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The University of Dublin

Fluvial Carbon Budgeting Across a Spectrum of Raised Bog Environments.

Peter Lebrocqy-Cox

Supervisors:

Prof. Laurence Gill, Dr. Shane Regan and Dr. Matthew Saunders

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An tSeirbhís Páirceanna Náisiúnta
agus Fiadhúlra
National Parks and Wildlife Service



Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhshaoil

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Table of Contents

1	Introduction	1
1.1	Fluvial Carbon of Peatlands.....	2
1.1.1	Particulate and Non-Particulate Organic Carbon.....	3
1.1.2	Evasion of CH ₄ and CO ₂	5
1.2	Ecohydrology of Raised Bogs	7
1.3	Project Aims	10
2	Methods and Equipment	11
2.1	Study Sites.....	11
2.1.1	Clara bog SAC	11
2.1.2	Garryduff.....	14
2.1.3	All Saints SAC.....	15
2.2	Equipment and Measurements	16
2.2.1	Discharge Measurements.	16
2.2.2	NPOC Measurements.....	17
2.2.3	Meteorological measurements.....	18
2.2.4	Micrometeorological measurements.....	19
2.2.5	Storativity measurements.....	20
2.2.6	Fluvial Gas Flux Evasion.....	22
2.3	Data Collection.....	25
2.4	Analysis	25
2.4.1	Flow	25
2.4.2	fDOM	27
2.4.3	Multivariate Analysis.....	28
2.4.4	NPOC Flux Measurements	28
2.4.5	Micrometeorological measurements.....	28
2.4.6	Storativity measurements from the microcosm experiments.....	29
2.4.7	Catchment area determination.....	30

2.4.8	Fluvial Gas Flux Evasion	30
3	Chapter 1 - Making Light Work: Using fDOM technology and multivariate analysis as a proxy to accurately estimate NPOC exports in temperate peatlands of varying conditions.....	32
3.1	Introduction	32
3.2	Methods and Equipment.....	36
3.2.1	Study Sites	36
3.2.2	Equipment and Measurements.....	36
3.2.3	Data Collection	36
3.2.4	Analysis.....	36
3.3	Results	37
3.3.1	fDOM	37
3.3.2	fDOM vs NPOC Linear Regression	38
3.3.3	fDOM vs NPOC Multivariate Analysis.....	41
3.3.4	Flux Measurements.....	44
3.4	Discussion.....	45
3.5	Conclusion.....	47
4	Chapter 2 - Insights into the hydrology and catchment delineation for three raised bogs in Ireland representing a range of ecological conditions.....	49
4.1	Introduction	49
4.2	Methods and Equipment.....	51
4.2.1	Study Sites	51
4.2.2	Equipment and Measurements.....	51
4.2.3	Data Collection	51
4.2.4	Analysis.....	52
4.3	Results	52
4.3.1	Evaluation of Eddy Covariance ET and PET	52
4.3.2	Comparison of the three peatlands across flow, hydrographs, effective rainfall and catchment	56

4.4	Discussion.....	63
4.5	Conclusion.....	66
5	Chapter 3 - Fluvial Carbon Exports for Irish raised bogs across a spectrum of conditions, investigating NPOC, CO ₂ and CH ₄	67
5.1	Introduction	67
5.2	Methods and Equipment	69
5.2.1	Study sites	69
5.2.2	Equipment and Measurements.....	69
5.2.3	Data Collection	69
5.2.4	Analysis.....	69
5.3	Results.....	70
5.3.1	Fluvial Gas Flux Evasion.....	70
5.3.2	NPOC Flux Estimations	73
5.4	Discussion.....	75
5.5	Conclusion.....	77
6	Discussion.....	79
6.1	The feasibility of using fDOM in-situ measurements as a proxy for NPOC concentration. 79	
6.2	The ecohydrology of three raised bog sites.....	80
6.3	The fluvial carbon exports the three bog sites	81
7	Conclusion & Recommendations for future research	83
8	References	86
9	Appendices.....	103
9.1	Appendix 1: Summary of peatland carbon studies.....	103
9.2	Appendix 2: Multivariate Analysis Equations	105
9.2.1	Proposed Theoretical Framework.....	105
9.2.2	Support Vector Regression (SVR)	106
9.3	Appendix 3: Chapter 1	108

9.3.1	Flow	108
9.3.2	Multivariate Analysis Results.....	115
9.4	Appendix 4: Chapter 2.....	120
9.4.1	Effective rainfall.....	120
9.4.2	Water table and storativity	123
9.5	Appendix 5: Muskingum Theory	133

Table of Figures

<i>Figure 1 Raised bog formation stages (Hammond, 1981).....</i>	<i>7</i>
<i>Figure 2 Clara Bog catchment and ecotopes. The discharge measurement spots are marked by the red X. Clara Upper (CLU) is the higher red x, Clara Lower (CLL) is the lower red X . The Eddy covariance tower is marked by the blue X. Map altered from Regan et al. (2020).</i>	<i>13</i>
<i>Figure 3 Garryduff Bog catchment. The discharge measurement spot is marked by the black X. The pump that is the closest to the flume and affects our study is marked by the blue X.</i>	<i>15</i>
<i>Figure 4 All Saints Bog catchment. The discharge measurement spots are marked by the two yellow triangles at the border of the catchment. The Eddy covariance tower and met station are placed at the red circle right of the centre of the catchment area.....</i>	<i>16</i>
<i>Figure 5 Installed flume in CL Upper natural stream.....</i>	<i>17</i>
<i>Figure 6 The steel drum microcosms which were installed on Clara, the silver one on the left had to be abandoned as it was too damaged during installation.....</i>	<i>21</i>
<i>Figure 7 The microcosms were installed at each of the ecotopes (GHG_locs). Bare peat was not measured.</i>	<i>21</i>
<i>Figure 8 The OTT sensor in AS was installed at Piezometer Network 29.....</i>	<i>22</i>
<i>Figure 9 The gas chamber</i>	<i>23</i>
<i>Figure 10 The water trap connected to the chamber and analyser.</i>	<i>23</i>
<i>Figure 11 The chamber placed on top of the collar which has been inserted tightly into a polystyrene insulation board which floats.</i>	<i>23</i>
<i>Figure 12 The LI – 7810 CH₄/CO₂/H₂O Trace Gas Analyser (LI-COR)</i>	<i>23</i>
<i>Figure 13 Chamber measuring in-situ at CL</i>	<i>23</i>
<i>Figure 14 The location of the chamber tests in CL - CL Upper (CL) and CL Lower (CLL)</i>	<i>24</i>
<i>Figure 15 The location of the chamber tests in Garryduff.....</i>	<i>24</i>
<i>Figure 16 fDOM (QSU) of Clara (a), Garryduff (b) and All Saints (c) with outliers removed and filled with linear interpolation.....</i>	<i>38</i>

Figure 17 CL corrected fDOM (QSU) plotted alongside the lab measured grab samples of NPOC (mg/L) (a)	
Garryduff corrected fDOM (QSU) plotted alongside the lab measured grab samples of NPOC (mg/L) (b)	
All Saints corrected fDOM (QSU) plotted alongside the lab measured grab samples of NPOC (mg/L) (c)	39
Figure 18 Scatter plots of the fully corrected fDOM vs lab measured NPOC, for CL, r squared: 0.427 (a),	
Garryduff, r squared: 0.000902 (b) and AS, r squared: 0.575 (c).	40
Figure 19 Predicted NPOC and measured NPOC timeseries for CL (a), GD (b) and AS (c).	41
Figure 20 The observed values of NPOC vs the estimated values based on linear regression and the CDF	
Inversion Method for CL (a), GD (b) and AS (c).	42
Figure 21 Time series of simulated NPOC and measured NPOC at CL (a), GD (b) and AS (c).	43
Figure 22 Scatterplot showing eddy covariance flux tower-based daily evapotranspiration rates (ET _{ec} in	
mm/day) versus potential evapotranspiration rates at CL (a) and AS (b). Note: Windspeed data used in the	
PET calculation was retrieved from the nearest Met Éireann weather station (Mullingar for CL and Gurteen	
for AS) as windspeed was not recorded at CL or AS.	54
Figure 23 Comparison of the trends in average daily ET and PET for the different months for CL (a) and AS (b).	
	54
Figure 24 Flow for CL Upper (a), Garryduff (b) and All Saints (c) flow monitoring sites across the whole	
measurement period including flume and OTT measurements.	56
Figure 25 The average half hourly flows (l/s) for each season per year in Clara (a), Garryduff (b) and All Saints	
(c).	57
Figure 26 Hydrographs for two heavy rain events during winter, December 2020 (a) and February 2020 (b) in	
Clara, December 2020 (c) and February 2023 (d) for Garryduff and December 2022 (e) and January 2023 (f)	
for All Saints.	59
Figure 27 Hydrographs for heavy rain events in summer, July 2021 (a) and July 2023 (b), for Clara, early July	
2020 (c) and late July 2020 (d) for Garryduff and July 2021 (e) and August 2021 (f) for All Saints.	60
Figure 28 The average effective rainfall (mm/day) for CL and AS for 2021 (a), 2022 (b) and 2023 (c).	62
Figure 29 The Daily values of C (combined CH ₄ and CO ₂ , both measured in gC/day), CH ₄ and CO ₂ export for	
CL (a) and GD (b).	71
Figure 30 The average CO ₂ and CH ₄ flux (g CO ₂ -C eq/m ² /day) per season for CL (a) and GD (b).	73
Figure 31 The monthly load of NPOC in kg exported across the measurement period in CL (a) and GD (b).	74
Figure 32 CL Upper flow data after basic filtering	108
Figure 33 CL Upper flow data after basic filtering and outlier detection and removal using β criterion of 1.5.	
	109
Figure 34 Water level (mm) plotted against flow (l/s) for CL Upper, r squared: 0.97	110
Figure 35 Garryduff flow data after basic filtering	110
Figure 36 Garryduff flow data after basic filtering and outlier detection and removal using β criterion of 2.5	
and a window of 50.	110
Figure 37 Water level data (mm) from the OTT sensor before Garryduff Flume	111
Figure 38 All Saints flow data after basic filtering	112

<i>Figure 39 All Saints flow data after basic filtering and outlier detection and removal using β criterion 2.5 (a) and a window of 50</i>	112
<i>Figure 40 Raw fDOM (QSU) for Clara (a), Garryduff (b) and All Saints (c).</i>	112
<i>Figure 41 CL fDOM (QSU) filtered for conductivity (a), CL fDOM (QSU) filtered for turbidity (b), CL fDOM (QSU) corrected for temperature (c) and CL fDOM (QSU) with outliers removed.</i>	113
<i>Figure 42 Garryduff fDOM (QSU) filtered for conductivity (a), Garryduff (QSU) corrected for turbidity (b), Garryduff fDOM (QSU) corrected for temperature (c) and Garryduff fDOM (QSU) with outliers removed (d).</i>	114
<i>Figure 43 All Saints fDOM (QSU) filtered for conductivity (a), All Saints fDOM (QSU) corrected for temperature (b), All Saints (QSU) corrected for turbidity (c) and All Saints fDOM (QSU) with outliers removed (d).</i>	114
<i>Figure 44 Scatter plot of CL, r squared: 0.874 (a), Garryduff, r squared: 0.977 (b) and All Saints, r squared: 0.382 (c) fDOM (QSU) vs fDOM Inner filter effects (QSU)</i>	115
<i>Figure 45 shows the observed values of NPOC vs the estimated values based on linear regression and the CDF Inversion Method for CL Upper.</i>	117
<i>Figure 46 shows the observed values of NPOC vs the estimated values based on linear regression and the CDF Inversion Method for Garryduff.</i>	119
<i>Figure 47 the observed values of NPOC vs the estimated values based on linear regression and the CDF Inversion Method for All Saints.</i>	120
<i>Figure 48 Clara flow with effective rainfall (mm/day)</i>	121
<i>Figure 49 All Saints flow with effective rainfall</i>	122
<i>Figure 50 Eddy covariance flux tower-based daily evapotranspiration rates (ETec in mm/day) and potential evapotranspiration rates (PET, Penman-Monteith FAO56 formulation [PM-FAO56, short grass reference]) at CL. Note: Windspeed data used in the PET calculation was retrieved from the nearest Met Éireann weather station (Mullingar) as windspeed was not recorded at All Saints. PET on days with missing was interpolated using monthly averages (mostly at the start of 2023).</i>	122
<i>Figure 51 Eddy covariance flux tower-based daily evapotranspiration rates (ETec in mm/day) and potential evapotranspiration rates (PET, Penman-Monteith FAO56 formulation [PM-FAO56, short grass reference]) at AS from March 2021 to December 2023. Note: Windspeed data used in the PET calculation was retrieved from the nearest Met Éireann weather station (Gurteen) as windspeed was not recorded at All Saints. PET on days with missing was interpolated using monthly averages (mostly at the end of 2023).</i>	123
<i>Figure 52 The water level data (m with respect to ground level) for CL marginal (a), sub-marginal (b), central ecotopes (c) and sub-central (d) ecotopes</i>	124
<i>Figure 53 The mean water level data (m with respect to ground level) for All Saints</i>	124
<i>Figure 54 The mean water level height (mm with respect to ground level) inside and outside the microcosm and the rainfall (mm) for the Central (a), Marginal (b) Sub-Central (c) and Sub-Marginal (d).</i>	128
<i>Figure 55 The storativity curves calculated from rainfall and water table changes (a) inside the microcosm at CL Central ecotope and (b) outside the microcosm, p-value (Welch's t test) = 0.04.</i>	130

Figure 56 The storativity curves calculated from rainfall and water table changes (a) inside the microcosm at CL Marginal and (b) outside the microcosm, p-value (Welch's t test) = 0.1498	132
Figure 57 The storativity curves from Swenson, Regan and Gill (2020), for inside the four microcosms at Abbeyleix Bog, Co. Laois - (a) Eriophorum Cutover, (b) Sub-Marginal, (c) Sub-Central, and (d) Sphagnum Cutover locations. The blue lines are the idealized storativity curves. The yellow dots indicate where rainfall data from offsite had to be used.	132
Figure 58 Daily potential evapotranspiration rates (PET, Penman-Monteith FAO56 formulation [PM-FAO56, short grass reference]) at GD from January 2021 to March 2023. Note: Net radiation data from All Saints was used in the calculation of PET as Gurteen Met Éireann weather station lacks records on it. PET on days with missing was interpolated using monthly average).	132

Table of Tables

Table 1 The characteristics of the ecotopes at Clara (Regan et al., 2020)	13
Table 2 The location and distance of rainfall data used for each study site. All weather data was taken from Met Eireann Historical Weather Data site.	19
Table 3 The number of evasion samples taken each month through the study period for CL and GD	31
Table 4 Comparison of the minimum, maximum and standard deviation of the NPOC outputs from autosamples, linear regression and multivariate analysis.....	44
Table 5 The derived NPOC fluxes (g/m ²) from the bogs using the continuous fDOM measurements converted into NPOC using linear regression and multivariate analysis was undertaken. Figures in bold are for full annual (12-month) monitoring.	44
Table 6 The Effective Rainfall (ER in mm) of the different sites depending on whether ETec or PET was used, where ER = Rainfall – ET.	55
Table 7 The catchment sizes of the sites calculated with PET and ETec as a comparison.	55
Table 8 The crop coefficients of CL, GD and AS using ETec values for each year.	56
Table 9 Comparison of annual ET for all sites. *For GD, ET was estimated using Kc from AS 2022.	61
Table 10 The catchments derived for the sites using discharge, ETec and rainfall.	63
Table 11 Average seasonal flux for CO ₂ and CH ₄ (g CO ₂ -C eq/m ² /day) and annual average for Clara	72
Table 12 Average seasonal flux for CO ₂ and CH ₄ (g CO ₂ -C eq/m ² /day) and annual average for Garryduff ...	72
Table 13 The CO ₂ and CH ₄ evasions for Garryduff and CL in 2022. 2022 was the only complete year of measurements.	72
Table 14 The Partial Rank Correlation Coefficients (PRCC) from the Monte Carlo sensitivity analysis of NPOC export to flow, NPOC and catchment for CL and GD.	73
Table 15 The NPOC flux (g C/m ²) for the sites during their measurement periods. The cells in green indicate which fluxes can be compared to each other for each year.	75
Table 16 Summary of peatland carbon study sites.	103

<i>Table 17 Summary of data from peatland carbon studies described in Appendix 1 Summary of peatland carbon studies</i>	<i>104</i>
<i>Table 18 The NSE goodness of fit results for the different models used for determining the variables that best described the relationship between fDOM and NPOC for CL, using different time windows. Where Y is fDOM, C is Conductivity, T is Water Temperature, Q is Discharge, R is Rainfall, E is the expectation function and Var is the variance of the data.</i>	<i>116</i>
<i>Table 19 The different models used for determining the variables that best described the relationship between fDOM and NPOC for GD. Where Y is fDOM, C is Conductivity, T is Water Temperature, Q is Discharge, R is Rainfall, E is the expectation function and Var is the variance of the data. Values are in NSE and the value in bold is the one that was used.</i>	<i>118</i>
<i>Table 20 The different models used for determining the variables that best described the relationship between fDOM and NPOC for AS. Where Y is fDOM, C is Conductivity, T is Water Temperature, Q is Discharge, R is Rainfall, E is the expectation function and Var is the variance of the data. Values are in NSE and the value in bold is the one that was used.</i>	<i>119</i>
<i>Table 21 The water level data for CL and All Saints, with mean, minimum and maximum values. *As there wasn't a complete year of data for 2022, the data from June – Dec 2022 was compared to the same period of 2023.</i>	<i>125</i>
<i>Table 22 The mean, minimum and maximum water level inside and outside the microcosms for each microcosm site at CL.....</i>	<i>126</i>

1 Introduction

Globally peatlands cover approximately 3% of Earth's land area and store ~44% of global soil carbon (IUCN, 2021) which is more carbon than is contained in the world's tropical rainforest biomass (Page, Rieley and Banks, 2011). Annually, they sequester approximately 0.37 gigatonnes of carbon dioxide (CO₂) (Yu *et al.*, 2011) which is about 17% of the total GHG emissions of the EU between 1990 and 2021 (Statista, 2023). Therefore, the conservation and restoration/rehabilitation of peatlands as high-carbon systems have been identified as a climate change mitigation option of immediate benefit (IPCC, 2023).

In Ireland, peatlands are estimated to store two-thirds of the total national soil carbon stock (Renou-Wilson *et al.*, 2022). When comparing Special Area of Conservation (SAC) raised bogs in 1994 to 2012/13, there has been an approximate loss of 37%, which is of particular concern as 60% of the intact raised bogs in Western Europe are located within Ireland (National Parks and Wildlife Service, 2017). It is estimated that around 80% of Irish peatlands have been damaged to some extent by anthropogenic disturbances such as draining or mining (Renou-Wilson *et al.*, 2022; Fluet-Chouinard *et al.*, 2023).

Given their importance for storage and sequestration, the rehabilitation of peatlands is a priority in the most recent Climate Action Plan of Ireland, aiming to rehabilitate 77,600 hectares of peatlands across numerous landowners and projects (Government of Ireland, 2023). The EU's Recovery and Resilience Facility, through the National Recovery and Resilience Plan, is investing up to €108 million in the Enhanced Decommissioning, Rehabilitation and Restoration Scheme (EDRRS) for the rehabilitation of 33,000 hectares of peatlands across 82 bogs owned by Bord na Móna (Department of Public Expenditure, NDP Delivery and Reform, 2021). Bord na Móna have currently rehabilitated over 19,700 hectares of bog as of 2024 (Bord na Móna, n.d.) as part of its decarbonisation and rehabilitation strategy. Coillte, Ireland's semi-state forestry company, has multiple projects on peatland restoration, such as the Wild Western Peatlands project which aims to restore and rehabilitate approximately 2,100 hectares of Atlantic blanket bog and wet heath (Coillte, 2020). The NPWS of the Department of Housing, Local Government and Heritage have also committed to invest €12 million in the rehabilitation and restoration of degraded wetlands across multiple project sites (Government of Ireland, 2023).

In light of the national emphasis on peatland restoration, there is a need to improve the technical basis for monitoring sites during rehabilitation to quantify the fluxes of carbon in the systems. This technical need is reflected in Action 12 of the Peatlands and Climate Change Action Plan 2030, '*Long-term greenhouse gas monitoring projects on peatlands (to include dissolved organic carbon)*

need to be established for all peatland in a continuum from intact sites through to sites with a thin coating of peat to allow for reporting of the success of restoration and rehabilitation in terms of greenhouse gas reduction' (Irish Peatland Conservation Council, 2021). One of the key principles of the National Peatlands Strategy (Principle 19) also identifies this as a need '*...The immediate priority will be to address research requirements in relation to rehabilitation, restoration and enhancement and to establish the information required to support the development of an informed policy position. This will include the development of a sound technical basis for analysis and reporting of greenhouse gas emissions and removals associated with wetlands'* (National Parks and Wildlife Service, 2015). In line with the commitments of the Peatland and Climate Change Action Plan 2030, The National Peatland Strategy and the Climate Action Plan 2023, it is important to better understand how to manage these systems to maintain and restore peat soils for carbon storage. This requires a knowledge of how carbon enters and leaves the system, through a comprehensive assessment of the Net Ecosystem Carbon Balance (NECB).

1.1 Fluvial Carbon of Peatlands

The Net Ecosystem Carbon Balance (NECB) of peatlands consist of net ecosystem exchange (NEE) (which is the balance between Gross Primary Productivity (GPP) and ecosystem respiration (ER) in terms of carbon dioxide); net methane (CH₄) consumption or efflux; and the net gain or loss of C in water inputs and runoff (including total organic carbon, dissolved inorganic carbon and CH₄) (Chapin *et al.*, 2006).

The NEE, the difference between fixation of C via photosynthesis and emission of C through ecosystem respiration, of peatland systems is relatively well-researched compared to the other components. In general, near natural sites have been found to assimilate between 47 and 205 g C/m²/year whereas degraded sites generally emit between 189 and 492 g C/m²/year (See Table 16 and Table 17, Appendix 1). However, the carbon losses via fluvial carbon pathways are not adequately quantified and remain a key knowledge gap. This area of research is important, as fluvial carbon has been shown to account for 15-50% of all Greenhouse Gas (GHG) emissions from drained and rewetted peatlands (Evans, Renou-Wilson and Strack, 2016) and in some cases changing annual carbon budgets of peatlands from sources of carbon to sinks of carbon when included (Billett *et al.*, 2006).

There are two pathways in which carbon can leave through fluvial pathways: in the form of dissolved or particulate carbon as water flows out of the system, and also as evaded gasses through the surface water to atmosphere exchange.

The following sections explore these different species of carbon and their roles in the GHG balance of peatlands.

1.1.1 Particulate and Non-Particulate Organic Carbon

Carbon enters water from organic soils when the water is in contact with the soils, which is then exported as Non-Particulate Organic Carbon (NPOC) and Particulate Organic Carbon (POC), differentiated based on their particle size (Hope, Billett and Cresser, 1994). This pathway has been shown to significantly influence the overall carbon balance of peatlands (Evans, Renou-Wilson and Strack, 2016). One example of this is Billett *et al.* (2004) where the water borne carbon flux was found to be 30 g C/m²/yr, which meant that the peatland was a net source of carbon, rather than sink. Additional studies have underlined the quantitative importance of NPOC, which was estimated to account for up 80% of total fluvial export (Roulet *et al.*, 2007; Nilsson *et al.*, 2008; Koehler, Sottocornola and Kiely, 2011; Prijac *et al.*, 2023).

In natural or near-natural peatlands the amount of POC exported tends to be small (Evans, Renou-Wilson and Strack, 2016) due to the small proportion of exposed peat soil and the soil in general being bound up or protected by overlying vegetation and water. However, POC export can be significant in active extraction sites (Worrall *et al.*, 2011). It should be noted that the sites in this study are in different stages of rehabilitation with no extraction occurring and therefore POC has not been included in this study, however given that it could be important, it is a potential route for further study.

NPOC plays an important role in the carbon balance of peatlands as any change in NPOC emissions will lead to a significant redistribution of the terrestrial carbon on a regional scale (Limpens *et al.*, 2008). NPOC is produced from the microbial decomposition of organic material and therefore one of the main drivers of its production are the biological and physical processes related to microbial activity (Armstrong *et al.*, 2012). However, the movement of water and its retention time in contact with the organic soil is also an important driver. Longer retention times and slow water movement lead to lower NPOC exports while shorter retention time and faster moving water leads to higher NPOC exports (Prijac *et al.*, 2023). The loss of NPOC from peat soil is controlled by the combination of production, diffusion, solubility, and transport (Fenner, Freeman and Worrall, 2009; Prijac *et al.*, 2023).

Due to the influence of biological agents, vegetation and physical soil properties on NPOC, there are significant temporal variations associated with NPOC, with higher NPOC detected in the summer months due to increased air and soil temperatures and water discharge rates (Regan *et al.*, 2020).

NPOC concentrations in surface waters have been increasing in the last decade in boreal and temperate areas in the Northern Hemisphere, with peatlands identified as one of the main sources of this NPOC (Roulet and Moore, 2006; Monteith *et al.*, 2007; Garmo *et al.*, 2014; de Wit *et al.*, 2016; Björnerås *et al.*, 2017; Kankaala *et al.*, 2019). Anthropogenic pressures such as land use change and climate change on peatlands are a driver of this increase in NPOC, due to the modification of water flows and water table levels (Moore *et al.*, 2013; Nieminen, Sarkkola and Laurén, 2017; Cook *et al.*, 2018; Brown, Goulsbra and Evans, 2019).

Typically, NPOC is measured using lab-based measurements that provide discrete results, and is often used to compare the accuracy of other NPOC estimation methods (Downing *et al.*, 2012; Lee *et al.*, 2015). The method is relatively simple, involving the collection of water samples on site, and then the analysis of the samples using High-Temperature Combustion (HTC). It does, however, requires on site frequent sampling which can be expensive and time consuming.

Auto sampling regimes can also be used to collect more frequent samples, whereby an autosampler is programmed to collect water samples, typically every hour, during a storm event. The issue with this is that it requires accurately predicting the exact timing of the storm events and also being out in the field during those conditions (Saraceno *et al.*, 2009; Pellerin *et al.*, 2012). It also requires the samples to be left out for the duration of the measurement, prolonging the time before the samples can be acidified and correctly stored before analysis.

For more continuous measurement of NPOC that don't require someone to collect water samples on site, ultraviolet-visible (UV-VIS) spectrophotometric sensors have been used with reasonable accuracy (Jeong *et al.*, 2012; Jollymore, Johnson and Hawthorne, 2012; Etheridge *et al.*, 2013; Lee *et al.*, 2015), as well as sensor technology that detect fluorescent Dissolved Organic Matter (fDOM). Both methods have been seen to perform similarly for the estimation of NPOC (Lee *et al.*, 2015; Wang *et al.*, 2021).

This study focusses on fDOM as a method of estimation for NPOC. The method has proven to be inexpensive and effective methods for coastal (Vodacek *et al.*, 1995; Coble, Del Castillo and Avril, 1998; Chen, 1999) and freshwater systems (Saraceno *et al.*, 2009; Pellerin *et al.*, 2012), with more recent deployment in boreal peatland systems (Prijać *et al.*, 2023). Because it is in situ, it can provide more high frequency data over a long period of time, including data during storm events (Saraceno *et al.*, 2009; Pellerin *et al.*, 2012). However, this method requires a determination of the relationship between fDOM and NPOC, which is site specific (Downing *et al.*, 2012; De Oliveira *et al.*, 2018), therefore the sensors need to be deployed on site for a while to compare the fDOM derived NPOC to grab samples NPOC. Additionally, there are important factors which can interfere

with the accuracy of these measurement systems that have to be accounted for as the fDOM method requires a lot of filtering of data before the relationship between fDOM and NPOC can be determined (Saraceno *et al.*, 2009). It also requires a lot of overseeing as they can be subject to damage and harsh weather conditions (Pellerin *et al.*, 2012). Peatlands are highly turbid due to particulates and dissolved matter which can pose a problem for the sensors which are typically deployed in clear water systems. Any suspended particles may scatter light while dissolved matter may absorb some of the light emitted by the sensors (Saraceno *et al.*, 2017). Additionally, pH and temperature can affect the intensity of the light emitted (Spencer, Bolton and Baker, 2007; De Oliveira *et al.*, 2018), although the pH that would likely affect this is not typically seen in most natural systems (Piana and Zahir, 2000; Patel-Sorrentino, Mounier and Benaim, 2002; Spencer, Bolton and Baker, 2007). Temperature has been shown to have an inverse relationship with fDOM: with higher temperatures there is a higher probability of excited electrons in the water, reducing fluorescence intensity (Henderson *et al.*, 2009a; De Oliveira *et al.*, 2018). Another important interaction is the inner filter effect (IFE) which is the distortion of band shape and/or a decrease in emission quantum yield (Downing *et al.*, 2012; De Oliveira *et al.*, 2018). Therefore, the important factors to account for when using fDOM readings as a proxy for NPOC are turbidity, temperature and IFE.

In the context of Irish peatlands, further research into fluvial carbon is important as it has been shown that the magnitude of the fluvial carbon flux is found to nearly double when peat is drained on the bog margin, reverting the bog into a significant source of carbon (Regan *et al.*, 2020). Given the various conditions of peatlands in Ireland, it is important to be able to quantify the movement of fluvial carbon in these systems in order to better understand their overall carbon cycle. However, due to the temporal variation of NPOC, there is a need for high temporal data using in situ measurements. Field-based sensors for measuring NPOC proxies, fDOM and turbidity, for boreal peatlands have been carried out, for NPOC concentrations between 0.9 and 24.2 mg/L (Prijac *et al.*, 2023). However, these methods have not yet been executed for temperate peatlands.

1.1.2 Evasion of CH₄ and CO₂

The role of evasion in overall C export for rivers, streams and lakes has been emphasised in many studies, with significant fluxes in CO₂ evasion seen for these systems, despite their overall low land surface cover (Cole and Caraco, 2001; Drake, Raymond and Spencer, 2018; Horgby *et al.*, 2019).

The evasion of methane (CH₄) and carbon dioxide (CO₂) from drainage channels and standing water is a less understood aspect of peatland emissions. Methane and carbon dioxide can be emitted directly from a water's surface to the atmosphere along a concentration gradient (Hope *et al.*,

2001; Billett *et al.*, 2004; Billett and Moore, 2008), which can create significant partial pressure differences across the air–water interface. Supersaturation of CO₂ and CH₄ therefore in the water is a driver of evasion of these gasses from the surface of water. However, the flow of water is also an important driver (Hope *et al.*, 2001; Billett *et al.*, 2004). A comparison of surface water gas concentration and evasion rates at open waters and flowing water show a significant correlation between evasion rate and concentration of CO₂ and CH₄ in open waters but not in water with more turbulence (Billett and Moore, 2008). This means that in open waters, the degassing of the water is driven by partial pressure but in areas with more surface turbulence, the degassing occurs due to the disturbance resulting in higher emissions. When measuring evasion with floating chambers, therefore, it must be taken into account that the chamber itself may be adding to the disturbances or indeed reducing the disturbances by shielding the water from wind.

Evasion of CH₄ varies between different peatland sites. Emissions from drainage ditches in peatland sites are higher than the emissions from the terrestrial peat surface within the sites (Minkinen and Laine, 2006). In one study, drainage ditches which covered approximately 5% of the land accounted for 84% of CH₄ emissions (Teh *et al.*, 2011). The intensity of land use has also been correlated to the increase in mean CH₄ emissions from drainage ditches, ranging from drained blanket bog and drained forested peatlands to grasslands and peat extraction sites (Evans, Renou-Wilson and Strack, 2016). There are two processes by which CH₄ is produced and emitted from drainage ditches. The first is methanogenesis (a process by which methane is produced) within the peat, which is then laterally transported into the ditches. The second is methanogenesis from within the drain's own sediment (Roulet and Moore, 2006). As to which one of these processes is the predominant source of CH₄ is still a matter of some debate (Evans, Renou-Wilson and Strack, 2016).

A study looking at the CO₂ emissions from multiple peat extraction sites showed no significant difference in CO₂ evasion between drainage ditches and drained peat soils (Sundh *et al.*, 2000). There is little research to date on how these emissions may differ between drained and undrained sites. One study looking at this question found that the mean CO₂ emissions for four undrained peatland sites was 12 g/C/m²/year, whereas four drained sites had a mean emission rate of 24 g C/m²/year (Rantakari *et al.*, 2010). It's important to note that as peatland drains tend to be slow moving, the CO₂ may not be evaded until further downstream where turbulence increases, meaning these emissions may be considered as off-site emissions.

Once the method of calculating NPOC is verified and CO₂ and CH₄ evasion is measured, there is a need to better understand the peatland ecohydrology to determine pathways of flow that will affect the carbon losses and gains through the water.

1.2 Ecohydrology of Raised Bogs

Natural, intact, raised bogs have a characteristic dome shape above a regional groundwater table (Figure 1). Raised bogs are ombrotrophic whereby the vegetation surface does not receive any direct inputs from the regional groundwater and mineral soils (Figure 1), making raised bogs low in mineral nutrients and poorly buffered, acidic systems.

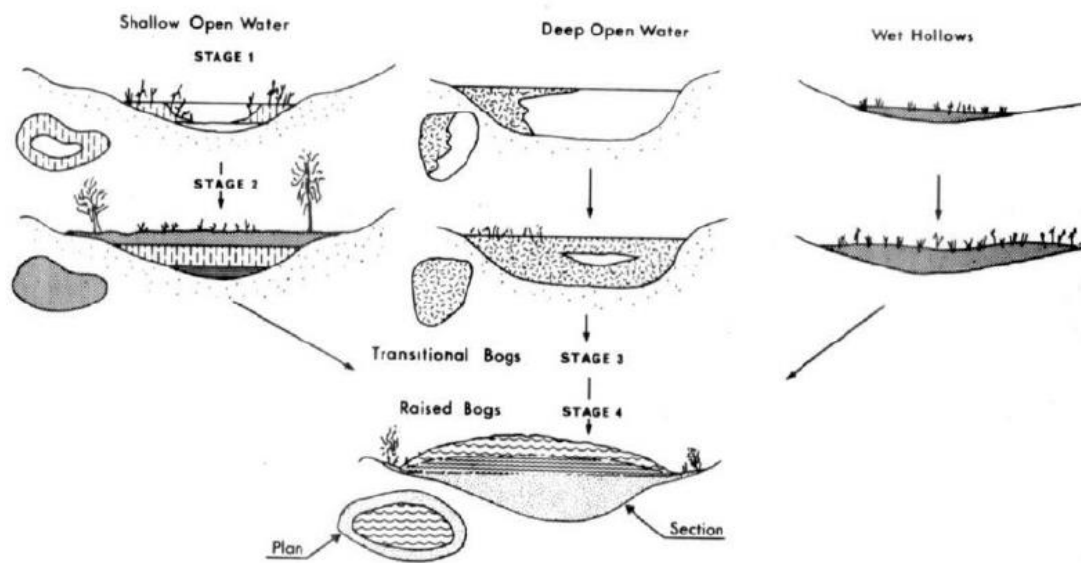


Figure 1 Raised bog formation stages (Hammond, 1981)

Though the raised bog is several meters above the more regional groundwater table, if the bog is intact, it is permanently saturated. This hydrology of the raised bogs can be understood by looking at the diplotelmic conceptual model of raised bogs (Ingram, 1978).

When conceptualising the ecohydrology of a raised bog system two main storages are usually considered that have different responses to precipitation inputs. The biggest storage is the catotelm, which sits on or in the regional groundwater body and consists of permanently saturated and well-decomposed compressed peat soil, with low hydraulic activity and has no peat forming aerobic microorganisms. The hydraulic connection between the groundwater body and the catotelm will vary across different raised bogs. Although in most cases the traditional view of these systems as being distinct from deeper groundwater seems to be the case, in some instances, where more permeable materials underlie them, deeper groundwater can affect the hydrology of the bog ecosystem through hydraulic gradients between the wetland and substrate materials. This can be more commonly seen in low-lying peatland ecosystems, such as fens (Lowry, Fratta and Anderson,

2009; Johansen, Pedersen and Jensen, 2011; Rossi *et al.*, 2012), where in these cases the positive upward hydraulic gradients leads to an actual recharge of water into the fens from the underlying aquifer. In contrast in raised bogs the hydraulic gradient may instead be providing upward hydrostatic pressure but without upward flow ingressing into the bog itself (Regan *et al.*, 2019).

The smallest of the two storages is the acrotelm, which has high hydraulic conductivity, an oscillating water table, variable water content, is subject to periodic entry of air after lowering of water table, is rich in peat forming aerobic bacteria and is mainly dominated by *Sphagnum spp.* mosses (Ingram, 1978). The acrotelm is considered the active layer as the residence time of water in this layer is much less than in the catotelm. While an acrotelm is a thin layer, it has a large effect on the hydrology due to its higher hydraulic conductivity (and transmissivity) and storativity compared to the catotelm (Boelter, 1968; Price, 2003; McCarter and Price, 2015; Swenson, Regan and Gill, 2020).

The dynamics of the water table relative to the ground level will determine the stability of the acrotelm. The conditions that favour the persistent high water tables are (Regan *et al.*, 2020):

1. Minimal downwards infiltration/seepage and fluid flow at depth.
2. Shallow topographic gradient limiting the velocity of discharge and increasing recharge.
3. Build-up of poorly humidified organic materials, which provide storativity in the upper peat.

The porous structure of the *Sphagnum* is conducive to runoff and storage processes. To maintain *Sphagnum* on the acrotelm, the mean water level needs to be within 10-15 cm of the surface all year round. The low threshold is a result of the evapotranspiration which is directly replaced by either precipitation or capillary transport from the water table (Robroek *et al.*, 2009). The ground level of a bog, however, is not static as the surface rises or falls as a result of rainfall, drought or gas volume (Ingram, 1983; Camporese *et al.*, 2006). This is an important aspect of maintaining the relatively narrow specifications for *Sphagnum spp.* growth in a healthy bog.

The catotelm has a more delayed response to precipitation and is far less transmissive than the acrotelm. Any disturbance or damage to the regional groundwater can have more significant effects on peatland hydrology than disturbance to surface hydrology (Regan *et al.*, 2020). The hydraulic conductivity (K) profile of peat controls the rate of subsurface drainage. This, combined with the hydrogeological properties of peat, control the water flow and storage processes in peatlands (Beckwith, Baird and Heathwaite, 2003; Price, 2003). A catotelm will naturally act as a barrier to vertical and lateral flow as long as it is saturated and intact.

For peatlands that have been extracted, the drainage required for these activities would alter the natural hydrology of the peat. Artificial drainage lowers the water table in the areas around the drain as the drains dissect the natural flow routes of water (Holden *et al.*, 2006). The drier conditions also alter the vegetation community of the peatland, favouring shrubs and trees over *Sphagnum* (Laine, Vasander and Laiho, 1995; Murphy, Laiho and Moore, 2009). The dry conditions also facilitate the oxidation of the peat, which leads to carbon being exported into the air or water in the form of CO₂ or NPOC (Rowson *et al.*, 2010). There is also increased sensitivity of runoff response to storm rainfall in drained peatlands (Holden, Chapman and Labadz, 2004; Holden *et al.*, 2006).

Restoration efforts in the form of rewetting affect the hydrology of the peatland as well, though this effect is dependent on how long the peatland was drained and extracted (Laine, Vasander and Laiho, 1995; Parry, Holden and Chapman, 2014). The damming of drains and rewetting of peatlands can increase the water table immediately around the dams, but less so the further away from the dam (Gaffney *et al.*, 2020). Even when the water table recovers, there may not be immediate vegetation recovery depending on the effectiveness of the damming and the season of restoration works, it can be between 3 and 15 years (González and Rochefort, 2014; Gaffney *et al.*, 2020). Simulation of the effect of drainage and rewetting, showed that most of the peat loss occurs between 50 and 100 years during drainage, most of which is not regained even after 200 years of rewetting (Young *et al.*, 2017), therefore the restoration process takes a significant amount of time, and it is also difficult to identify when the restoration process will rehabilitate the peatland to pre-drainage levels, if at all.

This project focuses on the following key aspects of water flow in a bog in relation to dissolved carbon and to better understand its ecohydrology: rainfall, evapotranspiration and runoff vs water that permeates the bog.

Given the importance of *Sphagnum* in the carbon cycle of a bog and its dependence on water levels, the study of the ecohydrology of bogs is important for better management of the bog sites in general and the understanding of climate change impacts. Understanding the ecohydrology of a bog requires insights into its inputs and outputs. Swenson *et al.* (2020) used microcosms combined with evapotranspiration and rainfall data in the field to understand the dynamics of shallow lateral flow of Abbeyleix bog. They found that the timing and magnitude of the lateral flow differed considerably between locations with differing ecological conditions. Where *Sphagnum* moss layer was present, the upstream catchment provided a slow continuous net lateral input of water supporting the water table during drought periods, however this was not observed in

locations lacking *Sphagnum*. In this study, we are using the microcosm methodology combined with active and calculated measurements of evapotranspiration, met station data and outflow data through flumes.

The sites in this study have differing ecohydrological conditions (further explained in Section 2.1), with Clara bog as a near natural site with typical bog vegetation, All Saints bog as a recently extracted site undergoing rehabilitation with sparse vegetation and Garryduff bog as a recently extracted site with water pump systems still in place, at the very beginning of rehabilitation. The impact of these differing conditions will be analysed in this study, in relation to fluvial carbon fluxes.

1.3 Project Aims

The aims of this project are to assess the impacts of peatland degradation and rehabilitation to better inform management or resilience to climate change by asking the following questions:

1. Can fDOM can be used as a proxy for NPOC in temperate raised bogs of high NPOC concentration and if so, to what accuracy?
2. What are the ecohydrological differences between three raised bogs under different levels of rehabilitation that may influence their fluvial carbon fluxes?
3. What are the differences in the overall fluvial carbon fluxes of these bogs and the drivers of these fluxes?

The specific objectives of this project which will achieve the overall project aims are:

1. To collect half hourly fDOM data using EXO 2 multi-Sonde fDOM sensors in 3 peatland sites for 2 years to compare to lab-measured NPOC from grab samples. The relationship between fDOM measurements and NPOC derived from lab-based measurements of in situ samples are compared, using simple linear regression and multivariate analysis as two methods of comparison.
2. To determine the ecohydrology of three raised bog sites based on management, active and calculated measurements of evapotranspiration, met station data and outflow data through flumes and one-dimensional microcosms.
3. To combine measurements of NPOC and evading CO₂ and CH₄ to determine the fluvial carbon export of two peatland sites in Ireland and how that contributes to their overall fluvial carbon fluxes.

2 Methods and Equipment

2.1 Study Sites

2.1.1 Clara bog SAC

Clara bog is located 53° 19'N, 7° 37'W in the midland region of Ireland. It is a raised bog in the Irish midlands and in the last 200 years its surface area has reduced by over 50% due, largely, to human activities such as land use change and peat extraction (Crushell *et al.*, 2008). It has an Atlantic temperate climate with an average annual rainfall of 1047 mm and an average annual temperature of 10.05 °C during this study period (Met Éireann, 2023b).

Clara bog is currently protected under the Habitats Directive as a Special Area of Conservation (SAC) under the European Missions Directive of 1992 and is a Ramsar Site of International Importance. The site also boasts a high biodiversity and is an important ecosystem for the red listed Curlew (*Numenius arquata*) and a breeding site for the amber listed Merlin (*Falco columbarius*).

In 1987, the bog was declared a Natural Nature Reserve and its restoration was undertaken by the insertion of over 6000 peat dams into existing drains between 1993 and 1996. However, peat cutting for domestic use was still allowed until 2008 (Crushell *et al.*, 2008). Peat cutting for domestic use has led to a 4% loss of area in Clara west and a 5% loss in Clara East between 1973 until 2017 (Regan *et al.*, 2020). Clara bog is considered a near-natural raised bog, having been relatively undisturbed in the last 20 years, making it a good case study for the hydrology of near natural raised bogs.

Clara bog is separated into two distinct hydrological catchments by a road that cuts through the site separating CL East from CL West. Clara East was extensively drained from the 1980s until 1996 when the work of blocking the drains was undertaken. Clara West is much more intact with just two drains, one running parallel to the road and the other at the southern margin. The blocking of the drains in Clara East has led to the areas of the site that have been restored to active raised bog. Clara West has changed morphologically with lakes and tension cracks forming. There has also been a loss in active raised bog in Clara West of more than 40% between 1991 and 2017. This study will focus on Clara West (Figure 2).

An esker and gravel complex bound the northern side of Clara bog, with finer gravel carbonate-rich till deposits on its southern side. Underneath these deposits lies a Mississippian Waulsortian Limestone bedrock. This bedrock acts as a moderately productive aquifer as groundwater can only pass-through faults and fissures within the matrix of the bedrock. Till deposits underlie

approximately 40% of the bog, with a thickness ranging from 4 to 6 m around the margins and cutover areas to between 8 to 10 m closer to the central areas of the bog. Depth to bedrock is between ~14 m, at a ridged area in the centre of the bog, to ~20 m, near the southern margin. The components of the till matrix are clay-silt and sand; the proportion of gravel in this matrix increases with depth. Areas of shallow peat depth, less than 3 m in depth, are associated with areas where till mounds underlie the peat which can be seen in the south-central area of the site. Areas of deep peat depth, 8 to 10 m in depth, have fine grained laminated lacustrine clay underneath which can be between 0.2 and greater than 4 m in thickness. Overlaying this are calcareous marl deposits in the south-eastern part of the site.

In the western and eastern areas of the site there are fine to coarse grained particles of sand, in layers less than 20 cm thick.

The vegetation succession in Clara is grouped into ecotopes which are vegetation communities with similar characteristic water table depths, fluctuations and hydrochemistry (van der Schaaf and Streefkerk, 2002). They classify the ecological quality of habitat areas and represent a hydrological sequence from dry to permanently saturated zones within the bog.

There are four main ecotopes that concern this study – central, sub-central, sub-marginal and marginal. Their main differences are based on the presence of hummocks and hollows, the thickness of the acrotelm, and the dominant plant species (Table 1). Marginal tends to have the thinnest or no acrotelm, mainly dominated by *Calluna vulgaris* and *Trichophorum cespitosum* whereas central has the most developed acrotelm and is dominated by the peat forming *Sphagnum cuspidatum*.

Table 1 The characteristics of the ecotopes at Clara (Regan et al., 2020)

Ecotope	Characteristics
Marginal	No hummocks and hollows Acrotelm usually absent or poorly developed (<0.05 m) Few or no peat-forming plant communities Vegetation dominated by <i>Calluna vulgaris</i> and <i>Trichophorum cespitosum</i>
Sub-marginal	Some differentiation between hummocks and hollows Hollows inundated during small fraction of the year Acrotelm absent or thin (<0.05 m) Hollows dominated by <i>Narthecium ossifragum</i> and <i>Sphagnum tenellum</i>
Sub-central	A micro-topography of hummocks, hollows and lawns, but no pools, dominated by <i>Sphagnum magellanicum</i> Lawns are dominant Acrotelm depth variable from 0.10 m to locally well developed 0.40 m
Central	A micro-topography of hummocks, hollows and pools Acrotelm moderately to well developed Depth of up to 0.5 m Pools, and hollows dominated by <i>Sphagnum cuspidatum</i>

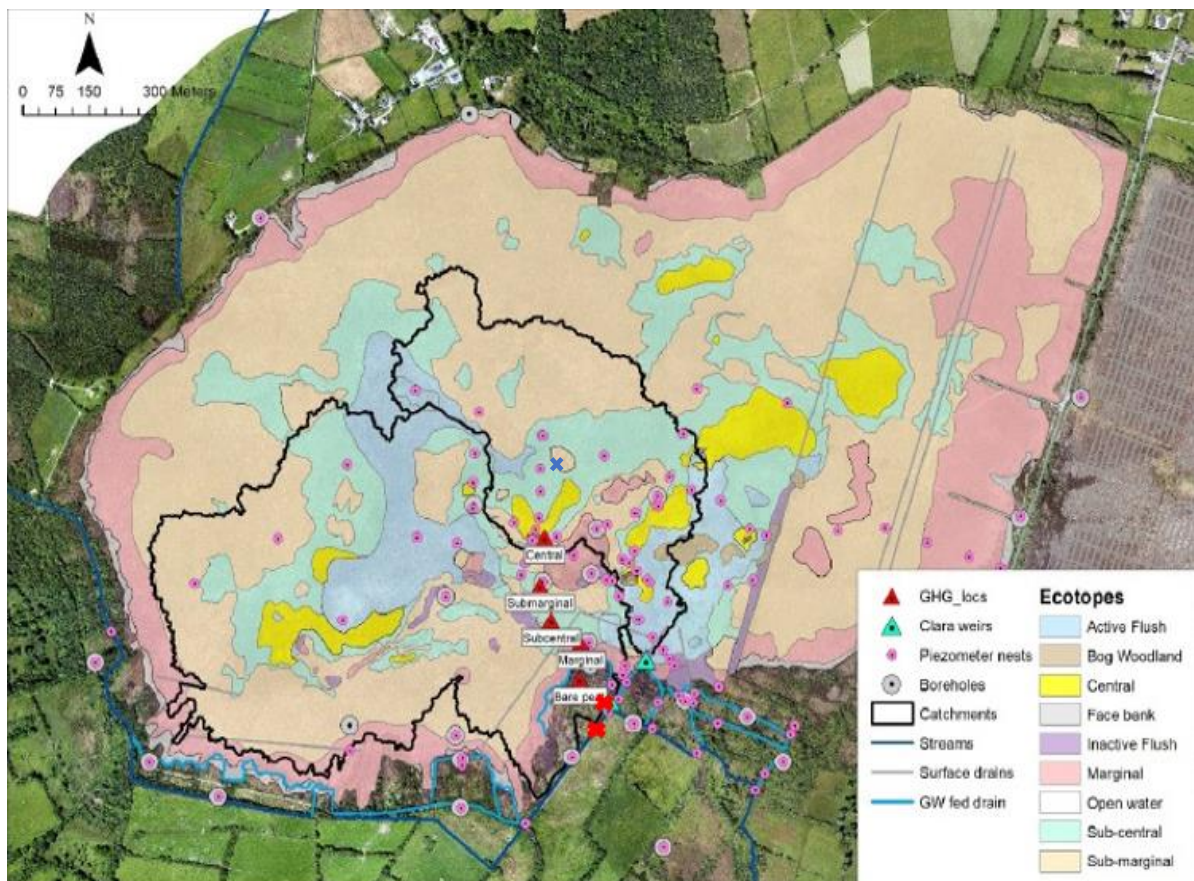


Figure 2 Clara Bog catchment and ecotopes. The discharge measurement spots are marked by the red X. Clara Upper (CLU) is the higher red x, Clara Lower (CLL) is the lower red X. The Eddy covariance tower is marked by the blue X. Map altered from Regan et al. (2020).

2.1.2 Garryduff

Garryduff is a raised bog located adjacent to the River Shannon in Clonfert, Co. Galway and several designated conservation sites. The draining and development of Garryduff bog began in 1960 with industrial peat production beginning in 1968 and ceased in 2019. Using Met Éireann data from the nearest station, Gurteen, the average annual rainfall and temperature have been 937 mm and 10.3°C respectively during this study period (Met Éireann, 2023b), the same figures as All Saints.

The underlying geology of Garryduff is mostly dark limestone and shale with the underlying soils and subsoils being classified as Raised bog cutover peat. Under the peat there are lacustrine deposits (marl) as well glacial deposits interbedded with glacio-fluvial deposits consisting of grey gravely clay and silt.

The site has three pumps which dominate the hydrology of the system, therefore the site did not have a natural eco-hydrological regime during the study period. At the beginning of the study period the bog sparsely consisted of vegetation as wet and dry grassland, bog woodland (Birch, spruce and Ash), some conifer trees, sedge/reed beds and gorse. Due to ceasing of the pumping of the site at the end of this study period, the extent and make up of the population is in the process changing. The majority of the footprint of former peat production during the study period was bare peat making up approximately 50% of the bog's area and containing active drainage channels.

Most of Garryduff Bog is classed as cutaway, there are now only small pockets with peat in excess of 2 m. The degraded nature of this raised bog site makes it a good representation of degraded raised bog hydrology.

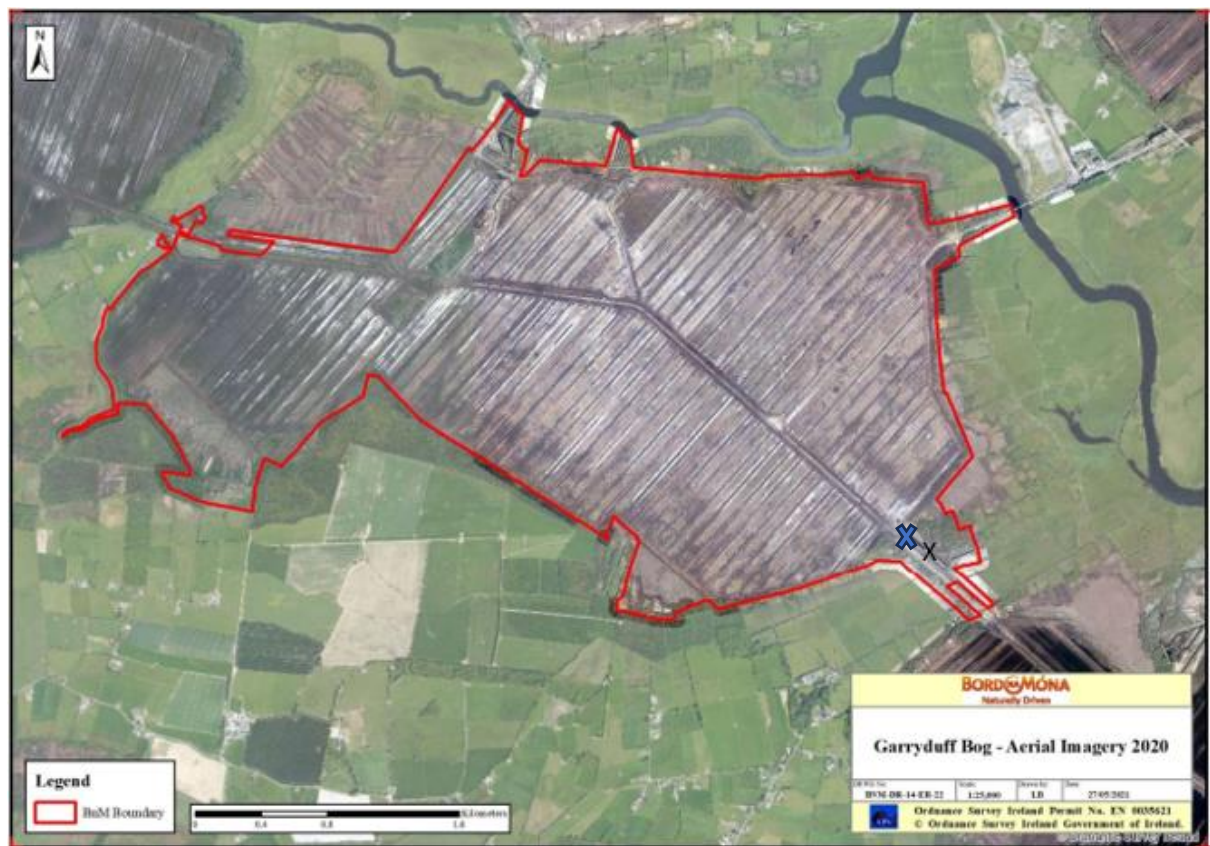


Figure 3 Garryduff Bog catchment. The discharge measurement spot is marked by the black X. The pump that is the closest to the flume and affects our study is marked by the blue X.

2.1.3 All Saints SAC

All Saints Bog is a lowland raised bog located about 5 km north-west of Birr in Co. Offaly. It is separated from the River Little Brosna callows by a fragmented esker ridge. The site is an SAC, protected under the Habitats Directive for its Orchid-rich calcareous grassland, raised bogs, Rhynchosporion vegetation and bog woodland. The bog lies on poorly productive limestone aquifer bedrock.

All Saints Bog features a large birch and pine dominated bog woodland covering 14.34 ha. Using Met Éireann data from the nearest station, Gurteen, the average annual rainfall and temperature have been 937 mm and 10.3°C respectively during this study period (Met Éireann, 2023b).

Up until recently, peat cutting (for use in horticulture), drainage and quarrying to the south of the high bog have been responsible for the degradation of the bog. The current conservation objective for All Saints Bog is to restore the area of active raised bog and bog woodland to the area present when the Habitats Directive came into force in 1994.

All Saints was selected to represent a rehabilitation site as it is currently going through the process of enhanced rehabilitation using berms / bunding (as shown on Figure 4).

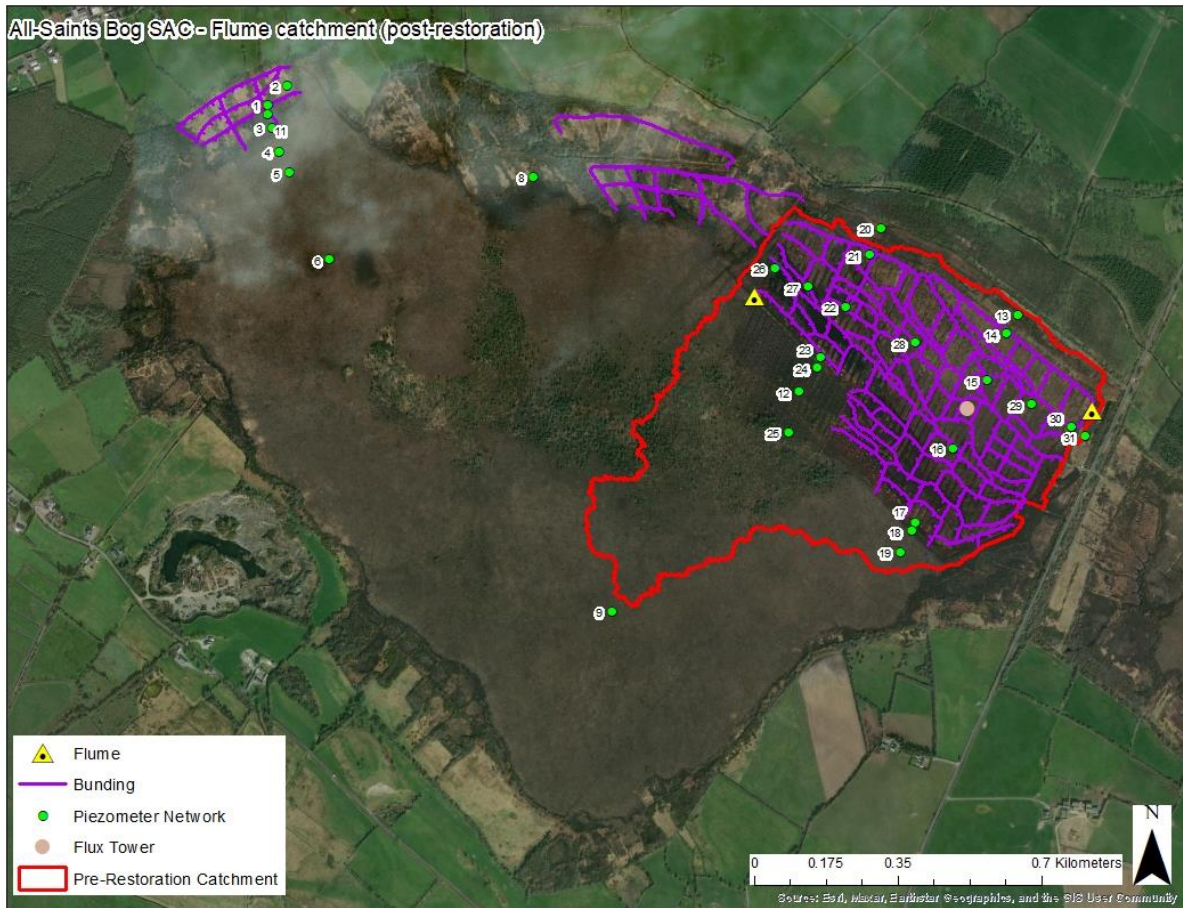


Figure 4 All Saints Bog catchment. The discharge measurement spots are marked by the two yellow triangles at the border of the catchment. The Eddy covariance tower and met station are placed at the red circle right of the centre of the catchment area.

2.2 Equipment and Measurements

2.2.1 Discharge Measurements.

Flumes were placed in stream outlets from exemplar sub-catchments for the different areas of three bogs under examination. In CL a Replogle, Bos, and Clemmens flume (RBC 13.17.06 with a maximum flow of 85 l/s) was installed measuring the discharge from a stream draining the upper part of the natural bog, called CL Upper (CLU). In GD, a larger flume (RBC 13.17.08 with a maximum flow of 145 l/s) was installed which was placed at the exit of a settling pond which was fed by two pumps that intermittently pumped out water from the bog draining to a sump. AS had a RBC 13.17.06 flume installed at the exit from the bog in a stream that was fed into by man made drains.



Figure 5 Installed flume in CL Upper natural stream

The pressure values (a proxy for water depth) in the stilling well were logging pressure every 15 minutes and the data were then logged telemetrically at one-hour intervals by a VanWalt DataHub. The flow was determined using a predetermined lab-based relationship between pressure and manual measurements of discharge (l/s) within the flume (as outlined in Section 2.4). The equation used differed slightly depending on the size of the flume.

The catchments that fed into the flumes were provided by the National Parks and Wildlife Service (NPWS) for CL and Bord na Mona (BnM) for GD and AS. These catchment areas were 0.269 km², 2.218 km² and 0.6811 km² respectively.

In addition, two OTT Orpheus Mini Level Loggers (OTT Loggers) were installed in front of the flumes in stilling wells made of PVC pipes as a backup system for measuring flow. The OTTs provided water level height based on the pressure of water above the sensor.

Pump run data for the operational periods of the two XFP 300J-CB3 pumps on Garryduff were obtained from Bord na Mona (BnM) as the pumps were managed by them. The flow rate from the pumps was back-calculated using a flood Muskingum routing methodology between the discharge point of the pumps and the flow monitoring location with the flume, as detailed in the Supplemental Information.

For the flume in Garryduff, where the overflowing of the flume was a semi regular event, manual measurements of flow were undertaken using an Acoustic Digital Current Meter for any flow that reached over 145 l/s.

2.2.2 NPOC Measurements

Fluorescent dissolved organic matter (fDOM) measurements (QSU) were taken every 30 minutes using EXO 2 multi-Sonde instruments (Xylem Inc, NY, USA) situated just before the flume in each site. The sonde was installed in a stilling well made from a PVC pipe that had been cut with slits (3

mm wide) to allow the water to flow in without large debris. The fDOM sensor measures the fraction of the NPOC that absorbs light in the UV range of 365 nm (± 5 nm) and emits light at 480 nm (± 40 nm) as per the manual (Xylem Water Solutions, 2019). The sonde had additional sensors measuring temperature ($^{\circ}\text{C}$), specific electrical conductivity ($\mu\text{S}/\text{cm}$), and turbidity (Formazin Nephelometric Unit (FNU)). A wiper installed on the sonde reduced the risk of biofouling of the sensors. The sensors were all removed, inspected and calibrated every 12 months in the lab every twelve months using a quinine sulphate standard.

Discrete water samples were taken every two weeks by hand. Autosamplers (Isco 3700 water sampler) were also deployed on each site to capture the short-term variation of NPOC, when a rain event was predicted. The samples were then filtered in the field through Minisart 0.45 μm syringe filters, acidified by adding two drops of 2 molar HCl and refrigerated until they could be analysed using Shimadzu TOC-L analyser, which uses the HTC method, with a manufacturers NPOC's detection limit of 0.5 mg/l. A further 10 ml of the filtered sample was set aside and placed in a separate container without acidification. This was then used to determine absorbance at 254 nm in the lab using a spectrophotometer, for later correction of the fDOM values.

2.2.3 Meteorological measurements

Two automated weather stations were installed in CL and AS to record key meteorological parameters, this was controlled by a CR3000 micrologger (Campbell Scientific, Shepshed, England). The measurements made included air temperature and relative humidity (HC2S3 Rotronic Hygroclip2, Campbell Scientific, Shepshed, England), wind speed and direction (RM Young, Traverse City, Michigan, USA), incident photosynthetically active radiation (Quantum sensors, Skye Instruments, Llandrindod, Wales), precipitation (tipping bucket rain gauge, RM Young, Traverse City, Michigan, USA), net radiation (NR-Lite 2, Kipp and Zonen, Delft, the Netherlands), soil heat flux (Hukseflux, Delft, the Netherlands), soil temperature (TCAV, Campbell Scientific, Shepshed, England) and volumetric soil water content (CS616 Water Reflectometer, Campbell Scientific, Shepshed, England). All atmospheric sensors were installed between 2-3 m above the ground, while all soil based sensors were located within a 5 m radius of the eddy covariance flux tower.

The tipping bucket rain gauge on CL did not return accurate results as it kept getting blocked by debris and the equipment itself was being managed by another study and as such precipitation data was taken from Horseleap for daily values and Mullingar for hourly values. For GD and AS, meteorological data from the nearest Met Eireann station in Gurteen was used. See Table 2 for details on data type and distance from the study sites.

Table 2 The location and distance of rainfall data used for each study site. All weather data was taken from Met Eireann Historical Weather Data site¹.

Study Site	Meteorological data source	Type	Distance from Study Site (km)
Clara	Met Eireann Horseleap	Daily Rain	~7.5
Clara	Met Eireann Mullingar	Hourly Rain	~30
Garryduff	Met Eireann Gurteen	Daily and Hourly	~25
All Saints	Met Eireann Gurteen	Daily and Hourly	~13

2.2.4 Micrometeorological measurements

Net ecosystem measurements of evapotranspiration were made using the Eddy Covariance (EC) technique for CL and AS. The EC instrumentation consisted of a three-dimensional sonic anemometer (Windmaster, Gill Instruments, Lymington, UK) and an enclosed infrared gas analyser (LI-7200, LICOR, Lincoln, Nebraska, USA). The EC sensors were installed on a tripod mast and a height of 3 m.

The acquisition of high frequency flux data was undertaken using a LICOR analyser interface unit and all data were subsequently post-processed using EddyPro software (Version 6.2.1). The eddy covariance data processing included spike removal and double coordinate rotation, while tests for turbulence and stationarity were also applied (Foken *et al.*, 2005; Reichstein *et al.*, 2005; Mauder *et al.*, 2008). The interdependency of turbulence criteria on flux estimation was assessed the ustar filtering approach of Papale *et al.* (2006). The flux footprint was assessed using a two-dimensional model by Kljun *et al.* (2004). Further information on flux analysis, quality control and gap-filling can be found in Ingle (2023).

In AS, an automated weather station was used to record key meteorological parameters, this was controlled using LI-COR data acquisition and retention modules (LI-COR, Nebraska USA), wind speed and direction (HS-50 Gill instruments, Hampshire, UK), incident photosynthetically active radiation (LI-COR Quantum sensor, LI-COR, Nebraska USA), precipitation (tipping bucket rain gauge, TR-525M, Texas Electronics, USA), net radiation (CNR4 Net Radiometer, Kipp and Zonen, Delft, the Netherlands), volumetric soil water content (Stevens Hydraprobe, Oregon, USA), soil based sensors which were located within a 10 m radius of the eddy covariance flux tower and post-processed using EddyPro software (Version 7.0.6) and Tovi (Version 2.8.1).

For GD, the crop coefficients of AS were used to determine an estimated evapotranspiration as outlined in Section 2.4.5.

¹ Available at: <https://www.met.ie/climate/available-data/historical-data>

2.2.5 Storativity measurements

To look at lateral flow, microcosms were set up in the sites. For the microcosms, 215 litre steel collars, with both floor and lid removed, were installed by inserting them into the peat to a depth of between 61.6 and 70.6 cm, leaving between 17 and 26 cm of barrel collar above the surface level of the bogs. In this way they became microcosms that would prevent lateral flow.

Two microcosms were initially installed in AS but unfortunately, the rehabilitation in AS meant that the microcosms were quickly flooded by the rewetting and were no longer usable. Additionally, there was an attempt to install two microcosms in GD but the shallow peat depth and compacted nature of the site made installation impossible. For CL, the microcosms were installed at each ecotope, as described in Table 1, to represent the hydrological differences between the ecotopes (Figure 7). One was also installed by the EC tower, sub-central, in the centre of the bog. Inside the microcosms OTT sensors and divers were installed in PVC pipes to measure the Water Level Height (WLH) from the surface of the bog. Outside the microcosm OTT sensors were already in place in PVC pipes to measure the WLH from the surface outside of the microcosms. A barro-diver was installed on the site to measure the atmospheric pressure to enable the compensation calculation for water depth from the raw diver data.

The water level data for CL were taken from the OTT sensors outside each microcosm. In AS, it was taken from an OTT sensor installed at point 29 in Figure 8. The area of the OTT in AS was not a banded area at the time of measurement but was fed into by banded areas.

The microcosm results were analysed and due to issues with getting on site rain data and installation of equipment, the storativity values produced unlikely/impossible values and therefore the results were not included in the analysis of the thesis. The results can be found in Appendix 3 Microcosms.



Figure 6 The steel drum microcosms which were installed on Clara, the silver one on the left had to be abandoned as it was too damaged during installation.

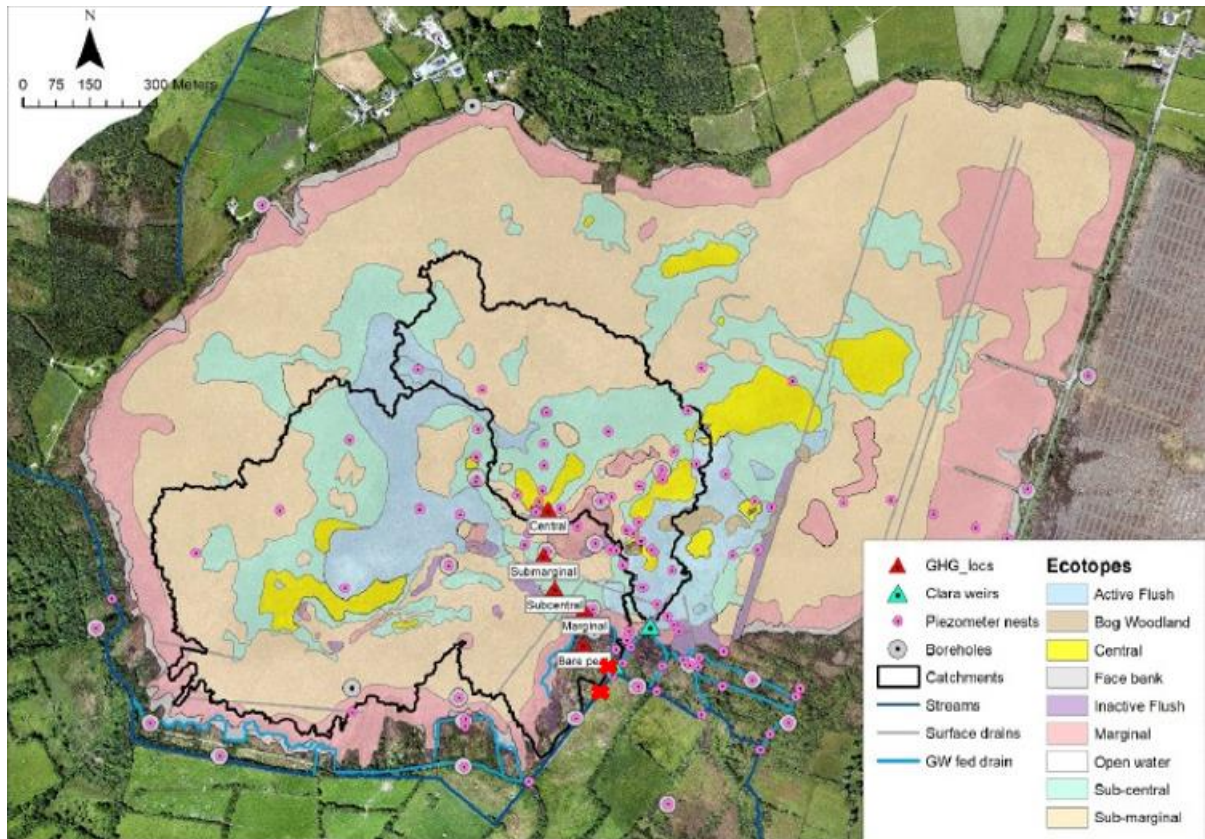


Figure 7 The microcosms were installed at each of the ecotopes (GHG_locs). Bare peat was not measured.

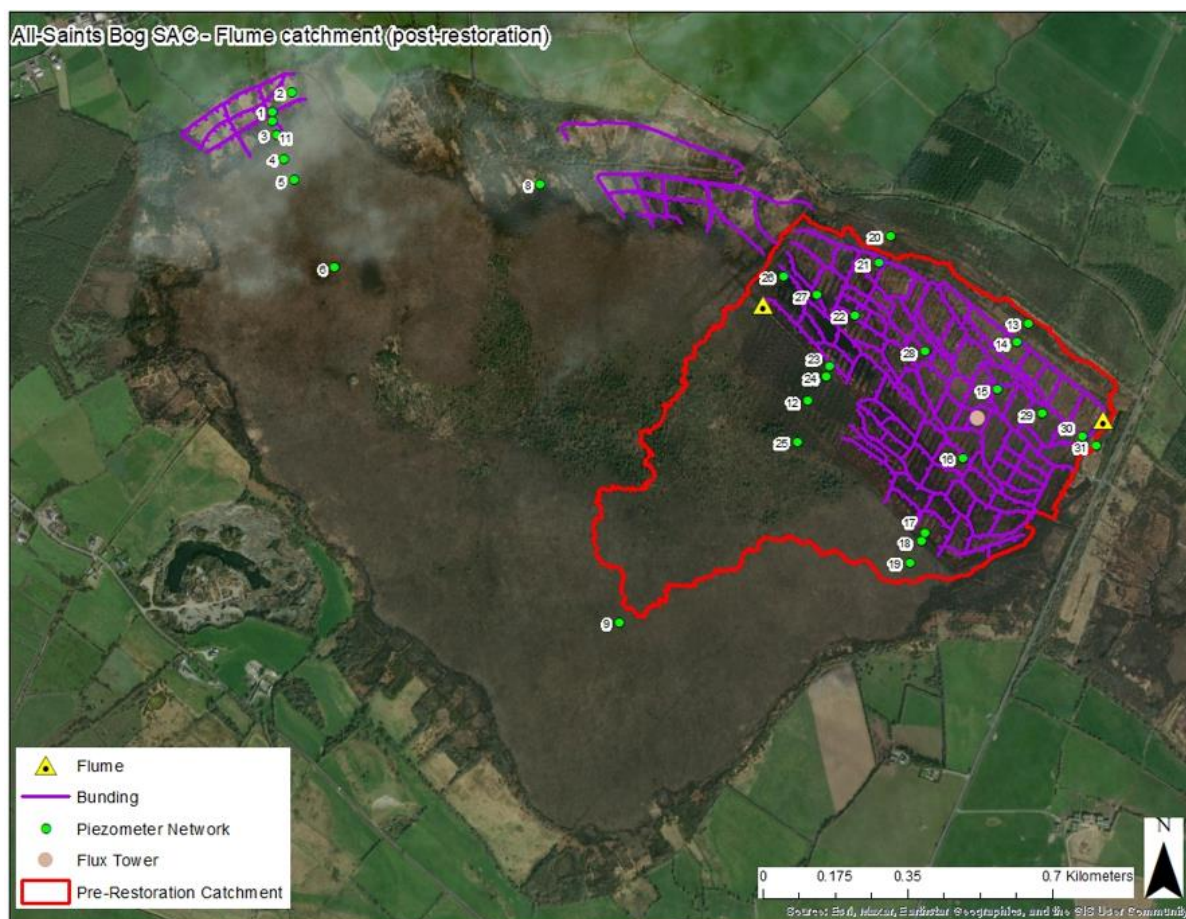


Figure 8 The OTT sensor in AS was installed at Piezometer Network 29.

2.2.6 Fluvial Gas Flux Evasion

A LI – 7810 CH₄/CO₂/H₂O Trace Gas Analyser (LI-COR) was used to measure the methane (CH₄) (ppb), carbon dioxide (CO₂) (ppm) and water vapour (H₂O) (ppm). The location of where the chamber measurements were taken for each site are presented in Figure 14 and Figure 15.

A chamber (Figure 9) was designed to be attached to the analyser with an incorporated water trap (Figure 10) to ensure that no water would enter the analyser. A floating collar was constructed using a polystyrene insulation board with a PVC pipe of diameter 25 cm (Figure 11). The total headspace volume of the chamber and pipe was 0.0052 m³. The surface area of the chamber was 0.0167 m² for the whole measurement period.

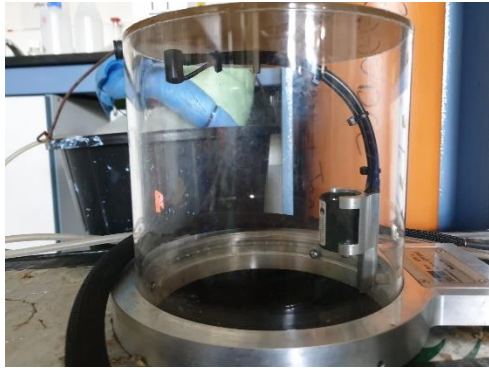


Figure 9 The gas chamber



Figure 10 The water trap connected to the chamber and analyser.



Figure 11 The chamber placed on top of the collar which has been inserted tightly into a polystyrene insulation board which floats.



Figure 12 The LI – 7810 CH₄/CO₂/H₂O Trace Gas Analyser (LI-COR)



Figure 13 Chamber measuring in-situ at CL

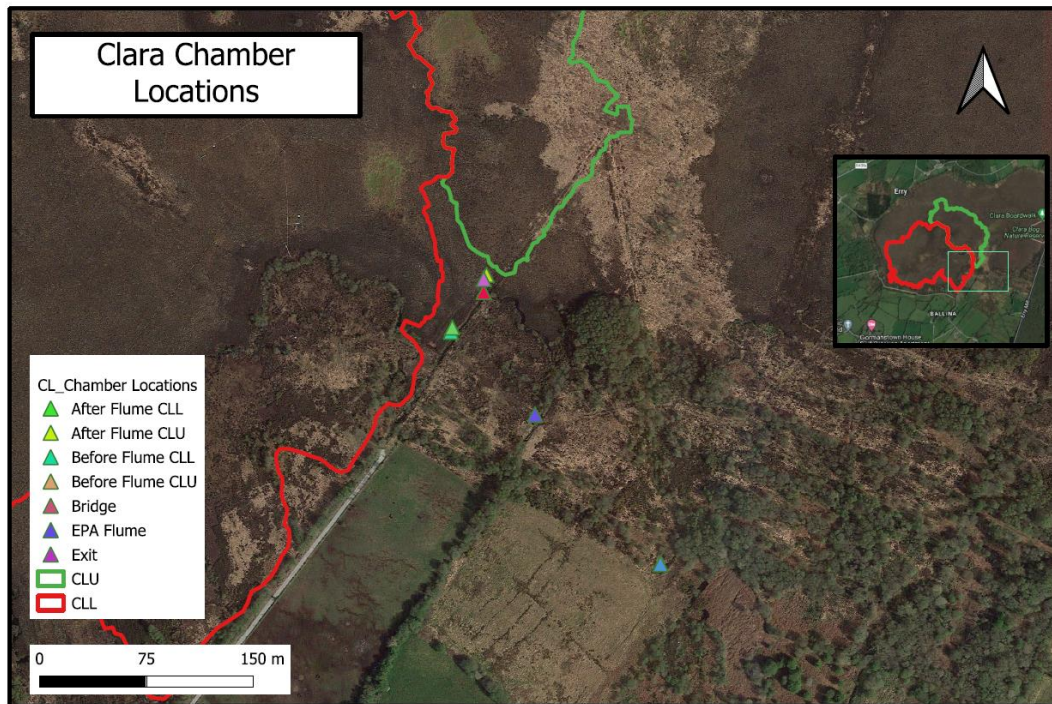


Figure 14 The location of the chamber tests in CL - CL Upper (CL) and CL Lower (CLL)

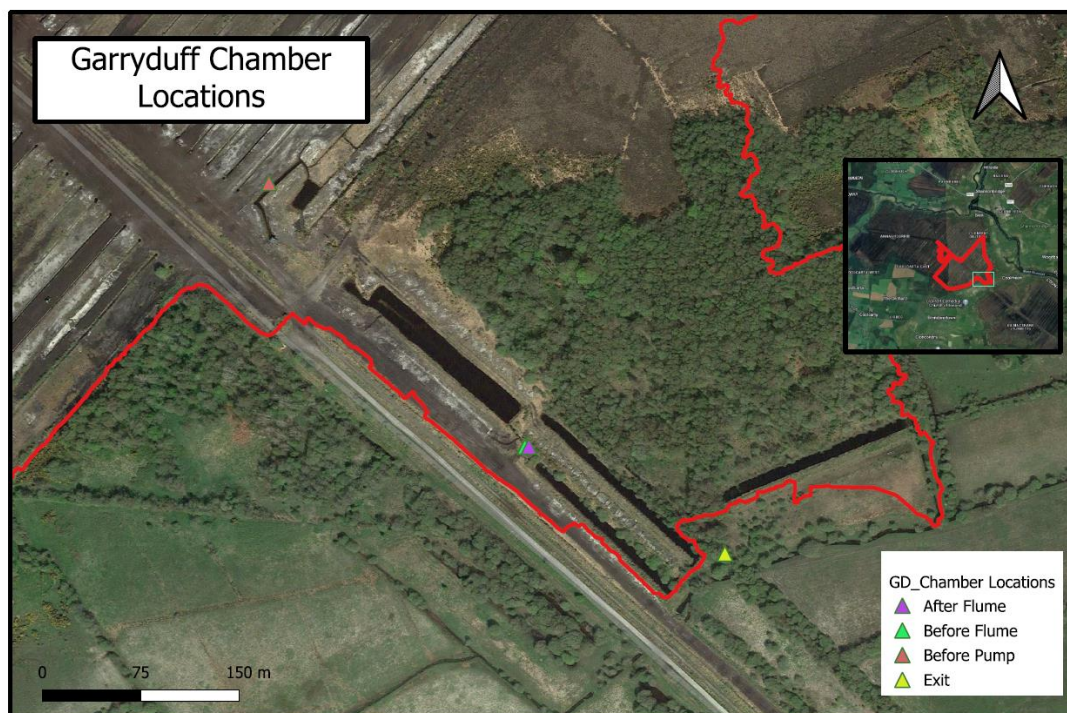


Figure 15 The location of the chamber tests in Garryduff

2.3 Data Collection

Flume data were telemetric and were logged online, downloaded from a Van Walt Server. Data from the Sondes were downloaded every two weeks when batteries were changed using the Xylem KorEXE software. NPOC and absorbance samples were taken at the same time. For AS, all NPOC samples were taken using Isco 3700 autosamplers over 24 to 72 hour periods.

The OTTs for WTH and flow were downloaded once a month during field visits and the water level (Diver) data was collected at the end of the study period.

Chamber measurements of fluvial gas flux evasion were taken every 2 to 4 weeks for 5 minute periods on a transect away from the flume. They were measured alongside Electrical Conductivity (EC) and temperature. In CL there were seven sampling points and in GD there were four. These were chosen based on accessibility and distance from each sampling point. These locations were chosen because they were drains leaving the site, as this study is interested in looking at the carbon export of water leaving the site. Sampling points at different points within the bog could also have been selected given more time.

2.4 Analysis

2.4.1 Flow

2.4.1.1 Basic Filtering

The collected data were loaded into R statistical software package. All times were rounded to the nearest 15 minutes. Most pressure values were very low, with outliers of 1 bar. Any pressure values over 1 bar were replaced with NA. Any measurements of flow over 85 or 145 l/s were changed to NA as that is the maximum capacity of the flume. Any negative measurements were changed to NA.

All NAs were filled using the pressure equation from the flume (Equation 1).

Equation 1

$$Q = 0.0000003 \times (((P \times 10197.16) - 4.4929)^3) + 0.0011 \times (((P \times 10197.16) - 4.4929)^2) + 0.0569 \times (P \times 10197.16 - 4.4929) - 0.4778$$

Where P is pressure and Q is discharge.

All negative flow values were changed to 0 and all values over 85 l/s were changed to 85 l/s for the flume in CL. For the flume in Garryduff, where the overflowing of the flume was a semi regular event, a new depth/flow relationship (Equation 2) was determined via manual measurements of

flow using measurements of cross-section depth and spot velocity measurements using an Acoustic Digital Current Meter for any flow that reached over 145 l/s.

Equation 2

$$Q < - (8870.9 \times P) - 112.91$$

Where P is pressure and Q is discharge.

2.4.1.2 Outlier detection and removal

The data still contained a series of high jumps and dips which were likely due to periodic obstructions of the pipes leading to the sensors during water flow by floating debris. To remove any such outliers, the outlier detection method of Bae and Ji (2019) was used. The outlier removal process includes an initial cutoff process to remove outliers out of the measurement range and an outlier detection process using modified Z-scores based on the median absolute deviation (MAD) of a robust estimator. MAD is considered a more robust measurement of the variability of a univariate sample of quantitative data, compared to using standard deviation, as it is very insensitive to outlier deviation (Huber and Ronchetti, 2009; Leys *et al.*, 2013).

Assuming the dataset is $X=\{x_1, x_2, \dots, x_n\}$ the MAD is defined as:

Equation 3

$$MAD(X)=Med\{|X-Med(X)|\}$$

where $Med(X)$ is a function for finding the median of the data set X . $MAD(X)$ shows the median value of absolute deviations between the individual observations of data set X and $Med(X)$.

The $MAD(X)$ value was then compared to the standard deviation, by normalising it ($MADN(X)$). As follows:

Equation 4

$$MADN(X)=MAD(X)/0.6745$$

The constant value 0.6745 is the 75% percentile of a normal distribution, which corresponds to the MAD of the standard normal distribution with a standard deviation of 1 (Iglewicz and Hoaglin, 1993; Maronna *et al.*, 2019). The $MADN(X)$ corresponds to the standard deviation of the normal distribution for the centre location of the data estimated by the sample median.

To detect outliers, $MADN(X)$ needs to be compared with the deviation of the individual observation x_i centered on the location estimated by the sample median. This was done by generating a

modified Z-score (M_i). This was then compared with the outlier rejection criterion β to determine if the data point is an outlier (Iglewicz and Hoaglin, 1993), as per Equation 5

Equation 5

$$M_i = |x_i - \text{Med}(X)| / \text{MADN}(X) < \beta$$

Iglewicz and Hoaglin (1993) suggested a rejection criterion, $\beta = 3.5$, based on the results of their simulation, however, Leys *et al.* (2013) reported that β can be determined differently according to the researcher's perspective, but suggested a β value of 2.5. In this case, two β values (2.5 and 0.5) were used to determine the effect of a range.

2.4.1.3 Hydrographs

For hydrographical analysis, for each of the sites rain events with more than one hour rain, with at least 10mm of rain were identified and reviewed to identify which rain events had a corresponding impact on the flow to analyse the link between the rain and flow. Two events per season, per site were identified as examples. Effective rainfall was also calculated for each during the study period to compare to flow. This was done by subtracting the daily ETec data from daily rain data.

2.4.2 fDOM

fDOM data was filtered initially using conductivity, with values of QSU corresponding to a conductivity of 2 or lower removed, as that conductivity indicates that the sensor was not submerged in the water. The fDOM data was then corrected for temperature using the method in De Oliveira *et al.* (2018). Any removed values were then filled in using linear interpolation. The data were then checked for outliers using the Bae and Ji (2019) method previously used for flow. The newly filtered data was then gap filled using linear interpolation.

The fDOM was then corrected for Inner Filter Effects (IFE) using UV254 using the method in De Oliveira *et al.* (2018). This method is important to account for any absorption of excited and emitted radiation by the sample matrix to ensure more accurate fDOM readings.

The relationship between the fDOM and the fDOM IFE was then used to create a correction for all values where measurements of UV254 was not available.

These corrected fDOM values were then plotted against NPOC lab measurements to determine the relationship from which predicted NPOC values could then be obtained.

2.4.3 Multivariate Analysis

The simple regression between continuous fDOM results and discrete NPOC measurements did not yield a consistent relationship and so an alternative multi-variate analysis approach was carried out between the two data sets to derive a more robust relationship.

The multivariate approach models the relationship between observed NPOC data and fDOM sensor data using an unknown relationship. By expressing the cumulative distribution function (CDF, a way to describe the distribution of a random variable by showing the accumulated probability up to each point) of NPOC data in terms of fDOM's CDF, it estimates both functions based on the data. Since the relationship between the two is unknown, the method assumes that the CDF of NPOC is a function of fDOM and other variables related to water quality. A support vector regression (SVR) model is then used to develop this complex relationship. SVR is typically used for regression analyses where complex relationships exist (Mammone, Turchi and Cristianini, 2009) and while there is a lot of trial and error involved in determining parameters (Yu, Chen and Chang, 2006), it has had successful application in hydrological modelling (Raghavendra. N and Deka, 2014; Granata, Gargano and De Marinis, 2016).

The SVR (Cortes and Vapnik, 1995) was used to predict an output (predicted NPOC) based on input data (precipitation, discharge, water temperature, fDOM and conductivity). It maps the input into a higher-dimensional space where the relationship with the output becomes linear. The model is optimized by balancing the complexity of the prediction function with minimizing the prediction error. A kernel function, specifically a Gaussian radial basis function, is used to transform the inputs, allowing the model to capture complex patterns in the data. The method adjusts parameters to find the best fit without overfitting or underfitting.

A breakdown of the equations used are in Appendix 2: Multivariate Analysis Equations.

2.4.4 NPOC Flux Measurements

The 30 minute continuous fDOM data were converted into NPOC (mg/l) values using the relationships derived by the SVR analytic approach. Each data point was then multiplied by the respective flow at the flumes to derive a continuous NPOC load profile (g/min) leaving the bogs. The NPOC flux was determined by getting the total annual load of NPOC for each outlet and dividing it by the respective catchment areas to yield an areal flux in g C/m².

2.4.5 Micrometeorological measurements

Water vapour data from the Eddy covariance tower measurements were processed using EddyProc and used to quantify evapotranspiration (ET).

The Penman-Monteith FAO56 (Allen *et al.*, 1988) method was used to calculate reference grass evapotranspiration (ET), also called potential evapotranspiration (PET) in this study.

$$ET_o = \frac{0.408\Delta(R_n - G) + \frac{900}{T}\gamma u_2 \delta e}{\Delta + \gamma(1 + 0.34u_2)}$$

Where:

ET_o = Reference evapotranspiration, Water volume evapotranspired (mm/day)

Δ = Rate of change of saturation specific humidity with air temperature. (Pa/K)

R_n = Net irradiance (MJ m²/day), the external source of energy flux

G = Ground heat flux (MJ m²/day), usually equivalent to zero on a day

T = Air temperature at 2m (K)

u_2 = Wind speed at 2m height (m/s)

δe = vapor pressure deficit (kPa)

γ = Psychrometric constant ($\gamma \approx 66$ Pa K⁻¹)

Data analysis was performed using R. While PET was calculated using the “Evapotranspiration” package in R (Guo, Westra and Peterson, 2022)

Annual Crop Coefficients (Kc) were derived by dividing the measured yearly value of ET by the PET.

2.4.6 Storativity measurements from the microcosm experiments

The storage properties within and outside the microcosms were determined using the water table fluctuation (WTF) method (Dettmann and Bechtold, 2016; Bourgault, Larocque and Garneau, 2017; Swenson, Regan and Gill, 2020). Storativity (also referred to as specific yield) is calculated during specific rainfall events in a peatland using the volume of rainfall and change in water table according to Equation 6

Equation 6

$$S(wt) = \frac{\Delta z}{\Delta V}$$

where $S(wt)$ is the storativity (no units) as a function of water table, Δz is the change in water table over a rainfall event (mm), and ΔV is the volumetric change (mm) ($\approx$ precipitation (P) over a rainfall event). Therefore, the storativity was calculated by dividing the change in water volume by change in rain depth.

Rainfall data were extracted from an offsite met station in Mullingar (Met Éireann, 2023b).

The specific rainfall events were defined as per Swenson *et al.* (2020) methodology. A rainfall event was defined as any event which:

- Had more than 1mm of rain per hour
- Was no longer than 7 hours in duration, to reduce the effect of lateral losses during the rainfall event.
- Had no other rain event less than 3 hours before or after it as per Bourgault, Larocque and Garneau (2017)

The water table height at the beginning and end of a rainfall event was calculated as well as the total rainfall during the event. These values were used to calculate storativity as per Equation 6. The storativity values for inside and outside the microcosms were compared to each other using Welch's t test, as there were uneven sample sizes.

2.4.7 Catchment area determination.

Catchments for each of the flumes were determined using Equation 7 where Q is cumulative discharge over a specified time period (usually a hydrological year), ET is the annual cumulative evapotranspiration and Rain is the cumulative rainfall. This gave catchment area in m² which was then converted into km².

Equation 7

$$Catchment = (Q + ET) \div Rai$$

Where Q is discharge, ET is evapotranspiration.

2.4.8 Fluvial Gas Flux Evasion

The slope of each 5 minute measurement period was used to determine the CO₂ and CH₄ flux based on the following equation:

Equation 8

$$\begin{aligned} & Slope \times 10^{-6} \times (Headspace\ Volume \times Atmospheric\ Pressure \times 100 \\ & \times Molecular\ Weight) / (8.314 \times (273.15 \\ & + Water\ Temp)) \times 10^{-6} \times (1/Surface\ Area) \end{aligned}$$

The CO₂ and CH₄ flux values in ppm/second were converted to g C eq/m²/day, using the quantity of carbon in each molecule (Equation 9).

Equation 9

$$\text{Flux (gC/m}^2\text{/day)} = \text{Flux (gCO}_2\text{/m}^2\text{/day)} * 0.27$$

$$\text{Flux (gC/m}^2\text{/day)} = \text{Flux (gCH}_4\text{/m}^2\text{/day)} * 0.75$$

The measurements of flux (g C/m²/day) for each month (see number of measurements taken per month for each site in Table 3) were averaged to get the average flux value per day for that month. Then the average daily flux was multiplied by the number of days in that month to get monthly total flux (g C/m²) and then these values were summed to get annual totals for 2022, the only complete year of measurement. The average flux value per day in each month was also averaged with the flux value per day in each month of that season to get the average daily flux value in each season. The seasons were defined according to Met Éireann's definitions of Irish seasons, December to February – winter, March to May – spring, June to August – summer and September to November – autumn (Met Éireann, 2023a).

Table 3 The number of evasion samples taken each month through the study period for CL and GD

CL		GD	
Nov-21	8	Nov-21	7
Jan-22	6	Dec-21	6
Mar-22	17	Apr-22	3
May-22	5	May-22	3
Jul-22	3	Jun-22	5
Sep-22	3	Sep-22	1
Oct-22	5	Oct-22	3
Nov-22	6	Nov-22	1
Dec-22	9	Dec-22	5
Jan-23	4	Jan-23	1
Feb-23	6		

3 Chapter 1 - Making Light Work: Using fDOM technology and multivariate analysis as a proxy to accurately estimate NPOC exports in temperate peatlands of varying conditions.

3.1 Introduction

Globally, peatlands cover approximately 3% of the land while storing between 25% to 33% of the Soil Organic Carbon (SOC) stock (Eswaran, Van Den Berg and Reich, 1993; Batjes, 1996), a number which accounts for approximately 600 Gigatons of carbon (Yu *et al.*, 2011; Hawken, 2017). Forests store a similar amount of carbon while covering approximately ten times the area (Frolking *et al.*, 2011).

In Ireland, peatlands are estimated to store two-thirds of the total national soil carbon stock (Renou-Wilson *et al.*, 2022). When comparing Special Area of Conservation (SAC) raised bogs in 1994 to 2012/13, there has been an approximate loss of 37%, which is of particular concern as 60% of the intact raised bogs in Western Europe are located within Ireland (National Parks and Wildlife Service, 2017). It is estimated that around 80% of Irish peatlands have been damaged to some extent by anthropogenic disturbances such as draining or mining (Renou-Wilson *et al.*, 2022; Fluet-Chouinard *et al.*, 2023).

There are consequences to the loss of these ecosystems and the carbon stock contained within. For example, in the UK 95% of the peatland area consists of blanket and raised bogs, which have been estimated to hold 3.2 billion tonnes of carbon. A loss of only 5% of the carbon stored within these systems would be equivalent to the entire Greenhouse Gas (GHG) emissions from anthropogenic sources in the UK annually (Bain *et al.*, 2011).

The Net Ecosystem Exchange (NEE) of peatland systems is relatively well-researched. In general, near natural sites have been found to assimilate between 47 and 205 g C/m²/year whereas degraded sites generally emit between 189 and 492 g C/m²/year (See Table 2 and Table 3, Appendix 1). However, the losses via fluvial carbon pathways are not adequately quantified and remain a knowledge gap. This area of research is important, as fluvial carbon has been shown to account for 15-50% of all Greenhouse Gas (GHG) emissions from drained and rewetted peatlands (Evans, Renou-Wilson and Strack, 2016) which in some cases changes annual budgets from carbon sources to carbon sinks (Billett and Moore, 2008).

Ingressing water that is in contact with organic soil becomes super-saturated with carbon, which is then exported as Non Particulate Organic Carbon (NPOC) and Particulate Organic Carbon (POC),

differentiated based on their particle size (Hope, Billett and Cresser, 1994). Studies have underlined the quantitative importance of fluvial carbon (Roulet *et al.*, 2007; Limpens *et al.*, 2008; Nilsson *et al.*, 2008; Koehler, Sottocornola and Kiely, 2011); additionally, carbon is released back to the atmosphere as carbon dioxide (CO₂) and methane (CH₄) from the fluvial water's surface. Depending on the density of drainage channels on the sites as well as peatland condition, this evading carbon may also be significant.

NPOC is produced from the decomposition of organic material and exuded from vegetation. The functional types of vegetation in peatlands correlates with NPOC, as both the current and past vegetation has been shown to influence the exports of NPOC (Armstrong *et al.*, 2012). The NPOC then accumulates in the pore water of peat soil. Its subsequent transport to drainage waters is controlled by hydrological factors and chemical solubility controls, such as pH.

The majority of studies have shown a positive correlation between NPOC concentrations and discharge within most types of ecosystems, for example, regression analysis has shown an increase in stream discharge from 0.1 to 10 l/s can lead to an increase in NPOC concentrations between 1.4 and 5.5 times (Hope, Billett and Cresser, 1994). This relationship, however, can be weaker depending on the ecosystem, with discharge only explaining 38.5% of the variation in NPOC in moorland streams in Scotland (Grieve, 1984) and less than 30% of the variation in NPOC in streams in Cumbria (Tipping, Hilton and James, 1988). This weaker relationship between discharge and NPOC in peat rich soils has also been confirmed by Clark *et al.* (2007). This may be due to the fact that streams fed by peatland catchments have two sources of water, water from the catotelm which has a longer residence time and surface runoff water from the acrotelm with a much shorter residence time and a more similar chemical signature to rainwater (Worrall *et al.*, 2011). During high precipitation events the surface runoff can then dilute the NPOC rich catotelm water leaving the peatland (Eimers, Buttle and Watmough, 2008). In temperate peatlands the seasonal variation in the relationship between discharge and NPOC concentration is mostly a result of the changes in the sources of NPOC from above ground vegetation and litter, driven by temperature (Inamdar *et al.*, 2006) rather than changes in hydrological flow paths.

The pH of a peatland may also affect the NPOC flux of the ecosystem. However, decreasing pH in already highly protonated soils will not have a significant effect in NPOC concentration as these soils will have limited scope for further reduction of organic matter solubility (Evans, Renou-Wilson and Strack, 2016).

In natural peatlands, the NPOC flux follows a clear latitudinal and climatic gradient differing by orders of magnitude from one end of the gradient to another with temperature likely acting as the

main fundamental control on NPOC flux (Evans, Renou-Wilson and Strack, 2016). The NPOC flux of subarctic or boreal peatland can be as low as $5 \text{ g C m}^{-2} \text{ year}^{-1}$ compared to tropical peatlands where the NPOC flux can be up to $60 \text{ g C m}^{-2} \text{ year}^{-1}$ (Evans, Renou-Wilson and Strack, 2016). In drained sites there is a significant increase in NPOC flux when compared to similar undrained sites. One systematic review showed a mean increase of NPOC flux from natural to drained sites of 62% and a decrease of NPOC flux in rewetted peatlands of 37% (Evans, Renou-Wilson and Strack, 2016).

Direct laboratory-based measurements of NPOC concentration are commonly derived from two methods. The first is to measure the NPOC concentration as Non-Purgeable Organic Carbon. The organic carbon is converted to carbon dioxide through the process of thermal oxidation, which is then measured by absorbance of infra-red radiation (Peacock *et al.*, 2014). The second way to measure NPOC directly in the laboratory is to measure the Total Carbon (TC) and Inorganic Carbon (IC). The NPOC concentration can then be derived by subtracting IC from TC (Peacock *et al.*, 2014). The problem with these measurements is that they are costly and time consuming. Although some cheaper alternatives exist like a method for measuring NPOC concentration using chemically induced changes in colour (Bartlett and Ross, 1988), there still is the problem of needing to go out on site to collect samples, therefore the data will not be high frequency.

NPOC concentration has also been measured using UV-visible spectroscopy based on the fact that light absorbed by water is highly dependent on the concentrations of NPOC (Korshin, Li and Benjamin, 1997). This method is commonly used in the water treatment industry as absorbance at 254 nm used as a proxy for NPOC. This works well because humic substances can make up 90% the NPOC in some lakes and wetlands, although it is important to note that this percentage can vary considerably (Thurman, 1985). These humic substances in turn absorb light in the UV part of the electromagnetic spectrum as well as in the visible spectrum to a lesser degree (Edzwald, Becker and Wattier, 1985). Wavelengths between 250 and 350 nm have also been used for measurements of NPOC concentration, however the standard 254nm was found to perform as well as other wavelengths of 230 and 263nm (Peacock *et al.*, 2014). Some studies have sought to calculate NPOC concentration using non site-specific calibrations (Worrall *et al.*, 2011). However, this can be difficult as any calibration may differ due to factors like land management, peat depth, soil type, vegetation and time as a result of the variability of NPOC structural characteristics (Wallage and Holden, 2010).

Fluorescent Dissolved Organic Matter (fDOM) sensors can be used to make high frequency, in situ NPOC concentration estimates for rivers and streams (Downing *et al.*, 2009, 2012; Pellerin *et al.*, 2012; Carpenter *et al.*, 2013; Goldman *et al.*, 2014; Mast *et al.*, 2016). Some studies that used

fDOM have found that fairly extensive post processing is needed for temperature, turbidity and Inner Filtering Effects (IFE) (Downing *et al.*, 2012; Saraceno *et al.*, 2017) as well as some specific corrections for sites and sensors (Hoffmeister *et al.*, 2020).

Temperature and pH may affect the fDOM measurements by altering the energy states of the fluorescing substances, diminishing the intensity of light output, which is known as fluorescence quenching (Baker, 2005; Spencer, Bolton and Baker, 2007). However, lab based studies of pH on natural samples and organic matter standards have shown that, within the ranges seen in most natural systems pH has a negligible impact on fluorescence wavelengths measured by most modern fDOM sensors (Patel-Sorrentino, Mounier and Benaim, 2002; Spencer, Bolton and Baker, 2007). In contrast the fact that DOM is inversely related to sample temperature is well established; higher temperatures increase the likelihood that excited electrons will revert to a ground state as a result of radiationless decay, reducing fluorescence emission intensity (Vodacek *et al.*, 1995; Zepp, Sheldon and Moran, 2004; Lakowicz, 2006). This results in decreases of ~1% per 1°C increase (Henderson *et al.*, 2009b). These results have been found to be similar in different sample types including quinine sulphate, which suggests that the relationship is independent of DOM composition within the excitation-emission wavelengths used by most commercial fDOM sensors (Downing *et al.*, 2012).

Finally, correcting for turbidity is argued to be critical for determining accurate measurements of fDOM due to light attenuation by suspended particles. Having a generic turbidity-based correction can mitigate errors to a certain degree but the development of a site specific equation is preferable (Saraceno *et al.*, 2017). However, there have been studies that have not accounted for turbidity at all and have used raw fDOM measurements as a proxy for NPOC with success in low turbidity systems where interference of the fDOM sensor was expected to be minimal (Wilson *et al.*, 2013; Ganju, Miselis and Aretxabaleta, 2014; Crawford *et al.*, 2015; Sobczak and Raymond, 2015; Watras *et al.*, 2015; Oestreich *et al.*, 2016).

In summary, there is a need to include NPOC losses within peatland systems, however a standardised methodology carrying out in situ measurements in raised bog systems does not yet exist. This study compares lab measurements to in situ measurements of fDOM to determine if the method provides sufficient accuracy. In situ measurements can be convenient as they don't necessitate regular site visits for sample collection, however the reliability and accuracy of these measurements must first be investigated before in situ measurements can be recommended as a suitable alternative to lab measurements of NPOC.

This study sets out to determine the relationship between fDOM measurements and NPOC derived from lab-based measurements of in situ samples, using simple linear regression and more complex multivariate analysis as two methods of comparison. This is to test whether fDOM can be used as a proxy for NPOC in raised bogs and if so, to what accuracy.

3.2 Methods and Equipment

3.2.1 Study Sites

The study sites for this section are as presented in Section 2.1, with all three study sites included; Clara (CL), Garryduff (GD) and All Saints (AS).

3.2.2 Equipment and Measurements

For this paper, the main equipment and measurements taken are discharge (via flumes at the sub-catchment outlets) and NPOC measurements (via fDOM Sondes and samples taken back to the laboratory for analysis) as described in Sections 2.2.1 and 2.2.2.

3.2.3 Data Collection

Hourly flume data were telemetric and logged online, downloaded from a Van Walt Server every two weeks. Data from the Sondes were downloaded every two weeks when batteries were changed using the Xylem KorEXE software. NPOC and absorbance samples were taken at the same time. Autosamplers were deployed on the 7/12/2021, 20/05/2022 for CL and 22/02/2021, 19/02/2022 for GD. For AS, all NPOC samples were taken exclusively using Isco 3700 autosamplers over 24 to 72 hour periods, this was done 3 times over one year (18/05/2022, 7/06/2022, 27/01/2023) with one single grab sample (7/04/2022). Data collection took place from June 2020 to January 2024.

3.2.4 Analysis

For the processing of flow from the discharge measurements the basic filtering and outlier detection and removal method as described in Sections 2.4.1.1 and 2.4.1.2 were used. Basic filtering involved the removal of NAs, rounding times to the nearest 15 minutes, removing any flow outside of the maximum capacity of the flumes and removing any negative values.

The outlier detection removed outliers out of the measurement range and used modified Z-scores based on the median absolute deviation (MAD) of a robust estimator, as described in Bae and Ji (2019). This research relies on the researcher determining site specific β scores that yielded the best results while removing the fewest possible data. The percentage of data points removed as outliers for CL, GD and AS were 0.05%, 1.99% and 1.69% respectively. These outliers likely occurred

from issues with the flume technology, as the inflow pipe can get blocked with debris and cause false readings.

For fDOM data, the filtering process was as described in Section 2.4.2, removing any periods where the Sonde was not submerged, and correcting for temperature and IFE effects, as per De Oliveira *et al.* (2018).

As the simple regression between continuous fDOM results and discrete DOM measurements did not yield a consistent relationship, an alternative multi-variate analysis approach was carried out between the two data sets to derive a more robust relationship. This process used an SVR relationship (Vapnik, 2000) as set out in Section 2.4.3.

The fDOM data was converted into NPOC (mg/l) as described in Section 0, and presented relative to the catchment areas of the sites in terms of areal flux (gC/m²).

3.3 Results

3.3.1 fDOM

Figure 16 a, b and c show the culmination of the filtering of the raw fDOM data for Clara, Garryduff and All Saints respectively. The breakdown of the filtering process is in Appendix 3 Flow. As per the methodology this included filtering and correction for conductivity, temperature, turbidity and outliers. Any missing data were then filled using linear interpolation for the sites to give the final time series across the monitoring points shown in Figure 16. CL (SD = 15.27 QSU) has less fluctuations in their timeseries than GD (SD = 35.31 QSU) and AS (SD = 44.59 QSU), likely due to the higher human disturbances at GD and AS such as water pumping and rehabilitation efforts. The range is greater in AS (70 to 398 QSU) and GD (48 to 321 QSU) than in CL (83 to 164 QSU). However, in AS the majority of this range is due to the dip and spike in measurements in August 2022, possibly due to a disturbance during rehabilitation efforts but no specific occurrence was reported.

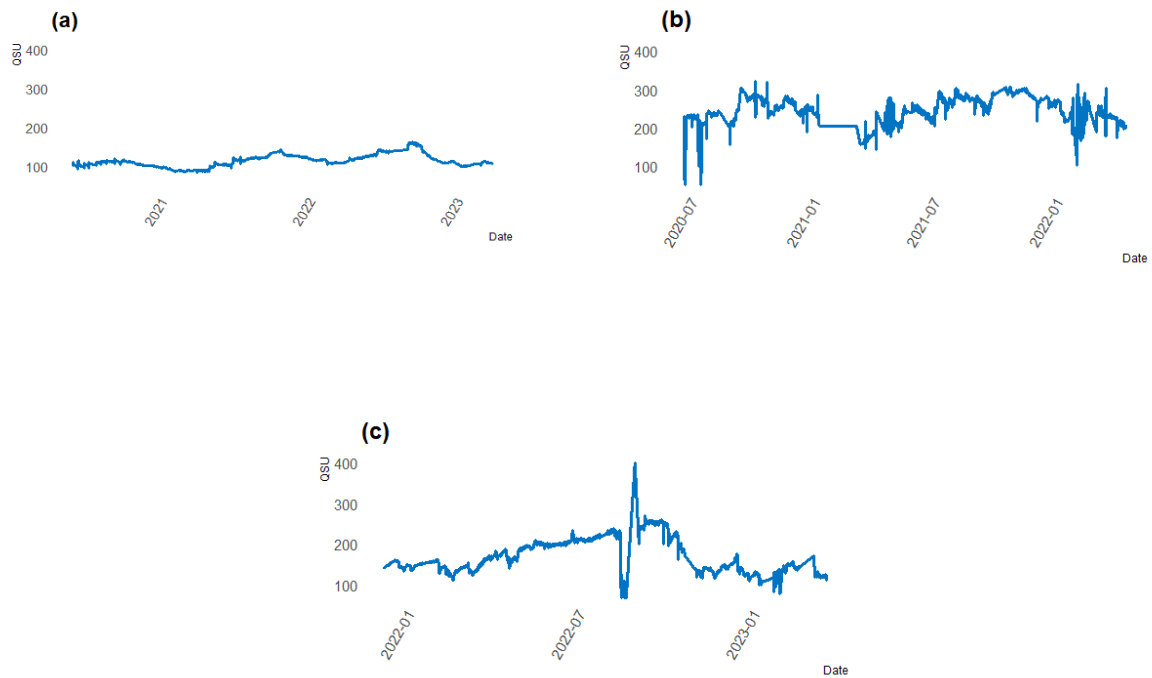


Figure 16 fDOM (QSU) of Clara (a), Garryduff (b) and All Saints (c) with outliers removed and filled with linear interpolation.

3.3.2 fDOM vs NPOC Linear Regression

Figure 17 shows the corrected values for fDOM plotted alongside the lab measured samples of NPOC from sites CL, GD and AS respectively. In CL, GD and AS 123, 90, and 62 samples of NPOC were collected respectively. Additionally, the samples in AS were almost exclusively collected using autosamplers whereas in the other sites single grab samples were taken every 2 to 4 weeks as well as autosamplers being deployed.

The lab measured NPOC values for CL reach their peaks for each year during the summer and fall to their lowest values during the winter (Figure 17a). The fDOM values reflect this pattern.

GD NPOC values increase and decrease along with the fDOM. However, the affect is less pronounced than in CL (Figure 17b) . This is likely due to the range of NPOC values being considerably smaller than in CL. In GD this range is between 15.99 mg/l to 29.04 mg/l. Whereas in CL this range is between 15.04 mg/l to 56.84 mg/l.

For AS, NPOC values follow the fDOM pattern (Figure 17c), however, it is also evident that the range of the NPOC values over each individual autosampling period is not represented in the fDOM data. This can also be seen in the autosampling periods for CL (Dec 2021 and Feb 2020) and GD (Feb 2021).

Within these types of raised bog systems, it is possible that previously established methods of determining the relationship between NPOC and fDOM may not capture the complexity of the sites. Nonetheless, there is an apparent correlation between the NPOC and corrected fDOM timeseries for CL and GD (Figure 17a and Figure 17b). In AS (Figure 17c) there is no apparent correlation in the time series, likely due to the fact that less consistent NPOC measurements were undertaken spaced over time for this site and as such there is a less continuous record of NPOC to compare.

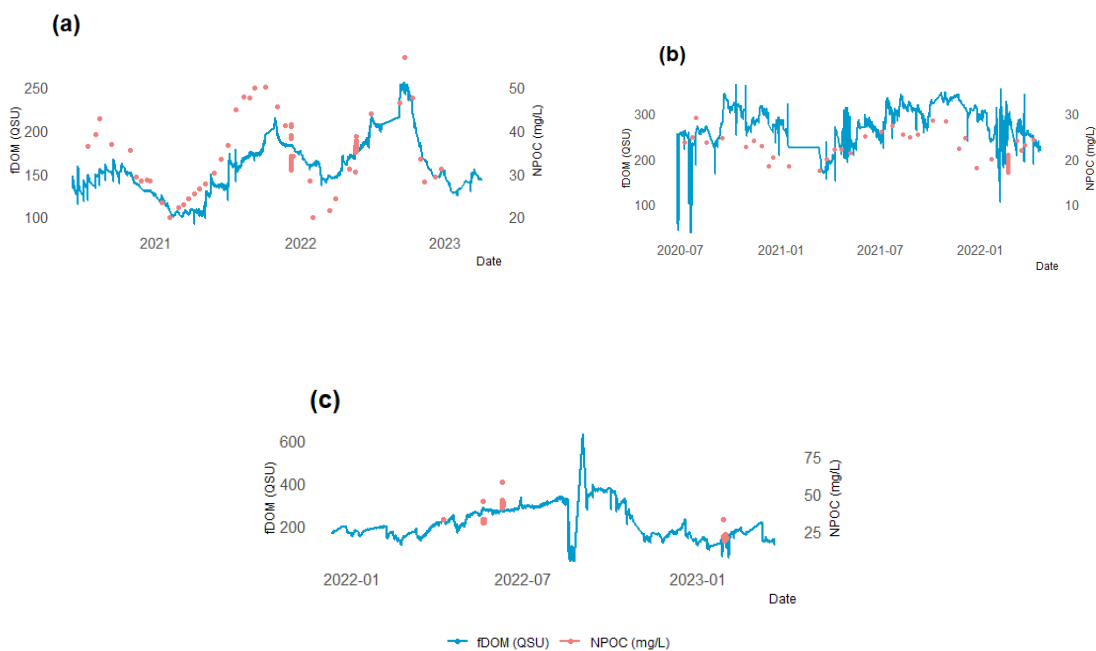


Figure 17 CL corrected fDOM (QSU) plotted alongside the lab measured grab samples of NPOC (mg/L) (a) Garryduff corrected fDOM (QSU) plotted alongside the lab measured grab samples of NPOC (mg/L) (b) All Saints corrected fDOM (QSU) plotted alongside the lab measured grab samples of NPOC (mg/L) (c)w

The measured NPOC and corrected fDOM data were plotted to create an initial estimated correlation between NPOC and fDOM for the three sites (Figure 18). For CL and AS, the relationship between the predicted and measured NPOC is statistically significant (p value $9.7e-13$ and $2.86e-12$ respectively) but not for GD (p value 0.83). However, despite the statistical significance as can be seen by the the r squared values of Figure 18 and time series trends in Figure 19, there still appears to be significant deviations in the predicted NPOC compared to the measured NPOC. AS shows the strongest correlation (r squared: 0.575), though likely due to the poor distribution of the data, with GD showing the weakest correlation (r squared: 0.000902), although no correlation is very strong. The weak correlation between the predicted NPOC and measured NPOC is also

supported by the Nash–Sutcliffe efficiency (NSE) metric for hydrological modelling for each site, AS and CL have the higher NSE (0.57 and 0.43 respectively) with GD having the lowest NSE (0.01). AS and CL qualify as models, though are not considered as good models (NSE > 0.75 is considered a good model according to Motovilov *et al.* (1999)), whereas GD does not qualify as a model.

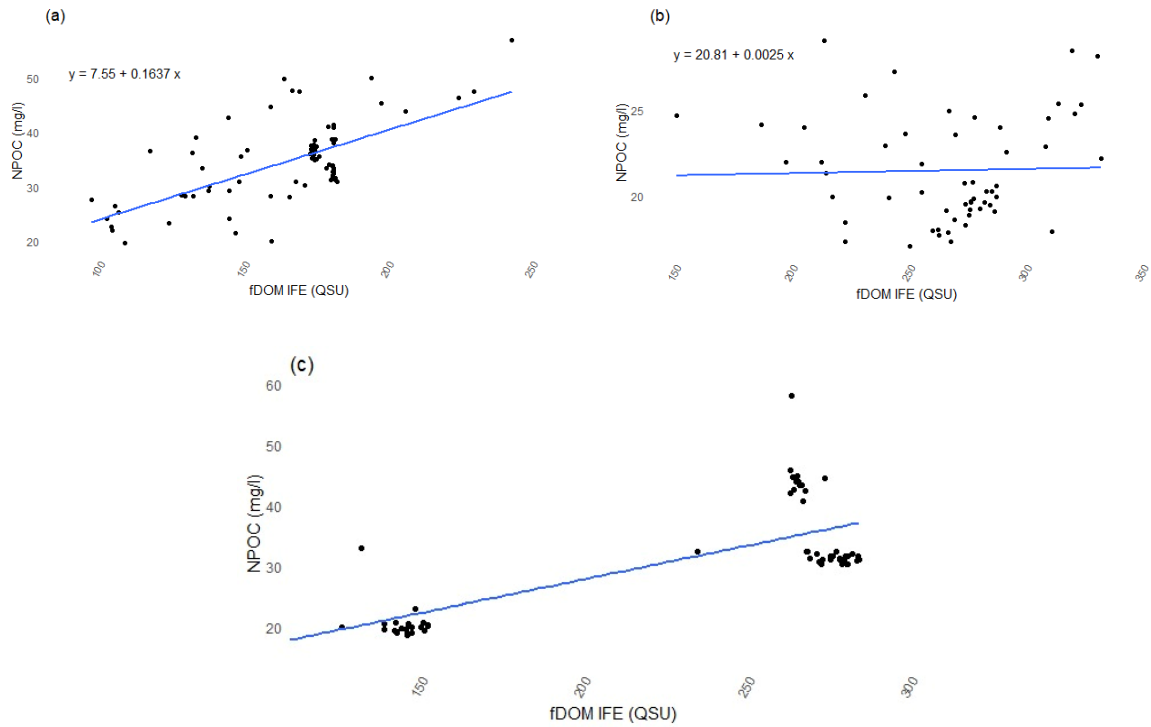


Figure 18 Scatter plots of the fully corrected fDOM vs lab measured NPOC, for CL, r squared: 0.427 (a), Garryduff, r squared: 0.000902 (b) and AS, r squared: 0.575 (c).

The predicted NPOC, derived from fDOM, follows a similar trend to the measured NPOC as fDOM did (Figure 19). For CL, both the predicted and the measured NPOC show similar fluctuations, ranging between 23 and 49 mg/l and 20 and 57 mg/l respectively, with a standard deviation of 5.09 and 7.08 respectively. For GD, the standard deviation and range for both predicted and measured NPOC (SD of 0.89 and 3.10 mg/l respectively and range of 16 and 23 mg/l and 17 and 29 mg/l respectively) is lower than CL, as can be seen in Figure 19b, it both NPOC values show less fluctuation compared to CL and AS. AS shows the highest standard deviation for both predicted and measured NPOC (9.10 and 9.62 mg/l respectively) as well as the highest range (8 to 76 mg/l and 19 mg/l respectively) of all the sites, likely due to its high fluctuations in 2022.

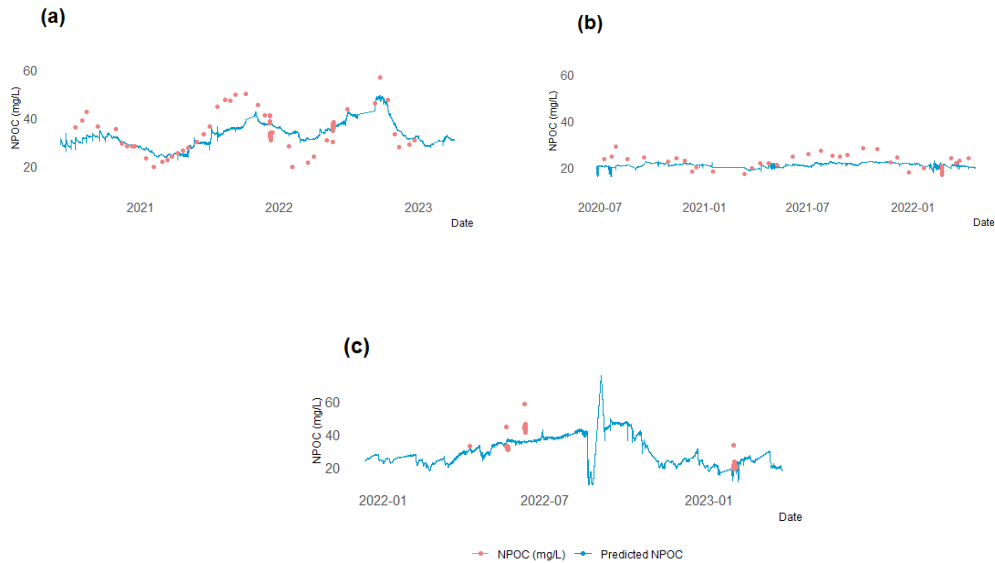


Figure 19 Predicted NPOC and measured NPOC timeseries for CL (a), GD (b) and AS (c).

3.3.3 fDOM vs NPOC Multivariate Analysis

The multi-variate approach was used for all sites determine which combination can be used to best to derive the optimum relationship between fDOM and NPOC, given the low r squared values between the predicted and measured NPOC as established in the previous section. This method uses the CDF Inversion Method.

For CL, functions of fDOM and rainfall considered over a 3-hour window were used to get the third highest value of NSE (0.811 compared to 0.814 for the 36-hour window and 0.821 for the 48-hour window). The reason that this value was used as opposed to the model that looked at fDOM expectation function and variability of fDOM and over a 48-hour window was that it only resulted in a very small difference in the NSE. The benefits of the smaller time window is that it requires considerably less data to develop the model, and also to simulate the model for future data and so the 3-hour window was used. For GD, functions of fDOM considered over a 36-hour window was used as it had the highest NSE (0.866). For AS, functions of fDOM and conductivity over a 12-hour window showed the best results (0.93). It should be noted that in AS the model was calibrated (on 7% of the data) and validated (on the remaining 30%) intermittently throughout the time series as opposed to the other two bog sites where the models were calibrated on the initial 70% of the data and validated on the final 30%. Overall, as can be seen in Figure 20, the chosen relationships show a higher correlation to the observed NPOC measurements for all sites compared to the linear regression method employed in Section 3.3.2, with all sites having an NSE higher than 0.75 which would be considered a good model (Motovilov *et al.*, 1999).

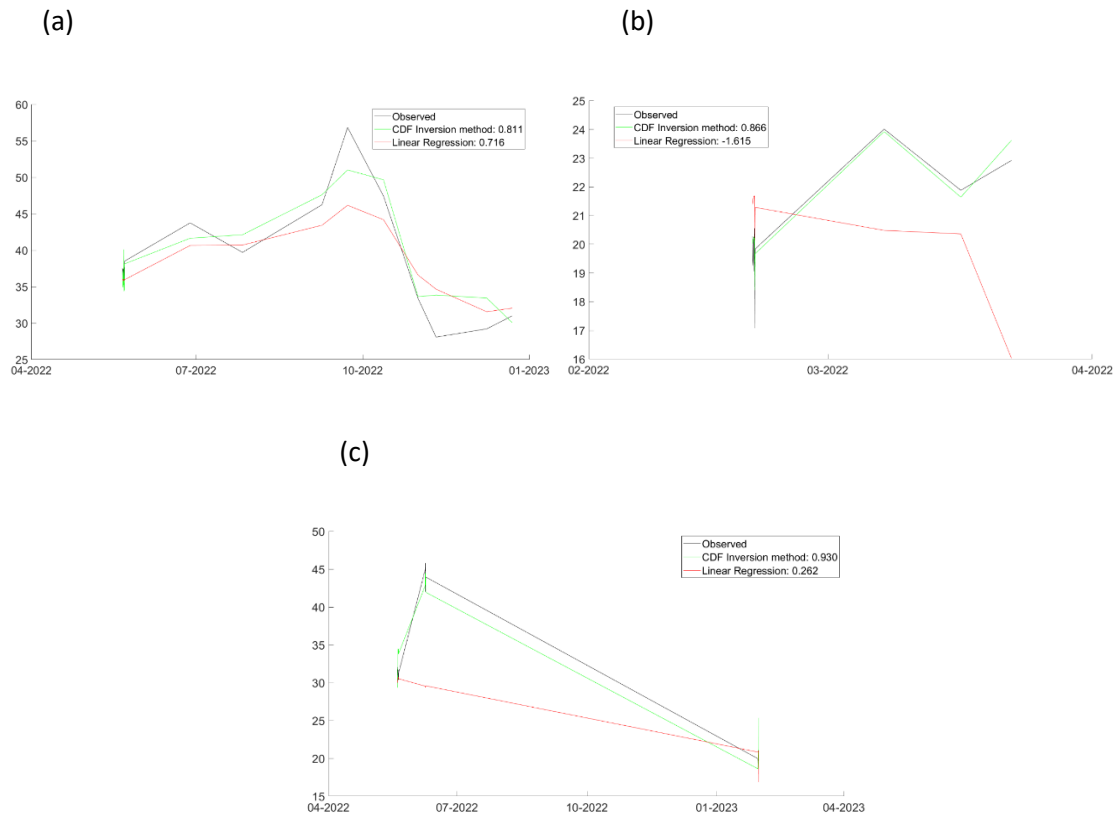


Figure 20 The observed values of NPOC vs the estimated values based on linear regression and the CDF Inversion Method for CL (a), GD (b) and AS (c).

After plotting the simulated and measured NPOC timeseries (Figure 21), it appears that despite the statistical significance and general accuracy of this method, the AS simulated and measured NPOC follow very different trends (Figure 21c). This may be because during the period where the predicted NPOC shows high fluctuation in August 2022 (Figure 19c), there is no measured NPOC values and the multivariate approach using NSE is sensitive to outliers and high fluctuations. Therefore, in this instance for AS, the lack of consistent measured NPOC data may be throwing off the analysis. For CL and GD, the trend in simulated NPOC appears to follow the trend in measured NPOC, with the exception of the end of 2021 in CL, when the fDOM sensor broke down and some data points were missing. This unfortunately coincided with a peak in NPOC, and as NSE is biased in predictions if the model misses peaks and troughs, the missing data at this important period likely lead to incorrect predictions for that period.

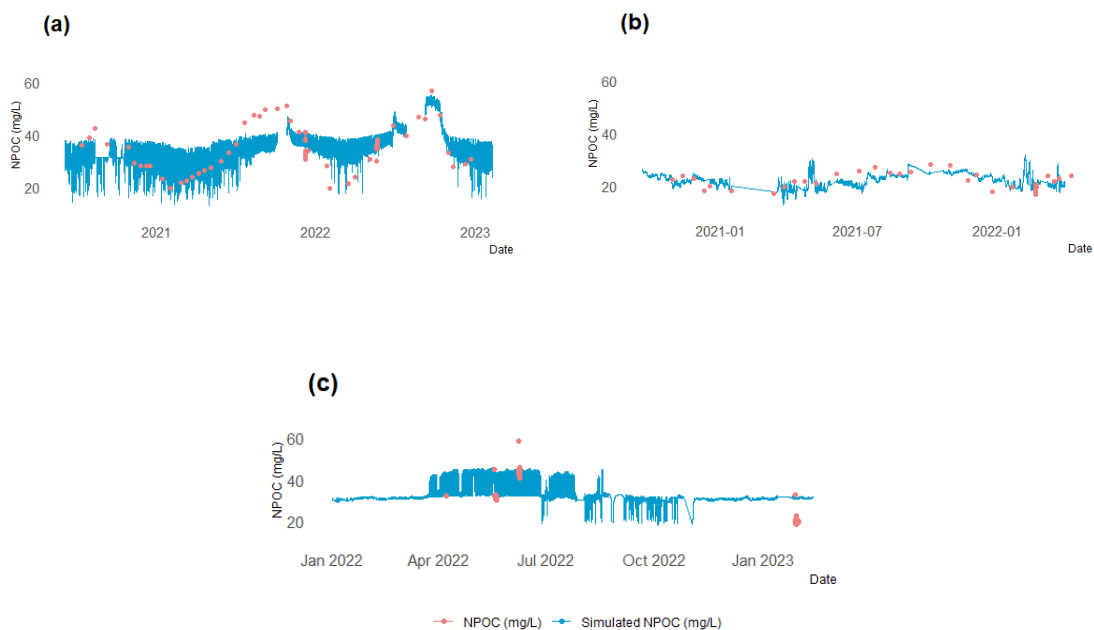


Figure 21 Time series of simulated NPOC and measured NPOC at CL (a), GD (b) and AS (c).

Overall though the model appears to follow the short-term variability seen in auto sampling regimes better than the linear model does. The NPOC derived from autosampling was used to compare to the NPOC derived from the linear and multivariate fDOM-NPOC relationships. The autosample data was selected as it has high frequency samples over a few days, which will show the short term variability of NPOC better than the grab samples taken every 2 weeks.

When looking the range and SD of NPOC from the three sources, the SD of the autosample NPOC is higher than both models for all sites. For CL and GD, the multivariate NPOC has a higher SD than the linear NPOC, therefore there is more variation in the multivariate NPOC data than in the linear NPOC data, although not as variable as the autosample NPOC. This indicates that the multivariate derived NPOC is closer to capturing the short term variability of NPOC in CL and GD than the linear regression derived NPOC. However, since very few autosampling regimes were taken (2 for CL and 1 for GD), it is possible that more autosampling regimes could be used to improve the multivariate model.

For AS, the linear NPOC has a higher SD than the multivariate NPOC. This is an indication that the AS multivariate model is not representative of the short changes in NPOC, as can be seen visually in the timeseries of simulated vs measured NPOC in Figure 21.

Table 4 Comparison of the minimum, maximum and standard deviation of the NPOC outputs from autosamples, linear regression and multivariate analysis.

		Min	Max	SD
CL	NPOC autosamples	30.3	41.3	2.8
	NPOC linear	35.7	37.6	0.6
	NPOC multivariate	34.2	40.09	1.2
AS	NPOC autosamples	18.6	58.1	9.1
	NPOC linear	15.7	37.2	7.4
	NPOC multivariate	30.5	44.8	5.7
GD	NPOC autosamples	17.1	20.8	1.1
	NPOC linear	20.7	21.5	0.2
	NPOC multivariate	20.01	20.7	0.34

3.3.4 Flux Measurements

The final derived flux values (gC/m^2) of each site's catchment area using the fDOM and NPOC correlation using linear regression and multivariate analysis are presented in Table 5. The mean change between the two methods for GD is 0.03 gC/m^2 , CL is 0.01 gC/m^2 and All Saints is 1.37 gC/m^2 . CL and GD overall shows the lowest change in flux values between the two methods, with AS showing the highest. This shows that the overall effect of the multivariate analysis on NPOC export value estimation seems to be low when compared to just using the NPOC values derived from the simple linear relationship between fDOM and measured NPOC as in Section 3.3.2.

Table 5 The derived NPOC fluxes (g/m^2) from the bogs using the continuous fDOM measurements converted into NPOC using linear regression and multivariate analysis was undertaken. Figures in bold are for full annual (12-month) monitoring.

	All Saints Flux (g C/m^2)		Garryduff Flux (g C/m^2)		Clara Flux (g C/m^2)	
Year	Linear Regression	MV Analysis	Linear Regression	MV Analysis	Linear Regression	MV Analysis
2020	NA	NA	4.12 ^a	4.25 ^a	8.16 ^b	7.93 ^b
2021	NA	NA	9.46	9.49	10.57	10.68
2022	10.63	12.00	4.16 ^c	4.21 ^c	9.44	9.29
2023	2.02 ^d	3.4 ^d	NA	NA	2.24 ^d	2.21 ^d
Full Year Averages	10.63	12.00	9.46	9.49	10.00	9.99

^a Sept to Dec 2020

^b June to Dec 2020

^c Jan to March 2022

^d Jan to Feb 2023

3.4 Discussion

This study set out to determine the feasibility of using fDOM in-situ measurements as a proxy for NPOC concentration in three temperate raised bogs of varying conditions.

The traditional linear regression methods for determining a relationship between NPOC and fDOM i.e. trying to correlate continuous fDOM measurements against periodic samples of lab measured NPOC as Downing *et al.* (2012) and De Oliveira *et al.* (2018) did not appear to work well in these peatland systems with high concentrations of NPOC. While the relationships were statistically significant for AS and CL, the lower sample of measured NPOC in AS makes correlation difficult. NSE coefficients indicated that the models for CL and AS qualify but are not good. This is likely due to the relatively high concentrations of NPOC in the runoff from these bog systems measured at the study sites. NPOC measurements were the only factor of all factors used for correcting fDOM that were not within the limits of the De Oliveira *et al.* (2018) method. In most previous studies determining the relationship between NPOC and fDOM the concentration of the NPOC was between 0.6 and 24.2 mg C/l (see Appendix 1: Summary of peatland carbon studies), whereas in this study the NPOC concentrations range between 15.04 and 58.12 mg C/l across the sites.

The NPOC concentration in a peatland runoff waterway is determined by numerous factors, including precipitation, soil moisture, flow discharge, temperature, and pH and the hysteresis between those processes (Hope, Billett and Cresser, 1994; Inamdar *et al.*, 2006; Clark *et al.*, 2007; Evans, Renou-Wilson and Strack, 2016). Multivariate analysis was therefore used to attempt to take into account some of these confounding variables and to derive a more nuanced and improved relationship between NPOC and fDOM.

When the multivariate approach was used based on a machine learning Support Vector Regression model, good models were determined for all three sites, according to NSE coefficients (all NSE coefficients were over 0.75). This indicates that using this method, fDOM can be used as a proxy for NPOC concentrations in these systems, with good accuracy. Although the annual measurements of flux did not change by much between models the multivariate approach appeared to capture the short-term variability of the NPOC concentrations better than the linear model, with the exception of AS. It may be an indication that more frequent auto sampling regimes could better correlate fDOM to these short-term changes in NPOC. However, in AS, where there was predominantly autosampling regimes, the seasonal changes in NPOC concentration were not as represented by the fDOM, as there were not enough consistent samples over the period, even if the model has a high NSE, we cannot be confident in the model due to the low samples. In general, this may represent the need for the combination of consistent grab sample

measurements as well as more frequent autosampling measurements for periods over 1 to 3 days. This, however, puts into question the feasibility of fDOM technology from an economic perspective, if consistent in situ measurements are required to determine the site specific relationship between fDOM and NPOC concentrations, given that fDOM is site specific (Downing *et al.*, 2012).

A strength of this model is that it is constantly adjusting the relationship between fDOM and NPOC over time, not relying on a fixed relationship. This is currently the first time, to this study's knowledge, that multivariate analysis was used to determine the relationship between fDOM and NPOC. Within the three study sites different models were used with high degree of certainty being reached. The fact that this model relies entirely on the fDOM and NPOC data may be due to other variables being "slow" variables, meaning they require more time to affect the NPOC, creating a lag between cause and effect, i.e. the hysteresis effect. Variables like changes in hydrology, soil carbon content and temperature have been shown to have a lag effect on NPOC (Freeman *et al.*, 2001; Holden and Burt, 2003; Daniels *et al.*, 2008; Broder and Biester, 2015; Dick *et al.*, 2015), therefore it can be assumed they have an affect on NPOC, but due to the lag effect, our model did not pick them up as predicting variables. Further study would be required to identify how these hysteresis effects could be picked up by the model.

The different approach to calibrating and validating the AS model was due to the drop in NPOC concentration at the end of the measurement period. This drop is possibly a result of the rehabilitation taking place on the site. During the beginning of the measurement period, there was a lot of rehabilitation occurring on the site, including the digging up of soil to create bunds. This disturbance of soil would have exposed carbon rich peat to the air, increasing decomposition of carbon into any water it comes in contact with (Moore *et al.*, 2013; Brown *et al.*, 2015; Rosset *et al.*, 2022). As the rehabilitation slowed down and the more extreme disturbance of the site reduced, less of the peat would have been exposed to decomposition, possibly explaining the NPOC concentration drop at the end of the measurement period in AS. However, this relationship would have to be confirmed with more consistent NPOC measurements to better capture the timeseries of the change.

Another limitation of this study is determining whether the UV range used for detecting fDOM as per the manual was suitable for these sites. The UV range can differ depending on the type of DOM in water, between 200nm and 500nm (Lebret *et al.*, 2018; He *et al.*, 2021), therefore a PARAFAC analysis specific to DOM in temperate raised bogs of different conditions could be necessary to ensure that the sensors are picking up DOM accurately (Zhang *et al.*, 2020).

The overall effect of the multivariate analysis on the annual export of NPOC for the sites appears to be minimal. Between pre and post multivariate analysis, there was a 0.01% decrease, 0.03% increase and 12.8% increase in flux for CL, GD and AS respectively. For CL and GD, this is a very small change and puts into question the overall usefulness of multivariate analysis for the calculation of annual NPOC export. However, given the greater statistical confidence in the multivariate analysis of the relationship between NPOC and fDOM, we can be more certain of the NPOC export results overall. For example, the multivariate analysis seems to better align with the short-term variability of NPOC concentration seen in the autosampling measurements compared to the linear relationship of NPOC and fDOM. While there was more of a change for AS, given the lack of confidence in the final result due to lack of consistent data, this may not be a useful case study for this technique.

3.5 Conclusion

In general, this study found that using a simple correlation between fDOM to NPOC, as per the methodology presented in Downing *et al.* (2012) and De Oliveira *et al.* (2018) does not provide sufficient accuracy for these temperate peatlands studied in Ireland. This is likely due to the fact that these sites have higher NPOC values than the sites studied previously using fDOM. Since there are multiple factors which influence the NPOC concentration in a peatland waterway such as precipitation, soil moisture, flow discharge, temperature, and pH and the hysteresis between those processes, multivariate analysis was used to attempt to account for them. Using the multivariate approach in this study a statistically significant relationship between fDOM and NPOC could be determined in all three sites.

A potential strength of this model is that it is constantly adjusting the relationship between fDOM and NPOC over time and thereby not relying on a fixed relationship. Within the three study sites different models were used with high degree of certainty being reached. The multivariate approach is a more statistically robust method of predicting NPOC from fDOM compared to a simple linear relationship in these sites, better representing the short-term changes in NPOC concentration seen in autosampling measurements. However, the annual measurements of NPOC export changed very little between the two methods of predicting NPOC, likely due to the export being based on an average over the year. This suggests that fDOM, in tandem with multivariate analysis can be beneficial in looking at the short-term changes of NPOC concentration in these raised bog systems, and therefore can be more assured of the final NPOC export calculations.

However, likely due to hysteresis, many of the important impact variables relating to NPOC were not taken into account by the models with the highest NSE. Therefore, while there appears to be

potential for this method, there is also a need to identify how it can pick up the impact of these important variables and whether this would in fact improve the models output.

Fundamentally, the findings of this study raises the question of the economic feasibility of the fDOM technology. Given that the relationship between fDOM and NPOC is site specific, if consistent measurements along with autosampling are required to accurately predict NPOC from fDOM in raised bog systems, is this method worth the economic cost? This will depend on the goal of any such study – if the goal is to better understand short term fluctuations in NPOC concentrations in raised bog systems, then this method may required. However, if the aim is to simply determine reasonable estimation of annual NPOC export, then there may not be a need to invest in this technology and method. Therefore, a cost benefit analysis would need to be carried out depending on the case.

Given the importance of the rehabilitation of peatlands in Ireland and Europe and the role of fluvial carbon in the overall carbon budget of peatlands, there is a need focus on the following aspects of future research, in relation to using proxies to estimate fluvial carbon fluxes: (1) the lag time between variables affecting NPOC concentration; (2) further determining of the frequency of measurements required; (3) the extent to which the fDOM systems can be improved to take into account short term changes in NPOC; (4) a PARAFAC analysis of UV absorption of DOM in raised bog systems of different conditions to more accurately estimate NPOC and; (5) the economic feasibility of this technology depending on the project goals.

4 Chapter 2 - Insights into the hydrology and catchment delineation for three raised bogs in Ireland representing a range of ecological conditions

4.1 Introduction

Globally peatlands cover approximately 3% of Earth's land area but store ~30% of global terrestrial carbon (Frolking *et al.*, 2011). Within the European Union (EU) this percentage jumps to over 50% (Tanneberger *et al.*, 2021). Drainage has a detrimental effect of peatlands resulting in a reduced capacity to store or even retain terrestrial carbon, water quality and biodiversity. In fact approximately 46% European peatlands have stopped accumulating peat all together (Tanneberger *et al.*, 2017). Ireland contains one of the highest concentrations of wetlands in Europe with approximately 60% of the remaining raised bog habitat area in the European Union (EU). However, only 9% of the original raised bog area is considered to be suitable for conservation and less than 1% of this area is actively forming peat (National Parks and Wildlife Service, 2017). Given their importance for carbon storage and sequestration, the rehabilitation of peatlands is a priority in the most recent Climate Action Plan of Ireland, aiming to rehabilitate 77,600 hectares of peatlands across numerous landowners and projects (Government of Ireland, 2023). This will require significant rewetting projects, which underlines the necessity of understanding the ecohydrology of peatland systems.

When conceptualising the ecohydrology of a raised bog system, two main storages are usually considered that have different responses to precipitation inputs. The biggest storage is the catotelm, which sits on or in the regional groundwater body and consists of permanently saturated and well-decomposed compressed peat soil, with low hydraulic activity and has no peat forming aerobic microorganisms. The hydraulic connection between the groundwater body and the catotelm will vary across different raised bogs. Typically, these systems are distinct from deeper groundwater, however, where more permeable materials underlie them, deeper groundwater can affect the hydrology of the bog ecosystem through hydraulic gradients between the wetland and substrate materials. This can be more commonly seen in low-lying peatland ecosystems, such as fens (Lowry, Fratta and Anderson, 2009; Johansen, Pedersen and Jensen, 2011; Rossi *et al.*, 2012) but in these cases the positive upward hydraulic gradients leads to an actual recharge of water into the fens from the underlying aquifer. Whereas in raised bogs the hydraulic gradient may instead be providing upward pressure without upward flow ingressing into the bog itself (Regan *et al.*, 2019).

The smallest of the two storages is the acrotelm, which has high hydraulic conductivity, an oscillating water table, variable water content, is subject to periodic entry of air after lowering of water table, is rich in peat forming aerobic bacteria and is mainly dominated by *Sphagnum spp.* mosses (Ingram, 1978). The acrotelm is considered the active layer as the residence time of water in this layer is much less than in the catotelm. While an acrotelm is a thin layer, it has a large effect on the hydrology due to its higher hydraulic conductivity (and transmissivity) compared to the catotelm.

An important component of acrotelm is the *Sphagnum spp.*, which, when there is an intact layer of the species in a bog, indicates an intact raised bog system. It has been described as a keystone species (Rocheft, 2000) and has been noted to be a major indicator of CO₂ assimilation on rehabilitated and rewetted bogs (Nugent *et al.*, 2018; Swenson *et al.*, 2019). The porous structure of the *Sphagnum spp.* is conducive to runoff and storage processes. To maintain *Sphagnum spp.* on the acrotelm, the mean water level needs to be within 10-15 cm of the surface, a low threshold due to evapotranspiration directly replaced by either precipitation or capillary transport from the water table (Robroek *et al.*, 2009). The ground level of a bog, however, is not static as the surface rises or falls as a result of rainfall, drought or gas volume (Ingram, 1983; Camporese *et al.*, 2006). This is an important aspect of maintaining the relatively narrow specifications for *Sphagnum spp.* growth in a healthy bog.

Any change to the regional groundwater level due to human interference or natural processes such as drought can have more significant effects on peatland hydrology than disturbance to surface hydrology (Regan *et al.*, 2020). The hydraulic conductivity (K) profile of peat controls the rate of subsurface drainage. This combined with the hydrogeological properties of peat, control the water flow and storage processes in peatlands (Beckwith, Baird and Heathwaite, 2003; Price, 2003).

In extracted peatlands, drainage disrupts natural hydrology, lowering the water table and redirecting water flows (Holden *et al.*, 2006). This drier environment favors shrubs and trees over *Sphagnum* moss, altering vegetation (Laine, Vasander and Laiho, 1995; Murphy, Laiho and Moore, 2009) and increasing peat oxidation, which releases CO₂ and NPOC into the air and water (Rowson *et al.*, 2010). Drained peatlands also show heightened runoff sensitivity to storm rainfall (Holden, Chapman and Labadz, 2004; Holden *et al.*, 2006). Restoration efforts, including rewetting and drain damming, impact hydrology depending on the duration of drainage, affecting nearby water tables (Gaffney *et al.*, 2020). Full vegetation recovery can take 3–15 years, influenced by dam effectiveness and restoration season (González and Rocheft, 2014; Gaffney *et al.*, 2020). Models

suggest that while most peat loss occurs within 50–100 years of drainage, only partial recovery is likely even after 200 years of rewetting (Young *et al.*, 2017) highlighting the extensive time required to potentially restore pre-drainage conditions.

Given the importance of *Sphagnum* in the carbon cycle of a bog and its dependence on water levels, the study of the ecohydrology of bogs is important for better management of the bog sites in general and the understanding of climate change impacts. Understanding the ecohydrology of a bog requires a knowledge of its inputs and outputs. Swenson, Regan and Gill (2020) used microcosms combined with evapotranspiration and rainfall data in the field to understand the dynamics of shallow lateral flow of Abbeyleigh bog in Ireland. They found that the timing and magnitude of the lateral flow differed considerably between locations with differing ecological conditions. Where *Sphagnum spp.* moss layer was present, the upstream catchment provided a slow continuous net lateral input of water supporting the water table during drought periods, however this was not observed in locations lacking *Sphagnum*. In this study, the microcosm methodology was used combined with measured and predicted measurements of evapotranspiration, met station data and outflow data through flumes. This combines the observations from the one-dimensional microcosms with the larger outputs of flow and ET with the input of rain to determine the ecohydrology of these sites and how they differ based on management.

This study set out to determine the differences between three raised bog sites of different management conditions - near natural, rehabilitation through bunds and degraded with rehabilitation works pending - based on their hydrological regimes.

4.2 Methods and Equipment

4.2.1 Study Sites

The study sites for this section are as presented in Section 2.1, with all three study sites included; Clara (CL), Garryduff (GD) and All Saints (AS).

4.2.2 Equipment and Measurements

This paper focused on discharge (Section 2.2.1), meteorological (Section 2.2.3, micrometeorological (Section 2.2.4) and storativity (Section 2.2.5) measurements.

4.2.3 Data Collection

Flume data were telemetric and were logged online. These data were downloaded from a Van Walt Server. The OTTs for WTH and flow were downloaded once a month during field visits and the diver data was collected at the end of the study period.

4.2.4 Analysis

For the processing of flow from the discharge measurements the basic filtering and outlier detection and removal method as described in Sections 2.4.1.1 and 2.4.1.2 were used. Basic filtering involved the removal of NAs, rounding times to the nearest 15 minutes, removing any flow outside of the maximum capacity of the flumes and removing any negative values.

The outlier detection removed outliers out of the measurement range and used modified Z-scores based on the median absolute deviation (MAD) of a robust estimator (Bae and Ji, 2019).

For micrometeorological analysis, the ET was quantified using water vapour data processed using EddyProc, with PET quantified using the Penman-Monteith FAO56 (Allen and Duffy, 1998) method (as in Section 2.4.5).

Storativity of the viable microcosms in CL was calculated using the WTF method as in Section 2.4.6. For the sub-central and sub-marginal sites much of the storativity results were either significantly under 0 or above 1, therefore these microcosm were not included in the storativity results.

The catchment area for each flume were calculated using Equation 7 in Section 2.4.7, with discharge, ET and rain.

For hydrographical analysis, for each of the sites rain events with more than one hour rain were identified and reviewed to identify which rain events had a corresponding impact on the flow to analyse the link between the rain and flow. Two events per season, per site were identified as examples. Effective rainfall was also calculated for each during the study period to compare to flow. This was done by subtracting the daily ETec data from daily rain data.

4.3 Results

4.3.1 Evaluation of Eddy Covariance ET and PET

The relationship between eddy covariance flux tower-based daily evapotranspiration rates (ETec in mm/day) and potential evapotranspiration rates for CL is similar for 2020 and 2021, with a deviation for 2022 and 2023 (Figure 22a). 2021 shows the higher r-squared value (0.80), therefore stronger relationship between ETec and PET. For AS, the relationship shows a higher r-squared value (0.57) for 2023 than 2022 and 2021 (Figure 22b), but overall, the relationship between ETec and PET has a lower r-squared in AS than CL. In AS, the relationship between ETec and PET also seems to improve in the year where the water level increases (2022 to 2023 had an increase of 0.24m increase in water table height, Appendix 3 Water table). As PET assumes an infinite supply of water (Pereira *et al.*, 1999, 2015), the higher the water availability, the closer the relationship

between the ETec and PET, which has been found by other evapotranspiration studies (Kar, Verma and Singh, 2006; Zeppel *et al.*, 2008; Liu *et al.*, 2017).

All r-squared values are above 0.5, which are generally considered to be acceptable for models (Santhi *et al.*, 2001; Van Liew, Arnold and Garbrecht, 2003; Moriasi *et al.*, 2007).

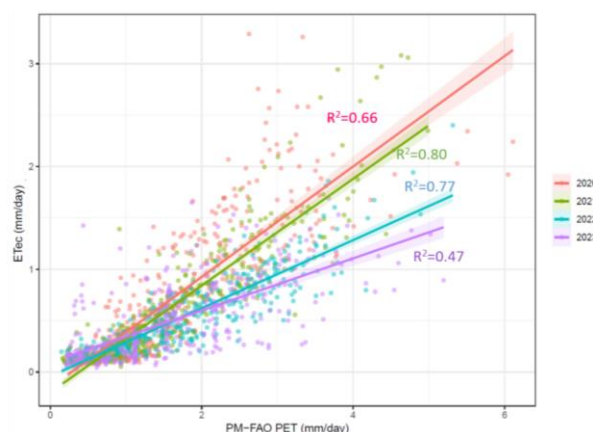
For GD, only PET values were available due to the lack of an EC tower on site. To remedy this, values for crop coefficient (Kc) for AS were used as an indicator for GD. Using these indicative crop coefficient values, estimated values of ETec were determined. The Kc of AS was considered to be the closest to GD, as both sites are mainly bare peat. Given that standard Kc values of the same vegetation types are often transferred between different locations and climates, it was reasoned that the Kc of two largely bare peat sites would be similar.

For all sites, the annual PET values are much higher than the ETec values (Table 9). For CL, the average annual PET is 615.74 mm compared to ETec of 242.58 mm. For AS, the average annual PET is 711.4mm compared to ETec of 269.6 mm. For GD, PET is 817.27mm compared to 261.525mm.

For CL, ETec appears to reduce slightly every year from 2020 but this pattern is not reflected in PET, with a decrease in PET in 2021 but a subsequent increase in 2022, followed by a decrease again in 2023. For AS, for the two full years that can be compared, ETec increases from 2022 to 2023, but PET reduces. For GD, PET and ETec both increase from 2021 to 2022 although that is due to the same crop coefficient being used to estimate ETec.

For CL and AS, the trends over the months show similar patterns for both ETec and PET, with lower values in the winter period and the peaks reached during the summer period (Figure 22).

(a)



(b)

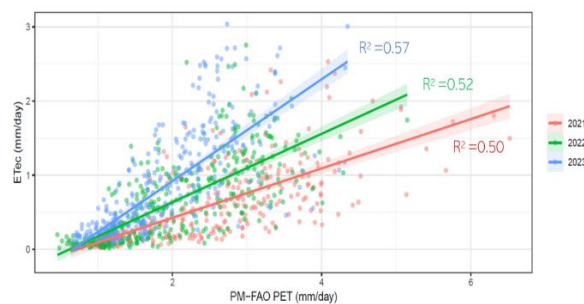
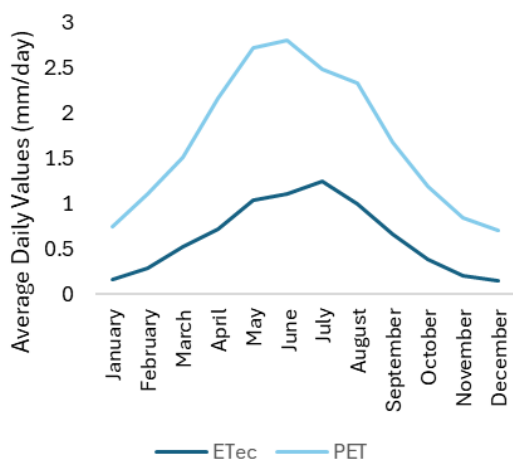


Figure 22 Scatterplot showing eddy covariance flux tower-based daily evapotranspiration rates (ET_{ec} in mm/day) versus potential evapotranspiration rates at CL (a) and AS (b). Note: Windspeed data used in the PET calculation was retrieved from the nearest Met Éireann weather station (Mullingar for CL and Gurteen for AS) as windspeed was not recorded at CL or AS.

(a)



(b)

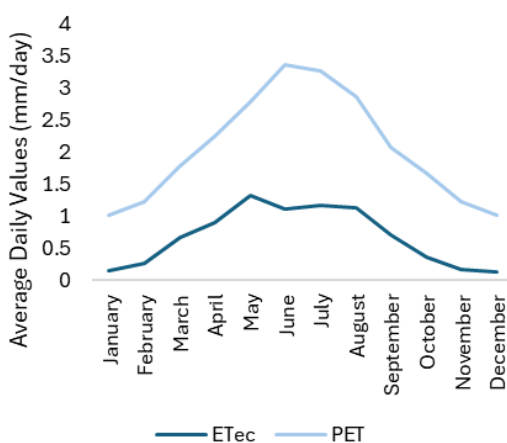


Figure 23 Comparison of the trends in average daily ET and PET for the different months for CL (a) and AS (b).

To better compare the ETec values to PET, effective rainfall and catchment sizes were calculated using both values. When using PET for effective rainfall (

Table 6), for GD and AS, some unlikely values for ER are derived such as 1.31mm for GD in 2021 and -65.97mm in 2022 for AS. Given the flow and the fact that these sites are wet for most of the year, these ER values would be unexpected. PET also provides unlikely or impossible estimations of catchment sizes when compared to ETec (Table 7), for GD PET derived catchment size significantly overestimates the size (1299.72 km² compared to the LIDAR derived catchment of 2.22 km²) and provides a negative value of catchment for AS. For CL however, PET provides a calculation of catchment size closer to the LIDAR estimation than ETec, although the ETec estimation is not too far off the LIDAR estimation.

The crop coefficients for CL and AS (Table 8) are similar to those seen in other peatland sites between 0.38 and 0.5 (Sottocornola and Kiely, 2010; Hirano *et al.*, 2016).

Given these results of effective rainfall, catchment size and crop coefficients, it was determined that ETec could be used going forward to compare these sites. For AS and GD the ETec and estimated Etec give the most the most likely results for catchment, effective rainfall and in the case of AS, crop coefficient. For CL, while PET did provide a catchment area closer to the LIDAR estimation, the crop coefficient derived from ETec is within the expected range and for comparison purposes to the other sites, ETec will be used for this site as well.

Table 6 The Effective Rainfall (ER in mm) of the different sites depending on whether ETec or PET was used, where ER = Rainfall – ET.

	CL		GD		AS	
	ERpet	ERetec	ERpet	ERetec	ERpet	ERetec
2020	380.24	734.86	-	-	-	-
2021	345.62	694.8	1.31	539.66	-	-
2022	355.64	797.6	96.15	669.29	-65.97	441.3
2023	240.54	647.24	-	-	183.24	559.51

Table 7 The catchment sizes of the sites calculated with PET and ETec as a comparison.

	CL (km ²)		Garryduff (km ²)		All Saints (km ²)	
	PET	ET	PET	ET	PET	ET
Average	0.26	0.126	652.78	1.76	-1.095	0.548
LIDAR	0.269		2.22		0.68	

Table 8 The crop coefficients of CL, GD and AS using ETec values for each year.

	2020	2021	2022		2023	
mm	CL	CL	CL	AS	CL	AS
ETec	293.14	238.2	196.4	240.7	182.76	298.49
PET	647.76	587.38	638.36	747.97	589.46	674.76
Crop Coefficient (Kc=ET/PET)	0.45	0.41	0.31	0.32	0.31	0.44

4.3.2 Comparison of the three peatlands across flow, hydrographs, effective rainfall and catchment

4.3.2.1 Flow

The final filtered and corrected flows for CL, GD and AS are shown in Figure 24. GD has the highest flow (median 23.02 l/s, maximum 907.2 l/s), AS has the second highest flow (median 1.64 l/s, maximum 110.52 l/s) with CL having the lowest flow of all study sites (median 0.86 l/s, maximum 45.6 l/s). In general, the bigger the catchment, the larger the flow, therefore the flows reflect the estimated catchment sizes of the three sites, with GD being the biggest catchment (6.075 km²) and CL being the smallest (0.126 km²).

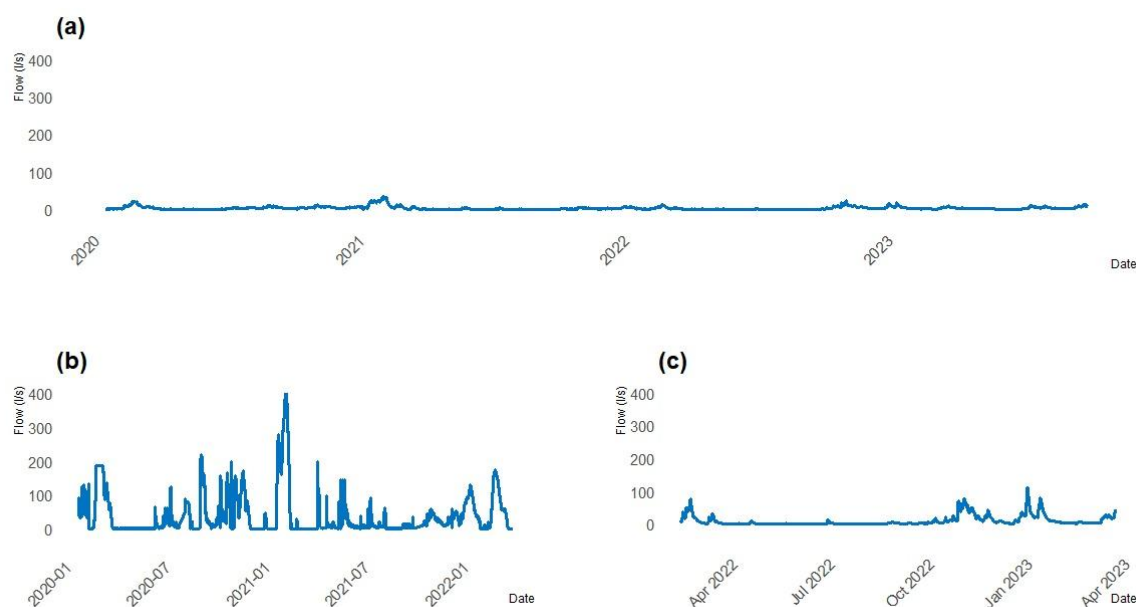


Figure 24 Flow for CL Upper (a), Garryduff (b) and All Saints (c) flow monitoring sites across the whole measurement period including flume and OTT measurements.

In terms of the average half hourly flows per season for each year measured, for CL and GD, the Winter of 2021 had the highest average half hourly flow of any season and any year for these two

sites. For AS, the highest average half hourly flow was seen in Autumn of 2023. For all sites, the highest average half hourly flow was seen in either Autumn or Winter.

CL and AS show similar patterns in their flows throughout the years per season, discounting 2020 where there is no data for AS. For Autumn, Spring and Summer, the pattern of the average half hourly flow per year in those seasons match both sites, with Winter 2021 being the exception. This could be due to the rehabilitation works on AS in 2021, which may have disturbed the natural flow regime of AS. The following winters in AS follow the same pattern as CL.

GD and CL also follow some similar patterns in the years that they can be compared. For Autumn, Summer and Winter, both sites follow similar patterns from 2020 to 2022, with a different pattern observed for each year in Spring. The similarities in flow patterns between the two sites however, are a result of different processes, as while rainfall affected both flows, the presence of the pump on GD means that the relationship between the rainfall and flow would be different to the one in CL.

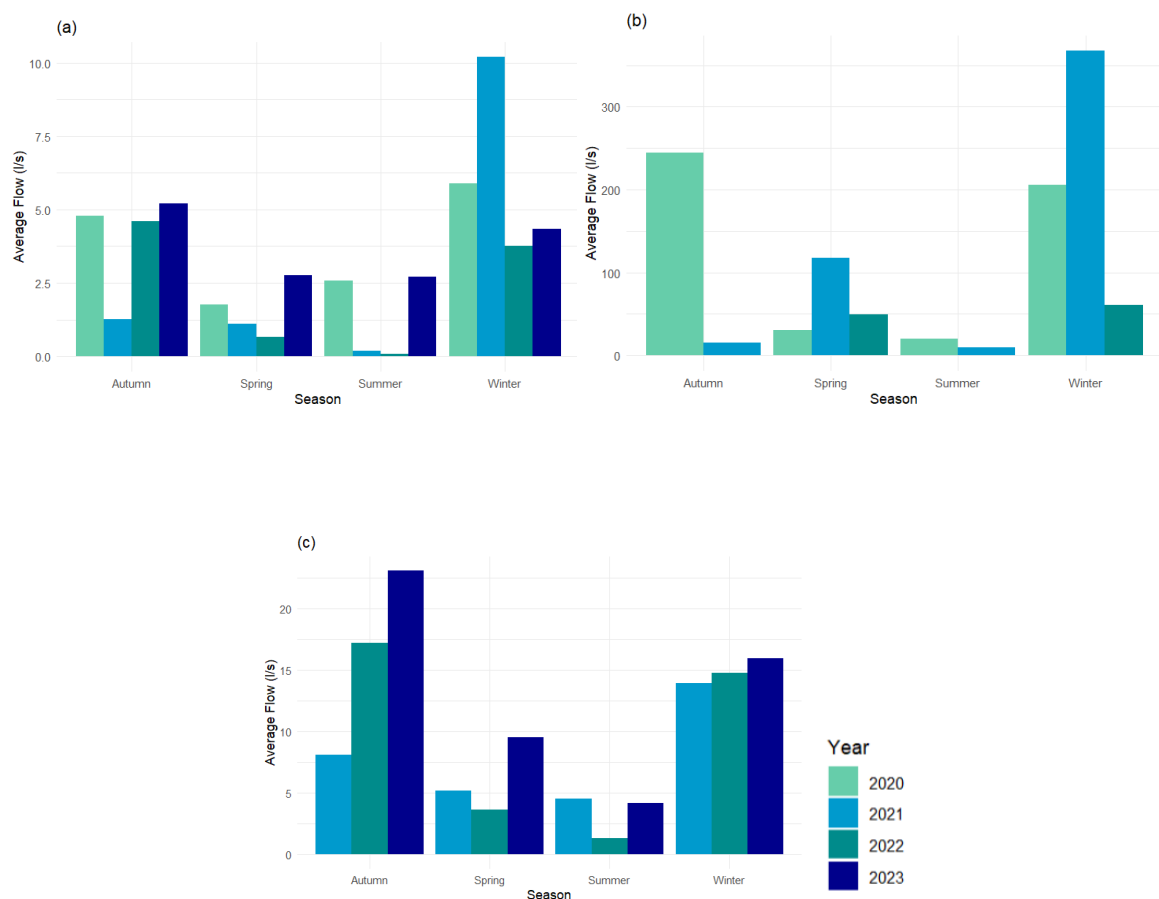


Figure 25 The average half hourly flows (l/s) for each season per year in Clara (a), Garryduff (b) and All Saints (c).

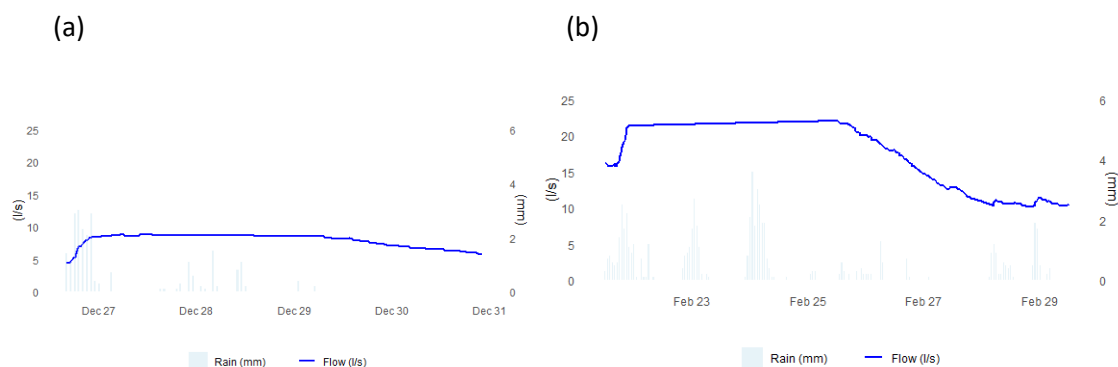
4.3.2.2 Hydrograph Analysis

The response of flow after winter rain events is different at each site. In general, the difference in volume of flow is different for the sites, with CL having the lowest volume overall, as previously established in Section 4.3.1.

For CL, overall the flow shows a less flashy response to a rain event than GD and AS in Winter (Figure 26), even though a similar amount of rain is falling. The first series of significant rain events were in December 2020 (Figure 26a). The main rain event which leads to an increase in flow (5 l/s increase between the beginning and end of the rain event) lasted 8 hours with a total of 16.4 mm of rain. The other rain events were very small with a total of 7.6 mm of rain, with no event exceeding 2.1 mm total and no obvious change in flow. The flow gradually reduces but not back to the level before the rain event, this is a similar pattern for the second winter rain event (Figure 26).

When comparing CL to AS, as the two sites with normal flow regimes without the presence of a pump, it seems clear that CL has less of a flashy response to similar rain events, and the flow more gradually decreases to pre rain event levels in CL than AS after the rain event.

GD has a specific flow response to rain events due to the presence of the pumps, this can be seen in Figure 26d, where the hourly flow response reflects the turning on and off of the pumps. Despite this, the increase in flow from the start of the rain event to the peak flow during the rain event in AS (Figure 26e and f) is similar to GD (55l/s increase and 50 l/s increase respectively). This indicates that the flow response to rain events in AS during the winter does not follow the pattern of the near natural site, CL.



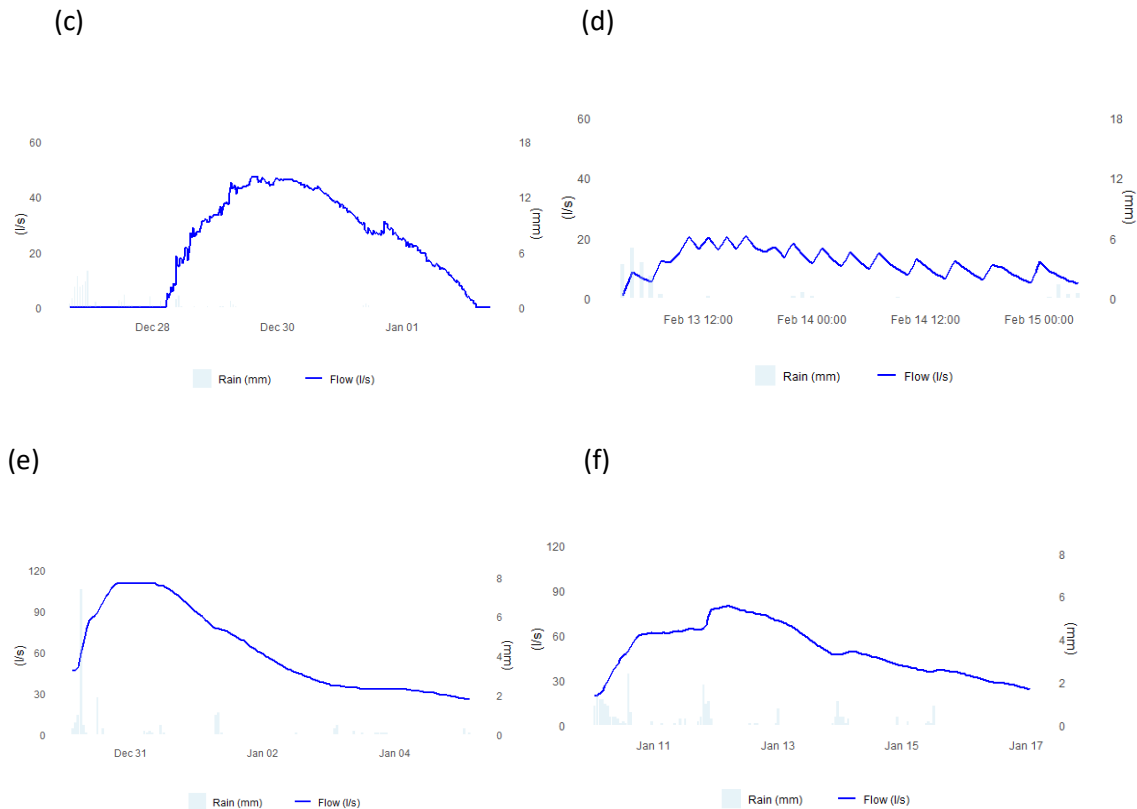


Figure 26 Hydrographs for two heavy rain events during winter, December 2020 (a) and February 2020 (b) in Clara, December 2020 (c) and February 2023 (d) for Garryduff and December 2022 (e) and January 2023 (f) for All Saints.

For summer rain events, CL and AS show similar responses to rainfall, even though the volume of flow is higher in AS than CL in general (Figure 27). For both rain events at both sites, there is an initial increase in flow followed by small increases and decreases due to other small rain events until an eventual decrease in flow back to pre-rain event levels. GD has a more flashy response to the rain events (from 0 l/s to 60 l/s almost instantaneously, Figure 27c) than CL and AS, with the second rain event (Figure 27d) showing less of a flashy response, however, the zig zag pattern is evident again as in winter.

Overall this shows that in winter, CL has the less flashy response with a gradual decrease in flow levels after the rain event, with AS and GD having more flashy responses, though AS shows more natural increases and decreases in flow than GD due to GD having a pump. For the summer, CL and AS have a more similar pattern to each other, while GD still shows a flashy response due to the pumps. This indicates that when the near natural site, CL, and the rehabilitation site, AS, are more saturated (during winter), their responses to rain events are different, but during drier periods, they seem to be more similar. This could be due to the impacts of rehabilitation efforts on AS and vegetation on CL.

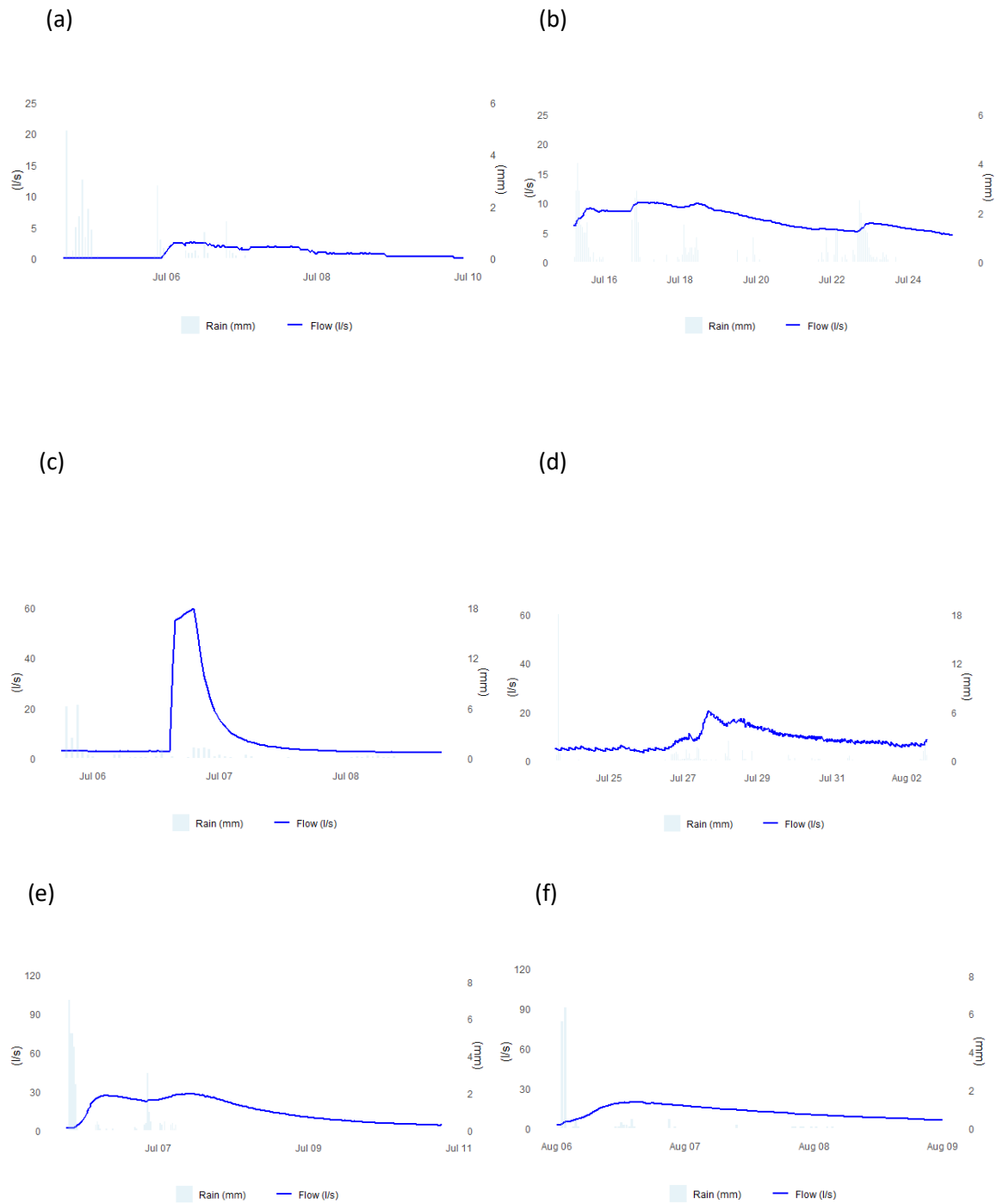


Figure 27 Hydrographs for heavy rain events in summer, July 2021 (a) and July 2023 (b), for Clara, early July 2020 (c) and late July 2020 (d) for Garryduff and July 2021 (e) and August 2021 (f) for All Saints.

4.3.2.3 ET and Effective Rainfall

Overall, in terms of ET, the sites have similar annual ET with CL having the lowest (227.63mm) and AS and GD having similar annual ET (see Table 9). GD and AS having similar ET is expected given that the crop coefficient of AS was used for GD and given their geographic proximity, their rainfall

levels were similar. In CL, lower ET than the mainly bare peat of GD and AS is expected due to the higher vegetation cover in CL, as *Sphagnum* has high water retention abilities (Hirano *et al.*, 2016).

Table 9 Comparison of annual ET for all sites. *For GD, ET was estimated using Kc from AS 2022.

Sites	ET (mm)				
	2020	2021	2022	2023	Average
CL	293.14	238.2	196.4	182.76	227.63
GD*		253.34	269.71		261.53
AS			240.7	298.49	269.6

When comparing the average effective rainfall (mm/day) of CL and AS from 2021 to 2023 (Figure 28), across all years, CL has higher effective rainfall for most months than AS, though they follow similar increasing and decreasing trends over the months, with the months with the lowest and highest average effective rainfall for each site being the same for 2022 and 2023 (2021 does not have a complete set of data for AS to compare). CL having higher effective rainfall than AS despite having similar rainfall is likely due to the presence of more *Sphagnum* in CL which has been shown to stabilise ET due to its water retention abilities (Hirano *et al.*, 2016).

The effective rainfall of GD was not compared no monthly values of ET were derived (as described in Section 4.3.1, GD only has monthly PET values, however those values were deemed to be inaccurate).

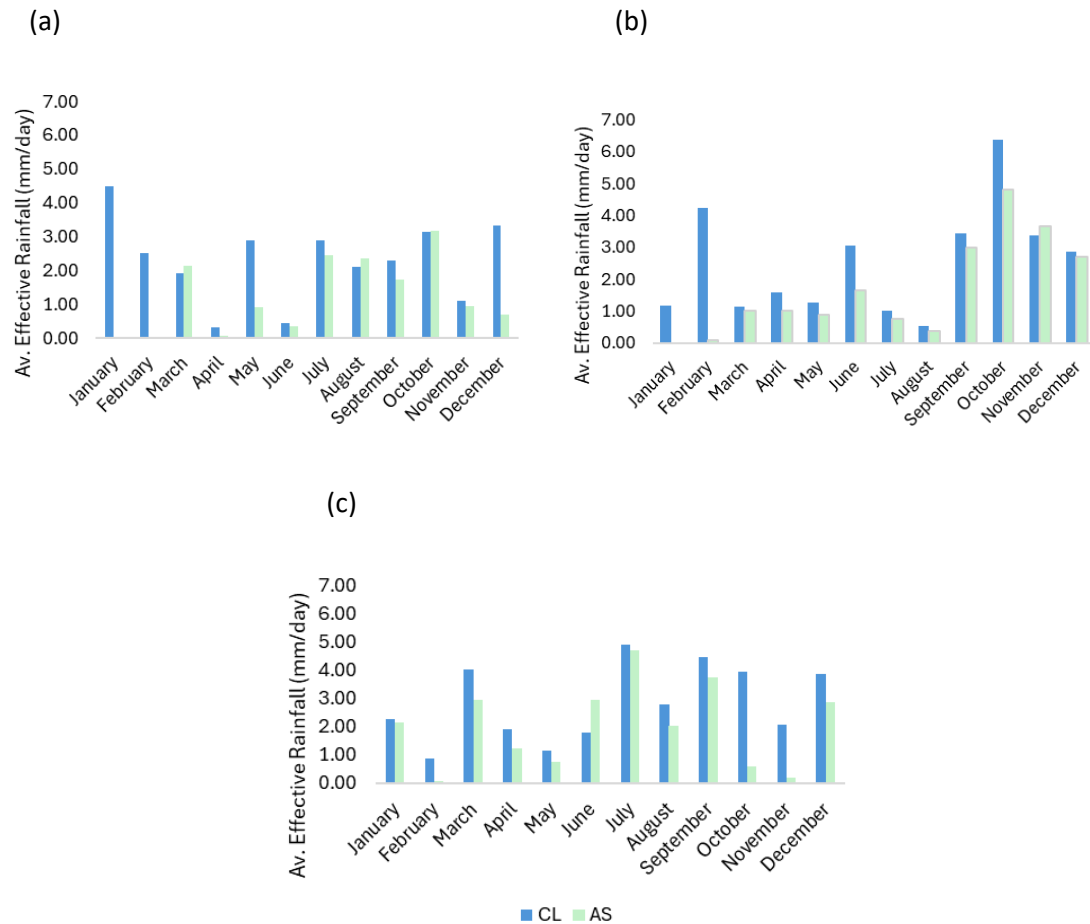


Figure 28 The average effective rainfall (mm/day) for CL and AS for 2021 (a), 2022 (b) and 2023 (c).

4.3.2.4 Catchment areas.

The revised catchments for the flumes based on the ET, discharge and rainfall are in Table 10. Overall GD is the bigger catchment, given that it has the highest flow of all the sites.

The calculated size of the CL catchment using the successive annual water balances changes minimally over the measurement period which is to be expected as the site is undergoing no active rehabilitation and as a protected near natural site should see no major disturbances.

The calculated area of All Saints' catchment changes a little throughout the measurement period. The changes are likely a result of the rehabilitation work, such as the installation of bunds and blocking of drains, increasing the catchment size of the site.

Table 10 The catchments derived for the sites using discharge, ETec and rainfall.

	CL (km ²)	Garryduff (km ²)	All Saints (km ²)
2020	0.152	-	-
2021	0.143	1.88	0.439
2022	0.089	-	0.656
2023	0.119	-	0.653
Average	0.126	1.88	0.548

4.4 Discussion

This study set out to compare three raised bog sites of different ecological conditions and management regimes based on their hydrology.

ET was an important factor in the hydrological analysis and the usefulness of eddy covariance derived ET (ETec) was investigated. Overall ETec showed good correlation to PET, with similar seasonal variation. It provided far more reasonable effective rainfall and catchment sizes for AS and GD, and expected crop coefficients for CL and AS. Although, the catchment derived from PET was closer to the LIDAR estimation provided by the NPWS for CL, the ETec derived catchment was still within the realm of possibility. It is important to note that LIDAR itself can struggle to capture fine scale topographic features such as hollows, hummocks and drains (Kalacska, Arroyo-Mora and Lucanus, 2021; Abdelmajeed and Juszczak, 2024) which are common in peatlands, therefore the ETec estimation not being as close to the LIDAR estimation as the PET estimation is not necessarily an indication of the ETec not being accurate enough. Ultimately, along with these considerations and the need for consistency for comparison, ETec was used for the ET calculations in all sites. There has been significant discussion in the hydrology field about the use of the Penman-Monteith FAO method (Allen *et al.*, 1988) versus in field measurements using lysimeters or eddy covariance towers. Both the Penman-Monteith and EC tower-based methods depend on a related energy balance model. The EC use high-frequency measurements of the vertical wind velocity and scalar quantities to determine the turbulent flux. A well-known disadvantage of the EC method is its energy closure problem. Depending on the site, the energy available to drive the fluxes can exceed the sum of the turbulent fluxes, often by 10-30% (Wilson *et al.*, 2002; Foken, 2008; Leuning *et al.*, 2012). The Penman-Monteith method is easy to implement and provides useful estimates, however the use of generalised crop coefficients limits its site-specific accuracy (Hunsaker *et al.*, 2003; Allen *et al.*, 2005; Gonzalez-Dugo *et al.*, 2009). The lysimeters are an easy, direct method of measuring ET, however, have the limitation that they are fixed and are not representative of a larger heterogenous area like the EC method is, unless enough lysimeters are deployed to provide

good spatial coverage (Rana and Katerji, 2000; Allen *et al.*, 2011). In the case of this study, we found that the catchment size and other research on the crop coefficients of other temperate peatlands (Sottocornola and Kiely, 2010; Hirano *et al.*, 2016) suggest that the ETec is more representative than the PET derived from the Penman-Monteith model. It could be paired with lysimeters to improve accuracy, but in the case of this study, this was not possible due to limited equipment. Another limitation of the ETec is that the method of diurnal water table fluctuations could not be applied to reflect the different plant life stages, community compositions and antecedent soil moisture conditions due to the sites not meeting the condition of having water levels below soil surface (Ahmad *et al.*, 2020). These are important aspects which are missing from the EC method of ET calculation (Carlson Mazur, Wiley and Wilcox, 2014) and should be considered for further study.

In general, the flow of the sites follows expected trends. GD has a higher flow, with CL having the lowest flow which is reflected by their catchment sizes, as GD has the largest catchment and CL the smallest. The larger the catchment size, the higher the flow. Catchment size calculations used in this study were based on the ETec, for comparability across the sites, however, this did not take into account the effect of groundwater on catchment size. This could be significant, as with CL, a study on its groundwater drainage showed that in areas where there is no basal sealing layer, the peatland is more connected to the regional groundwater system (Regan *et al.*, 2019). The calculation of catchment size is dependent on the peatland's inputs and outputs. If groundwater is an important part of the hydrology of a peatland, then if it is left out of the calculation, the catchment size result may not be representative. Further study would focus on the impact of groundwater as well as surface water in the calculation of catchment size of these peatlands.

The flow response to rain events in Winter and Summer provided interesting insight into the specific conditions of the sites. CL and AS show similar responses to rain events in the Summer (a less flashy response with a gradual decrease in flow), however AS is flashier than CL in the Winter. CL has much higher *Sphagnum* cover, which has much higher hydraulic conductivity and sub-surface transmissivity when compared to a well-decomposed peat soil (McCarter and Price, 2015; Hirano *et al.*, 2016). During Winter when water levels are higher, rainfall events lead to more runoff in the absence of vegetation cover (Shantz and Price, 2006; McCarter and Price, 2013; Swenson, Regan and Gill, 2020). In the Summer, when water levels are low, the rain most likely percolates into the acrotelm for both sites, therefore their responses to rain events are similar. Overall, the magnitude of the flow after a rainfall event in AS is much higher than in CL (up to 40 l/s increase after a rainfall event in All Saints compared to up to 10 l/s increase in Clara despite similar rainfall). This is likely due to the continuous layer of *Sphagnum* moss which has high water retention abilities

and is also reflective of their catchment sizes. This indicates that the rehabilitation efforts on AS with the bunds don't appear to be fully replicating the flow regimes of the more natural site as of yet. It is clear that GD has a much different response to rain events than AS and CL. This is to be expected given the presence of the pumps, as they are the predominant driver of the flow regime on the site. The flow tended to go from 0 l/s up to 60 l/s almost instantaneously, as the pumps only turn on when the water level reaches a certain point. This means that the water is stored before it is released therefore, there is little gradual increase in flow on the site. Therefore, a pumped site like GD has a less direct relationship between rain events and flow compared to sites with a more natural flow regime like CL and AS.

The trends in ET and effective rainfall are expected for these sites. CL has more vegetation cover, and due to the water retention capacity of *Sphagnum* (McCarter and Price, 2015; Hirano *et al.*, 2016), it has lower ET and therefore higher effective rainfall than the other sites. When comparing CL to AS (GD had no monthly ET data due to lack of eddy covariance on site), the similarity in the monthly effective rainfall trends, when the ETec trends are different, indicates the driving effect of precipitation being similar for both sites.

Understanding the ecohydrology of bogs across a spectrum of conditions and under different management regimes requires getting to grips with the different aspects that feed into and make up the ecohydrology of these systems. An analysis of their flow, precipitation and evapotranspiration provided useful insights into these bogs, as two of them have natural flow regimes (CL and AS) but differentiated by their vegetation cover and the other, GD, has a pump system which is the main driver of its flow regime. These conditions are reflected in the hydrological assessment of this study. In general, the more vegetated bog with a natural flow regime, CL, has lower ET, higher effective rainfall and lower flow than AS, which also has a natural flow regime but has little vegetation cover, highlighting the important role of water retaining vegetation such as *Sphagnum* in controlling the hydrology of a bog. GD, the mined site which has pumps, shows that the hydrology of sites managed like this will mainly be driven by these pumps.

Further study to better understand the differences between bogs of different conditions and their drivers would ensure that all sites use the same equipment where possible, as in this study GD did not have an EC tower and monthly ET values, and therefore, effective rainfall could not be compared to the other sites. In the case of the ETec methodology, the use of lysimeters in conjunction with eddy covariance for the measurement of ET on an ecotope scale could help to understand the drivers of ET on each site on a smaller scale, thereby explaining the differences between the sites, and their management regimes, better. However, given the cost of eddy

covariance technology, it would be beneficial to develop a model to allow for the estimation of ET based on site specific variables such as vegetation types, water availability etc. Another aspect of micro scale hydrology that would be important to include is lateral flow, as understanding the interaction between macro and micro scale hydrological processes has been shown to be important for predicting climate change impacts, the restoration and management of peatlands and the physiological process of *Sphagnum* (Price, 2003; Moore, Morris and Waddington, 2015; Swenson, Regan and Gill, 2020). This was attempted in this study (See Appendix 3 Microcosms), however meaningful results were not gained due to time constraints and flaws in installation. Additionally, the impact of groundwater systems on these sites should be investigated, to provide a more holistic picture of the movement of water through the sites.

4.5 Conclusion

The aim of this study was to compare three raised bog sites of different ecological conditions and management regimes based on their hydrology. CL is a near natural site, AS is a site of active rehabilitation and GD is an actively pumped degraded site.

A key difference between the three raised bog sites can be seen in their flow. In general, the flow of each site reflected their estimated catchment size with GD being the biggest site, showing larger flows than the others. CL, the near natural site, has a less flashy response to rain than the other sites, due to its vegetation cover. AS has flashier winter trends suggesting that the rehabilitation efforts on AS with the bunds don't appear to be fully replicating the flow regimes of the more natural site as of yet. GD flow is predominantly affected by the pumps and has a much flashier response to rain events due to this. CL also has lower ET and higher effective rainfall, again as a result of its vegetation cover. These results highlight the significance of vegetation cover on hydrology, however, there is a need to include more micro scale hydrological analysis for lateral flow to further understand this significance. The improved understanding of the micro and macro scale hydrology of peatlands in different conditions is important to better determine the pathways in which different exports such as carbon and heavy might leach out of these systems.

5 Chapter 3 - Fluvial Carbon Exports for Irish raised bogs across a spectrum of conditions, investigating NPOC, CO₂ and CH₄.

5.1 Introduction

Globally peatlands store more carbon than is contained in the world's tropical rainforest biomass (Page and Baird, 2016), while only covering 3% of Earth's land area (Frolking et al., 2011). In Ireland, peatlands are estimated to store two-thirds of the total national carbon stock (Renou-Wilson et al., 2022). The conservation of peatlands has been recognised as beneficial for climate change mitigation (IPCC, 2023) and the rehabilitation of peatlands is a priority in the most recent Climate Action Plan of Ireland (Government of Ireland, 2023). Despite this recognition, it has been estimated that around 80% of Irish peatlands have been damaged to some extent by anthropogenic disturbances such as draining or mining (Renou-Wilson et al., 2022). Given the global and national emphasis on peatland rehabilitation to mitigate climate change, it is important to better understand how to manage these systems to maintain and restore peat soils for carbon storage. This requires a knowledge of how carbon enters and leaves the system – The Net Ecosystem Carbon Balance (NECB).

The NECB of peatlands consists of net ecosystem exchange of carbon dioxide (CO₂) (NEE); net methane (CH₄) consumption or efflux; lateral biomass export assumed to be negligible in these systems; and the net gain or loss of C in water inputs and runoff (including total organic carbon, dissolved inorganic carbon and CH₄) (Chapin et al., 2006).

While the NEE of peatland systems is relatively well-researched, the losses via fluvial carbon pathways are rarely quantified in studies on carbon budgets and remain a knowledge gap (Webb *et al.*, 2018). This area of research is important, as fluvial carbon has been shown to account for 15-50% of all Greenhouse Gas (GHG) emissions from drained and rewetted peatlands (Evans et al., 2016) and in some cases changing annual budgets from carbon sources to carbon sinks (Billett et al., 2006).

There are two pathways in which carbon can leave through fluvial pathways, through – the dissolved or particulate carbon leaving with the water as it flows out of the system and as evaded gasses through the surface of the water. When ingressing water comes in contact with organic soil, it becomes super-saturated with carbon, which is then exported as Non Particulate Organic Carbon (NPOC) and Particulate Organic Carbon (POC), differentiated based on their particle size (Hope et al., 1994). NPOC is produced from the decomposition of organic material and exuded from

vegetation. This NPOC then accumulates in the pore water of peat soil and its subsequent transport to drainage waters is controlled by hydrological factors such as flow and chemical solubility controls, such as pH.

High frequency in-situ measurements of NPOC can be estimated using Fluorescent Dissolved Organic Matter (fDOM) sensors (Carpenter et al., 2013, Downing et al., 2009, Downing et al., 2012, Goldman et al., 2014, Mast et al., 2016, Pellerin et al., 2012). This process has been tested on Irish temperate peatlands in Ireland (see Section 3) and has been used in this paper to model the NPOC exports of the two sites.

In natural or near-natural peatlands the amount of particulate organic carbon (POC) exported tends to be small (Evans et al., 2016) due to the small proportion of exposed peat soil and the soil in general being bound up/protected by overlying vegetation and water. POC export can be significant in extraction sites (Worrall *et al.*, 2011), however the sites in this study are in different stages of rehabilitation with no extraction occurring and therefore POC has not been included in this study.

Additional losses of carbon through fluvial pathways occur through the evasion of CO₂ and CH₄ from the fluvial water's surface. Depending on the density of drainage channels on the sites as well as peatland condition, this evading carbon may also be significant. In UK peatlands, it is estimated the evading carbon from the surface of the bog can make up to 80% of total NPOC loss (Billett, Garnett and Dinsmore, 2015). The evasion of CO₂ and CH₄ from drainage channels and standing water is a less understood aspect of peatland emissions with little published measurements of these factors (Aitova *et al.*, 2022). The gasses can be evaded directly from a water's surface to the atmosphere along a concentration gradient (Billett and Moore, 2008), which can create significant partial pressure differences across the air–water interface. Supersaturation of CO₂ and CH₄ and turbulence of water are therefore drivers of evasion of these gasses from the surface of water. The flow of water is also an important driver, a significant correlation between evasion rate and concentration of CO₂ and CH₄ in open waters but not in water with more turbulence has been demonstrated (Billett and Moore, 2008). This means that in open waters, the degassing of the water is driven by partial pressure but in areas with more surface turbulence, the degassing occurs due to the disturbance, an important consideration while taking measurements with gas chambers.

This study combines measurements of NPOC and evading CO₂ and CH₄ to determine the fluvial carbon export of two peatland sites in Ireland: Clara Bog, Co. Offaly and Garryduff bog, Co. Galway. NPOC was calculated using fDOM as proxy, processed for temperature, turbidity and Inner Filtering

Effects (IFE) as in Section 3, as well as some specific corrections for sites and sensors (Hoffmeister et al., 2020). The measurements were taken from the beginning of 2020 to the end of 2023. Evading CO₂ and CH₄ were measured in situ using a LI-COR portable CO₂ and CH₄ gas analyser over a one year period at two to four week intervals. The calculations of NPOC and evading CO₂ and CH₄ were then used to determine the fluvial carbon exports of these two bogs over the study period.

5.2 Methods and Equipment

5.2.1 Study sites

The study sites for this section are as presented in Section 2.1, with all three study sites included; CL, Garryduff and All Saints.

5.2.2 Equipment and Measurements

For this paper, data from the discharge (Section 2.2.1), NPOC (Section 2.2.2), meteorological (Section 2.2.3), micrometeorological (Section 2.2.4) and the fluvial gas flux evasion (Section 2.2.6) measurements were used.

5.2.3 Data Collection

Flume data were telemetric and were logged online, these data were downloaded from a Van Walt Server. Data from the sondes were downloaded every two weeks when batteries were changed using the Xylem KorEXE software. NPOC and absorbance samples were taken at the same time. For AS all NPOC samples were taken using Isco 3700 autosamplers over 24 to 72 hour periods.

Chamber measurements were taken every 2 to 4 weeks for 5 minute periods on a transect away from the flume. They were measured alongside Electro Conductivity (EC) and temperature. In CL there were seven sampling points and in GD there were four. These were chosen based on accessibility and distance from each sampling point. AS was not assessed due to time constraints and the ongoing rehabilitation works.

5.2.4 Analysis

For the processing of flow from the discharge measurements the basic filtering and outlier detection and removal method as described in Sections 2.4.1.1 and 2.4.1.2 were used. Basic filtering involved the removal of NAs, rounding times to the nearest 15 minutes, removing any flow outside of the maximum capacity of the flumes and removing any negative values.

The outlier detection removed outliers out of the measurement range and used modified Z-scores based on the median absolute deviation (MAD) of a robust estimator (Bae and Ji, 2019).

For fDOM, the filtering process was as described in Section 2.4.2, removing any periods where the sonde was not submerged, and correcting for temperature and IFE effects as per De Oliveira et al. (2018).

As the simple regression between continuous fDOM results and discrete DOM measurements did not yield a consistent relationship, an alternative multi-variate analysis approach was carried out between the two data sets to derive a more robust relationship. This process used an SVR relationship (Vapnik, 2000) as set out in Section 2.4.3.

The NPOC flux was determined as in Section 0, by getting the total annual load of NPOC and dividing it by the catchment areas. This was then converted into grams.

The CO₂ and CH₄ flux from the water surface was calculated using the slope of each 5 minute measurement period as in Equation 8 of Section 2.4.8. The total monthly flux was calculated and then the total daytime flux for the seasons were compared (Section 2.4.8.).

5.3 Results

5.3.1 Fluvial Gas Flux Evasion

For this a total of 14 and 12 transects were taken over the course of a year on CL and GD respectively. The aim was to take at least 2 measurements per season.

The daily values of C (combined CH₄ and CO₂, both measured in gC/day), CH₄ and CO₂ export were plotted based on the transect taken for each day (Figure 29). On all days CH₄ contributed the least to the export. For CL, the gas flux peaks at November and April, with dips in between, whereas for GD, the peaks are at November of each year.

The difference between average daily flux in C, CH₄ and CO₂ between CL and GD are statistically significant (Wilcoxon rank-sum exact test for non parametric statistical testing of two independent groups of different sample size; p-value of 0.000186, 0.0005, 0.002 respectively).

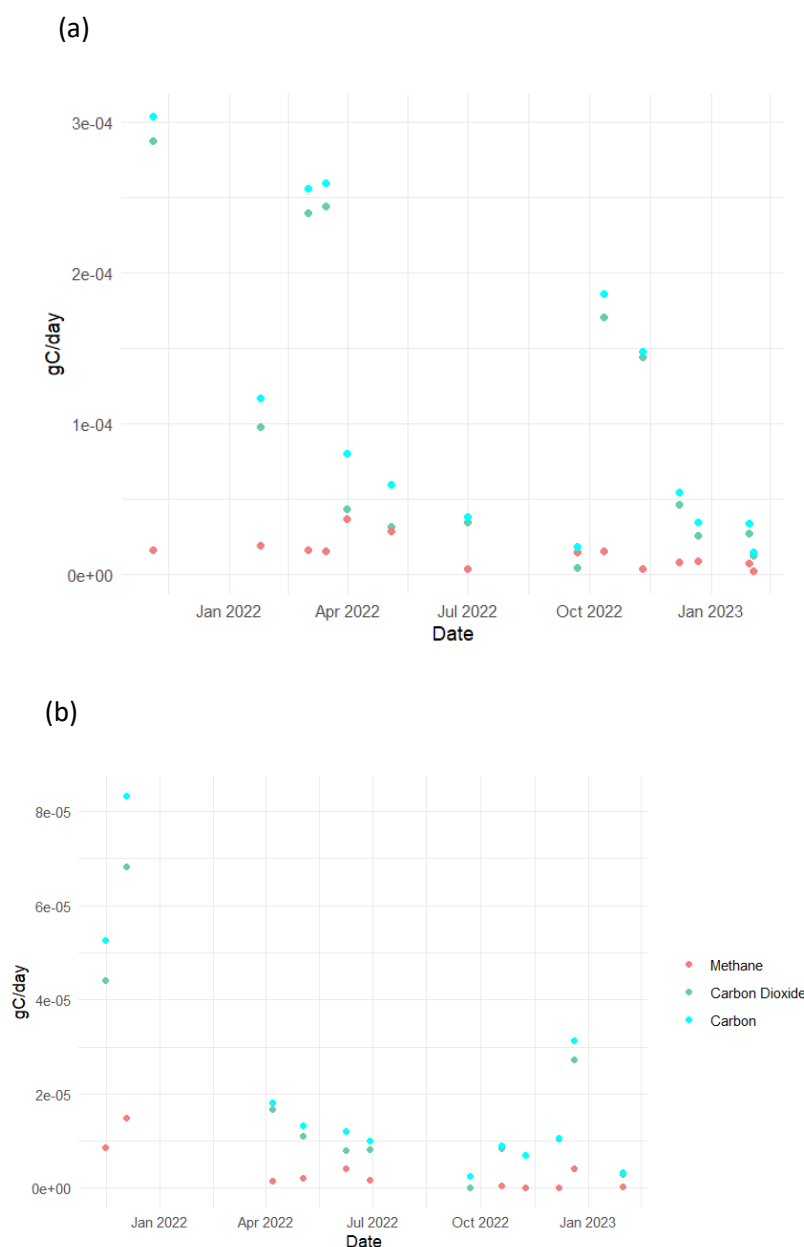


Figure 29 The Daily values of C (combined CH₄ and CO₂, both measured in gC/day), CH₄ and CO₂ export for CL (a) and GD (b).

On average, CL shows higher flux for CO₂ equivalents (g CO₂-C eq/m²/day) than GD (Table 11 and Table 12). For CL, Autumn shows the highest flux (1.64×10^{-4} g CO₂-C eq/m²/day) of all seasons on average, with Spring being the second highest (1.2×10^{-4} g CO₂-C eq/m²/day). In GD, Winter shows the highest flux (3.79×10^{-5} g CO₂-C eq/m²/day), with Autumn being the second highest (1.78×10^{-5} g CO₂-C eq/m²/day).

Overall, the flux in GD was lower than in CL (0.0046 gC/m² compared to 0.036 gC/m² for 2022). A direct comparison may be difficult given that there was an uneven sample of data taken for each site, and were not taken always taken on the same day at each site due to time constraints.

Table 11 Average seasonal flux for CO₂ and CH₄ (g CO₂-C eq/m²/day) and annual average for Clara

	Average		
	CO ₂ Flux (g CO ₂ -C eq/m ² /day) x 10 ⁻⁶	CH ₄ Flux (g CO ₂ -C eq/m ² /day) x 10 ⁻⁶	Total Flux (g CO ₂ -C eq/m ² /day) x 10 ⁻⁶
Winter	43.0	9.2	52.2
Spring	9.58	26.6	122.0
Summer	34.7	3.35	38.0
Autumn	152.0	12.3	164.0
Average daily flux for the site	81.3	12.9	94.2

Table 12 Average seasonal flux for CO₂ and CH₄ (g CO₂-C eq/m²/day) and annual average for Garryduff

	Average		
	CO ₂ Flux (g CO ₂ -C eq/m ² /day) x 10 ⁻⁶	CH ₄ Flux (g CO ₂ -C eq/m ² /day) x 10 ⁻⁶	Total Flux (g CO ₂ -C eq/m ² /day) x 10 ⁻⁶
Winter	3.17	6.2	37.9
Spring	13.9	1.8	15.7
Summer	8.2	2.8	10.9
Autumn	14.9	2.9	17.8
Average daily flux for the site	17.2	3.4	20.6

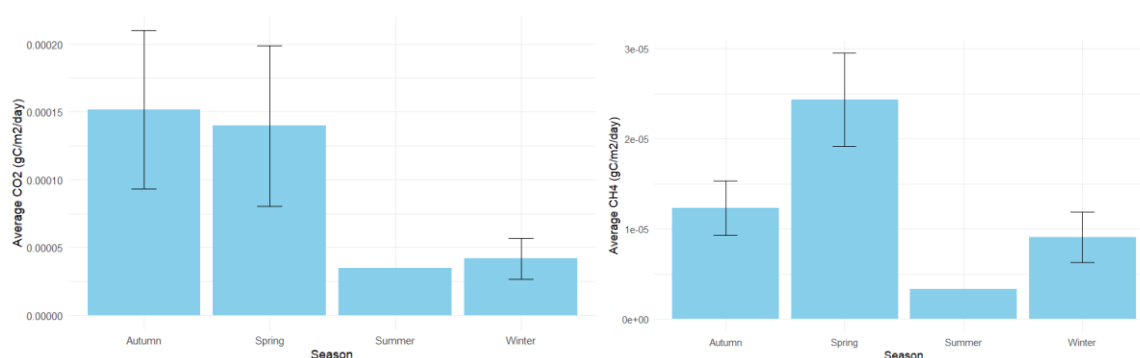
Table 13 The CO₂ and CH₄ evasions for Garryduff and CL in 2022. 2022 was the only complete year of measurements.

	Garryduff		CL	
	CO ₂ Flux (g CO ₂ -C eq/m ²)	CH ₄ Flux (g CH ₄ -C eq/m ²)	CO ₂ Flux (g CO ₂ -C eq/m ²)	CH ₄ Flux (g CH ₄ -C eq/m ²)
2022	0.0039	0.0007	0.031	0.005
Total Flux (gC/m ²)	0.0046		0.036	

For CL, the highest CO₂ and CH₄ flux was measured in Autumn and Spring, which coincide with the growing season in CL. It should be noted that for Clara there was only one summer measurement due to technical issues, therefore not much of a trend can be derived for the summer period.

For GD, both CO₂ and CH₄ flux was highest in Winter, likely driven by the flow as the higher flow rate during winter due to the pumps causing increased turbulence and therefore evasion of the gasses (Billett and Moore, 2008).

(a)



(b)

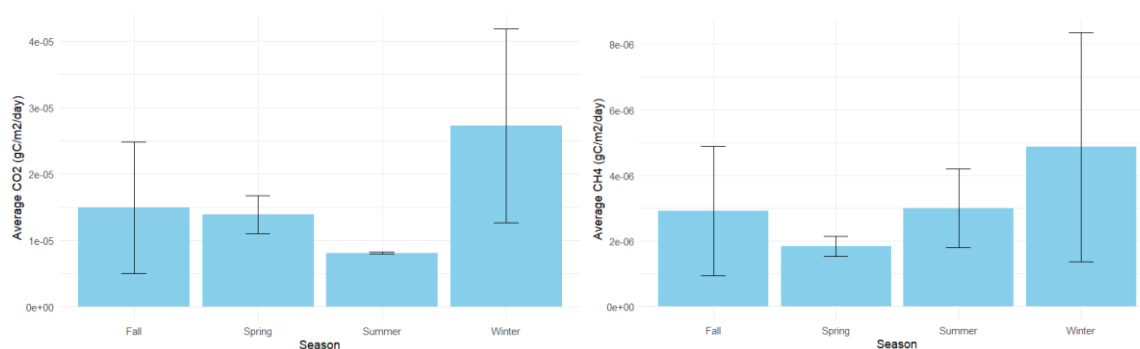


Figure 30 The average CO₂ and CH₄ flux (g CO₂-C eq/m²/day) per season for CL (a) and GD (b).

5.3.2 NPOC Flux Estimations

5.3.2.1 Monte Carlo sensitivity

The PRCC for total NPOC export (gC/m²) sensitivity to the variables indicate that flow (l/s), followed by NPOC (mg/l) is the most influential variable for total NPOC export estimation for both sites (Table 14). Flow and NPOC have a strong positive impact on the model, whereas catchment has a weaker negative impact for both sites. For GD, the catchment is a much weaker influencing variable than for CL (-0.38 and -0.68 respectively). This is likely due to the difference in catchment size between the two sites, as CL is much smaller than GD and therefore any change in catchment size to CL will be more significant as a proportion of its overall catchment size. Otherwise, the effects of flow and NPOC on the NPOC export is similar for both sites, with a slightly stronger positive impact of both variables on NPOC export in GD.

Table 14 The Partial Rank Correlation Coefficients (PRCC) from the Monte Carlo sensitivity analysis of NPOC export to flow, NPOC and catchment for CL and GD.

Variable	CL	GD
Flow	0.95	0.98
NPOC	0.85	0.87
Catchment	-0.68	-0.38

5.3.2.2 NPOC Flux for CL and GD

The monthly fluxes for NPOC were calculated by multiplying the outlet flow by the NPOC concentration at an hourly timestep and then summing these up to produce the cumulative totals per month.

For both sites, it can be seen that the Summer/Autumn months show lower monthly loads (kgC) than the Winter/Spring months (Figure 30).

For CL, the mean standard deviation for the monthly NPOC export was 0.10 kgC and for GD it was 1.38 kgC. Overall, given the total load of the NPOC exports for the sites, the standard deviation is minimal.

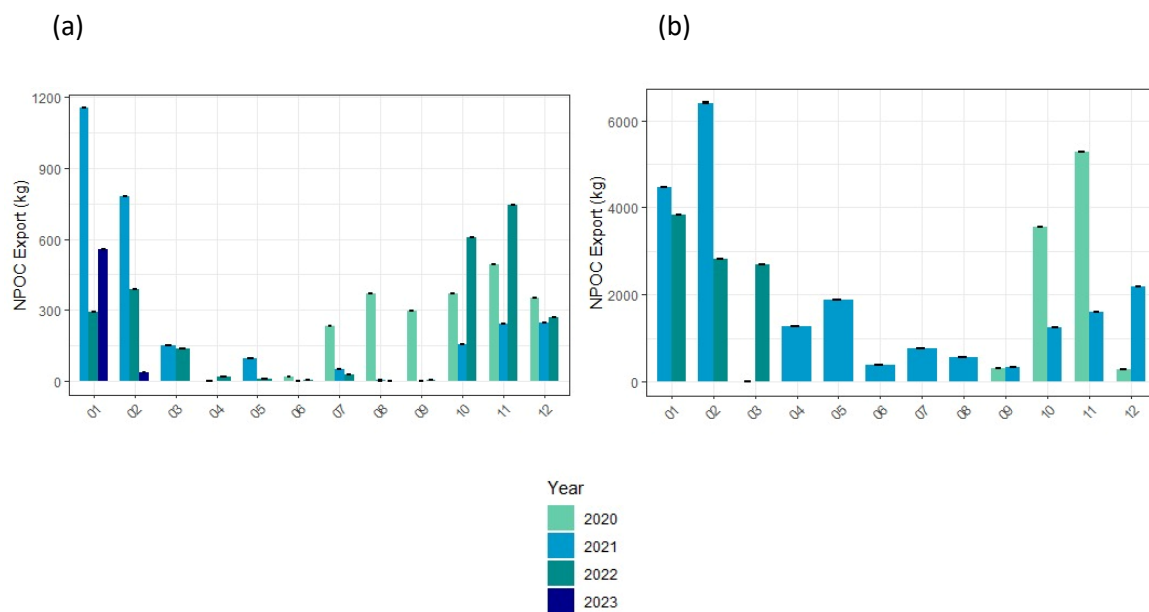


Figure 31 The monthly load of NPOC in kg exported across the measurement period in CL (a) and GD (b).

The annual flux NPOC values (gC/m^2) for the sites are presented in Table 15. For the final three months of 2020 GD has an export 6.32 gC/m^2 less than CL. For 2021, which is the only year for which we have a complete annual account at GD, the flux is 14.09 gC/m^2 less than CL. For 2022 there are full year measurements for AS and CL showing a difference of 8.17 gC/m^2 between the sites. The pumps were turned off after the third month in GD. For 2023 the first two months of the year were measured for both AS and CL and found a difference of 1.25 gC/m^2 .

Table 15 The NPOC flux (g C/m²) for the sites during their measurement periods. The cells in green indicate which fluxes can be compared to each other for each year.

Year	Garryduff Flux (g C/m ²)	Clara Flux (g C/m ²)
Sept- Dec 2020	5.35	10.14
2021	11.93	22.79
2022	5.29	19.81
Jan – Feb 2023	NA	4.71

5.4 Discussion

This study set out to determine components of the fluvial carbon export between two raised bog sites; CL which was in a near natural state and GD which was in a degraded state but in the initial stages of rehabilitation.

The chamber experiments looking at the evasion of CH₄ and CO₂ show that this flux for CL is larger than that of GD (0.036 gC/m² and 0.0046 gC/m² respectively). As CL had a higher water level overall, this is consistent with the literature that highlights where the water table is increased, C loss from surface waters increase (Billett and Moore, 2008; D'Acunha *et al.*, 2019). Additionally, the higher NPOC concentration in CL will drive more evasion, as the more saturated the water is, the more evasion of these gases there is (Waddington and Roulet, 1996; Billett and Moore, 2008; D'Acunha *et al.*, 2019). The drivers of the evasion at these two sites are likely different, GD overall has more flow and turbulence due to the pumps, therefore its evasion will be more linked to flow velocity and depth, whereas for CL where the water is less mobile and has more pools, the evasion is likely mainly driven by its surface water gas concentration (Billett and Moore, 2008). CL had higher gas evasion in the summer months which could be due to higher microbial activity during warmer periods (Roehm and Roulet, 2003; Pelletier *et al.*, 2014), however for GD Winter showed the higher evasion, again possibly indicating the role of the flow velocity and turbulence as a driver of evasion at this site.

The values of CH₄ and CO₂ are a small proportion of the measured values for NPOC, accounting for less than 1% in both sites, with CO₂ being the biggest contributor to carbon loss compared to CH₄ in both sites. Overall, this is in agreement with other studies which have shown that NPOC is the far bigger contributor to fluvial carbon export compared to the evasion of CO₂ and CH₄ (Billett *et al.*, 2010; Evans, Renou-Wilson and Strack, 2016). There have been studies in boreal peatlands that showed much higher concentrations of CH₄ and CO₂ evasion, between 22 and 66 gC/m²/ year (Repo *et al.*, 2007; Pelletier *et al.*, 2015; Kuhn *et al.*, 2018; D'Acunha *et al.*, 2019) but are closer to the values calculated for an ombotrophic bog, Mer Bleue, in Canada of 3.9 gC/m²/ year for CO₂ and

between 0.012 and 0.055 gC/m²/ year for CH₄. The low evasion values in this study could be due to the limitations in measurements during the study. Unfortunately, the pumps in GD turned off in the early months of the year where measurement was being undertaken, meaning that the values for evaded carbon while pumping was active cannot be known. The measurements in this study were also taken at points where the water was exiting the bog to determine the amount of carbon leaving the system. However, given that differences in C fluxes between the different parts of bogs have been emphasised by other studies (Waddington and Roulet, 1996; Hope *et al.*, 2001; Strack *et al.*, 2006; D'Acunha *et al.*, 2019), it may be useful to take samples from water pools at different points of the bog for a better understanding of the evasion of gasses on these sites. Additionally, given the small sample size of measurements, especially for Summer, the evasion results in this study would mainly be preliminary estimates. The high diurnal dynamics of evasion, specifically of CO₂ (Peter *et al.*, 2014), also indicates the importance of capturing the diurnal variation in evasion as well.

The use of fDOM to estimate the NPOC export has allowed for this study to analyse the response of NPOC concentrations at a higher temporal scale than would have been possible if taking samples back to the laboratory for analysis. The time series of NPOC concentrations show that although the concentrations increase during the summer and spring months the flow increases during the winter and autumn months resulting in the most load being exported during the period of lowest concentration. This push and pull of the two determinates of load means that different seasons have different predominant drivers, a relationship that holds for both sites. In general, this fits with other studies on the role of discharge on increased NPOC export, for example Urban *et al.* (1989) found that in a fen with lower NPOC concentrations there was higher NPOC export than two bogs with higher NPOC concentrations due to the higher discharge in the fen. Similarly, Pastor *et al.* (2003) used mesocosms from boreal peatlands to alter discharge rate and found that lower discharge led to lower NPOC export, despite high NPOC concentration.

All values of NPOC flux for the sites are similar to the mean flux for temperate peatlands, 24.2 gC/m²/yr, with a range of 1.4 to 94.8 gC/m²/yr (Rosset *et al.*, 2022). For 2021, the flux of CL, the smaller and more natural site, was higher than in comparison to GD, the site that has not undergone rehabilitation yet (22.79 gC/m² compared to 11.93 gC/m² respectively). This is not in agreement with global studies on NPOC exports of peatlands of disturbed and undisturbed conditions, which show that NPOC exports from disturbed sites are significantly higher than undisturbed sites (Rosset *et al.*, 2022). This may be due to the fact that in GD, vegetation cover is much lower than in CL, as it is composed of mainly exposed peat with some vegetation incursion. The vegetation may mean that the intake of carbon is higher due to photosynthesis and that there

is more vegetation available for microbial activity which lead to higher fluvial losses (Pastor *et al.*, 2003; Billett *et al.*, 2006; Clark *et al.*, 2007) as the majority of NPOC tends to be derived from recently fixed plant materials (Palmer *et al.*, 2001; Evans *et al.*, 2007; Billett *et al.*, 2010). When inspecting GD on site, in many places throughout the bog, the peat depth was less than a meter, meaning that there would be less organic soil for the water to interact with.

Another important aspect of the NPOC flux is the residence time. The residence time of rainfall can differ depending on the season due to the different saturation levels of the soil. In general, the greater residence time in summer means that the water is spending more time in the soil and, as such, absorbing more of the NPOC before leaving (Moore *et al.*, 2013). This would explain the trends in CL more than GD, given that the pumps dictate residence time in GD.

The emissions from CH₄ and CO₂ evasion would likely make little difference to the NPOC result. This may have been different when the pumps were on in 2020 and 2021, due to an increase in the turbulent movement of the water and thus potentially higher rates of degassing, but it seems unlikely that the flux would have increased by an amount to have made up for the double increase between CL and GD during 2020 and 2021.

A more in-depth study of the difference in the evasion of gas from surface waters, and its influence on overall fluvial carbon export, between two bogs of different conditions would focus on more consistent measurements for each month, including diurnal measurements (although this would require in situ equipment for the night measurements, and therefore capacity for this has to be assessed) and at different sampling points on the bogs. Furthermore, it is possible that taking POC measurements could be beneficial although it seems unlikely from the literature suggesting that it is negligible compared to NPOC (Evans, Renou-Wilson and Strack, 2016; Pickard *et al.*, 2022).

Ultimately though fluvial carbon is just a part of the NECB. The near natural site appears to have a higher fluvial carbon flux, however, it is likely it is taking in more carbon due its higher vegetation cover throughout its lifetime (D'Acunha *et al.*, 2019). This highlights the importance of looking at NECB rather than individual components of NECB when trying to understand the carbon flux of a peatland.

5.5 Conclusion

In this study, two raised bog sites were analysed: Clara (near natural) and Garryduff (mined). The fluxes of fluvial carbon from the sites show that Clara has the highest flux of all sites. This may be due to the natural processes in the near natural site meaning that the accumulation of carbon through increased plant growth is allowing for more carbon to leach out of the system through

water when these plants degrade. Whereas the more degraded system has less vegetation to assimilate carbon and therefore export it. The more degraded sites also have less peat depths due to mining, possibly contributing to less labile carbon rich peat available to interact with water. Additionally, the remaining peat has very low hydraulic conductivity and so the water won't move through it easily leading to a lot of quick surface flow. These findings highlight the importance of considering Net Ecosystem Exchange for peatland systems, rather than focussing on individual aspects of carbon flux, as while a site may export more carbon through water, it is possible it is taking in more carbon as well through its vegetation.

Comparing NPOC with CH₄ and CO₂ evasion supports other study findings that evasion is very small compared to NPOC, therefore a small contributor to fluvial carbon exports in temperate peatlands, however a more in-depth study of the relationship between the two at sites of different conditions would be required to confirm this finding for these types of sites.

6 Discussion

This study set out to answer :

1. Can fDOM can be used as a proxy for NPOC in temperate raised bogs of high NPOC concentration and if so, to what accuracy?
2. What are the ecohydrological differences between three raised bogs under different levels of rehabilitation that may influence their fluvial carbon fluxes?
3. What are the differences in the overall fluvial carbon fluxes of these bogs and the drivers of these fluxes?

6.1 The feasibility of using fDOM in-situ measurements as a proxy for NPOC concentration.

The traditional methods for determining a relationship between NPOC and fDOM i.e. trying to correlate continuous fDOM measurements against periodic samples of lab measured NPOC as Downing *et al.* (2012) and De Oliveira *et al.* (2018) provided statistically significant relationships for AS and CL, the NSE coefficients indicated that the models for CL and AS qualify but are not good.

The NPOC concentration in a peatland runoff waterway is determined by numerous factors, including precipitation, soil moisture, flow discharge, temperature, and pH and the hysteresis between those processes (Hope, Billett and Cresser, 1994; Inamdar *et al.*, 2006; Clark *et al.*, 2007; Evans, Renou-Wilson and Strack, 2016). Multivariate analysis was therefore used to attempt to take into account some of these confounding variables and to derive a more nuanced and improved relationship between NPOC and fDOM.

This approach produced good models for all three sites, according to NSE coefficients (all NSE coefficients were over 0.75). This indicates that using this method, fDOM can be used as a proxy for NPOC concentrations in these systems, with good accuracy. Although the annual measurements of flux did not change by much between models the multivariate approach appeared to capture the short-term variability of the NPOC concentrations better than the linear model. It may be an indication that more frequent auto sampling regimes could better correlate fDOM to these short term changes in NPOC. However, in AS, where there was predominantly autosampling regimes, the seasonal changes in NPOC concentration were not as represented by the fDOM, as there were not enough consistent samples over the period, even if the model has a high NSE, we cannot be confident in the model due to the low samples. In general, this may represent the need for the combination of consistent grab sample measurements as well as more

frequent autosampling measurements for periods over 1 to 3 days. This, however, puts into question the feasibility of fDOM technology from an economic perspective, if consistent in situ measurements are required to determine the site specific relationship between fDOM and NPOC concentrations, given that fDOM is site specific (Downing *et al.*, 2012).

The model however may not capture the effect of 'slow' but important variables as it relies mainly on fDOM and NPOC data. Variables like changes in hydrology, soil carbon content and temperature have been shown to have a lag effect on NPOC (Freeman *et al.*, 2001; Holden and Burt, 2003; Daniels *et al.*, 2008; Broder and Biester, 2015; Dick *et al.*, 2015), therefore it can be assumed they have an effect on NPOC, but due to the lag effect, our model did not pick them up as predicting variables. Further study would be required to identify how these hysteresis effects could be picked up by the model.

In general, the multivariate approach generated a good model use NSE coefficients as a measure, however, for the overall NPOC export, it did not lead to any major changes when compared to the linear model derived NPOC exports. It did however, provide more accurate results for short term variability, therefore its usefulness may depend on the goal of a study, whether it is to look at overall NPOC exports or short term responses. Given the likely need for more consistent autosampling as well as consistent grab sampling to derive the site specific relationship between fDOM and NPOC, the economic cost of the fDOM technology may not be justified, again, that depends on the goals of the study.

6.2 The ecohydrology of three raised bog sites

Overall, ET is a really important aspect in understanding the hydrological differences of these bog sites, specifically the catchment sizes and the effective rainfall. Overall, eddy covariance derived ET, ETec showed good correlation to PET, providing more reasonable/plausible results for catchment size and effective rainfall for GD and AS. For CL, while PET provided a closer catchment size calculation to LIDAR estimation, the ETec estimations were still plausible and for comparison to GD and AS, ETec was deemed a suitable estimation of ET for these sites. Lysimeters in conjunction with ETec could be used to derive a model which better represents ET on an ecotope scale as well as the macro scale ET.

Understanding the ecohydrology of bogs across a spectrum of conditions and under different management regimes requires getting to grips with the different aspects that feed into and make up the ecohydrology of these systems. An analysis of their flow, precipitation and evapotranspiration provided useful insights into these bogs, as two of them have natural flow regimes (CL and AS) but differentiated by their vegetation cover and the other, GD, has a pump

system which is the main driver of its flow regime. These conditions are reflected in the hydrological assessment of this study. In general, the more vegetated bog with a natural flow regime, CL, has lower ET, higher effective rainfall and lower flow than AS, which also has a natural flow regime but has little vegetation cover, highlighting the important role of water retaining vegetation such as *Sphagnum* in controlling the hydrology of a bog. GD, the mined site which has pumps, shows that the hydrology of sites managed like this will mainly be driven by these pumps.

Further study to better understand the differences between bogs of different conditions and their drivers would ensure that all sites use the same equipment where possible, as in this study GD did not have an EC tower and monthly ET values, and therefore, effective rainfall could not be compared to the other sites. In the case of the ETec methodology, the use of lysimeters in conjunction with eddy covariance for the measurement of ET on an ecotope scale could help to understand the drivers of ET on each site on a smaller scale, thereby explaining the differences between the sites, and their management regimes, better. However, given the cost of eddy covariance technology, it would be beneficial to develop a model to allow for the estimation of ET based on site specific variables such as vegetation types, water availability etc. Another aspect of micro scale hydrology that would be important to include is lateral flow, as understanding the interaction between macro and micro scale hydrological processes has been shown to be important for predicting climate change impacts, the restoration and management of peatlands and the physiological process of *Sphagnum* (Price, 2003; Moore, Morris and Waddington, 2015; Swenson, Regan and Gill, 2020). This was attempted in this study (see Appendix 3 Microcosms), however meaningful results were not gained due to time constraints.

6.3 The fluvial carbon exports the three bog sites

In general, CL, the near natural site, has higher NPOC and higher CH₄ and CO₂ flux than GD, the more degraded site. This is a function of the higher vegetation cover on CL. The vegetation may mean that the intake of carbon is higher due to photosynthesis and that there is more vegetation available for microbial activity which lead to higher fluvial losses (Pastor *et al.*, 2003; Billett *et al.*, 2006; Clark *et al.*, 2007) as the majority of NPOC tends to be derived from recently fixed plant materials (Palmer *et al.*, 2001; Evans *et al.*, 2007; Billett *et al.*, 2010). The higher NPOC concentration in CL will drive more evasion, as the more saturated the water is, the more evasion of these gases there is (Waddington and Roulet, 1996; Billett and Moore, 2008; D'Acunha *et al.*, 2019). The drivers of the evasion at these two sites are likely different, GD overall has more flow and turbulence due to the pumps, therefore its evasion will be more linked to flow velocity and depth, whereas for CL where the water is less mobile and has more pools, the evasion is likely mainly driven by its surface water gas concentration (Billett and Moore, 2008).

In terms of the impact of gas evasion on overall NPOC export, they contributed less than 1% in both sites, with CO₂ being the biggest contributor to carbon loss compared to CH₄ in both sites. Overall, this is in agreement with other studies which have shown that NPOC is the far bigger contributor to fluvial carbon export compared to the evasion of CO₂ and CH₄ (Billett *et al.*, 2010; Evans, Renou-Wilson and Strack, 2016). The low evasion values in this study, compared to others (Repo *et al.*, 2007; Pelletier *et al.*, 2015; Kuhn *et al.*, 2018; D'Acunha *et al.*, 2019), could be due to the limitations in measurements during the study.

The measurements in this study were taken at points where the water was exiting the bog to determine the amount of carbon leaving the system. However, given that differences in C fluxes between the different parts of bogs have been emphasised by other studies (Waddington and Roulet, 1996; Hope *et al.*, 2001; Strack *et al.*, 2006; D'Acunha *et al.*, 2019), it may be useful to take samples from water pools at different points of the bog for a better understanding of the evasion of gasses on these sites. Additionally, given the small sample size of measurements, especially for Summer, the evasion results in this study would mainly be preliminary estimates.

In terms of overall NPOC export, although the concentrations increase during the summer and spring months, the flow increases during the winter and autumn months result in the most load being exported during the period of lowest concentration. In general, this fits with other studies on the role of discharge on increased NPOC export that found that higher discharge led to higher NPOC export even in low NPOC concentration (Urban, Bayley and Eisenreich, 1989; Pastor *et al.*, 2003).

While the NPOC flux for the sites are similar to the mean flux for temperate peatlands, 24.2 gC/m²/yr, with a range of 1.4 to 94.8 gC/m²/yr (Rosset *et al.*, 2022), the flux of CL, the smaller and more natural site, was higher than in comparison to GD, the site that has not undergone rehabilitation yet (22.79 gC/m² compared to 11.93 gC/m² respectively). Generally, it would be expect for NPOC exports from disturbed sites to be significantly higher than undisturbed sites (Rosset *et al.*, 2022). However, in GD, vegetation cover is much lower than in CL, as it is composed of mainly exposed peat with some vegetation incursion. The vegetation may mean that the intake of carbon is higher due to photosynthesis and that there is more vegetation available for microbial activity which lead to higher fluvial losses (Pastor *et al.*, 2003; Billett *et al.*, 2006; Clark *et al.*, 2007) as the majority of NPOC tends to be derived from recently fixed plant materials (Palmer *et al.*, 2001; Evans *et al.*, 2007; Billett *et al.*, 2010). Additionally, when inspecting GD on site, in many places throughout the bog, the peat depth was less than a meter, meaning that there would be less organic soil for the water to interact with.

A more in-depth study of the difference in the evasion of gas from surface waters, and its influence on overall fluvial carbon export, between two bogs of different conditions would focus on more consistent measurements for each month and at different sampling points on the bogs. Furthermore, it is possible that taking POC measurements could be beneficial although it seems unlikely from the literature suggesting that it is negligible compared to NPOC (Evans, Renou-Wilson and Strack, 2016; Pickard *et al.*, 2022).

These results indicate the importance of looking at all components of NECB in conjunction with each other. The more rehabilitated site appears to be exporting more fluvial carbon, however, it is likely it is taking in more carbon due its higher vegetation cover throughout its lifetime (D'Acunha *et al.*, 2019). This highlights the importance of looking at NECB rather than individual components of NECB when trying to understand the carbon flux of a peatland.

Ultimately, this study concludes that using fDOM as a proxy for NPOC can give high temporal accurate estimations, which can feed into a better understanding of how the NPOC concentrations change over short periods of time, provided that there are a suitable number of lab sampled NPOC to derive the fDOM NPOC relationship. However, understanding the change in concentration of NPOC in these systems is only half of the story. Defining what is driving those changes is also important. The attempt to better profile the ecohydrology has given a context for the concentration changes that are picked up by the fDOM sensor. This has allowed for a better analysis of the fluvial carbon export of these bogs based on their management and hopefully can provide a more accurate estimation of their NECB in the future.

7 Conclusion & Recommendations for future research

In general, this study set out to determine the feasibility of using in-situ fDOM measurements as a proxy for NPOC, the relationship of which was used to predict the fluvial carbon budget of the three raised bog sites, taking into account the effects of ET, flow, evading fluvial carbon and precipitation.

Simple correlation between fDOM and NPOC, as per the methodology presented in Downing *et al.* (2012) and De Oliveira *et al.* (2018) does not provide sufficient accuracy for these temperate peatlands studied in Ireland, likely due to the lack of consideration of multiple complex factors within these bog sites such as precipitation, soil moisture, flow discharge, temperature, and pH and the hysteresis between those processes. A multivariate approach which takes these factors into account provides a statistically significant relationship between fDOM and NPOC in all three sites. This method allows for site specific factors to be taken into account, constantly adjusting the

relationship between fDOM and NPOC over time, and providing better estimation of short term changes in NPOC concentrations, although for overall annual NPOC export, the changes between the linear correlation derived NPOC export and the multivariate derived NPOC export are minimal. However, there is more confidence in multivariate derived NPOC estimations. Given the need for consistent grab and auto sampling measurements to define the site specific relationship between fDOM and NPOC, a cost benefit analysis of the fDOM technology should be carried out based on what the specific aims of the project are.

Once the relationship between fDOM and NPOC was determined, the hydrology of the bogs was analysed to determine the influence of this in the NPOC exports. An analysis of their flow, precipitation and evapotranspiration provided useful insights into these bogs, as two of them have natural flow regimes (Clara and All Saints) but differentiated by their vegetation cover and the other, Garryduff, has a pump system which is the main driver of its flow regime. These conditions are reflected in the hydrological assessment of this study. In general, the more vegetated bog with a natural flow regime, Clara, has lower ET, higher effective rainfall and lower flow than All Saints, which also has a natural flow regime but has little vegetation cover, highlighting the important role of water retaining vegetation such as *Sphagnum* in controlling the hydrology of a bog. Garryduff, the mined site which has pumps, shows that the hydrology of sites managed like this will mainly be driven by these pumps.

While Clara has higher NPOC flux, given its low discharge, it has lower NPOC export than Garryduff. Both sites show higher export in the Winter due to the high discharge rate, despite lower NPOC concentrations than in the Summer. For both sites, CO₂ and CH₄ evasion were less than 1% of total NPOC export, however, given some issues in evasion measurement the role of evasion in fluvial carbon export for these sites could be improved with more consistent measurements at different areas of the bogs.

Overall, this study has shown the benefit of using in situ fDOM measurements as a proxy to predict NPOC using multi variate analysis in temperate raised bog systems. By taking into account the different pathways of water movement through these systems, we can better understand the drivers of fluvial carbon flux. The near natural site appears to have higher fluvial carbon flux than the degraded sites but they likely take in more carbon to begin with, highlighting the importance of considering Net Ecosystem Exchange for peatland systems, rather than focussing on individual aspects of carbon flux, as while a site may have higher flux, it is possible it is taking in more carbon as well.

Recommendations for Future Research

Given the importance of the rehabilitation of peatlands in Ireland and Europe and the role of fluvial carbon in the overall carbon budget of peatlands, there is a need focus on the following aspects of future research:

1. For fDOM, further determining of the frequency of measurements required – in this study, it was clear that it is important to have more frequent measurements of NPOC to compare to fDOM to fully account for seasonal variability.
2. Determining the cost benefit analysis of fDOM technology considering the amount of data required for validation.
3. A PARAFAC analysis of UV absorption of DOM in raised bog systems of different conditions.
4. The lag time between variables affecting NPOC concentration – this study found that with multivariate analysis it was difficult to determine the effect of confounding variables such as pH and conductivity, and the lag time of the effect of these variables.
5. Development of a model that better captures evapotranspiration on these types of temperate peatlands, would be beneficial for understanding the ecohydrology more fully.
6. More in depth analysis of lateral flow impact on discharge in these systems, using microcosms.
7. More prolonged and consistent chamber measurements of CO₂ and CH₄ evasion of degraded sites, at different locations within each site.
8. Carrying out Net Ecosystem Carbon Balance studies for these peatland sites – as the near natural site has a higher flux of fluvial carbon, it is clear that in only considering the carbon losses, the net flux of carbon is not understood. A full study on the NECB of these peatlands is recommended to understand these sites more holistically.

8 References

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9 Appendices

9.1 Appendix 1: Summary of peatland carbon studies

Table 16 Summary of peatland carbon study sites.

Site Description							NPOC		POC		CH4		NEE		CO2-e		Study
Site Location	Latitude and Longitude	Status	Management	Climate	Catchment size	Study Period	Methods	Frequency	Methods	Frequency	Methods	Frequency	Methods	Frequency	Methods	Frequency	
Mer Bleue, Ontario, Canada	45.411°N, 75.481°W	Natural	Active Management	Northern Peatland	≈4.8 km ²	6 yr	Direct measurements	Weekly for 4 years and sporadic for two years of the study period.	NA	NA	Chamber measurements	NA	Eddy Covariance	30 minute intervals	NA	NA	(Roulet <i>et al.</i> , 2007)
Bellacorick Co. Mayo, Ireland	54°7'29.9" N, 9°33'22.2" W	Rehabilitation	Rewetting	Temperate Peatland	NA	5 yr	Estimates calculated at micro site scale but not upscaled.	NA	NA	NA	Chamber Measurements	Monthly	Chamber measurements	3-9 measurements per collar per day	NA	NA	Wilson <i>et al.</i> , 2016
Mer Bleue, Ontario, Canada	45°24' N, 75°30' W	Natural	Active Management	Northern Peatland	NA	1 yr	NA	NA	NA	NA	NA	NA	Eddy Covariance	30 minute intervals	NA	NA	Lafleur <i>et al.</i> , 2001
Fajemyr, Sweden	56°15' N, 13°33' E	Natural	Active Management	Temperate Peatland	NA	1 yr	NA	NA	NA	NA	NA	NA	Eddy Covariance	30 minute intervals	NA	NA	Lund <i>et al.</i> , 2007
Lanesborough, Co. Longford, Ireland	53°39' N, 7°56' W	Degraded	Drained Grassland, Nutrient Rich	Temperate Peatland	0.03 km ² - 0.05 km ²	2 yr	Direct Measurements	Fortnightly/Monthly	Direct Measurements	Fortnightly/Monthly	Chamber measurements	Fortnightly/Monthly	Chamber measurements	Fortnightly (summer), Monthly (Winter)	Chamber	Fortnightly/Monthly	Renou - Wilson <i>et al.</i> , 2014

Table 17 Summary of data from peatland carbon studies described in Appendix 1 Summary of peatland carbon studies

Site	Mean Annual Temperature	Mean Annual Precipitation	Water Table	NEE	NPOC	NPOC as a Proportion of NECB	POC	CH ₄	CO ₂ -e	NECB	Study
Mer Bleue, Ontario, Canada (1)	6.0 ± 0.8 °C	943 mm	NA	-40.2 ± 40.5 g m ⁻² yr ⁻¹	14.9 ± 3.1 g m ⁻² yr ⁻¹		NA	3.7 ± 0.5 g CH ₄ m ⁻² yr ⁻¹	NA	-21.5 ± 39 g C m ⁻² yr ⁻¹	Roulet <i>et al.</i> , 2007
Bellacorick, Co. Mayo, Ireland	10.3 °C	1245 mm	NA	-104 ± 80 g C m ⁻² yr ⁻¹	NA	NA	NA	9 ± 2 g C m ⁻² yr ⁻¹	NA	NA	Wilson <i>et al.</i> , 2016
Mer Bleue, Ontario, Canada (2)	5.8°C	910 mm	NA	-248 ± 68 g CO ₂ m ⁻² yr ⁻¹	NA	NA	NA	NA	NA	NA	Lafleur <i>et al.</i> , 2001
Fajemyr, Sweden	6.2°C	700 mm	NA	-78.6 ± 20.0 g CO ₂ m ⁻² yr ⁻¹	NA	NA	NA	NA	NA	NA	Lund <i>et al.</i> , 2007
Lanesborough, Co. Longford, Ireland	9.1°C	941 mm	NA	233 g C m ⁻² yr ⁻¹	37.7 g C m ⁻² yr ⁻¹		7.57 g C m ⁻² yr ⁻¹	NA	24.1 g C m ⁻² yr ⁻¹	663 g C m ⁻² yr ⁻¹	Renou-Wilson <i>et al.</i> , 2014
Glenvar, Co. Donegal, Ireland	9.8°C	1076 mm	NA	188 g C m ⁻² yr ⁻¹	11.5 g C m ⁻² yr ⁻¹		4.2 g C m ⁻² yr ⁻¹	1.35 g C m ⁻² yr ⁻¹	15.95 g C m ⁻² yr ⁻¹	267 g C m ⁻² yr ⁻¹	Renou-Wilson <i>et al.</i> , 2014
Glenvar, Co. Donegal, Ireland	9.8°C	1077 mm	NA	59 g C m ⁻² yr ⁻¹	11.5 g C m ⁻² yr ⁻¹		4.2 g C m ⁻² yr ⁻²	NA	15.95 g C m ⁻² yr ⁻¹	267 g C m ⁻² yr ⁻¹	Renou-Wilson <i>et al.</i> , 2015
Luther Marsh Wildlife Management Area, Ontario Canada	6.6°C	905 mm	NA	-680 ± 202 g CO ₂ m ⁻² yr ⁻¹	NA	NA	NA	22 ± 8 g CH ₄ m ⁻² yr ⁻¹	NA	NA	Berger <i>et al.</i> , 2019
Burns Bog, Canada	10.4°C	1189 mm	Between - 30 cm and 30cm	-179 ± 26.2 g CO ₂ m ⁻² yr ⁻¹	NA	NA	NA	17 ± 1 g CH ₄ m ⁻² yr ⁻¹	NA	NA	Sung-Ching Lee <i>et al.</i> , 2016
The Cross Loch, Scotland	8°C	1000 mm	0.1 ± 0.06 m	-114 g C m ⁻² yr ⁻¹	NA	NA	NA	NA	NA	NA	Hambley <i>et al.</i> , 2019

9.2 Appendix 2: Multivariate Analysis Equations

9.2.1 Proposed Theoretical Framework

This study denotes the observed NPOC data by the random variable X and the fDOM sensor data by the random variable Y . Assuming the relationship between those two variables is given as $Y = g(X)$ where $g(\cdot)$ is an unknown function, the random variable X can therefore be expressed as $X = g^{-1}(Y)$.

The cumulative distribution function $F_X(\cdot)$ of X can be expressed as:

Equation 10

$$F_X(x) = P(X \leq x) = P(g^{-1}(Y) \leq x) = P(Y \leq g(x))$$

Assuming that the cumulative distribution function of Y is expressed as $F_Y(\cdot)$, Equation 10 becomes:

Equation 11

$$F_X(x) = P(Y \leq g(x)) = F_Y(g(x))$$

Hence, a datapoint x can be expressed as:

Equation 12

$$x = F_X^{-1}[F_Y(g(x))]$$

Based on the discrete NPOC and continuous fDOM sensor data $F_X(\cdot)$ and $F_Y(\cdot)$ are estimated. However, since $g(x)$ is not known *a priori*, a different relationship needs to be developed.

This study assumes that an estimate of $F_Y(g(x))$ is a function of the non-exceedance probability $F_Y(y)$ along with a set of other variables Θ . Θ can be the moments of the fDOM sensor data such as, $y, EY, E[Y - EY]^2, E[Y - EY]^3, E[Y - EY]^4$, moments of other variables influencing the water quality concentration such as conductivity, discharge, water temperature, rainfall etc.

The relationship is considered as, $F_Y(g(x)) = f(F_Y(y), y, \Theta)$. However, since $F_Y(g(x)) = F_X(x)$, the function $f(\cdot)$ is obtained based on the following equation:

Equation 13

$$F_X(x) = f(F_Y(y), y, \Theta)$$

Since the function $f(\cdot)$ can assume a highly nonlinear form, a support vector regression (SVR) model has been used to develop the relationship.

9.2.2 Support Vector Regression (SVR)

A SVR relationship was developed for each site in terms of input vector (predictor) $\mathbf{x}_t = [x_{t,1}, \dots, x_{t,m}] \in \mathbb{R}^m$ where m denotes the number of predictors, and output (predictand) $y_t \in \mathbb{R}$ corresponding to time $t = \{1, 2, \dots, N\}$.

The relationship between $\mathbf{x}_t$ and y_t can be expressed as:

Equation 14

$$y_t = f(\mathbf{x}_t) + \varepsilon_t$$

where $\{f(\cdot); \mathbb{R}^m \rightarrow \mathbb{R}\}$ is a nonlinear transformation function, and ε_t is white noise whose expected value $E[\varepsilon_t]$ is zero.

Let the function $\phi(\cdot)$ map $\mathbf{x}_t$ at a higher p -dimensional space, where a linear relationship exists between $\phi(\mathbf{x}_t)$ and y_t . The linear relationship can be expressed as:

Equation 15

$$[y_t]_{1 \times 1} = [\phi(\mathbf{x}_t)]_{1 \times p} [\mathbf{w}]_{p \times 1} + [b]_{1 \times 1}$$

where the weights $[\mathbf{w}]_{p \times 1} = [w_1 \ w_2 \ \dots \ w_p]^T$.

The parameters $w_1, w_2, \dots, w_p$ and b can be estimated by optimizing the following objective function:

Equation 16

$$L(\mathbf{w}, \mathbf{e}) = \min_{\mathbf{w}, b, \mathbf{e}} \left[\frac{1}{2} \mathbf{w}^T \mathbf{w} + C \frac{1}{2} \sum_{t=1}^n e_t^2 \right]$$

where error $e_t = y_t - \phi(\mathbf{x}_t) \mathbf{w} - b$ and $[\mathbf{e}]_{N \times 1} = [e_1 \ e_2 \ \dots \ e_N]^T$. C is a SVR parameter considered to be the weight associated to the sum of squares of error e_t at a given time. Choosing high values of the parameter reduces (increases) the error in model prediction by overfitting (under fitting) the model.

Minimization of the term $\frac{1}{2} \mathbf{w}^T \mathbf{w}$ ensures that the model is not over-fitted, while minimization of the term $C \frac{1}{2} \sum_{t=1}^n e_t^2$ ensures that the model prediction error is not significantly high.

Introducing Lagrange multipliers, the optimization problem becomes:

Equation 17

$$L(\mathbf{w}, b, \mathbf{e}; \boldsymbol{\alpha}) = L(\mathbf{w}, \mathbf{e}) - \sum_{t=1}^N \alpha_t \{\phi(\mathbf{x}_t) \mathbf{w} + b + e_t - y_t\}$$

where α_t are the Lagrange multipliers and $[\alpha]_{N \times 1} = [\alpha_1 \ \alpha_2 \ \cdots \ \alpha_N]^T$. The optimal solution can be obtained by optimizing the function $L(\mathbf{w}, b, \mathbf{e}; \alpha)$ using the following conditions:

Equation 18

$$\begin{aligned} \frac{\partial L(\mathbf{w}, b, \mathbf{e}; \alpha)}{\partial \mathbf{w}} = 0; &\Rightarrow \mathbf{w} = \sum_{t=1}^N \alpha_t \phi(\mathbf{x}_t) \\ \frac{\partial L(\mathbf{w}, b, \mathbf{e}; \alpha)}{\partial b} = 0; &\Rightarrow \sum_{t=1}^N \alpha_t = 0 \\ \frac{\partial L(\mathbf{w}, b, \mathbf{e}; \alpha)}{\partial e_t} = 0; &\Rightarrow \alpha_t = C \times e_t \forall t \\ \frac{\partial L(\mathbf{w}, b, \mathbf{e}; \alpha)}{\partial \alpha_t} = 0; &\Rightarrow \mathbf{w}^T \phi(\mathbf{x}_t) + b + e_t - y_t = 0 \forall t \end{aligned}$$

Based on those conditions we get:

Equation 19

$$\begin{aligned} \sum_{t=1}^N \alpha_t &= 0 \\ \sum_{t'=1}^N \alpha_{t'} \phi(\mathbf{x}_{t'})^T \phi(\mathbf{x}_t) + b + \frac{\alpha_t}{C} &= y_t; \text{ for } \forall t=1, \dots, N \end{aligned}$$

where $\phi(\mathbf{x}_t)^T \cdot \phi(\mathbf{x}_t)$ is the dot product of the input vector in the high-dimensional transformed space. The dot product can be expressed by a Kernel function (Vapnik, 1995) given as:

Equation 20

$$\phi(\mathbf{x}_i)^T \cdot \phi(\mathbf{x}_j) = K(\mathbf{x}_i, \mathbf{x}_j)$$

This study considers a Gaussian radial basis kernel (RBF) function for analysis, which can be expressed as:

Equation 21

$$K(\mathbf{x}_i, \mathbf{x}_j) = e^{-\gamma \|\mathbf{x}_i - \mathbf{x}_j\|^2}, \quad \gamma > 0$$

The reason for choosing a RBF function instead of a polynomial is that the RBF function gives access to any analytic functions, and it is parsimonious. For chosen values of γ and C , values of $\{\alpha_t, t = 1, \dots, N\}$ and b are estimated.

9.3 Appendix 3: Chapter 1

9.3.1 Flow

Figure 32 shows the time series data of flow from the near natural CL (CL) stream with basic filtering before any outlier detection and removal has been undertaken, revealing significant jumps in data which are assumed to be outliers due to the speed at which the values increased and decreased. Figure 33 shows the time series data of flow after the outlier detection and removal was undertaken, using value of 1.5 for β with a window of 1040 preceding values. This window was chosen as there were 1040 values for 2019 which were not going to be used in the study and as such it was decided to use them as the window before removing them from the data. This removed approximately 4% of the data points in the final flow data set. This was well below the percentage of outliers detected when using a β of 1 in Bae and Ji (2019) where, when using a β between 1 and 2.5, the percentage of outliers detected were between 31.83% and 8.05% respectively.

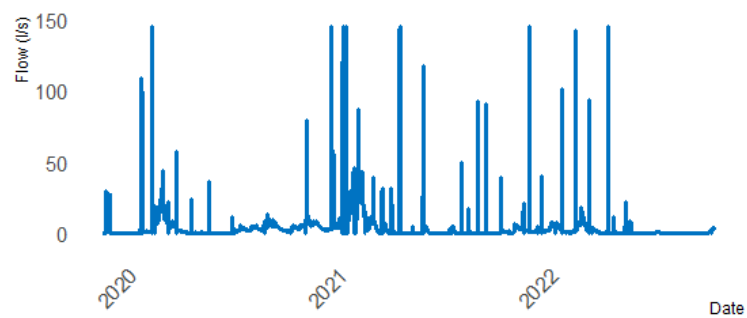


Figure 32 CL Upper flow data after basic filtering

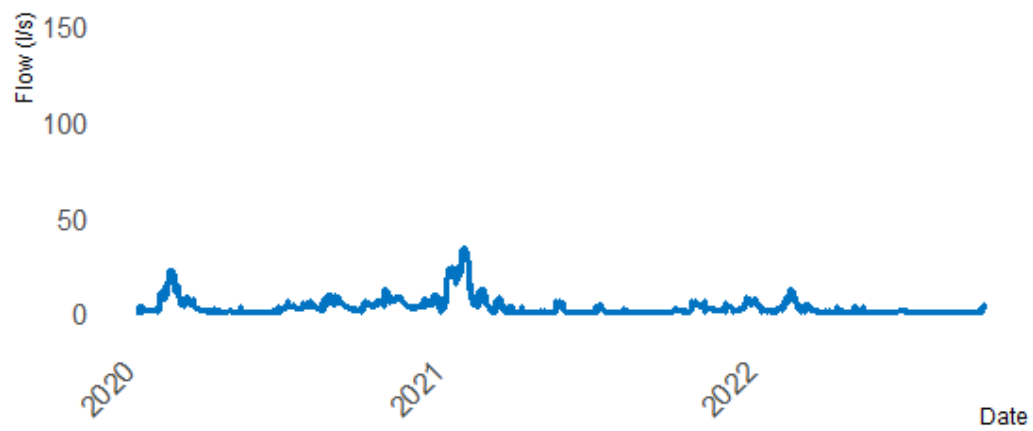


Figure 33 CL Upper flow data after basic filtering and outlier detection and removal using β criterion of 1.5.

The logger in CL stopped working after 09/10/2022, as such, the OTT sensors were used to measure flow for the end of the measurement period for CL.

In Figure 34 water depth measured by the OTT was compared to flow values from the flume when both were active to determine the relationship between the water depth and the flow, using Equation 22.

Equation 22

$$Q = 1.43 + 191.97(\text{depth}) + 38.48(\text{depth})^2$$

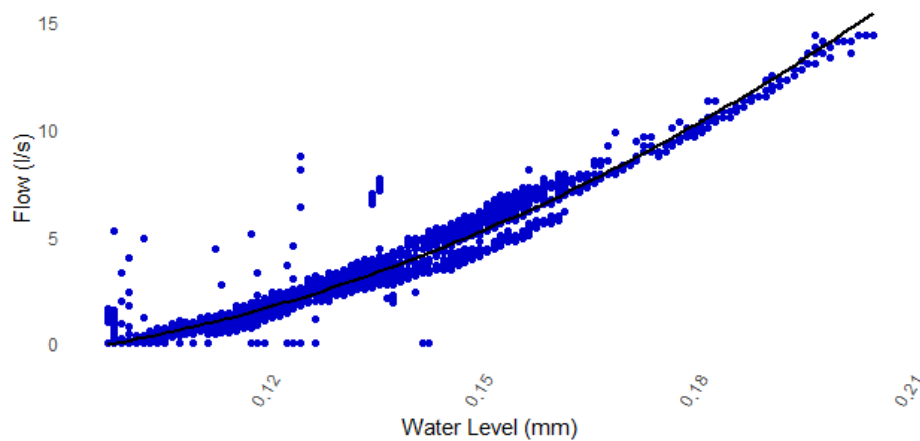


Figure 34 Water level (mm) plotted against flow (l/s) for CL Upper, r squared: 0.97

Figure 35 shows the time series data of flow from the near natural Garryduff drain with basic filtering before any outlier detection and removal had been undertaken. Figure 36 shows the time series data of flow after the outlier detection and removal was undertaken, using value of 2.5 for β with a window of 50 preceding values. This removed 0.18% of the data from the dataset.

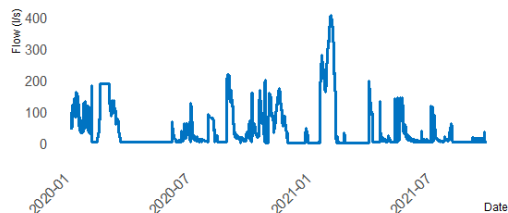


Figure 35 Garryduff flow data after basic filtering

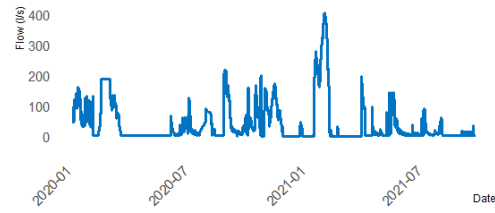


Figure 36 Garryduff flow data after basic filtering and outlier detection and removal using β criterion of 2.5 and a window of 50.

The logger in GD went missing from the site on the 30/09/2021, as such, the OTT sensors were used to measure flow for the end of the measurement period for GD. Figure 37 shows the raw OTT Water Level data for GD.

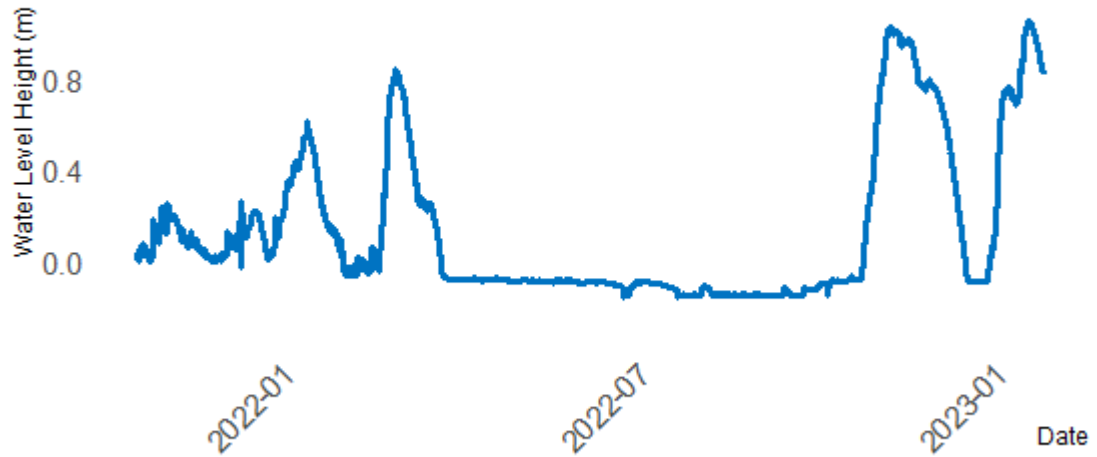


Figure 37 Water level data (mm) from the OTT sensor before Garryduff Flume

The OTT flow was determined using the flood Muskingum routing methodology (see Appendix 5: Muskingum Theory), which derived the following relationship between flow and depth at the flume (Equation 23), where x is equal to the OTT water depth values.

Equation 23

$$Q = 195.12x + 9.7731$$

Figure 38 shows the time series data of flow from the AS drain with basic filtering before any outlier detection and removal has been undertaken. Figure 39 shows the time series data of flow after the outlier detection and removal was undertaken, using value of 2.5 for β with a window of 50 preceding values. This removed 0.34% of the data from the dataframe.

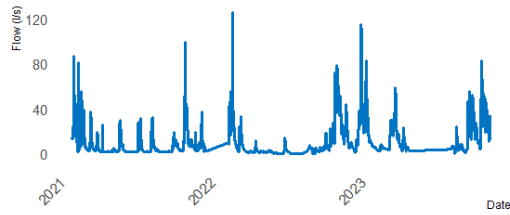


Figure 38 All Saints flow data after basic filtering

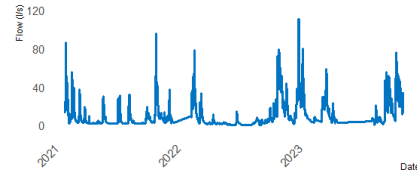


Figure 39 All Saints flow data after basic filtering and outlier detection and removal using β criterion 2.5 (a) and a window of 50

Figure 40 shows the raw fDOM data before any corrections for the three study sites were applied. The periods of missing data for AS are due to fDOM removal and flume diversion as a result of rehabilitation being undertaken on the site. There were also some periods in both GD and CL where measurements were interrupted due to technical issues. However, these periods were not as prolonged and occurred far less frequently.

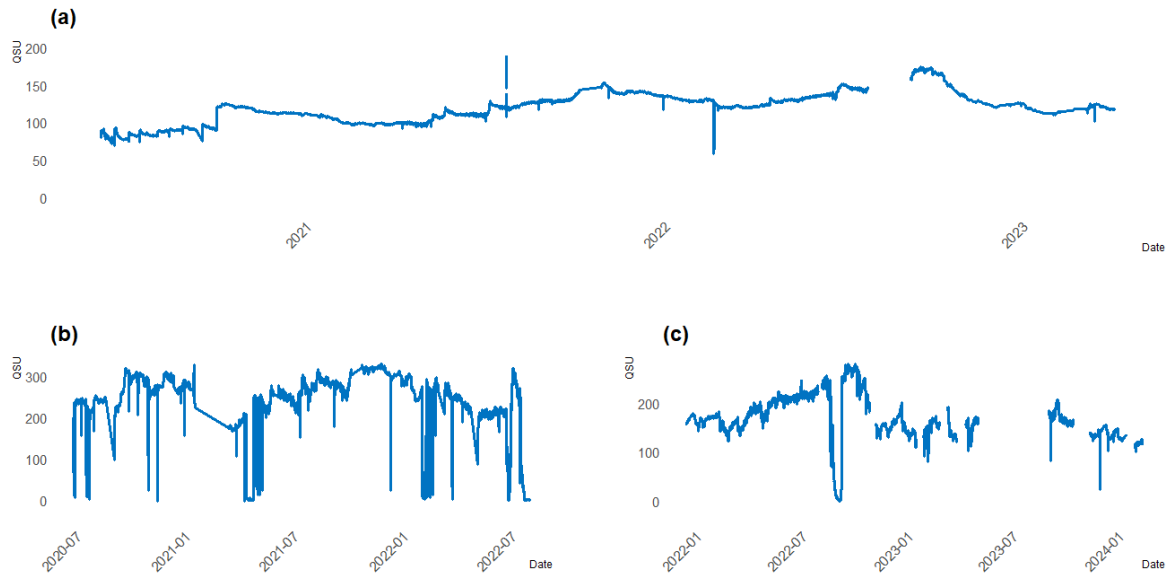


Figure 40 Raw fDOM (QSU) for Clara (a), Garryduff (b) and All Saints (c).

Figure 41 (a) shows the CL fDOM data after removing any fDOM values that corresponded to conductivity values that indicated that the sensors were not submerged ($>=2$).

Figure 41(b) and (c) show the corrections of fDOM using De Oliveira *et al.* (2018) equations for temperature and turbidity.

Missing values were filled based on linear interpolation and outliers were removed using the rolling median (Figure 41 (d)). A β of 0.5 and a window of 25 was used which removed 0.05% of data points.

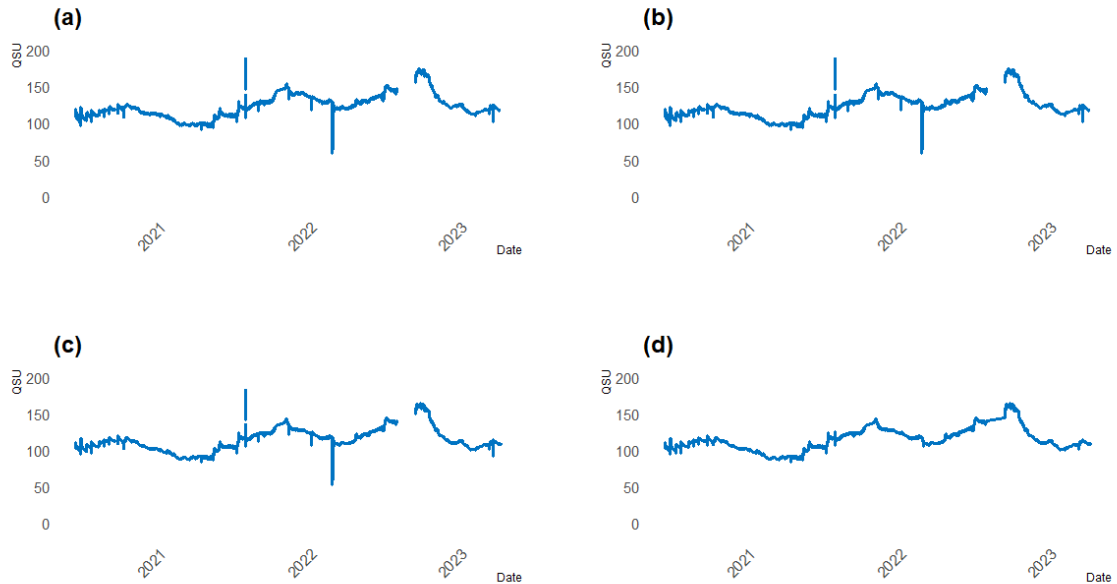


Figure 41 CL fDOM (QSU) filtered for conductivity (a), CL fDOM (QSU) filtered for turbidity (b), CL fDOM (QSU) corrected for temperature (c) and CL fDOM (QSU) with outliers removed.

Figure 42 and Figure 43 show the same filtering and correction process for the GD and AS sites. For GD, a β of 1 and a window of 75 was used which removed 1.99% of data points (Figure 42d). For AS, a β of 2.5 was used and as it was decided to only use the data from 2022 up until March of 2023 all the 2021 data was used as the window of 1029. This removed 1.69% of data points.

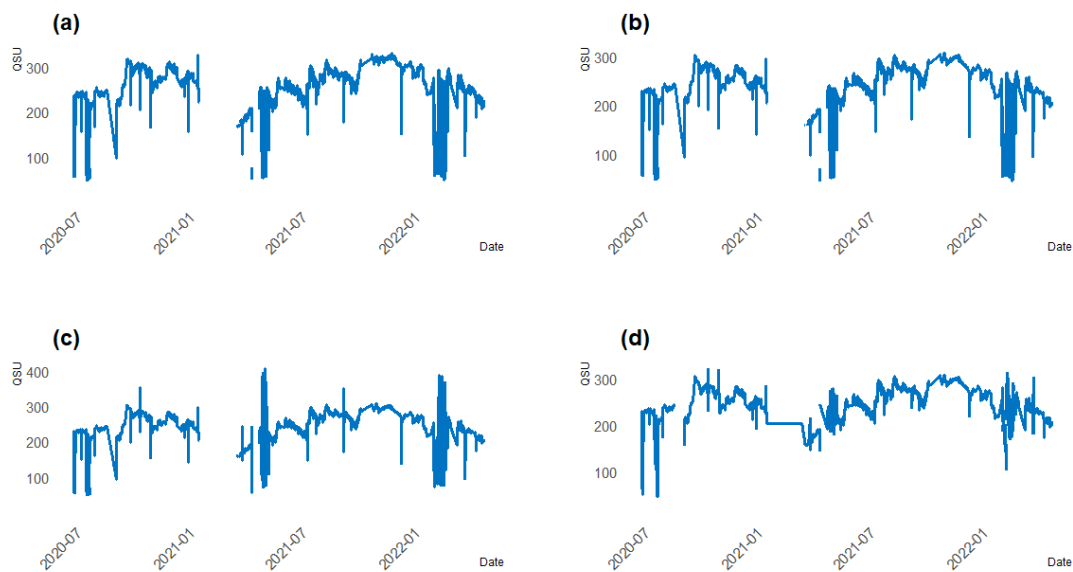


Figure 42 Garryduff fDOM (QSU) filtered for conductivity (a), Garryduff (QSU) corrected for turbidity (b), Garryduff fDOM (QSU) corrected for temperature (c) and Garryduff fDOM (QSU) with outliers removed (d).

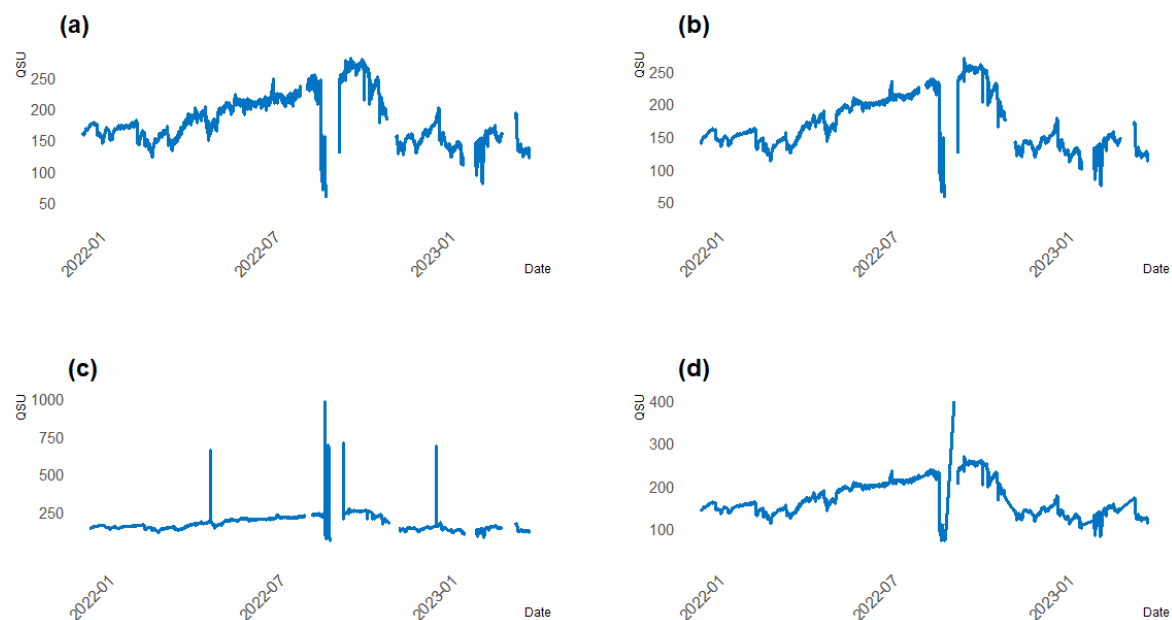


Figure 43 All Saints fDOM (QSU) filtered for conductivity (a), All Saints fDOM (QSU) corrected for temperature (b), All Saints (QSU) corrected for turbidity (c) and All Saints fDOM (QSU) with outliers removed (d).

Figure 44 shows the relationship between fDOM measured and fDOM corrected for IFE using the equation from De Oliveira *et al.* (2018) These relationships were then used to correct fDOM values.

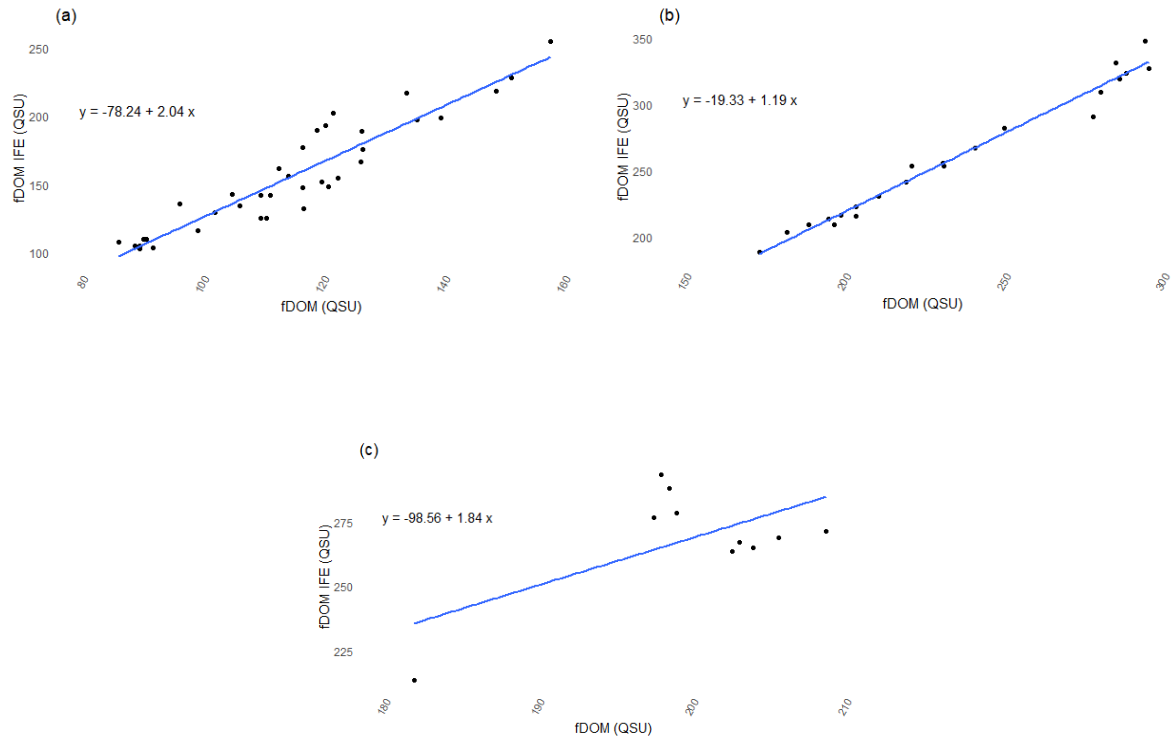


Figure 44 Scatter plot of CL, r squared: 0.874 (a), Garryduff, r squared: 0.977 (b) and All Saints, r squared: 0.382 (c) fDOM (QSU) vs fDOM Inner filter effects (QSU)

9.3.2 Multivariate Analysis Results

9.3.2.1 Clara

Table 18 shows the different variables that were used in the SVR based multi-variate modelling approach to determine which combination can be used to best to derive the optimum relationship between fDOM and NPOC for CL. In this case EY (fDOM) and ER (rainfall) considered over a 3 hour window were used to get the second highest value of NSE. The reason that this value was used as opposed to the model that looked at fDOM expectation function and variability of fDOM and over a 36 hour window was that it only resulted in a very small difference in the NSE; the benefits of

the smaller time window is that it requires considerably less data to develop the model, and also to simulate the model for future data and so the 3-hour window was used.

Table 18 The NSE goodness of fit results for the different models used for determining the variables that best described the relationship between fDOM and NPOC for CL, using different time windows. Where Y is fDOM, C is Conductivity, T is Water Temperature, Q is Discharge, R is Rainfall, E is the expectation function and Var is the variance of the data.

	Window assessed					
	3-hrs	6-hrs	12-hrs	24-hrs	36-hrs	48-hrs
Fy, y	0.790	0.764	0.674	0.649	0.691	0.698
Fy, y, EY	0.809	0.794	0.758	0.742	0.755	0.757
Fy, y, EY, Var(Y)	0.667	0.727	0.772	0.807	0.814	0.776
Fy, y, EY, Var(Y), E[Y-EY]³, E[Y-EY]⁴	0.662	0.731	0.764	0.813	0.778	0.724
Fy, y, EY, E[C]	0.791	0.798	0.775	0.807	0.809	0.821
Fy, y, EY, ET	0.216	0.296	0.413	0.354	0.336	0.339
Fy, y, EY, EQ	0.657	0.538	0.480	0.459	0.435	0.424
Fy, y, EY, ER	0.811	0.579	0.704	0.312	0.698	0.661
Fy, y, EY, EC, ET, EQ, ER	0.495	0.475	0.495	0.453	0.476	0.475
Fy, y, EY, EC, ET, EQ, ER, Var(C), Var(T), Var(Q), Var(R)	0.500	0.413	0.442	0.407	0.499	0.541
Fy, y, All moments (mean, Var, third and fourth of Y, C, T, Q, R	0.476	0.358	0.392	0.356	0.497	0.605

The CDF Inversion method improves on the linear regression showing it to be statistically significant.

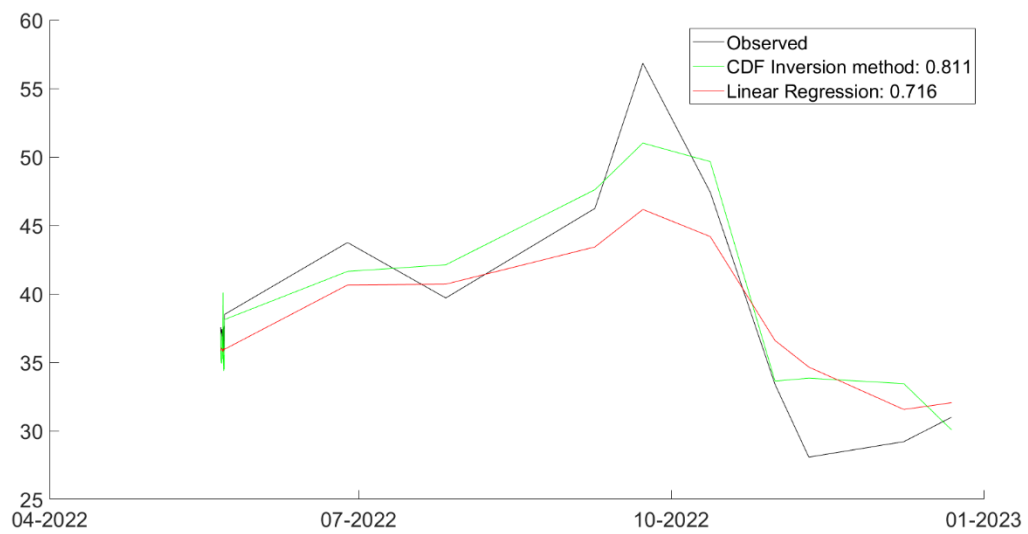


Figure 45 shows the observed values of NPOC vs the estimated values based on linear regression and the CDF Inversion Method for CL Upper.

9.3.2.2 Garryduff

Table 19 shows the different models used for determining the variables that best described the relationship between fDOM and NPOC. For the Garryduff bog runoff EY, Var(Y) over a 36-hour window was used as it had the highest NSE.

Table 19 The different models used for determining the variables that best described the relationship between $fDOM$ and NPOC for GD. Where Y is $fDOM$, C is Conductivity, T is Water Temperature, Q is Discharge, R is Rainfall, E is the expectation function and Var is the variance of the data. Values are in NSE and the value in bold is the one that was used.

	3-hrs	6-hrs	12-hrs	24-hrs	36-hrs	48-hrs
Fy, y	-0.626	-0.491	-0.438	-0.210	-0.178	-0.230
Fy, y, EY	-0.539	-0.356	-0.284	-0.181	-0.169	-0.275
Fy, y, EY, Var(Y)	-0.275	0.450	0.649	0.725	0.866	0.827
Fy, y, EY, Var(Y), $E[Y-EY]^3$, $E[Y-EY]^4$	-1.760	-0.333	0.620	0.487	0.752	-0.157
Fy, y, EY, E[C]	-0.389	-0.313	-0.178	-0.071	-0.135	-0.098
Fy, y, EY, ET	-0.291	-0.244	0.038	-0.105	-0.142	-0.124
Fy, y, EY, EQ	-0.499	-0.228	-0.070	0.201	0.323	0.243
Fy, y, EY, ER	-0.448	-0.188	0.067	0.464	0.562	0.779
Fy, y, EY, EC, ET, EQ, ER	-0.134	0.037	0.235	0.522	0.456	0.305
Fy, y, EY, EC, ET, EQ, ER, Var(C), Var(T), Var(Q), Var(R)	-0.525	-0.035	0.321	0.025	-0.007	0.133
Fy, y, All moments (mean, Var, third and fourth of Y, C, T, Q, R)	-1.011	-0.189	0.707	0.288	0.412	0.349

Figure 46 shows the observed values of NPOC vs the estimated values based on linear regression (NSE of -1.615) and the CDF Inversion Method (NSE of 0.866) for GD. The CDF Inversion method improves on the linear regression showing it to be statistically significant.

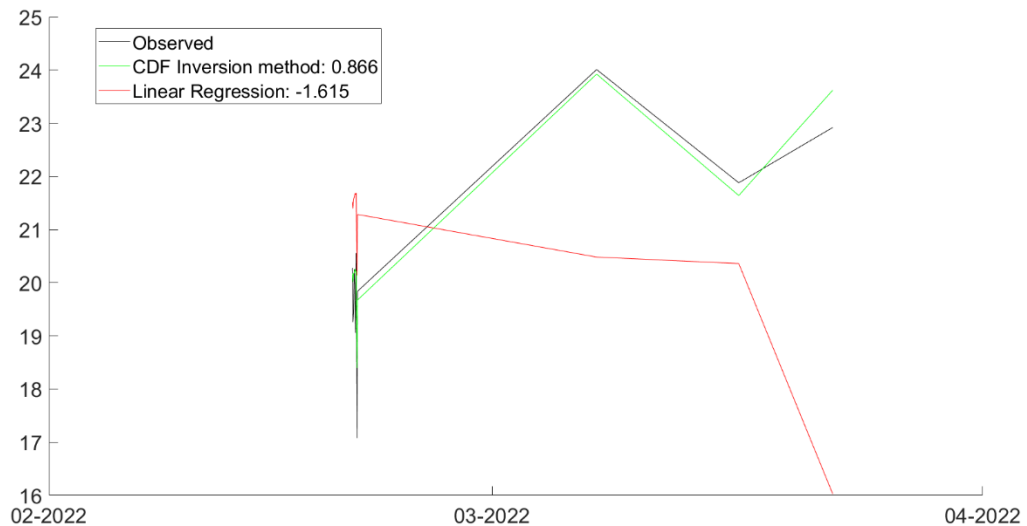


Figure 46 shows the observed values of NPOC vs the estimated values based on linear regression and the CDF Inversion Method for Garryduff.

9.3.2.3 All Saints

Table 20 shows the different variables that were used in the SVR based multi-variate modelling approach to determine which combination can be used to best derive the optimum relationship between fDOM and NPOC for AS. In this case the model that used EY (expectations function of fDOM) and [E]C (the expectation function of conductivity) over a 12-hour window showed the best results (NSE of 0.93). It should be noted that in AS the model was calibrated (on 7% of the data) and validated (on the remaining 30%) intermittently throughout the time series as opposed to the other two bog sites where the models were calibrated on the initial 70% of the data and validated on the final 30%.

Table 20 The different models used for determining the variables that best described the relationship between fDOM and NPOC for AS. Where Y is fDOM, C is Conductivity, T is Water Temperature, Q is Discharge, R is Rainfall, E is the expectation function and Var is the variance of the data. Values are in NSE and the value in bold is the one that was used.

NSE	3-hrs	6-hrs	12-hrs	24-hrs	36-hrs	48-hrs
Fy, y	0.9296	0.4796	0.7163	0.1861	0.6120	0.5836
Fy, y, EY	0.2624	0.6773	0.8490	0.4282	0.7151	0.6776
Fy, y, EY, Var(Y)	0.5445	0.6292	0.8152	0.5514	0.8264	0.7243
Fy, y, EY, Var(Y), E[Y-EY] ³ , E[Y-EY] ⁴	0.6026	0.7152	0.6480	0.6440	0.8053	0.7037
Fy, y, EY, E[C]	0.6557	0.8125	0.9304	0.6546	0.7357	0.6996
Fy, y, EY, ET	0.6170	0.7199	0.7403	0.4570	0.7280	0.7073
Fy, y, EY, EQ	0.7588	0.7070	0.6992	0.7330	0.8066	0.7748
Fy, y, EY, ER	0.6017	0.6945	0.2480	0.8624	0.6988	0.7670
Fy, y, EY, EC, ET, EQ, ER	0.7264	0.6996	0.4235	0.9301	0.8016	0.8003
Fy, y, EY, EC, ET, EQ, ER, Var(C), Var(T), Var(Q), Var(R)	0.4999	0.5448	0.6857	0.8989	0.8720	0.8238
Fy, y, All moments (mean, Var, third and fourth of Y, C, T, Q, R	0.4913	0.3900	0.4852	0.9427	0.8299	0.8474

Figure 47 shows the observed values of NPOC vs the estimated values based on linear regression (NSE of 0.262) and the CDF Inversion Method (NSE of 0.93) for AS. The CDF Inversion method improves on the linear regression showing it to be statistically significant.

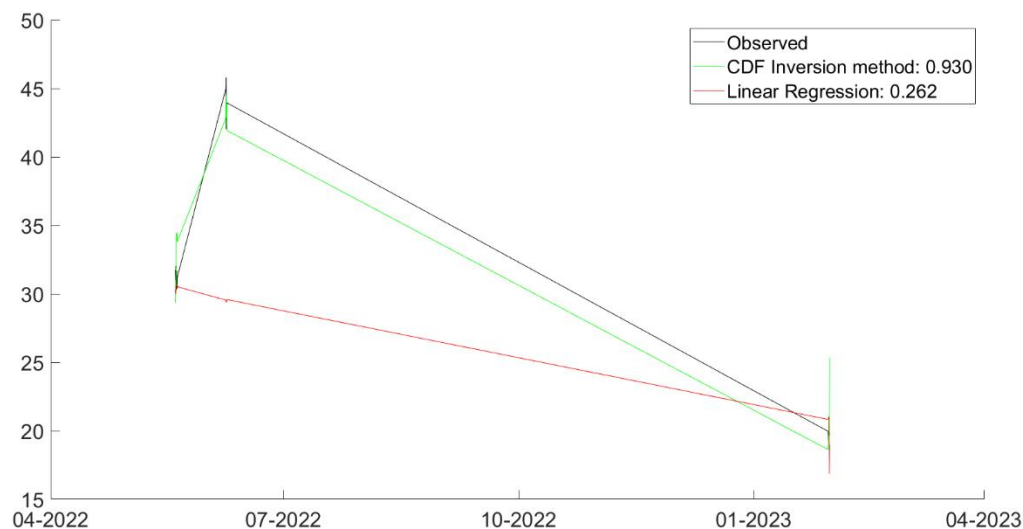


Figure 47 the observed values of NPOC vs the estimated values based on linear regression and the CDF Inversion Method for All Saints.

9.4 Appendix 4: Chapter 2

9.4.1 Effective rainfall

When looking at the effective rainfall trends compared to the flow trends (Figure 48), the high intensity peaks in effective rainfall are met by the peaks in flow. Higher intensity of effective rainfall is seen during the winter period of each year, during which the peak flow is also seen. The trends in effective rainfall differ between the years (Figure 48). In general, for 2020 and 2021, the periods of lower effective rainfall are in the late spring to mid-summer months, with the highest periods in the late autumn to winter period. In 2022, however, effective rainfall is lowest in the July and August period, with the highest effective rainfall in October. 2023 follows similar trends to 2020 and 2022 with the exception of July which shows the highest average effective rainfall and total rainfall for the whole year, with the second lowest effective rainfall for the year in February.

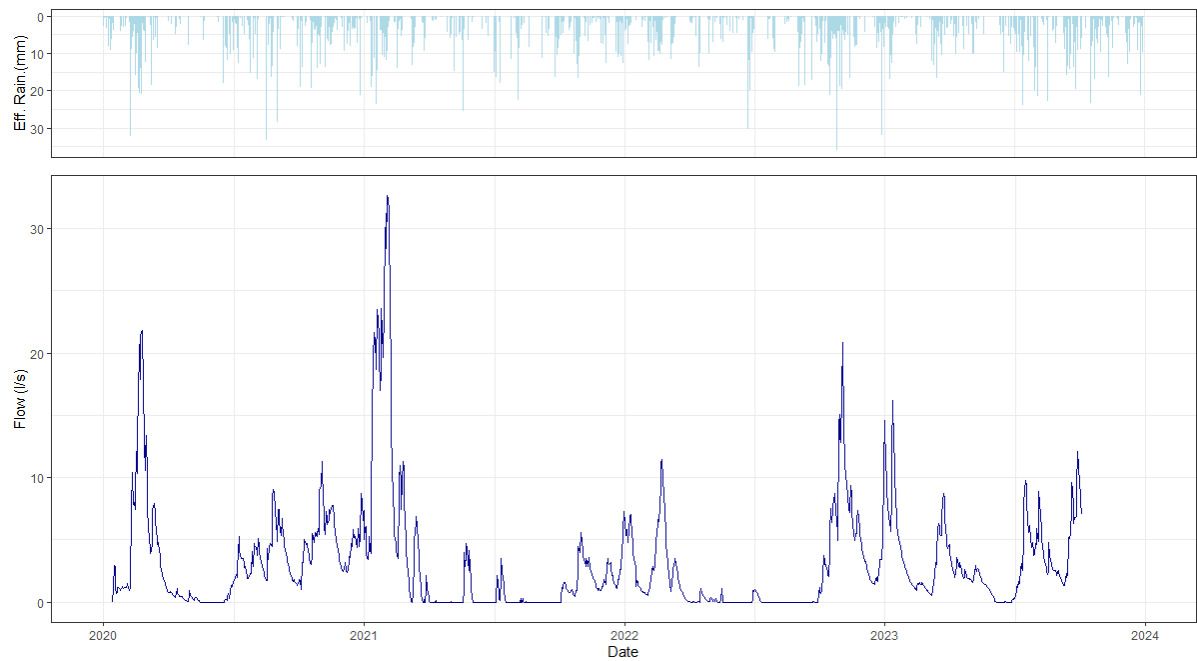


Figure 48 Clara flow with effective rainfall (mm/day)

When looking at the effective rainfall trends compared to the flow trends for AS (Figure 49), the high intensity peaks in effective rainfall generally follow the flow trends.

In 2021, the period of lowest average effective rainfall per month (mm/day) and total effective rainfall was between April to June, with the highest values in August and October (Figure 49). In 2022, however, August and July had the lowest effective rainfall. The highest values were in October and November. In 2023, the lowest effective rainfall was in February and May, with the highest in July and September. October and November showed quite low effective rainfall, however flow is quite high for that period.

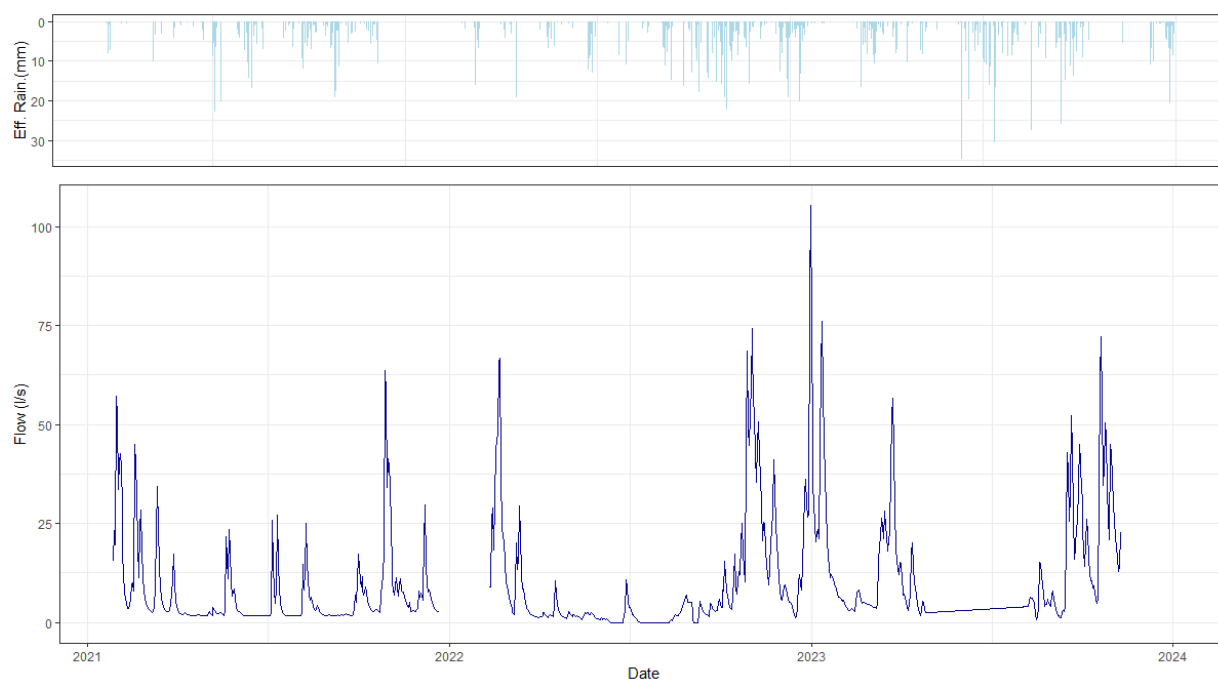


Figure 49 All Saints flow with effective rainfall

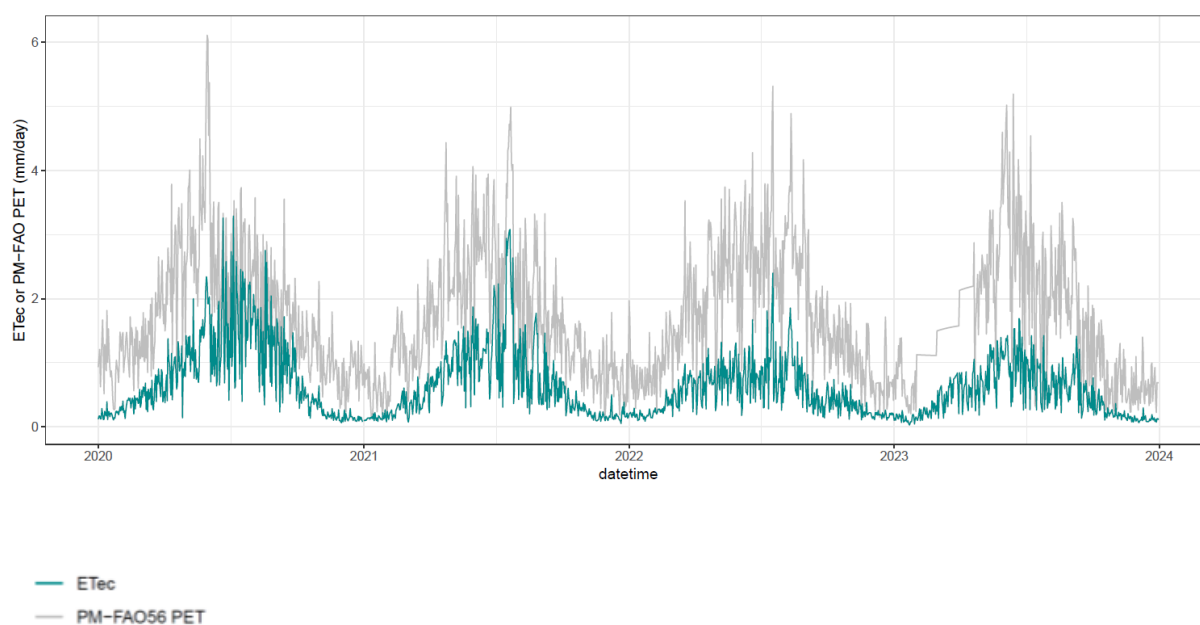


Figure 50 Eddy covariance flux tower-based daily evapotranspiration rates (ETec in mm/day) and potential evapotranspiration rates (PET, Penman-Monteith FAO56 formulation [PM-FAO56, short grass reference]) at CL. Note: Windspeed data used in the PET calculation was retrieved from the nearest Met Éireann weather station (Mullingar) as

windspeed was not recorded at All Saints. PET on days with missing was interpolated using monthly averages (mostly at the start of 2023).

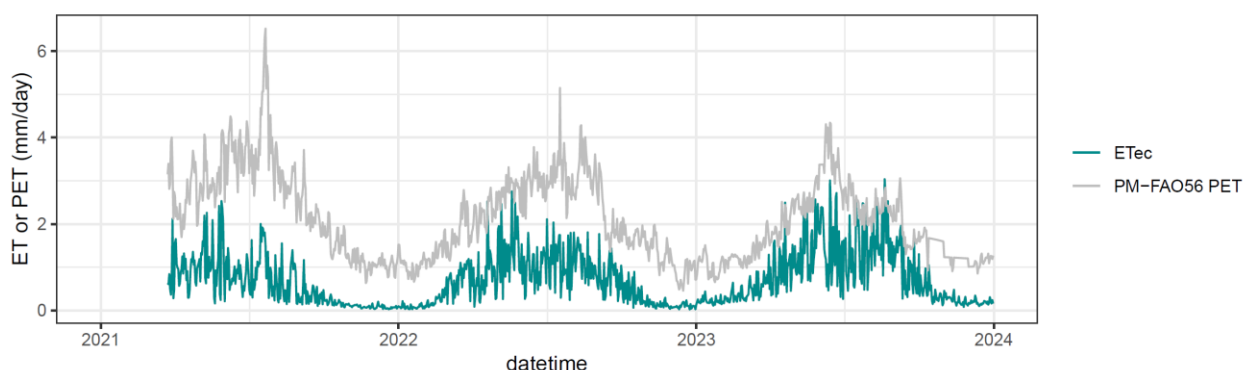


Figure 51 Eddy covariance flux tower-based daily evapotranspiration rates (ETec in mm/day) and potential evapotranspiration rates (PET, Penman-Monteith FAO56 formulation [PM-FAO56, short grass reference]) at AS from March 2021 to December 2023. Note: Windspeed data used in the PET calculation was retrieved from the nearest Met Éireann weather station (Gurteen) as windspeed was not recorded at All Saints. PET on days with missing was interpolated using monthly averages (mostly at the end of 2023).

9.4.2 Water table and storativity

9.4.2.1 Water table

The water level with respect to ground level for Clara and All Saints are presented in Figure 52 and Figure 53.

Overall, in Clara, the Marginal ecotope experienced lower water level data (mean level 0.44 m below ground level for 2022) than the other ecotopes, although only one complete year of data was available for marginal (Table 21). The Sub-Marginal and Sub-Central ecotopes sites showed similarly higher water levels (0.008 and 0.011 m below ground level), with Central showing slightly lower water levels than both on average (between 0.13 and 0.14 m below ground level). The inter year variation in water levels for Clara appear to be low, with slightly lower water levels in 2021 for Sub-Marginal and Sub-Central.

In All Saints, the water level on average is lower than in Clara (between 0.09 and 0.33 m below ground level), with the June to December period in 2023 having higher water levels (0.09 m below ground level) than the same period in 2022 (0.33 m below ground level).



Figure 52 The water level data (m with respect to ground level) for CL marginal (a), sub-marginal (b), central ecotopes (c) and sub-central (d) ecotopes.

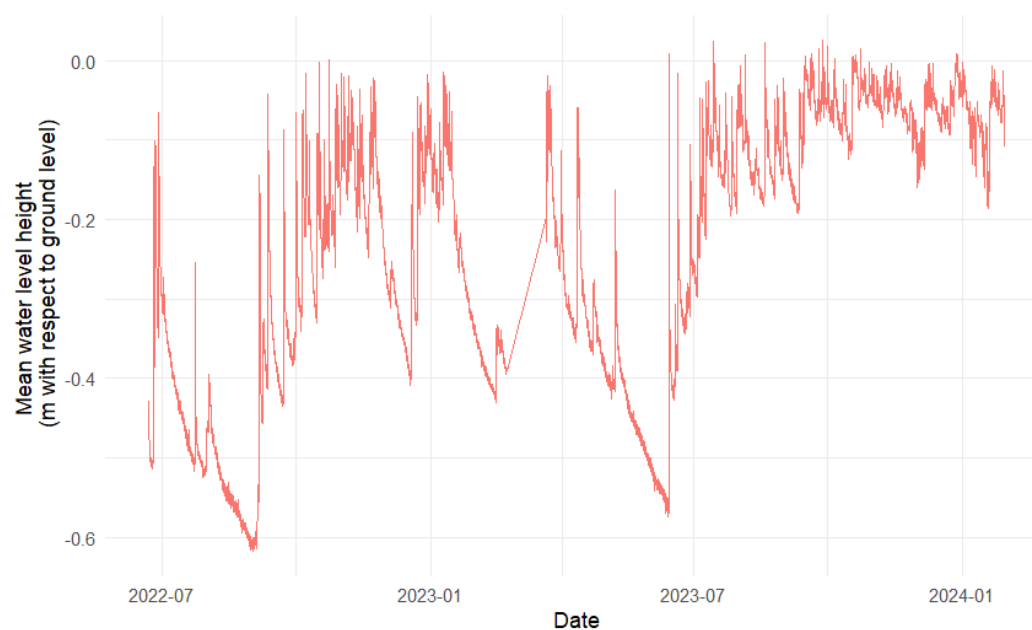


Figure 53 The mean water level data (m with respect to ground level) for All Saints.

Table 21 The water level data for CL and All Saints, with mean, minimum and maximum values. *As there wasn't a complete year of data for 2022, the data from June – Dec 2022 was compared to the same period of 2023.

		Water Level Height (m with respect to ground level)		
	Year	Mean	Min	Max
Clara Marginal	2022	-0.44	-0.75	0.00
Clara Sub-marginal	2020	-0.01	-0.03	0.00
	2021	-0.01	-0.02	0.00
	2022	-0.01	-0.03	0.00
Clara Central	2020	-0.13	-0.27	0.00
	2021	-0.14	-0.22	-0.03
	2022	-0.13	-0.24	-0.02
Clara Sub-central	2020	-0.008	-0.028	0.000
	2021	-0.011	-0.024	-0.002
	2022	-0.011	-0.033	-0.003
Average for Clara	2020	-0.05	-0.11	0.00
	2021	-0.05	-0.09	-0.01
	2022	-0.15	-0.26	-0.01
All Saints	2022 Jun-Dec	-0.33	-0.62	0.00
	2023 June - Dec	-0.09	-0.30	0.03
	2023	-0.20	-0.57	0.03

9.4.2.2 Microcosms

At the microcosm sites, the mean water level height (mm with respect to ground level) inside and outside the microcosms are presented in Figure 54. The minimum and maximum water level inside and outside the microcosms for each ecotope site are presented in Table 22. The sub-marginal ecotope and sub-central had the highest water level inside (215.92 and 249.2 mm respectively) and outside (-8.15 and -9.44 mm respectively) the microcosms.

For the Central ecotope site, the trends for water levels inside and outside the microcosm are less similar, with higher peaks inside the microcosm and the water level height outside the microcosm being lower than outside for most of the period (Figure 54(a)). For the Marginal ecotope, water levels both inside and outside the microcosm follow similar trends, with more fluctuations and higher peaks seen inside the microcosm (Figure 54(b)).

Both the Sub-Central and Sub-Marginal show matching trends inside and outside the microcosm, however the values outside the microcosm are on a much smaller scale than inside the microcosm (Figure 54 (c) and (d)). For example, the values for Sub-Central inside range from -38.64 and 376.84 mm and for outside range from -30.9 and -9.44 mm. Therefore, while the water levels inside and outside the microcosms at Sub-Central and Sub-Marginal follow the same patterns, the water levels outside the microcosm have a much lower range.

Table 22 The mean, minimum and maximum water level inside and outside the microcosms for each microcosm site at CL

	Water level (mm with respect to ground level)					
	Inside			Outside		
	Min	Max	Mean	Min	Max	Mean
Central	-126	190	23.17	-223	0	-100.9
Marginal	-220	75	-71.21	-220	0	-102.8
Sub-central	-38.64	376.84	215.93	-30.9	0	-9.437
Sub-marginal	-27.6	415.7	249.2	-27.6	0	-8.154

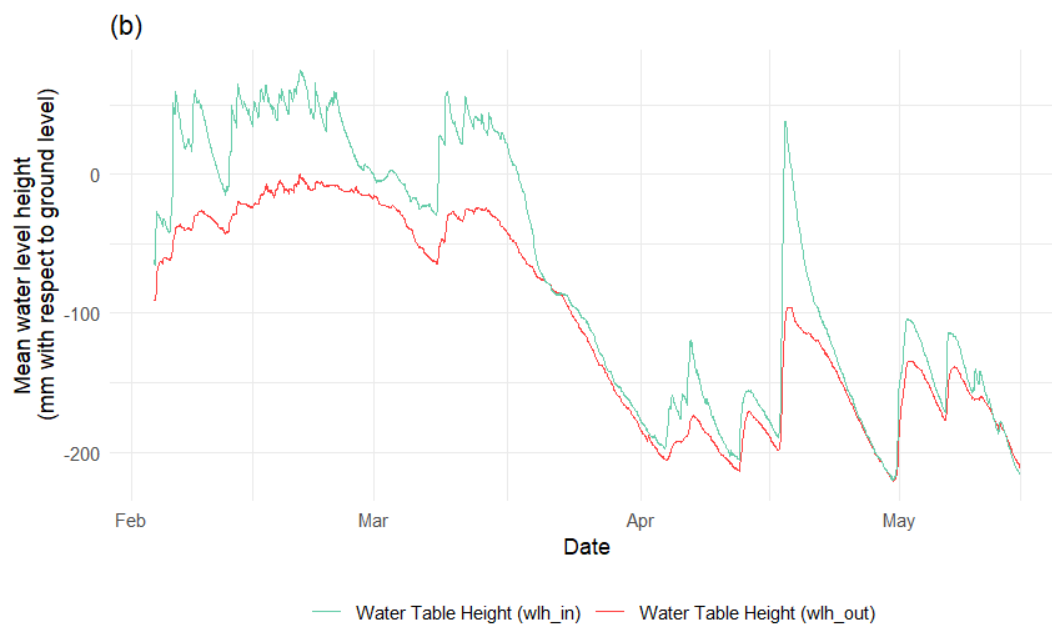
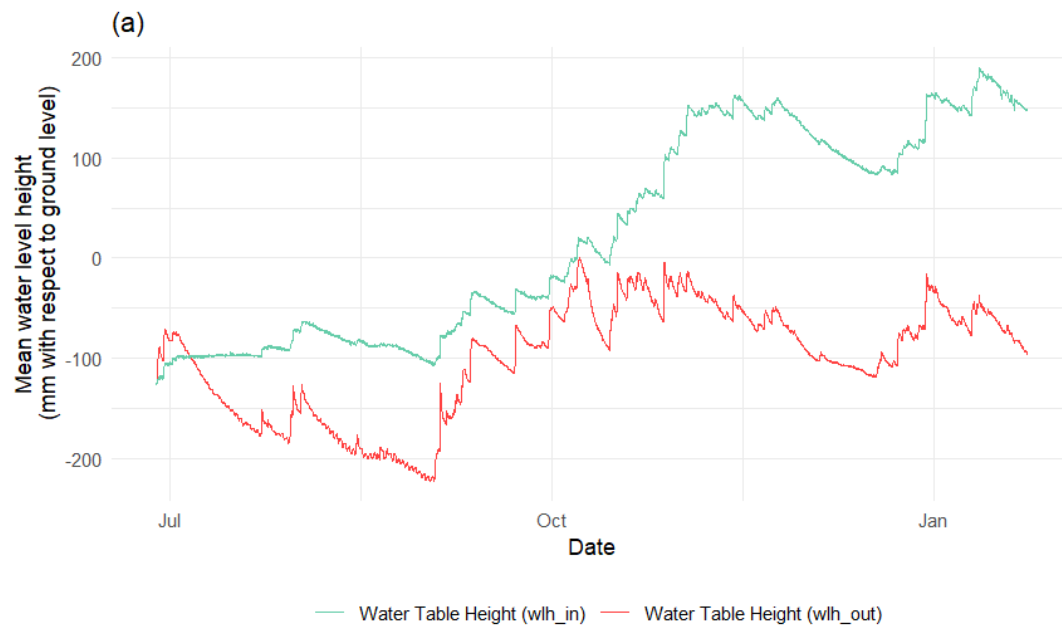




Figure 54 The mean water level height (mm with respect to ground level) inside and outside the microcosm and the rainfall (mm) for the Central (a), Marginal (b) Sub-Central (c) and Sub-Marginal (d).

For the storativity measurements, 104 and 43 rainfall events were found over the observation period for Central and Marginal respectively, with 165 rainfall events for Sub-Central and Sub-Marginal. Only a few storativity data points were output from these data for central and marginal (Figure 55 and Figure 56), however for Sub-Central and Sub-Marginal much of the storativity results were either significantly under 0 or above 1, therefore the data were not deemed to be useful.

The mean water level height inside and outside the microcosms in the Central ecotope were statistically significantly different (Welch's t test, p-value = 0.04, Figure 55) but not for Marginal (Welch's t test, p-value = 0.1498, Figure 56).

It should be noted that of 32 storativity values calculated for Central inside the microcosm, only 9 were within the expected range between 0 and 1 (although any values between 0 and 1.2 were presented here as per Swenson, Regan and Gill (2020)). For the Marginal ecotope location, 17 storativity values were calculated and 10 were within the expected range. Many rainfall events identified had a higher corresponding water level at the start of the rainfall event than at the end of the rainfall event, which indicates that something may have been wrong with the OTT loggers.

When comparing the storativity curves of this study to the storativity curves of Swenson, Regan and Gill (2020) in Abbeylax Bog, it is clear that this study has much less usable data points, indicating that there may have been issues either with the setting up of the microcosm sites and/or the measurement of the water level and data collection (Figure 57).

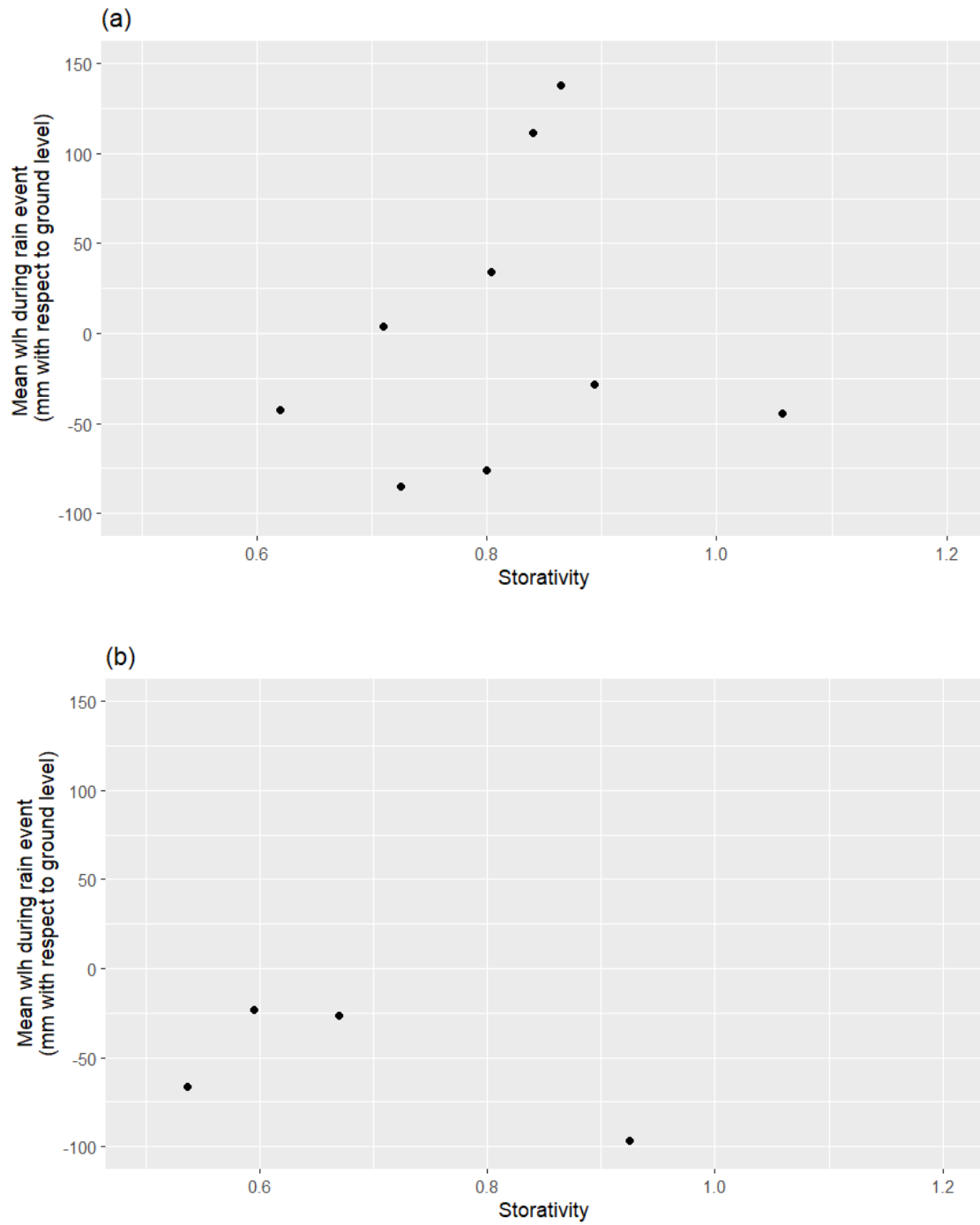


Figure 55 The storativity curves calculated from rainfall and water table changes (a) inside the microcosm at CL Central ecotope and (b) outside the microcosm, p -value (Welch's t test) = 0.04.

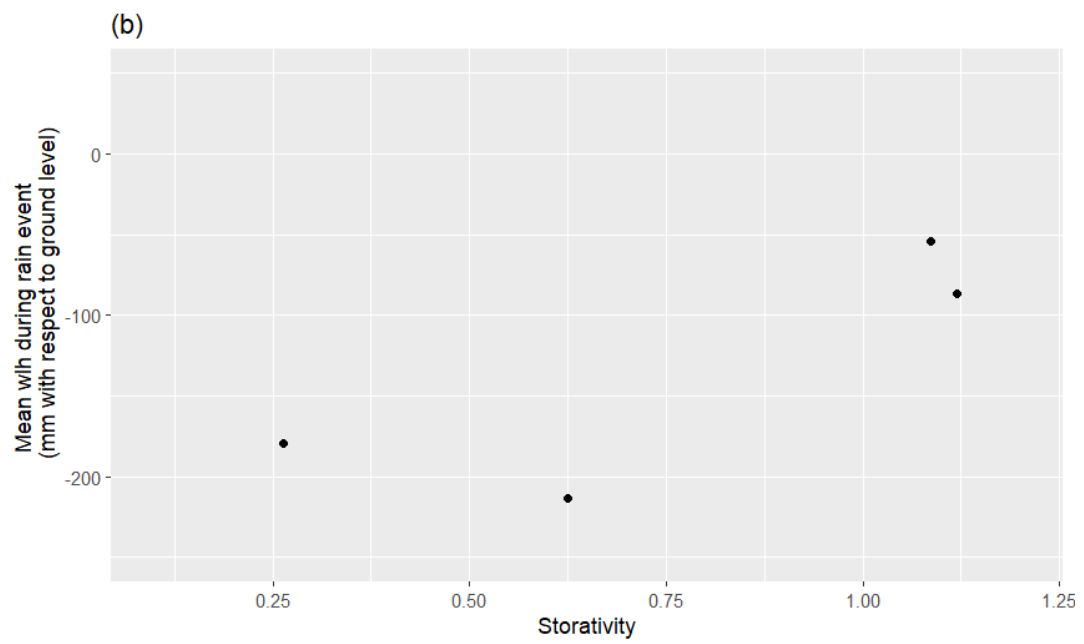
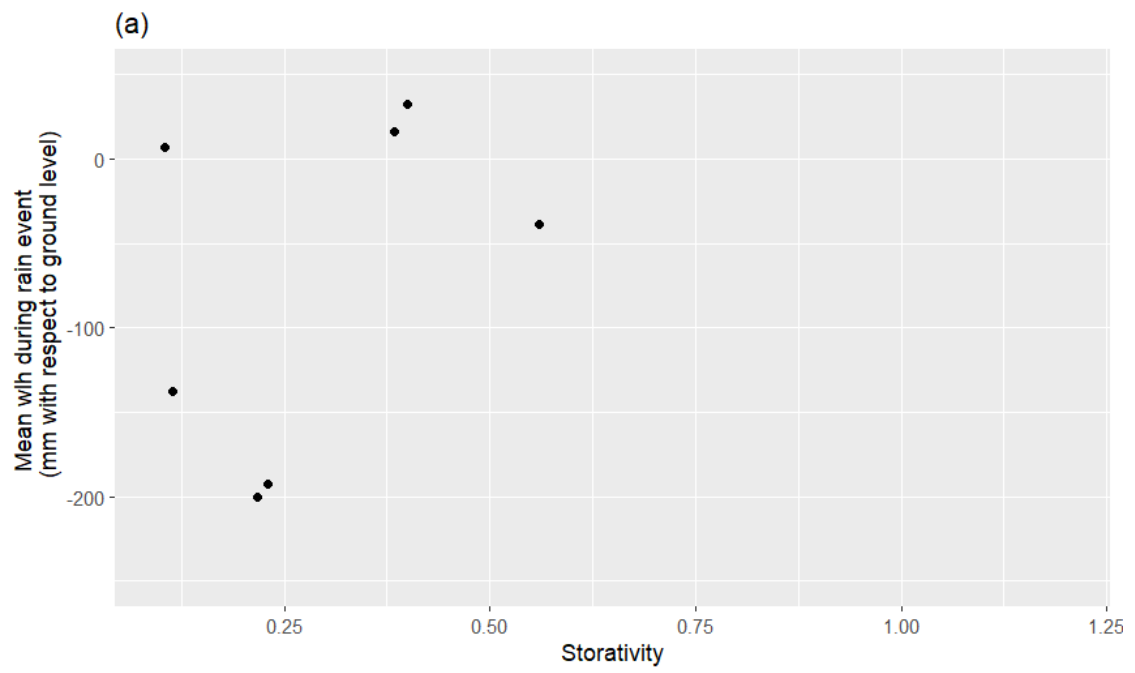


Figure 56 The storativity curves calculated from rainfall and water table changes (a) inside the microcosm at CL Marginal and (b) outside the microcosm, p -value (Welch's t test) = 0.1498

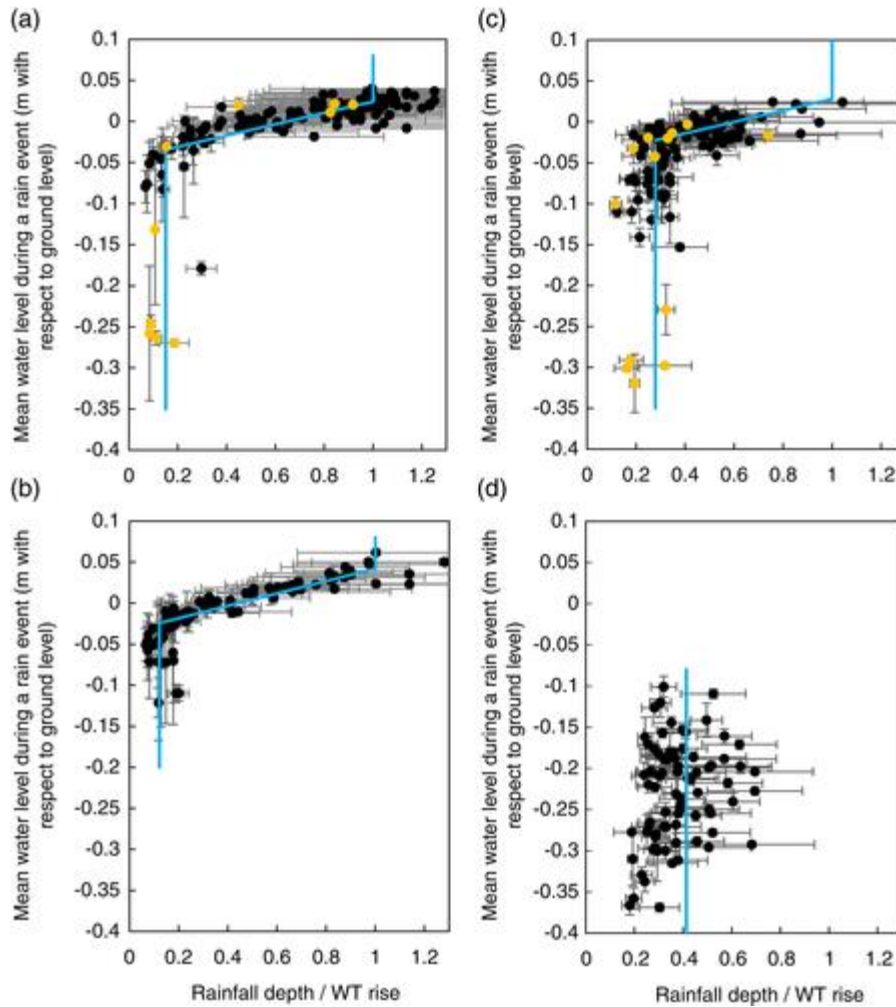


Figure 57 The storativity curves from Swenson, Regan and Gill (2020), for inside the four microcosms at Abbeyleix Bog, Co. Laois - (a) *Eriophorum* Cutover, (b) Sub-Marginal, (c) Sub-Central, and (d) *Sphagnum* Cutover locations. The blue lines are the idealized storativity curves. The yellow dots indicate where rainfall data from offsite had to be used.

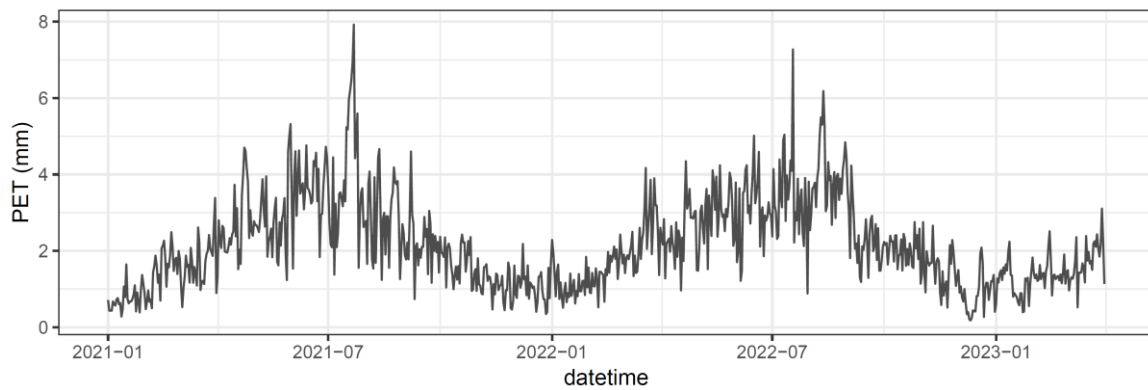


Figure 58 Daily potential evapotranspiration rates (PET, Penman-Monteith FAO56 formulation [PM-FAO56, short grass reference]) at GD from January 2021 to March 2023. Note: Net radiation

data from All Saints was used in the calculation of PET as Gurteen Met Éireann weather station lacks records on it. PET on days with missing was interpolated using monthly average).

9.5 Appendix 5: Muskingum Theory

The level logger in the flume at the outlet of Garryduff (GD) used to determine flow by the VanWalt DataHub went missing from the site on the 30/09/2021. However, an OTT Orpheus Mini Level Loggers (OTT Loggers) had been placed in front of the flume in a PVC stilling well as a backup system for measuring flow. A methodology needed to be found to produce a rating curve for this new level logger position in order to determine the flow from the site. There was a short period when there were both pump on/off data and OTT water level measurements between 15th to 18th October 2021. Equally, there was a short period of time when there was pump on/off data and flume flow measurements (before the probe was stolen) between 25th to 26th September.

The pumps discharge flow from a deep up and into a small lagoon from where the water then flow into the outlet channel where the lagoon is situated (approximately 300 m away from the pump sump. So, the methodology adopted to determine flow from the OTT sensors was as follows.

- Use the pump on/off data with the Flume flow data between 25-26th September to derive a Muskingum flood routing relationship for the mini-catchment (i.e., between where the pump discharges and the lagoon and the outlet at the flume).
- Use the Muskingum routing model to generate flows at the flume between 15th to 18th October 2021.
- Use these flow values with the OTT water level values to derive a rating curve for discharge versus water level at the flume for the OTT sensor.

Muskingum Flood routing approach is based on a so-called storage routing concept. For any inlet jump in flow into a catchment (inflow, I) there is a lag before the flow comes out of the catchment at the other end (see Figure S1).

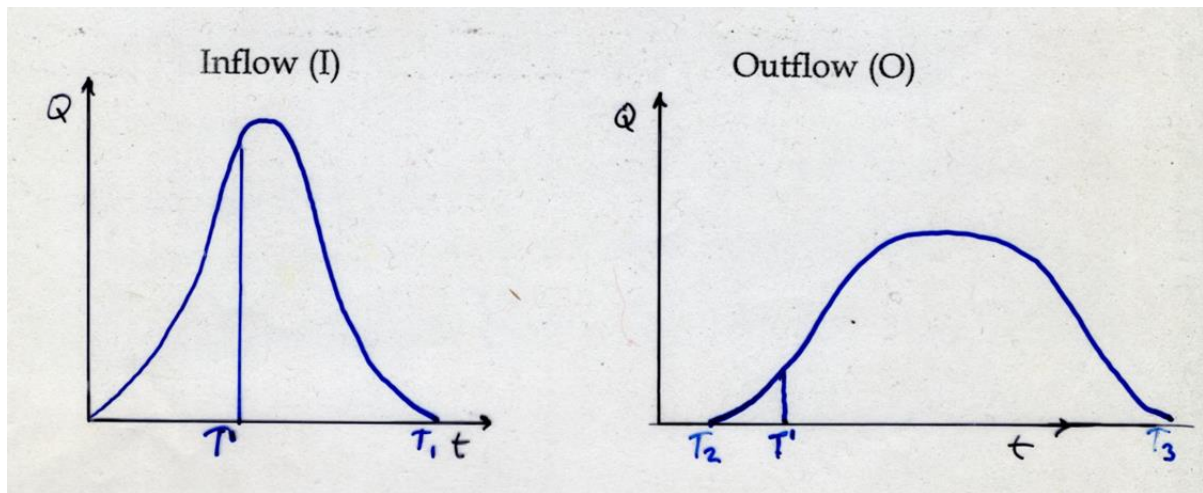


Figure S1. Typical inflow versus outflow for a catchment.

$$\text{The total flood volume } V = \int_0^{t_1} I \, dt = \int_{t_2}^{t_3} O \, dt$$

$$I_{(t')} = \int_0^{t'} I \, dt \quad O_{(t')} = \int_0^{t'} O \, dt \quad \text{Difference} = \text{storage volume}$$

$$\text{Storage volume at time } t' = S_{(t')} = \int_0^{t'} (I - O) \, dt$$

$$\frac{dS}{dt} = I - O \quad \text{continuity equation}$$

$$S_2 - S_1 = \frac{(I_1 + I_2)\Delta t}{2} - \frac{(O_1 + O_2)\Delta t}{2}$$

$$\text{The Muskingum river routing method assumes: } S = f_1(O) + f_2(I - O)$$

And that $f_1(O)$ and $f_2(I - O)$ are both straight line functions.

$$f_1(O) = K O \quad f_2(I - O) = b(I - O)$$

$$\text{Predicted outflow at the end of each time step} \quad O_2 = c_1 I_1 + c_2 I_2 + c_3 O_1$$

Where:

$$c_1 = \frac{\Delta T + 2Kx}{\Delta T + 2K - 2Kx} \quad c_2 = \frac{\Delta T - 2Kx}{\Delta T + 2K - 2Kx} \quad c_3 = \frac{\Delta T + 2K - 2Kx}{\Delta T + 2K - 2Kx}$$

Step 1

Using the inflow (pump data) and outflow (flume data) for 25th and 26th September 2020 yielded the following calculation of temporary storage (Table S.1). The x coefficients were then varied until the plot of storage (S) versus $XI + (1-x)O$ minimised the hysteresis and closed up to a straight line as possible (see Figure S2). The K coefficient was then determined from the gradient of this line. The c_1 , c_2 and c_3 Muskingum coefficients were then determined from the optimised x and K coefficients.

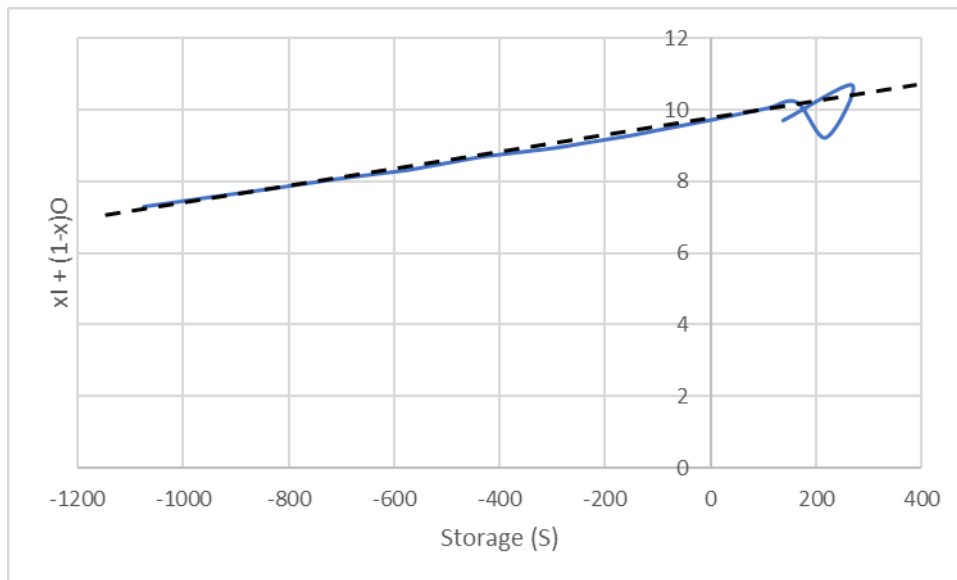


Figure S2. Plot of storage (S) versus $XI + (1-x)O$ for the Garryduff outlet catchment to determine Muskingum coefficients.

Table 1. Muskingum coefficient determination

Time	Inflow (I)	Outflow (O)	I - O	Storage (S)	$xI + (1-x)O$		
0	35	7.81	27.19	135.95	9.7133	x	0.07
5	35	8.87	26.13	266.6	10.6991		
10		9.93	-9.93	216.95	9.2349	K	430
15		10.99	-10.99	162	10.2207		
20		10.82	-10.82	107.91667	10.0595	c_1	0.081014
25		10.64	-10.64	54.7	9.8983	c_2	-0.06859
30		10.47	-10.47	2.35	9.7371	c_3	0.987575
35		10.31	-10.31	-49.216667	9.5914	ΔT	5
40		10.16	-10.16	-100	9.4457		
45		10.00	-10.00	-150	9.3		1
50		9.87	-9.87	-199.36667	9.1822		
55		9.75	-9.75	-248.1	9.0644		
60		9.62	-9.62	-296.2	8.9466		
65		9.53	-9.53	-343.85	8.8629		
70		9.44	-9.44	-391.05	8.7792		
75		9.35	-9.35	-437.8	8.6955		
80		9.22	-9.22	-483.9	8.5746		
85		9.09	-9.09	-529.35	8.4537		
90		8.96	-8.96	-574.15	8.3328		
95		8.87	-8.87	-618.51667	8.2522		
100		8.79	-8.79	-662.45	8.1716		
105		8.7	-8.70	-705.95	8.091		
110		8.60	-8.60	-748.95	7.998		
115		8.50	-8.50	-791.45	7.905		
120		8.4	-8.40	-833.45	7.812		
125		8.31	-8.31	-875	7.7283		
130		8.22	-8.22	-916.1	7.6446		
135		8.13	-8.13	-956.75	7.5609		
140		8.04	-8.04	-996.95	7.4772		
145		7.95	-7.95	-1036.7	7.3935		
150		7.86	-7.86	-1076	7.3098		

Hence, the flood routing model for the outflow catchment is:

$$O_2 = 0.081 I_1 - 0.069 I_2 + 0.988 O_1$$

This equation was then used to route the pump inflow data to generate an outflow time series to compare against what was actually measured at the flume as a check (see Figure S3).

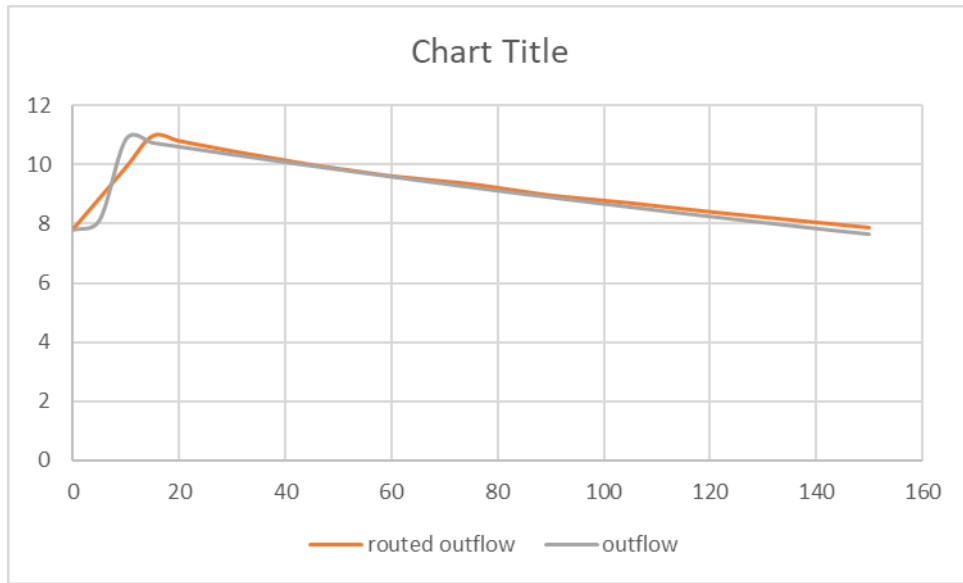


Figure S3. Routed outflow versus measured outflow at Garryduff flume.

Step 2

The time series between the pump flow data and comparative OTT levels at the flume between 15th to 18th October 2021 are shown on Figure S4.

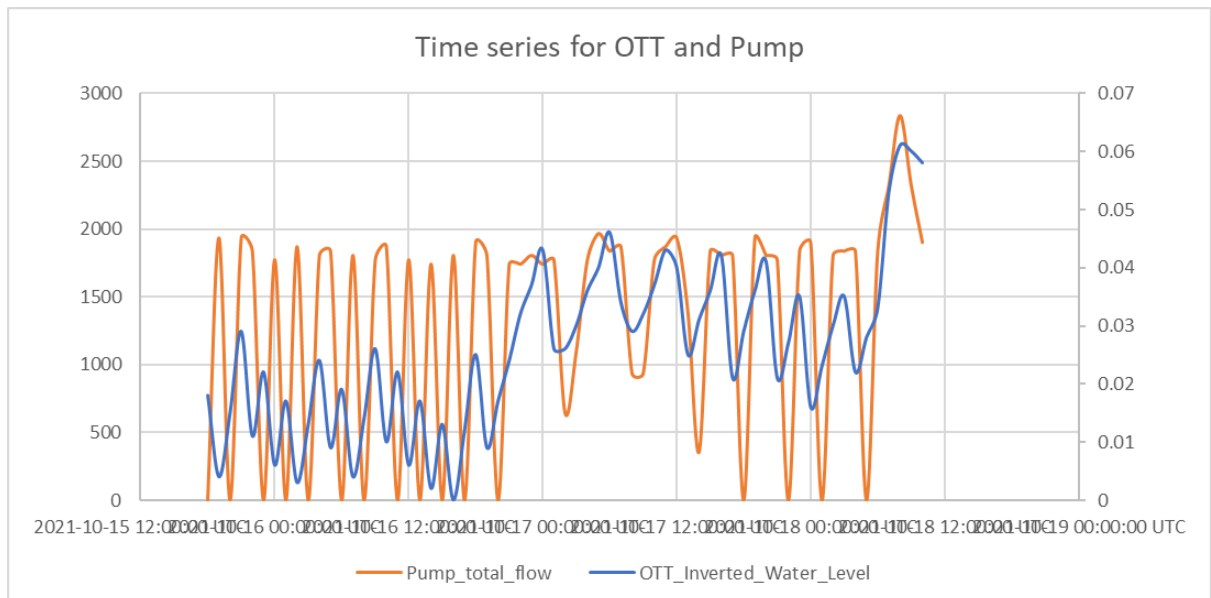


Figure S4. Garryduff Pump flow data and comparative OTT levels at the outlet flume.

The pump (inflow) data was then routed through the small lagoon catchment to produce outflow data (Figure S5) at the flume using the Muskingum derived catchment equation.

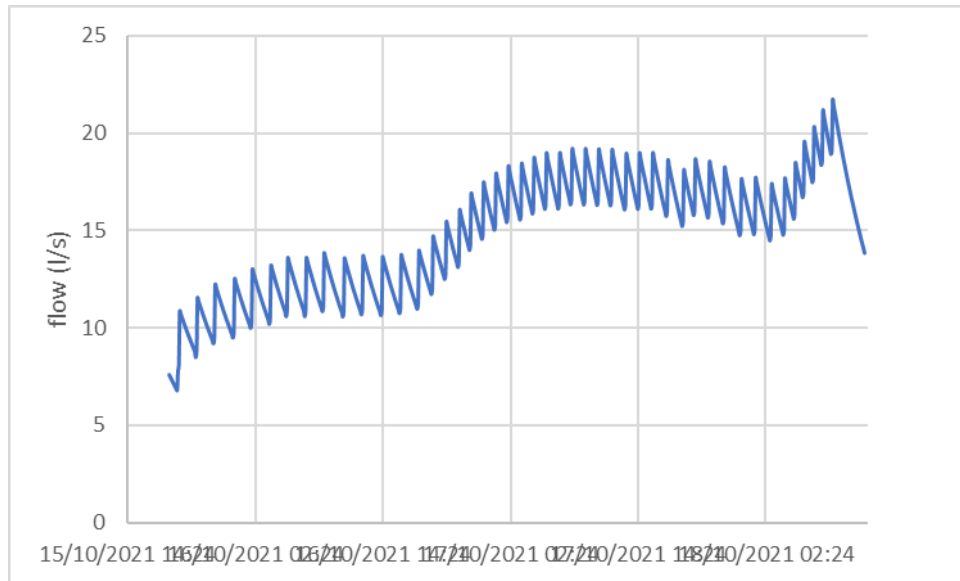


Figure S5. Modelled outflow at flume (15th to 18th October 2021).

Step 3

The modelled outflow values at the flume were cross correlated with the OTT water levels at the same time to produce the rating curve (Figure S6) with best fit lines (a linear and quadratic equation).

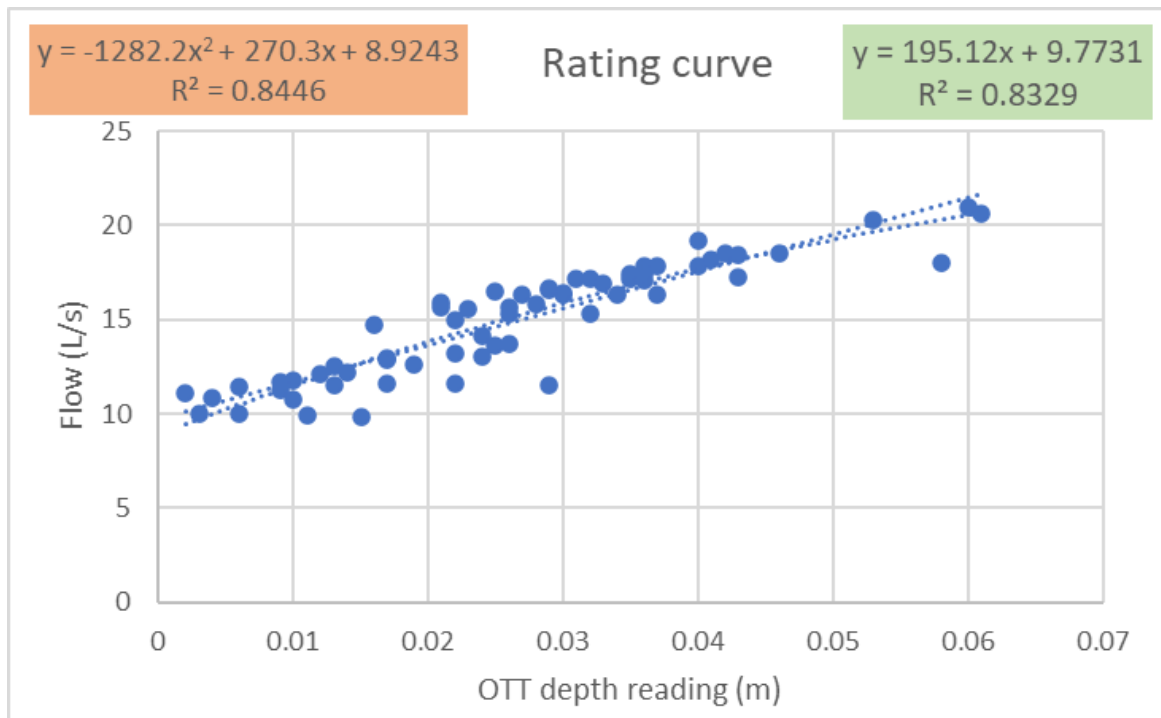


Figure S6. Rating curve for OTT water level sensor at Garryduff flume.