt is that which produces greatest efficacy with least risk. Based on these criteria it is clear from the dose calculations that alum treatment of TP in the water column is by far the best, and cheapest, option. However, only dosing the lakes based on water column P would have little long-term effect if the main load to the lakes is internal from enriched sediments. There are two methods of establishing the importance of the internal load (Søndergaard et al. 2003), one for lakes which stratify and develop an anoxic layer at the sediment water interface (Nürnberg, 1984), and shallow lakes (<5m) which do not stratify (Jeppesen et al. 1997). In shallow non-stratifying lakes with annual TP concentration greater than 100 μ g/L, Jeppesen et al. (1997) used 234 Danish lakes to determine that the internal load was important if the summer TP concentration was more than twice the winter concentration. Gibson (1996) showed that the internal load was important in 17 shallow Irish lakes if the summer concentration was twice that in the winter at >50 μ g/L. Based on the TP data for the chosen lakes, two of the selected shallow lakes may demonstrate this cycle, Corcaghan and Greagh, Corcaghan to a greater degree. It may be that, in these two lakes, during anoxic periods of high productivity available P may become available to be released into the water column. Grove, a shallow lake, and Coolyermer (maximum depth 13.5m) have higher TP concentrations in winter and generally lower in summer. This is consistent with seasonal uptake and release by algae but shows no evidence of an important internal load from sediment. Lambs is a deep lake (maximum depth 31.5m) which shows small spikes in concentration in early and late summer (30/5 and 02/09) but no subsequent decrease in winter, this is consistent with no important internal load.

4.5. Dose conclusions

Although Corcaghan and Greagh show some evidence of internal load, it was determined that for maximum efficacy, with minimum risk to lake fauna and flora, the lake water TP concentration dose calculation would be used for all lakes. Table 9 shows the tonnes of alum required and cost for chemicals required for remediation for each lake.



Lake	TP mg/L	Alum (T) required @ 42.35g Al/kg	Alum cost (£)		
Coolyermer	0.053	10.2	1,286		
Corcaghan	0.119	2.6	322		
Greagh	0.077	1.8	230		
Grove	0.057	0.3	39		
Lambs	0.067	16.0	2,020		

Table 9 - Amount and cost of alum required for each lake.



5. Dosing approval and negotiations

This section reviews the negotiations which took place with regulatory authorities to allow for deployment of chemicals to the lakes and for removal of fish for research purposes. It also includes a generic risk assessment for each lake for the use of P fixing chemicals in accordance with work package AT.1.1.

5.1. Background

It is acknowledged that reduction of lake nutrient loads to improve lake water quality may have a lag time of up to 20 years or more, and internal loads have the potential to maintain lakes in a perpetually eutrophic state for decades. Over one third of inter-drumlin lakes, such as those selected for remediation, have no significant outflow and these eutrophic lakes with enriched sediments have the potential to recycle nutrients continually into the water column. The addition of a chemical salt, such as Alum, which has been decided as the chemical of choice for this project, can rapidly reduce the phosphorus concentration by flocculation which settles to the lake sediment. The addition of chemical salts can also cause an immediate decrease in chlorophyll concentration and in addition reduce the incidence of further algal blooms and the effects of eutrophication in the long term.

5.2. Negotiations for permission to dose

As metal salts had only been used once in Ireland before, Foy (1985) applied alum to White Lough in Co Tyrone in 1980, it was necessary to obtain permission from the regulatory bodies from each jurisdiction before dosing the lakes. Each lake was regarded, and the governing bodies concerned were contacted to inform them as to nature of permissions sought, i.e., application of alum. At that time a full hydrological year of data had been collected and the dosage calculations for each lake had been made, the eco toxicological report had also been written and all of this sent to the parties concerned prior to our meeting.

A meeting took place on 17/11/2020. The key organizations were Monaghan County Council, Environmental Protection Agency, Northern Ireland Environment Agency, Irish Water, and Inland Fisheries Ireland.

In addition to the reports which had been sent prior to the meeting, details of pre and post dose monitoring protocol (Table 10), a generic risk assessment for metals salts, dosing method and a local formal risk assessment for each lake was presented to the panel as given below.



Before Remediation	After Remediation
Al, Fe, Mn, pH, TP, Chla and alkalinity in mixed layer water sample every other day for 5 days	Al, Fe, Mn, pH, TP, Chla and alkalinity in mixed layer water sample every other day for 8 days, then fortnightly for one month and monthly for 18 months following remediation
Zooplankton abundance in 3 vertical net hauls every other day for 5 days	Zooplankton abundance in 3 vertical net hauls after one week, two weeks and one month
Concentration of aluminium measured in gills of fish species from each lake	Concentration of aluminium measured in gills of fish species from each lake after one week, one month and two months

Table 10 - Protocol for pre and post dosing monitoring of lakes

Formal risk assessment of the effects of aluminium and iron salts on lakes

This is a generic risk assessment that uses the exposure-risk (dose-response) relationship and ecotoxicological results to derive a protective threshold for aluminium and iron. The thresholds are compared to the doses needed to remediate the five CatchmentCARE lakes and the findings assessed, using, as well, information on the biota found in eutrophic Irish lakes. There are no results for some fish and macroinvertebrate species.

The assessment is that the risk of using aluminium and iron salts to immobilize phosphorus should be low. For aluminium, the protective threshold is 3.0 mg Al/L and the dose 0.5 to 1.8 mg Al/L and for iron 10.0 mg Fe/L and 5 to 10 mg Fe/L.

Ecological effects of aluminium and iron salts in lakes

The results of whole-lake case studies into the ecological effects of remediating lakes using aluminium and iron salts are presented as they are the most relevant evidence of the effects. There are more studies for aluminium than for iron.

The evidence is that there are almost no ecological effects, based on zooplankton, benthic macroinvertebrates, fish and macrophytes. With aluminium, there was a reduction in a fish condition index for one species in one lake and the temporary accumulation of aluminium in the tissue of two fish in another lake.

As the doses of aluminium salts to the five selected lakes are all much less than the 3.0 mg Al/L , highest dose is Corcaghan 1.35 mg Al/L, the risk to the lakes is considered negligible.

A local risk assessment for each lake was also provided for the negotiations which looked at each lake in closer detail assessing any activities taking place in, on or around the lake such as fishing, water abstraction, cattle drinking, leisure pursuits, outflow, chemical spill, amenity or access and assesses them for risk, likelihood, impact and mitigation.

Catchment

Details of how we would dose the lakes was given to the parties involved so they would understand how we were reducing the risk to the lake and surrounding area. Clinty chemicals, who provide the alum for N. Ireland Water treatment plants would be used as the Alum supplier for the project. They would deliver the aluminium sulphate solution in IBCs to a safe location near lake boat access point. Each of these contains 1000 litres or 1.3 tonnes of alum @42.35g Aluminium/kg.

As an example of the dosing method Grove would be the first, and smallest, lake to be dosed.

Grove only required 0.3 tonnes (228 litres) of chemical. This quantity would be pumped using a Honda WMP chemical pump from the roadside, via suitable piping, to an empty IBC on board the boat. In the case of Grove this would be made easier by filling the onboard tank from concrete pier which extends into lake on the SW corner. As the chemical is corrosive, metal pipework and fittings would be avoided, and suitable plastic equipment would be used throughout.

As the near shore of the lake would not be dosed, the area above the fine-grained sediments was estimated using bathymetric maps of the lake. The total distance to be travelled by the boat during chemical application was calculated using equally spaced sweeps of the lake along the length of the dosing area, like mowing a lawn. As the dose (litres) was known, the boat speed (m/s) and flow rate of the chemical dose (ml/s) was determined prior to deployment for each lake.

Using the Honda WMP20 and plastic piping, the chemical would be pumped directly into the lake, just below the lake surface at the stern of the boat adjacent to the engine. The propeller would mix the chemical with the lake water as the boat moved forward. A floc would form almost instantly as the fixing of the P in the lake takes place.

Having been presented with all of the above information and following some detailed questioning and several online and in person meetings, permission to dose the lakes was finally granted on 17th November 2020. However, IFI then informed us that as we were removing fish from the lakes for scientific purposes that additional Section 14 approval was required. This was to lead to a considerable delay.



5.3. Section 14 approval

We were advised by IFI during our lake dosing permission meeting that we would require Section 14 application as our proposed fish sampling would fall within the scope of the 2010/63/EU directive (on the protection of animals used for scientific purposes) which was transposed into Irish law in December 2012 by SI No 543 of 2012. This only came to our attention because the fish we were removing from each lake were going to be analysed for aluminium before and after dosing. The Health Products Regulatory Authority (HPRA) Section 14 approval is required for:

- A. Carrying out procedures on animals
- B. Designing procedures or projects with animals
- C. Taking care of animals
- D. Killing animals for research

Dr David Kelly, an expert in the field, was engaged by the project to catch the fish from each lake according to project design, using fyke and gill nets. Although he has been doing this type of work for many years for monitoring purposes, he did not hold the necessary Section 14 licence for Ireland and so it was necessary for him to complete the qualification in order to carry out the fish catch and kill for the project. We attempted to find other biologists who already held the qualification and could do the work to expedite the process but were not able to find anyone, as it is quite skilled work with a limited number of operatives.

Following much negotiation with IFI Dr Kelly applied for the first available HPRA section 14 course and qualified in June 2021, once he had received his certification, we applied for a licence to fish each lake. As we were dosing Grove first, as it was the smallest and required the least chemical, we applied to DECC, of which IFI is part, on the 24/06/21. Permission was finally granted on the 24/08 21. Following on from this we applied for the other lakes on the 30/08/21, permission on these lakes was granted on the 03/11/21. Any future projects requiring fish removal for research should build these delays into project timeframes and apply for Section 14 approval as soon as possible.

5.4. Impact of delays on project deliverables

The global Covid-19 pandemic which resulted in travel restrictions, problems with suppliers, communication issues with project partners, lone working and laboratory closures meant that there was a delay in the dosing of the lakes. The initial project proposal had been to dose up to six lakes, however, due to a delay of over one year with the pandemic and waiting for dosing and Section 14 approvals three lakes were dosed. These were Grove at the end of 2021, and Greagh and Corcaghan in early 2022.



6. Lake monitoring

6.1. Background

It is acknowledged that reduction of lake nutrient loads to improve lake water quality may have a lag time of up to 20 years or more, and internal loads have the potential to maintain lakes in a perpetually eutrophic state for decades. Over one third of inter-drumlin lakes, such as those selected for remediation, have no significant outflow and these eutrophic lakes with enriched sediments have the potential to recycle nutrients continually into the water column. The addition of a chemical salt, such as Alum, which had been decided as the chemical of choice for this project, can rapidly reduce the phosphorus concentration by flocculation which settles to the lake sediment. The addition of chemical salts can also cause an immediate decrease in chlorophyll concentration and in addition reduce the incidence of further algal blooms and the effects of eutrophication in the long term.

6.2. Monitoring schedule

Regular monthly water samples were taken from each lake using a line throw at 1m depth and these samples were analysed for alkalinity, chlorophyll *a*, iron, aluminium, and manganese concentrations. However, as changes in lake water quality can occur very rapidly when chemical salts are added a more intense period of sampling was required before, on and after the day the lakes were dosed. In addition to the monthly water sampling which was carried out by Ulster University staff prior to and up to present as shown on Figure 3, the pre and post dosing protocol as shown in Table 11 was also followed.

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29.5.21	28.6.21	28.7.21	27.8.21	26.9.21	26.10.21	25,11,21	25,12,21	24.1.22	23.2.22	25.3.22	24.4.22	24.5.22	23.6.22	23.7.22	22.8.22	21.9.22	21.10.22	20,11.22	20.12.22	19,1,23	18.2.23	20,3,23

Figure 3 - The sampling dates for the three lakes up to March 2023. The dosing date is shown by the yellow circle for each lake. Grove was dosed 19/10/21, Greagh 17/11/21 and Corcaghan 19/01/22.

In addition to the intense water sampling undertaken by the Ulster University team, Dr David Kelly, a fish biologist was employed to catch fish from each lake for research purposes, five from each species present, one week before dosing and one week, two weeks and two months after. The zooplankton and fish samples are yet to be analysed. This work will be carried out by a PhD student Juan Bennett who is being sponsored by Ulster University. When complete the results will be presented in conference form and contained in his doctoral thesis.

Before Remediation	After Remediation
Al, Fe, Mn, pH, TP, Chla and alkalinity in mixed layer water sample every other day for 5 days	Al, Fe, Mn, pH, TP, Chla and alkalinity in mixed layer water sample every other day for 8 days, then fortnightly for one month and monthly for 18 months following remediation
Zooplankton abundance in 3 vertical net hauls every other day for 5 days	Zooplankton abundance in 3 vertical net hauls after one week, two weeks and one month
Concentration of aluminium measured in gills of fish species from each lake	Concentration of aluminium measured in gills of fish species from each lake after one week, one month and two months

Table 11 - Protocol	for	ore and	nost dosina	monitorina	of lakes
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7. Lake Dosing

7.1. Background

It was necessary to devise a dosing method that would suit project lakes accessibility, size, and dose requirements. The maximum dose required was for Corcaghan Lough (2.6 tonnes), so the dosing method, and risk assessment, was designed around this lake.

7.2. Method

Aluminium Sulphate is acidic and so specialised pumps, piping, storage equipment, protective clothing and eyewear were required. Chemical storage tanks with bunds, Honda WMP 20 chemical pumps and Goodyear piping with no metal fittings were used to design a system to dispense the salts to the lake. A large storage tank was kept on shore which was used to replenish a smaller tank which was securely located on the boat. One Honda WMP 20 pump was kept on shore to pump from the bund for refilling the boat tank via Goodyear hosing when the boat was brought to shore, and a second pump was secured on the boat which was set at the required flow rate prior to dosing. The flow rate had been determined on a previous occasion by filling the boat tank with water to the volume of chemical required for each lake and then covering the lake area while adjusting flow rate to determine the flow rate setting. During this period of trial and error it was also realised that if the chemical was dispensed next to the propeller of the boat ti would assist in mixing the chemical into the lake water. The alum chemical was delivered to lake side in industrial bulk containers (IBCs) and 25L drums by Clinty Chemicals with a cost of £4,932 for the three lakes, including delivery charges (£0.154 per litre of 8% alum).

The three lakes Grove, Greagh and Corcaghan were dosed between October 2021 and January 2022 using 0.3, 1.8 and 2.6 tonnes of alum, respectively.

7.3. Grove

This was the first of the lakes to be dosed as it was the smallest and required the least amount of chemical, 0.3 tonnes. Grove is a 1 ha lough which lies just west of Emyvale, in County Monaghan, mean depth 3 m and maximum depth 6.5 m (Figures 4 and 5).





Figure 4 - Grove Lough prior to dosing.



Figure 5 – Grove Lough being dosed with 0.3 tonnes of Alum on 19/10/2021. Note the floc plume precipitating out as alum is mixed into the water column by the boat propellor. When dispensing the chemical salts, the boat travelled in sweeps 7-8m apart, across the long axis and then short axis in a grid pattern. In this way the chemical is dispersed most evenly throughout the lake water column.



7.4. Greagh

Greagh is a 3 ha lough which lies adjacent to Corcaghan, mean depth 3.5 m and maximum depth 7 m. Although not currently used for abstraction, water from the lake can be pumped to Corcaghan in times of drought. The level of the lake is maintained by a weir, the outflow from which discharges into the Magherarney River when the lake is at capacity. It is surrounded by grassland agriculture with fringing vegetation of willow and alder and had easy vehicle and boat access (Figure 6). Greagh was dosed on the 17/11/21 using 1.8 tonnes of alum.



Figure 6 - Dosing equipment on Greagh Lough 17/11/21

7.5. Corcaghan

Corcaghan is a 4 ha lough in County Monaghan, mean depth 3 m and maximum depth 5 m. It has no inflow or outflow but is used for water abstraction by Irish Water. It is surrounded by grassland agriculture with fringing vegetation of alder and thorn and has easy vehicle and boat access (Figure 7). Corcaghan was dosed on the 19/01/22 using 2.6 tonnes of alum.





Figure 7 - First sweep of the boat dispensing alum on Corcaghan on 19/01/22.



8. Results

The last lake, Corcaghan, was dosed on the 19/01/2022 and monthly monitoring has continued since then. The results below show the changes in the main indicator factors for water quality in the lake since dosing for aluminium, chlorophyll-a and total phosphorus concentration. Other variables from the project have yet to be analysed including zooplankton and fish tissue. These results will augment the data once completed, in addition to further monthly lake water monitoring which will continue until the end of 2023.

8.1. Aluminium

Figure 8 shows the aluminium concentrations in the three lakes from May 2021 until March 2023. There is a sharp increase immediately following dosing but a rapid reduction to pre dosing concentrations, suggesting that aluminium had been deposited in the precipitated floc and remained locked in the sediments (Paul et al., 2008; Wauer and Teien, 2010) thus maintaining the water column at a safe concentration for lake biota. All lakes indicated a spike in April 2022 which cannot be explained other than sampling error as the lake levels were lower than normal and the sampler may have collected lake sediment when retrieving samples thus elevating the concentration when analysis was carried out.



Figure 8 - Aluminium concentration (μ g/l) of the three dosed lakes. Dashed lines show the dosing date for each lake according to legend colour.

8.2. Chlorophyll-a

Chlorophyll-a for the lakes is shown in Figure 9. This variable is a key indicator of phytoplankton/algae concentration and high values, greater than 25 μ g/l, indicate that the ecosystem is eutrophic, (Kasprzak et al., 2008; Li et al., 2017). Figure 9 shows a marked improvement in all lakes post remediation, especially in Grove Lough, which is the most typical of



the inter-drumlin lakes dosed. After the application in Grove the concentration fell from 25 μ g/l to roughly 5 μ g/l in less than one month. Chlorophyll-a concentrations for all lakes were also reduced in the months between May and September between 2021 (pre-dosing) and 2022 (post-dosing). The average for these six months fell from: Corcaghan 66 to 17 μ g/l, Greagh 35 to 11 μ g/l and Grove 10 to 2 μ g/l between 2021 and 2022. It is acknowledged that this is only one year's data, and this improvement may be short-lived, however, continued monitoring of the lakes will demonstrate whether they continue to have improved chlorophyll concentrations post remediation.



Figure 9 -Chlorophyll a concentration ($\mu g/l$) in the three dosed lakes. Dashed lines show dosing date for each lake according to legend colour.

8.3. Total phosphorus

The results for reductions in TP were less clear, but the summer concentration spikes observed in Greagh and Corcaghan in 2019 and 2021 were less extreme suggesting that the internal loading from the sediment had been reduced (Figure 10). Also, overall, there appears to be a smoothing of the data with less overall "noise" and variation throughout the year in all lakes. Again, it will remain to be seen whether this pattern continues for another year and whether internal loading returns as a potential issue in Greagh and Corcaghan. This will be indicated if the summer concentrations are more than double the winter concentrations if the winter concentrations are over 50 μ g/l (Gibson, 1996). The continued sampling regime for the remainder of this year will show if this is the case.





Figure 10 - TP concentration for the three dosed lakes. The smoother peaks post dosing, particularly in Greagh and Greagh are suggestive of reduced internal loading due to phosphorus being locked in the sediment because of the alum dosing.



9. Discussion

Cooke et al. (1993) stated that a P remediation project could be said to have been a success if it had: reduced phosphorus release for a substantial number of years, reduced the total phosphorus concentration, and if there were no toxic effects to aquatic species. The reasons for project failures have usually been insufficient reduction in external loads or incorrect calculation of dosage. Huser et al. (2016) found that up to 80% of treatment longevity was explained by Al dose. Their analysis of 114 lakes showed treatments which varied in longevity from 1 to more than 40 years in effectiveness. In each of these treatments most of the documented research reported null or minimal effects on aquatic biota with only temporary declines in certain groups of fish or macroinvertebrates and populations recovering to original densities shortly after treatment.

Using measures of success proposed by Cooke at al. (1993), and applying them to the current results, it may be assumed that there is some reduction in phosphorus release shown by smoothing of the TP curves for Greagh and Corcaghan in particular, although it remains to be seen how long this effect will last following a single, low alum dose. There is also some indication of a reduction in TP concentration in all lakes although the chlorophyll-a results show a much clearer pattern of change and to date there is no indication of any negative effects on aquatic species. This will be properly quantified when further analysis is carried out in further (doctoral) research.

Chemical lake remediation is literally a bottom-up approach, fixing phosphorus in the sediment of the lakes and making it unavailable for recycling into the water column (Hickey and Gibbs, 2009). This can only ever be a short-term fix if a top-down perspective is not taken, i.e., catchment management measures need to be adopted to reduce overall nutrient inputs to lakes otherwise any lake remediation can only be a temporary improvement and repeat applications will be necessary.

When the dose calculations for this project were being made it was clear from the literature that there were two methods of calculating the dose for each lake, the lake water TP method, and the sediment available P method, both of which are given earlier in the report. The differences in the dose concentration (mg/l) for each method in each lake was: Grove 0.65/2.24, Greagh 0.86/ 21.7, Corcaghan 1.35/12.17 for the water TP method and sediment method respectively.

As chemical remediation of lakes is not an established method in Ireland, and it took almost two years of negotiations with environmental agencies and stakeholders to obtain permission to dose, it was decided that the least risk option should be adopted i.e., the lesser dose of the lake water TP method.

On hindsight however, given that it had been determined by the ecotoxicology report that there was a protective threshold of 3mg/l Al, this higher concentration could have been applied to all of the lakes with no anticipated impact on any lake biota, and there may have been a more marked reduction in TP concentration. This is especially poignant when it is considered that Huser et al. (2016) stated the dose concentration has the most impact, over 80%, on the outcome of any



restoration. Also, Wauer and Teien (2010) state that concentrations of up to 14 mg/l of alum have been used to remediate lakes in N. America with little or no effect on benthic fauna or fish. On reflection, a higher dose should have been used for greater effect.

PhD researcher Juan Bennett who has been sponsored by Ulster University will continue the lake monitoring and perform fish toxicity studies from pre and post dose monitoring.

9.1. Legacy

In addition to this report, the work completed by the School of Geography and Environmental Sciences, Ulster University for CatchmentCARE has provided a general methodology for lake scoping, dose calculations, ecotoxicology reporting and monitoring, and which can be used by other agencies considering metal salts as a potential eutrophication remediation technique. Although not a fix all method, i.e., only suitable for smaller lakes above a specific alkalinity, it is a highly transferable method with wide ranging potential use across many Irish catchments.

The method devised by Ulster University has shown that, even at the most cautious of doses, improvements in lake water quality are possible. Further monitoring will give insights into the length of improvement time following a single, low concentration alum dose.

10. References

- Ahlgren, G., 1970. Limnological studies of Lake Norrviken, a eutrophicated Swedish Lake: II. Phytoplankton and its production. Schweiz. Z. Hydrologie 32, 353–396. <u>https://doi.org/10.1007/BF02502554</u>
- Bakker, E.S., Van Donk, E., Immers, A.K., 2016. Lake restoration by in-lake iron addition: a synopsis of iron impact on aquatic organisms and shallow lake ecosystems. Aquat Ecol 50, 121–135. https://doi.org/10.1007/s10452-015-9552-1
- Bengtsson, L., 1975. Phosphorus release from a highly eutrophic lake sediment: With 5 figures and 4 tables in the text. SIL Proceedings, 1922-2010 19, 1107–1116. https://doi.org/10.1080/03680770.1974.11896162
- Bradley, C. et al., 2015. Water quality in Ireland 2010-2012. Environmental Protection Agency, Wexford
- Cooke, G.D., Kennedy, R.D., 1981. Precipitation and Inactivation of Phosphorus as a Lake Restoration Technique. USEPA-600/3-81-012.
- Cooke, G.D., Welch, E.B., Martin, A.B., Fulmer, D.G., Hyde, J.B., Schrieve, G.D., 1993. Effectiveness of Al, Ca, and Fe salts for control of internal phosphorus loading in shallow and deep lakes. Hydrobiologia 253, 323–335. <u>https://doi.org/10.1007/BF00050758</u>
- Cooke, G.D., Welch, E.B., Peterson, S.A., Nichols, S.A., 2005. Restoration and management of lakes and reservoirs, third ed. ed. CRC/Taylor & Francis, Boca Raton (Fla.).
- Department of Agriculture, Environment and Rural Affairs (DAERA), 2021. Water Framework Directive Statistics Report. Belfast.
- Environmental Protection Agency (EPA), 2021. Water quality in 2020: An indicators report. Environmental Protection Agency, Wexford
- Foy, R.H., 1985. Phosphorus inactivation in a eutrophic lake by the direct addition of ferric aluminium sulphate: impact on iron and phosphorus 15, 613-629. https://doi.org/10.1111/j.1365-2427.1985.tb00232.x
- Gibbs, M.M., Hickey, C.W., Özkundakci, D., 2011. Sustainability assessment and comparison of efficacy of four P-inactivation agents for managing internal phosphorus loads in lakes: sediment incubations. Hydrobiologia 658, 253–275. <u>https://doi.org/10.1007/s10750-010-0477-3</u>
- Gibson, C.E., Foy, R.H., Bailey-Watts, A.E., 1996. An analysis of the total phosphorus cycle in some temperate lakes: the response to enrichment. Freshwater Biology 35, 525–532. https://doi.org/10.1111/j.1365-2427.1996.tb01766.x
- Hansen, J., Reitzel, K., Jensen, H.S., Andersen, F.Ø., 2003. Effects of aluminum, iron, oxygen and nitrate additions on phosphorus release from the sediment of a Danish softwater lake. Hydrobiologia 492, 139–149. <u>https://doi.org/10.1023/A:1024826131327</u>
- Hickey, C.W., Gibbs, M.M., 2009. Lake sediment phosphorus release management—Decision support and risk assessment framework. New Zealand Journal of Marine and Freshwater Research 43, 819–856. <u>https://doi.org/10.1080/00288330909510043</u>
- Huser, B.J., Egemose, S., Harper, H., Hupfer, M., Jensen, H., Pilgrim, K.M., Reitzel, K., Rydin, E., Futter, M., 2016. Longevity and effectiveness of aluminum addition to reduce sediment phosphorus release and restore lake water quality. Water Research 97, 122–132. <u>https://doi.org/10.1016/j.watres.2015.06.051</u>
- Jensen, H.S., Kristensen, P., Jeppesen, E., Skytthe, A., 1992. Iron:phosphorus ratio in surface sediment as an indicator of phosphate release from aerobic sediments in shallow lakes, in: Hart, B.T., Sly, P.G. (Eds.), Sediment/Water Interactions. Springer Netherlands, Dordrecht, pp. 731–743. <u>https://doi.org/10.1007/978-94-011-2783-7_66</u>

- Jeppesen, E., Jensen, J.P., Sondergaard, M., Lauridsen, T.L., 2005. Response of fish and plankton to nutrient loading reduction in eight shallow Danish lakes with special emphasis on seasonal dynamics. Freshwater Biol 50, 1616–1627. <u>https://doi.org/10.1111/j.1365-2427.2005.01413.x</u>
- Jeppesen, E., Peder Jensen, J., Søndergaard, M., Lauridsen, T., Junge Pedersen, L., Jensen, L., 1997. Top-down control in freshwater lakes: the role of nutrient state, submerged macrophytes and water depth, in: Kufel, L., Prejs, A., Rybak, J.I. (Eds.), Shallow Lakes '95. Springer Netherlands, Dordrecht, pp. 151–164. <u>https://doi.org/10.1007/978-94-011-5648-6_17</u>
- Kasprzak, P., Padisák, J., Koschel, R., Krienitz, L., Gervais, F., 2008. Chlorophyll a concentration across a trophic gradient of lakes: An estimator of phytoplankton biomass? Limnologica 38, 327–338. <u>https://doi.org/10.1016/j.limno.2008.07.002</u>
- Kennedy, R.H., Cook, G.D., 1982. Control of lake phosphorus with aluminium sulphate. Dose determination and application techniques. J Am Water Resources Assoc 18, 389–395. https://doi.org/10.1111/j.1752-1688.1982.tb00005.x
- Larsen, D.P., Sickle, J.V., Malueg, K.W., Smith, P.D., 1979. The effect of wastewater phosphorus removal on shagawa lake, Minnesota: phosphorus supplies, lake phosphorus and chlorophyll a. Water Research 13, 1259–1272. <u>https://doi.org/10.1016/0043-1354(79)90170-2</u>
- Li, X., Sha, J., Wang, Z.-L., 2017. Chlorophyll-A Prediction of Lakes with Different Water Quality Patterns in China Based on Hybrid Neural Networks. Water 9, 524. <u>https://doi.org/10.3390/w9070524</u>
- McGarrigle, M.L. et al., 2009. Water quality in Ireland 2007–2009. Environmental Protection Agency, Wexford
- Nürnberg, G.K., 1984. The prediction of internal phosphorus load in lakes with anoxic hypolimnia1: Internal P load. Limnol. Oceanogr. 29, 111–124. <u>https://doi.org/10.4319/lo.1984.29.1.0111</u>
- Paul, W.J., Hamilton, D.P., Gibbs, M.M., 2008. Low-dose alum application trialled as a management tool for internal nutrient loads in Lake Okaro, New Zealand. New Zealand Journal of Marine and Freshwater Research 42, 207–217. <u>https://doi.org/10.1080/00288330809509949</u>
- Peters, A., Crane, M., Adams, W. 2011. Effects of iron on benthic macroinvertebrate communities in the field 86, 591-595. <u>https://doi.org/10.1007/s00128-011-0283-2</u>
- Psenner, R., Pucsko, R., 1988. Phosphorus fractionation: advantages and limits of the method for the study of sediment P origins and interactions. Arch Hydrobiol Beih Ergebn Limnol 30, 43– 59.
- Rydin, E., Huser, B., Welch, E.B., 2000. Amount of phosphorus inactivated by alum treatments in Washington lakes. Limnol. Oceanogr. 45, 226–230. https://doi.org/10.4319/lo.2000.45.1.0226
- Rydin, E., Welch, E.B., 1999. Dosing Alum to Wisconsin Lake Sediments Based on *in vitro* Formation of Aluminum Bound Phosphate. Lake and Reservoir Management 15, 324–331. <u>https://doi.org/10.1080/07438149909354127</u>
- Smolders, A.J.P., Lamers, L.P.M., Moonen, M., Zwaga, K., Roelofs, J.G.M., 2001. Controlling phosphate release from phosphate-enriched sediments by adding various iron compounds. Biogeochemistry 54, 219–228. <u>https://doi.org/10.1023/A:1010660401527</u>
- Søndergaard, M., Jensen, J.P., Jeppesen, E., 2003. Role of sediment and internal loading of phosphorus in shallow lakes. Hydrobiologia 506–509, 135–145. <u>https://doi.org/10.1023/B:HYDR.0000008611.12704.dd</u>
- Sparling, D.W., Lowe, T.P., 1996. Environmental Hazards of Aluminum to Plants, Invertebrates, Fish, and Wildlife, in: Ware, G.W., Gunther, F.A. (Eds.), Reviews of Environmental Contamination and Toxicology, Reviews of Environmental Contamination and Toxicology. Springer New York, New York, NY, pp. 1–127. <u>https://doi.org/10.1007/978-1-4612-2354-2_1</u>



Wauer, G., Teien, H.-C., 2010. Risk of acute toxicity for fish during aluminium application to hardwater lakes. Science of The Total Environment 408, 4020–4025. https://doi.org/10.1016/j.scitotenv.2010.05.033