

CARBON FLUX FROM ERODING PEATLANDS IN THE PEAK DISTRICT

Richard Pawson & Dr Martin Evans

*Upland Environments Research Unit,
School of Environment and Development,
The University of Manchester.*

This report presents some of the key findings of the research undertaken as part of the Small Project Grant awarded by the Moors for the Future partnership, 2005. The research provides part of ongoing field and laboratory investigations for my PhD thesis. As this research is currently incomplete, this report provides summary results and key findings so far. A full version of results, analysis and discussion will be provided in the form of my final thesis.

Richard Pawson

CONTENTS

	Page
1.0 Introduction	4
2.0 Aims and scope of research	5
3.0 Methodologies	
3.1 POC:DOC interactions in turbulent sediment-water mix	5
3.2 POC oxidation in floodplain environments	6
3.3 Characterisation of POC portion of suspended sediment loads	7
3.4 High Temporal Resolution investigation of POC:DOC ratios from an eroding peatland	8
3.5 Laboratory Analysis	9
4.0 Results and Discussion	11
4.1 POC:DOC interactions in turbulent sediment-water mix	11
4.2 POC oxidation in floodplain environments	13
4.3 Characterisation of POC portion of suspended sediment loads	15
4.4 High Temporal Resolution investigation of POC:DOC ratios from an eroding peatland	17
5.0 Conclusions	22
6.0 Acknowledgments	22
7.0 References	23

1.0 INTRODUCTION

In recent years extensive research has been carried out in many blanket peat catchments following the realisation of the importance of this land cover type in the carbon balance. Northern peatlands represents somewhere between 30 and 50% of the Earth's total soil carbon store, which is nearly equivalent to the total amount of carbon in the atmosphere (Charman, 2002). Following the Kyoto Protocol, signatory countries are committed to reducing their greenhouse gas emissions by 5% from their 1990 levels. In order to achieve this each country can offset their emissions levels by encouraging accelerated sequestration of carbon. As such there has been much effort into improving understanding of the dynamics of these peatlands, with attempts often made to calculate the specific carbon budget of a given catchment (e.g. Worrall et al. 2003).

Though most aspects of the peatland carbon store have received extensive research interest, little research has focused on the particulate organic carbon (POC) portion of fluvial export, particularly in comparison to the dissolved portion (DOC). Significantly, much of the work that has been undertaken to assess POC export has been based on field samples taken on time scales that do not account for the highly episodic nature of sediment loss in upland catchments, perhaps resulting in underestimates of this portion of carbon flux. Furthermore, there appears to have been little work dedicated to assessment of carbon budgets in actively eroding peatlands, such as many areas of the Southern Pennines, UK. In such settings, the importance of POC relative to DOC export is likely to be further enhanced in comparison to more intact, accumulating systems.

As such, this research has been designed to assess specifically the role of particulate carbon losses in comparison to dissolved loads. The work entails both field and laboratory projects designed to investigate the relative significance of each portion, the interactions between the two forms of OC and the potential for POC oxidation and loss to the atmosphere. It is hoped that improved understanding of POC fluxes will facilitate future planning and decision making in the UK uplands.

2.0 AIMS AND SCOPE OF RESEARCH

1. Experimental investigation of the interactions of POC and DOC in simulated turbulent river flow
2. Assessment of the potential direct oxidation losses from flood plain deposition of carbon rich sediments
3. Characterisation of OC portion for sediment load from an actively eroding peatland
4. High resolution field analysis of the relative fluxes of POC and DOC: from event scale to a two week intensive period

The field site used for parts 2 – 4 of the project is the Upper North Grain (UNG) catchment. This is part of the National Trust High Peak Estate located in the Peak District, South Pennines, UK. Located at altitudes between 490 and 541 m OD and receiving 1200 mm rainfall pa, it is a classic location for blanket bog formation, (Lindsay *et al.* 1988). The catchment is relatively small, draining an area of 0.38 km² and is dominated by sheep farming (Rothwell *et al.* 2005), which grazes the main vegetation assemblage of Heather, Bilberry and Cotton Grass. The catchment is heavily eroded with Bower Type I gullies, which in the upper reaches occur solely in peat stratigraphy that often reach several metres in depth. In the lower reaches gullies cut into the underlying bedrock, which is commonly sandstones of the Millstone Grit Series that dominate this area of the Pennines, (Rothwell *et al.* 2005).

3.0 METHODOLOGIES

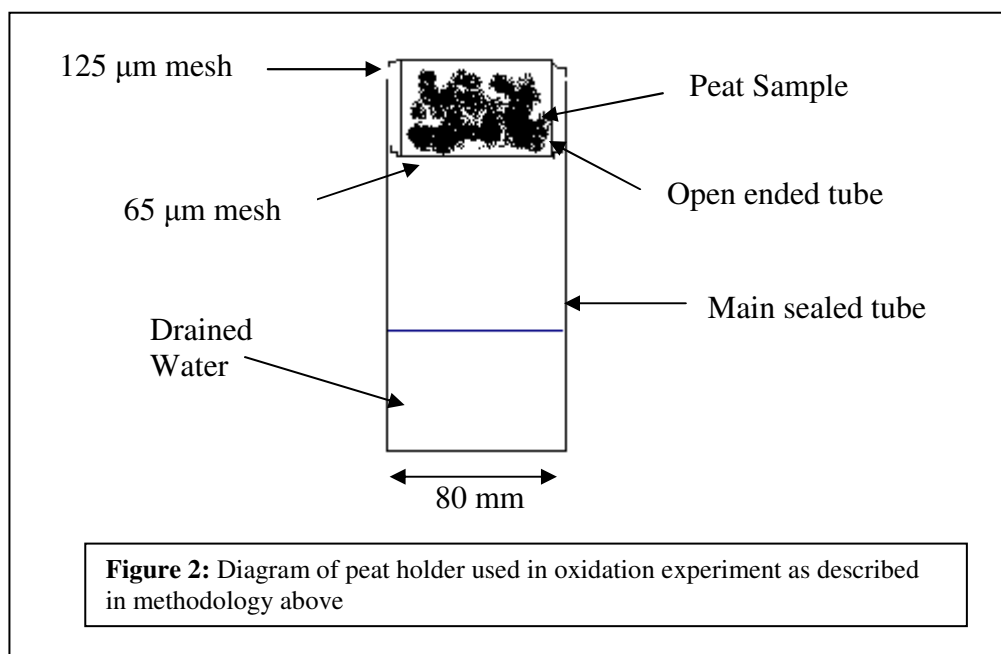
3.1 POC:DOC interactions in turbulent sediment-water mix

To assess the interactions between POC and DOC during transport, experiments were run to simulate the conditions that carbon rich sediments are subject to during turbulent river flow. This entailed mixing experiments of a variety of sediment concentrations in two ‘end-member’ water types. Sediments used were gulley wall peat sediments from a degrading peatland system. This was identified as a likely input to the channel and so the sediment

type that may provide an in-channel DOC source. Water types were rainwater and baseflow river water, representing the hydrological inputs and outputs of the system respectively. These various mixes were attached to vibrating clamps and sampled at a range of times over a 24 hours period. Analysis of water was undertaken using the methods outlined below, (see Laboratory Analysis). This allowed the analysis of the potential for POC to dissolve to form DOC in a variety of water-sediment scenarios. This is significant not only to improve our understanding of POC interactions in the environment, but also for improved understanding of DOC sourcing. DOC is a major issue for water companies due to its effect on water quality both visually and chemically.

3.2 POC oxidation in floodplain environments

Deposition of OC rich sediments following storm events provides an obvious potential location for direct loss of POC to the atmosphere via oxidation. To assess the potential for POC to be oxidised, a year long experiment was undertaken analysing the mass lost in known quantities of peat in specially designed pods exposed to natural conditions over a variety of timescales (See Figure 1).



By generation of a simple mass balance equation, the net loss of peat by weight was inferred as the loss of carbon to the atmosphere. Loss of mass by other means (e.g. rain splash erosion) was prevented by the use of fine (125 μm) mesh covering the pods of sediment. These pods were also allowed to drain by use of fine (64 μm) mesh on the base. This water was collected in a vessel and so could be analysed for DOC. This allowed the inclusion into the mass balance equation of the dissolution of POC and also allowed episodic drying and rewetting of the sediments, as would be the natural conditions in the field. This experiment is essential if POC is to be discussed with reference to atmospheric carbon cycling. If sediments eroded from peat systems are simply transported and deposited without loss of carbon to the atmosphere, then the flux of POC from peatlands may not be of great significance to wider global carbon cycles.

3.3 Characterisation of POC portion of suspended sediment loads

Due to the cost of OC sediment analysis, when investigating of the flux of POC at high temporal resolutions (and so include the episodic losses of storm events), an understanding of OC proportions in suspended sediments is essential. Previous work has suggested figures of ~ 35 % OC in upland suspended sediment concentrations (SSC's) (Worrall et al. 2003), but it is necessary to characterise POC contents on a catchment specific basis if we are to obtain an accurate understanding on POC and DOC proportions. As such, a variety of suspended sediment samples were analysed from UNG to obtain an average OC load for SSC. This could then be applied to SSC data obtained for a range of timescales in the catchment. Water samples used in this analysis included:

- Storm samples extracted during high discharge events
- Baseflow samples removed on a routine basis
- Over 300 quasi-continuous samples obtained during a two week intensive monitoring period (outlined below)

Samples were extracted using a range of methods, including Sigma 900 automatic water samplers (AWS), rising stage samplers and site visits. The samples used span an annual period and are taken at a full range of channel stages. This is to provide as broad a suite of sediment samples as possible and so a more accurate 'average' example of suspended sediment types. The water samples were filtered to remove sediments which were analysed as outline in 'Laboratory Analysis'.

In addition to actual suspended sediment analysis, a survey of carbon contents of source materials making up suspended sediments was undertaken. This allowed the identification and evaluation of inorganic carbon properties of sediments, which could be applied to calculate total POC. Sediment sources for the UNG catchment were identified as shale's and sandstones of the Millstone Grit series, periglacial head deposits dominated by these bedrock strata and peat sediments. A selection of each of these sediment types was collected from a wide spatial area in the catchment. Rock types and head deposits (the main inorganic carbon component) were sampled from 5 sites throughout the channel network. For completeness, a range of peat samples (n=>15) have also been analysed to determine average OC concentrations of peats in the catchment. Samples were analysed as outlined in section 3.5.1 'Sediment Analysis'.

3.4 High Temporal Resolution investigation of POC:DOC ratios from an eroding peatland

As mentioned, the temporal scale of previous POC flux analysis is perhaps unsuitable for the episodic nature of this component of the peatland carbon flux. As such, higher resolution investigation of POC and DOC ratios is essential if we are to improve our understanding of fluvial OC flux and estimate accurate carbon budgets. This is also essential in light of predicted environmental changes to more erosive climates in the UK uplands. Here, the results of POC and DOC fluxes for two field campaigns are presented. The first of these is the analysis of storm specific events from October 2004 to April 2005 in the UNG catchment. AWS samplers were used to extract water samples following a significant rise in stage during storm flow. These samples were then filtered and analysed for DOC and SSC

as outlined below. This allowed the comparison of POC and DOC flux on an inter-storm level. Following this, a two week intensive field study was undertaken in the spring of 2005 where field samples were extracted via AWS samplers every hour for 14 days. This generated a data set of over 300 water samples on a quasi-continuous basis. This allowed the calculation of a total flux of each component of the carbon flux, which allowed comparisons with other field studies. This data set was also used to display the episodic nature of POC export by extraction of POC and DOC data at different time scales. For this, hourly, 12 hourly and 24 hourly data sets of all possible combinations were used to calculate total flux by using interpolation methods such as those used in the literature, all based around algorithms from Walling and Webb (1985). To compare the accuracy of these interpolation methods (and display the problems of interpolating POC flux), an ‘actual load’ was calculated using an adaptation of Walling and Webb Method 3.

In addition to the intensive collection of field water samples, a range of field data was also logged throughout each of these campaigns. This data includes stage, which was then used to calculate discharge for the monitoring site. This is essential for flux estimation. In addition, pH, conductivity and turbidity were also logged using Sentry II data loggers and a range of probes produced by the Intelysis group. This data will be used in the future for further DOC and POC calibration on increased temporal scales.

3.5 LABORATORY METHODS

Water samples were vacuum filtered using weighed Whatman GF/C glass microfibre filter paper circles to separate the suspended sediment fraction over 1.2 μm . Water volume of filtrate was measured. Filter papers were dried for 1 week at room temperature in a dark room to restrict any potential oxidation of organic matter. Room temperature was chosen as previous experiments had shown a positive linear relationship between drying temperature and peat weight loss, (Pawson, *unpub. data*) attributed to organic carbon oxidation. The filter papers were then re-weighed to determine suspended sediment concentration (SSC) as a function of water volume. The separated water and sediments were then analysed.

Sediment Analysis

Sediment samples of over 50 mg were milled using a silicon carbide grinder in a 240 V Glen Crest mill. This homogenised the sediment and filter paper and allowed repeated analysis of samples to determine reproducibility of analytical techniques. Filter papers with less than 50 mg of sediment were left intact as some analysis techniques required more than this amount of sediment for accuracy. All samples were analysed for total carbon and total inorganic carbon using an SSM (Solids Module) of the Shimadzu TOC-V Series Analyser. From these results, POC content was determined by total carbon minus total inorganic carbon. For samples with over 50 mg sediment, loss on ignition (LOI) tests were undertaken to determine the total organic load of the sediment sample. This entailed weighing sediment samples which were then ignited in a furnace at 500°C for 1 hour and then reweighed. The loss in weight was interpreted as the % organics in the sample. As LOI data could not be obtained from low sediment concentrations, further sampling was carried out to determine the organic load at each site for low flow sampling times. This was achieved by taking larger water samples of up to 18 litres. These water samples were filtered by the methods outlined above using one filter paper per site. This meant that greater quantities of sediment were deposited on the filter paper for these lower SSC's and so LOI tests could be carried out as described. As such, results can be provided for total carbon, total inorganic carbon, total organic carbon contents and total organic/mineral content of sediments sampled from river water.

Water Analysis

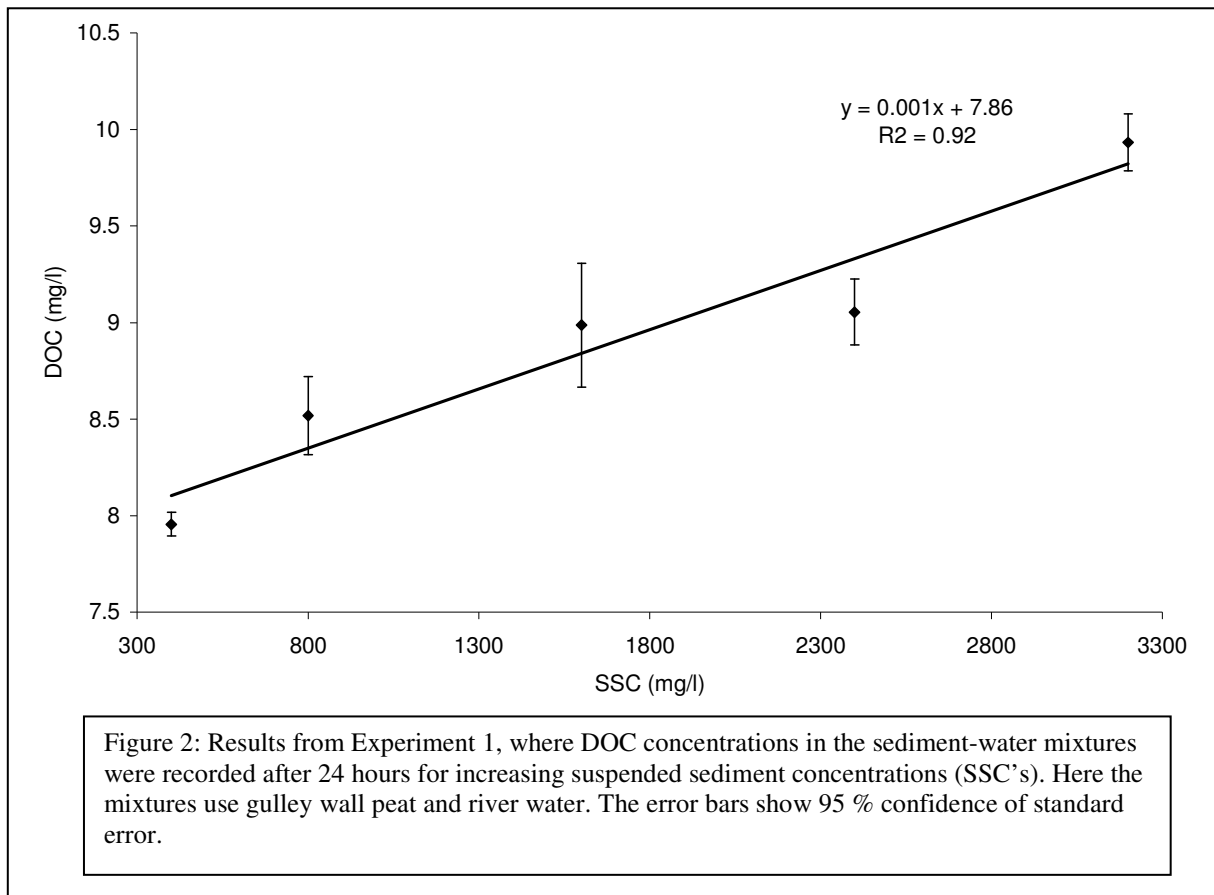
The remaining water was filtered once more using 0.45 µm Whatman membranes. Sub-samples were analysed for TOC (Total Organic Carbon) using the OCT-1 Sampler of the Shimadzu TOC-V Series Analyser. This size filtration was used as a common definition for the DOC includes colloidal carbon, (Koelmans and Prevo, 2003). The operational definition of DOC is therefore TOC < 0.45 µm. Samples were also analysed for pH and conductivity.

4.0 RESULTS AND DISCUSSION

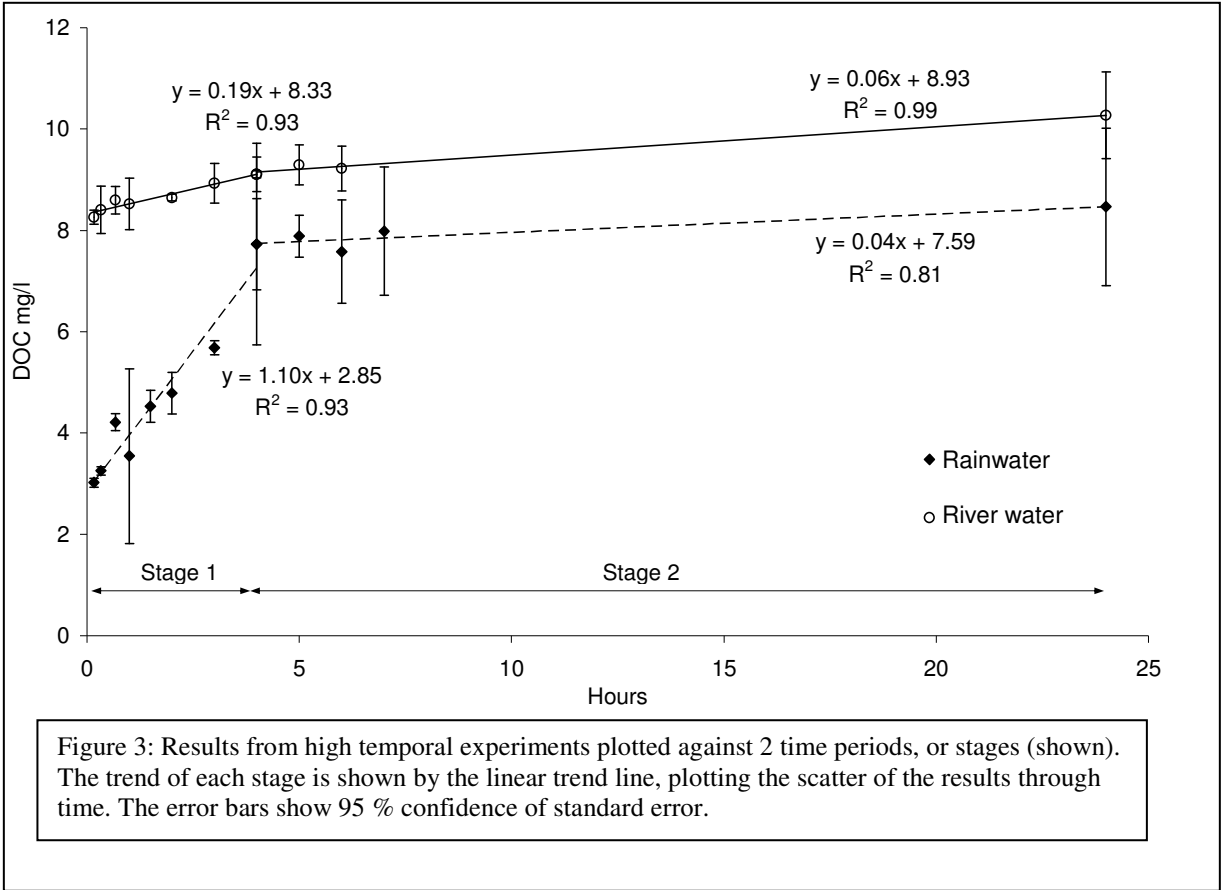
The following sections provide brief summary results and some key observations for each project.

4.1 POC:DOC interactions in turbulent sediment-water mix

The first experiment undertaken in this project was to test the potential for DOC concentrations to increase in a range of SSC's in water mixes. Figure 2 presents the results from one of these experiments, where final DOC concentration after 24 hours of agitation is plotted against SSC. This shows a strong correlation between SSC and total DOC concentration, with an r^2 value of 92 %, suggesting that the increase of DOC in a sediment and river water mix is controlled directly by the amount of suspended sediments available and suggests that carbon rich sediments may provide an in-channel source of DOC.



Following these results, a further experiment investigated the nature of these DOC increases by sampling water from two distinct mixes at decreasing regularity. The two water types were rainwater and baseflow river water mixed with SSC of 800 mg/l. The results from this experiment are plotted in Figure 3 below.



These results show once again that DOC concentrations can be increased when carbon rich sediments are available in mixing water samples. More significantly, these increases are not necessarily linear over time, particularly for those observations of rainwater mixes. Instead, a rapid increase of DOC concentrations from 0.64 mg/l to 7.73 mg/l is achieved within 4 hours of mixing for rainwater samples. River water samples also show a greater rate of increase during this period, obtaining a higher concentration of 9.11 mg/l although a lower overall increase from 7.36 mg/l. These distinct changes in rate suggest a two stage process

of DOC increase, drawing comparisons to similar work by Aguilar and Thibodeaux (2005) and Koelmans and Prevo (2003). The exact nature of these processes requires further investigation, which is currently planned for some time in spring 2006. In brief summary, these results show a direct link between OC rich sediments and DOC concentrations. This potential ‘in-channel source’ may be of some degree of significance when considering the levels of increases observed in rainwater and the rapidity of concentration increases.

4.2 POC oxidation in floodplain environments

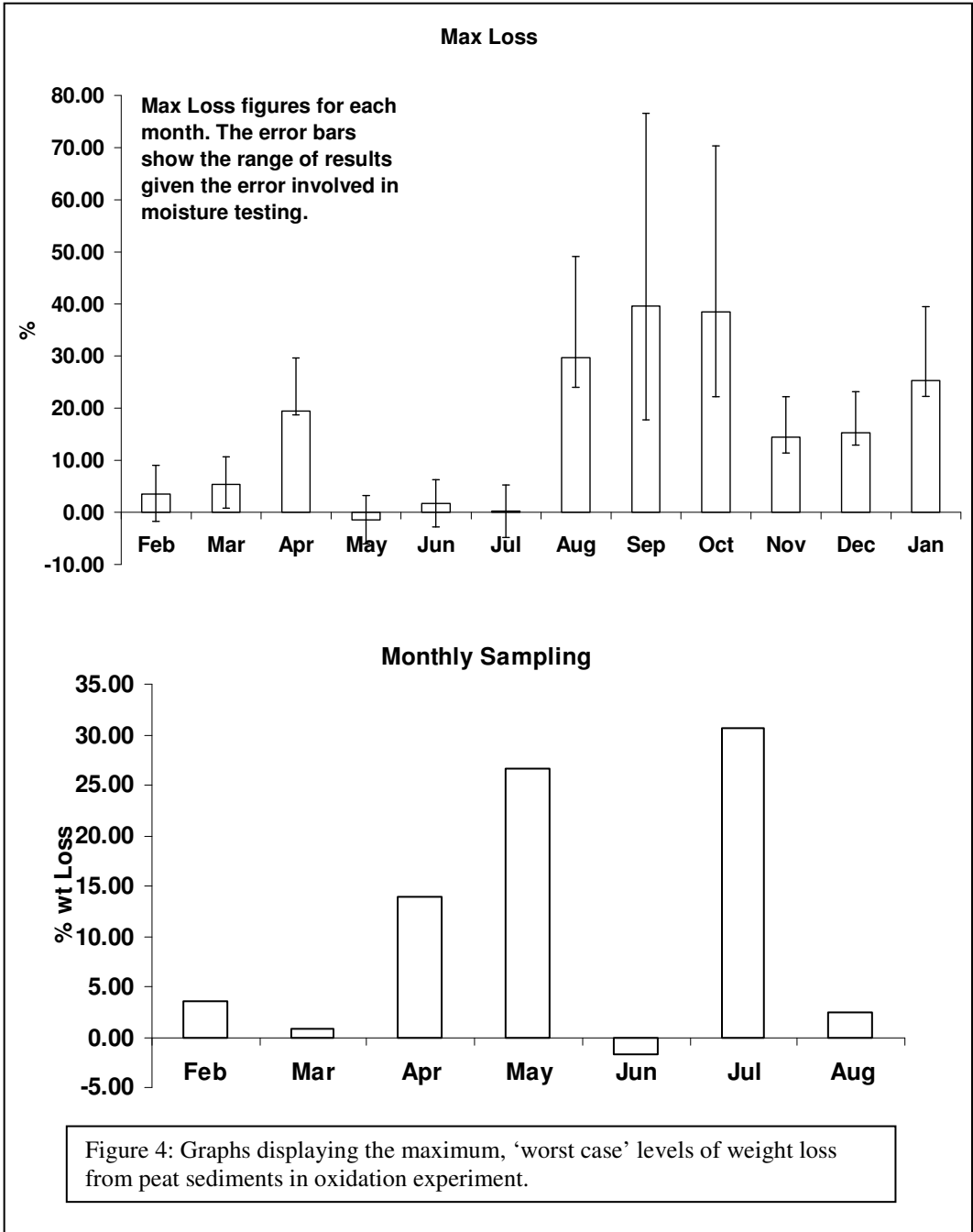
Using the methodology outlined above, multiple samples were set up in January 2005 and have been removed periodically for re-weighing until February 2006. New samples have been exposed from month to month (Table 2, monthly sampling), along with exposed samples being removed after one month, two months, three months etc (Table 1, annual sampling). These results are displayed in Tables 1 and 2, and the general trend of both data sets shown in Figure 4. The mean of the multiple samples and the sample with maximum percent loss – or ‘worst case scenario’ – are presented.

1. Annual Sampling			2. Monthly Sampling		
	Mean % Dry Loss	Max % Dry Loss		Mean % Dry Loss	Max % Dry Loss
Feb	3.24	7.58	Feb	3.18	3.48
Mar	3.79	7.97	Mar	-0.06	0.77
Apr	4.07	8.51	Apr	4.62	13.94
May	-4.58	0.29	May	6.55	26.58
Jun	-7.88	-3.0	Jun	-3.89	-1.82
Jul	-15.34	-10.12	Jul	9.68	30.64
Aug	20.6	24.0	Aug	0.18	2.39
Sep	35.65	38.3			
Oct	11.41	15.4			
Nov	4.33	8.45			
Dec	5.75	9.87			

Tables 1 and 2: Results of weight loss of samples as percent. Max % loss is the biggest weight change from the multiple samples.

The first two months of the study provided very interesting data suggesting a significant loss of weight of these samples exposed to atmospheric conditions for both the month to month

and longer period timescales. However, after this period, the results begun to vary considerably, and in some cases the sediment samples appear to have actually gained weight, (see Table 1). Firstly, this was attributed to sampling error or inaccuracies of sampling methods. However, having modelled the various variables of the calculation (i.e. the wet sediment weights, dry sediment weights and moisture contents etc.), it has become clear that the factor that most influences the final weight estimation is the moisture calculation. By changing this by as little as 0.5 % we have observed a significant change to the final peat weight, in some cases changing the result from a net loss to a net gain.



Great care has been taken calculating these moisture contents, with 25 replicates used in some cases and error calculated to $\pm 0.2 \%$ (95% confidence). Increasing this precision further appears unlikely. As such, month to month sampling was terminated in August after 8 months of data. Annual sampling is continuing in the hope of identifying some broad scale trends. However, in the most recent of samples collected there appears to be evidence of bacterial or algae-like growth in the form of green colouration of the inside of the meshes. With such high precision measurement of weight and potentially accurate calculation of moisture contents, it may be that the observed increases of mass of the sediments are actually caused by organic growth in the samples. This is, of course, a likely scenario. By exposing these sediments to floodplain conditions we are allowing them the very same condition in which they originally grew and formed. In fact, by virtue of investigating oxidation on flood plans we are actually expecting organic growth. As such, these results are perhaps best considered in terms of worst case scenarios on monthly scales and total overall losses on annual scales. As such, we can summarise that POC has the potential to loose up to $\sim 38 \%$ mass in the floodplain setting in worst cases, and that total annual losses can be as much as $\sim 10 \%$ including organic growth factors.

4.3 Characterisation of POC portion of suspended sediment loads

Following extraction and analysis of source rock samples from the UNG catchment, the results for total carbon are presented in Table 3. Total carbon is used here as although organic carbon may be present in rock types such as shale, this project is concerned with the export of POC from the peatland carbon store, and as such carbon contents should be corrected where possible to present only that portion of carbon export. The results draw similar conclusions to those in Spears and Amin (1981), with carbon contents of $2.3 \pm 1.5 \%$ for shale, $0.17 \pm 0.07 \%$ for sandstone and $1.09 \pm 0.73 \%$ for head deposits.

Shale's			
Site	wt sed	wt C	TC %
5	78.4	3.089	3.94
7	60.9	0.7962	1.31

8	95	0.8097	0.85
9	94.9	2.353	2.48
10	64	1.854	2.90
Mean			2.30
	Confidence level (95%)		1.541

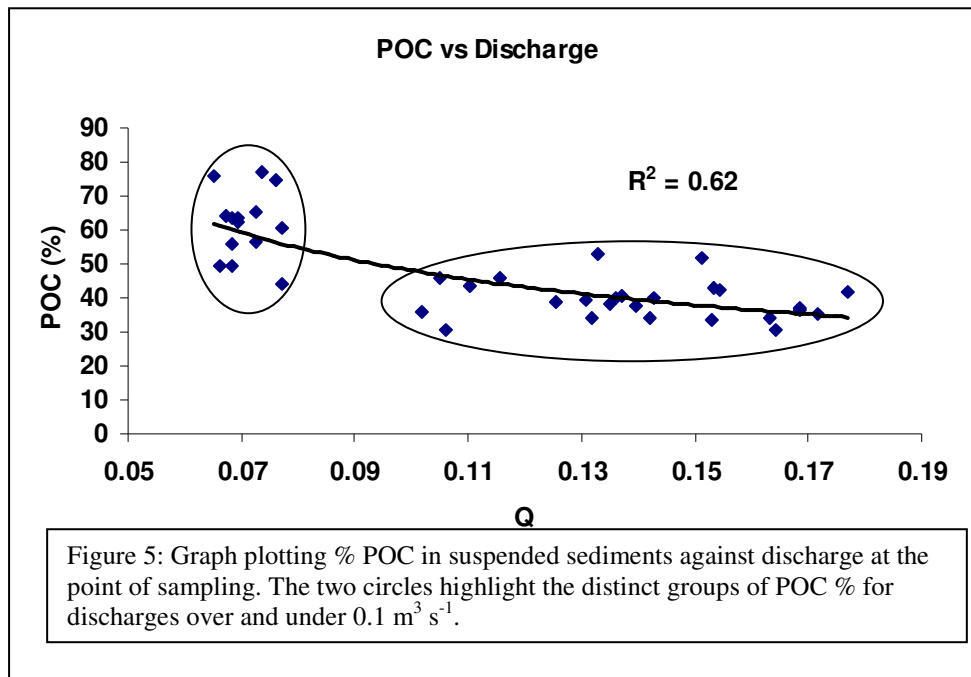
Sandstones			
Site	wt sed	wt C	TC %
5	130.8	0.2036	0.16
7	150.8	0.1408	0.09
8	112.3	0.2891	0.26
9	126.5	0.1935	0.15
10	136.5	0.2856	0.21
Mean			0.17
	Confidence level (95%)		0.077

Head Deposits			
Site	wt sed	wt C	TC %
5	124.3	2.02	1.63
7	138.1	0.9026	0.65
8	101.7	0.6252	0.61
9	81.4	1.462	1.80
10	78.7	0.5878	0.75
Mean			1.09
	Confidence level (95%)		0.713

Peat samples were found to have a mean TOC (Total Organic Carbon) content of 50.9 ± 1.7 % (n=15), concurrent with results from Worrall et al. 2003 after Francis 1987. There is no evidence of significant spatial variability of these results.

Results from the analysis of suspended sediment chemistry from a broad range of samples from UNG show that the % POC in a given suspended sediment sample has a mean value of 47.24 ± 4.1 % (n=40). These results ranged from 30.75 % to 77.13 % TOC. The reason for this wide range is due to the variety of discharge and SSC. If we consider discharge and POC alone (Figure 5) it is clear discharge plays some role in controlling POC proportions in SSC's. Quite simply, with increased discharge we see a reduction of POC in suspended sediments, which is inevitable due to the increased mobility of mineral matter such as quartz

grains from sandstone sources. This results in a reduction of the % POC in the suspended sediment. At lower discharges, much less mineral matter is mobilised and suspended sediments are therefore dominated by carbon rich organic matter.

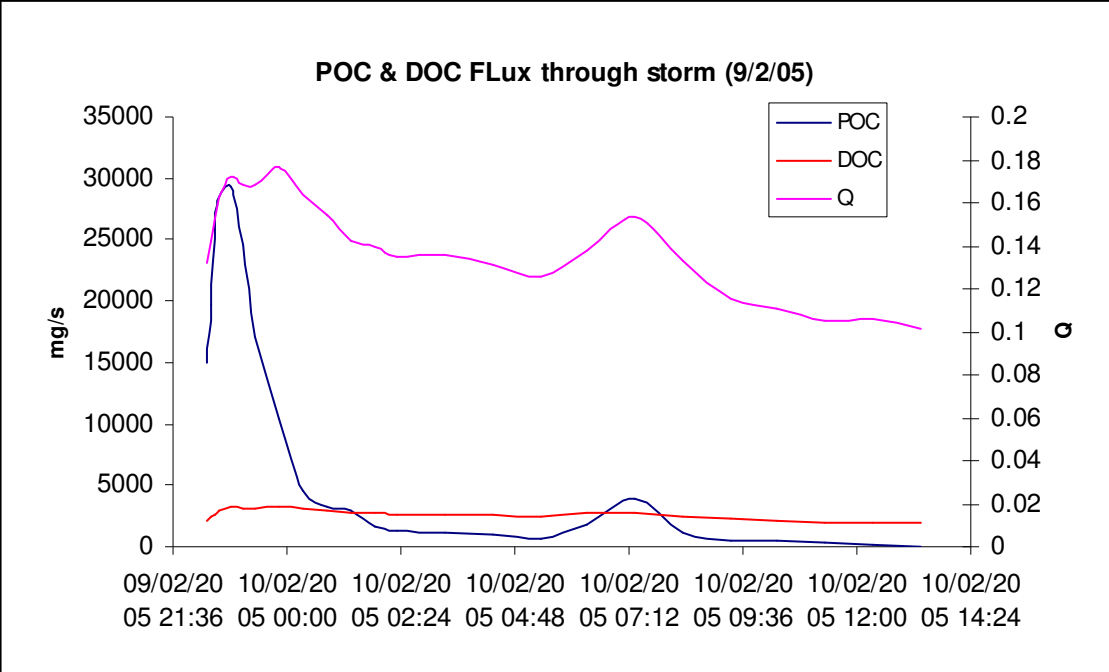


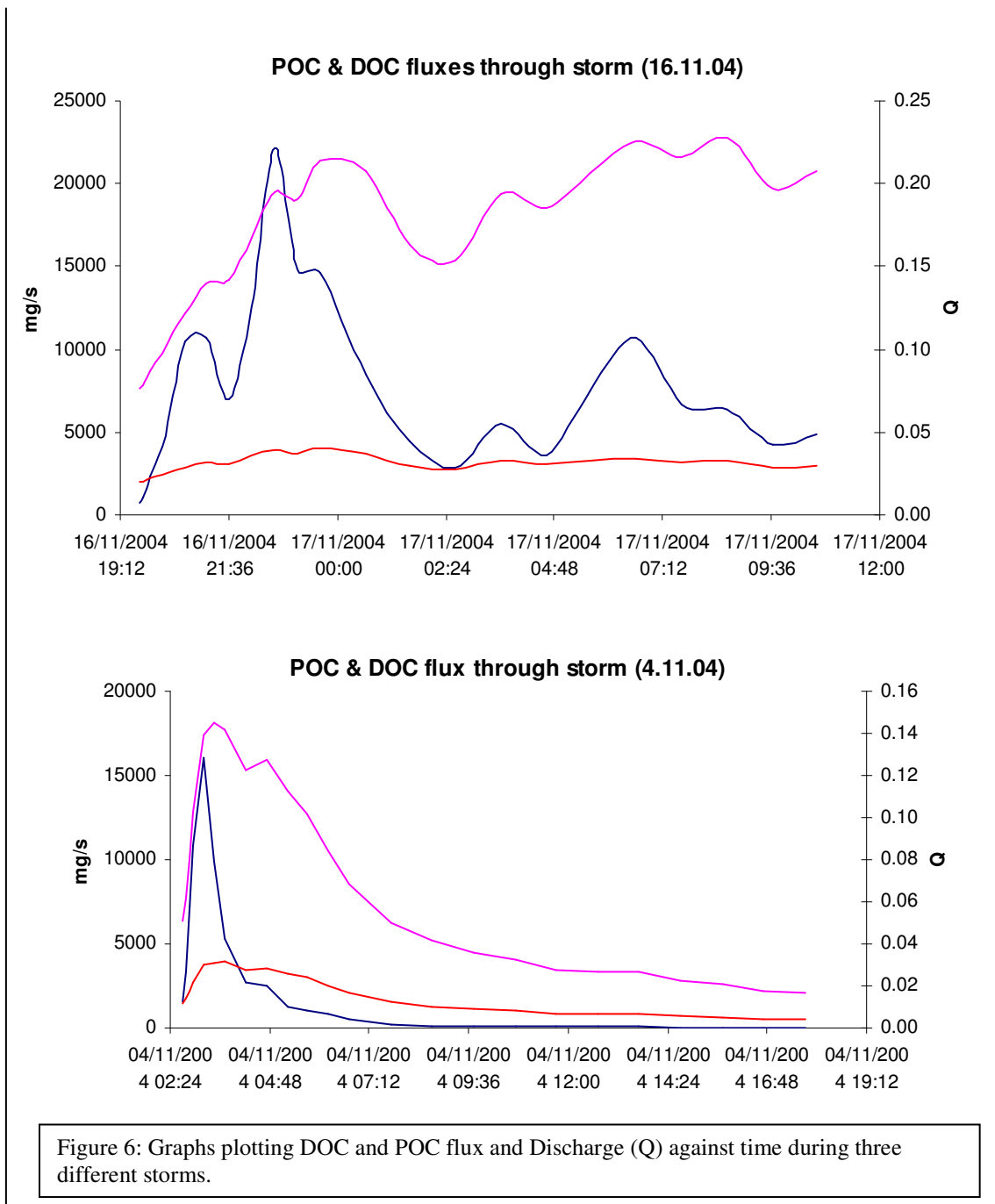
The correlation of this data allows us to predict potential OC contents dependant on discharge at the point of sampling. For low flow discharge below $0.1 \text{ m}^3 \text{ s}^{-1}$, concentrations of $60.9 \pm 5.5 \%$ are used for POC determination. For discharge over $0.1 \text{ m}^3 \text{ s}^{-1}$, concentrations of $38.8 \pm 2.2 \%$ are used. The error is calculated to 95 % confidence and can be used for predicting the range of potential POC concentrations, (i.e. min/max POC flux). Alternatively, the mean value given above of $47.24 \pm 4.1 \%$ for all this data can be used indiscriminately of discharge. Further work is planed to test these calibrations.

4.4 High Temporal Resolution investigation of POC:DOC ratios from an eroding peatland

Figure 6 presents graphs plotting three storm events. The graphs plot the instantaneous flux of POC and DOC as mg s^{-1} against stream discharge over time. It is clear from these

examples that during higher discharge events such as this, the POC portion of OC flux can be more significant than the DOC export due to the increased sediment transport and erosivity. It is also clear that the nature of POC export during episodic events is complex and that where possible; POC flux should not be averaged. POC fluxes appear highly variable on both intra-storm and inter-storm scales. To summarise these storms, it appears that DOC fluxes remain fairly constant while POC flux changes dramatically with a waning of discharge, as would be expected from previous observations of SSC and discharge relationships. Significantly, as we are able to calculate flux of each component, it is possible to quantify the amount of carbon export via each form for each storm event. During the storm on 9/2/05 a total of 305.3 kg of OC is measured to have been transported through this point in the UNG catchment. Of this, POC contributes 166.93 kg (54.67 %) while DOC contributes the remaining 138.37 kg (45.33 %). For the event on 16/11/05, a total of 622.04 kg of OC was exported, of which POC represented 70.67 % (439.56 kg), DOC 29.33 % (182.47 kg). Finally, during the event on 4.11.04, a total of 147.87 kg of OC was exported, of that 60.06 kg was particulate (40.61 %) and 87.82 kg was dissolved (59.39 %).





The results from the intensive 14 day monitoring period also suggest that estimated POC flux is highly variable dependant on the sampling regime. Table 4 summarises total flux results produced for each of the 35 possible data sets. These data sets were generated from the complete set of over 300 samples. Daily samples were extracted from the full data set for every possible hour of sampling. For example, the first data set was every day at 09:00, the

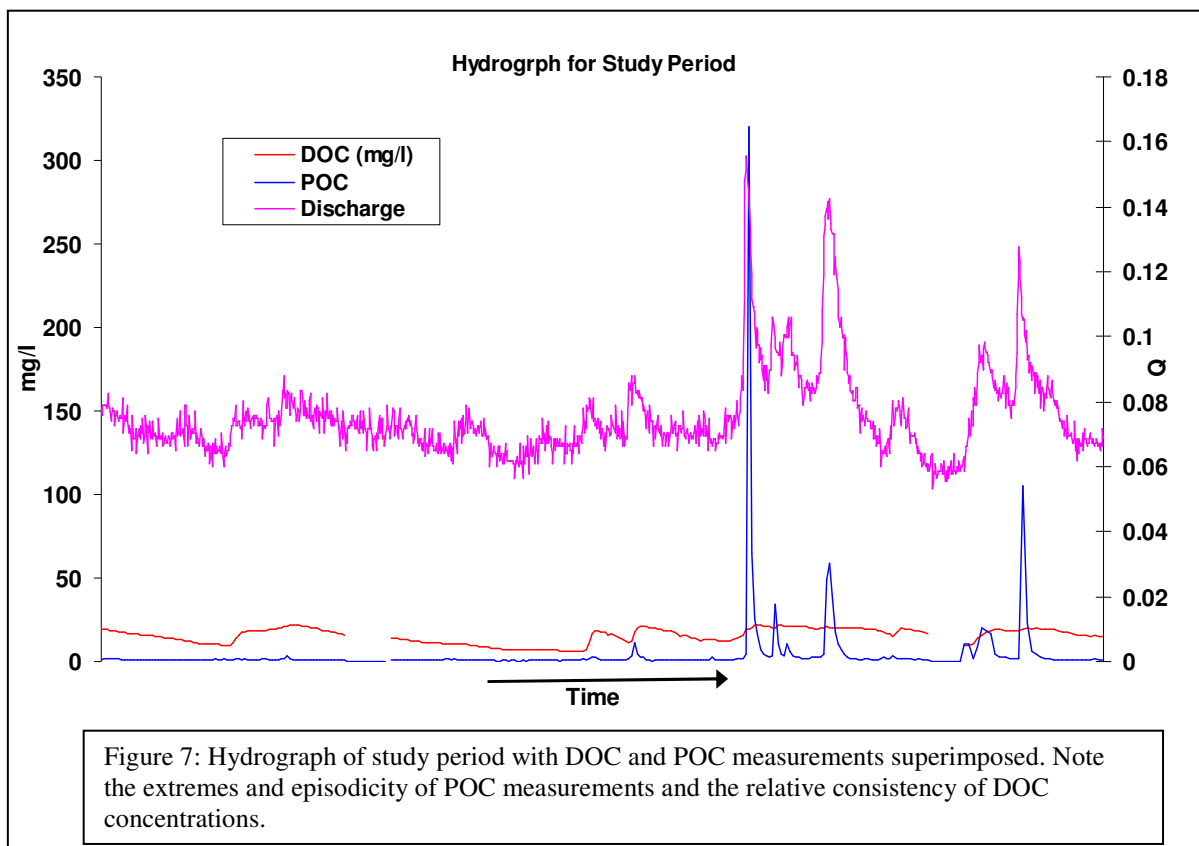
second every day at 10:00 and so on creating 24 possible sets of samples. For a twice daily regime, this was achieved in the same way but every 12 hours and thus produced half the number of data sets (12).

For all these results, it should be remembered that the sample period is exactly the same, and that each prediction of total load could have been produced had only those samples been taken. In other words, by reducing the temporal resolution of the samples, we see a reduction in the accuracy of the predicted total load. This can be either a massive underestimate or overestimate from the ‘actual load’.

DOC flux (kg)								
	Once Daily (n=14)				Twice Daily (n=28)			
	Method 1	Method 2	Method 4	Method 5	Method 1	Method 2	Method 4	Method 5
Min	1277.9021	1301.1484	1352.2394	1376.838	1372.77	1403.9227	1377.8118	1415.8136
Max	1584.5609	1634.248	1470.986	1527.5422	1446.738	1505.7566	1427.5417	1486.0933
Range	306.65882	333.09961	118.74664	150.70423	73.967978	101.83386	49.729882	70.27975
Actual Load = 1386.63 kg								
POC flux (kg)								
	Once Daily				Twice Daily			
	Method 1	Method 2	Method 4	Method 5	Method 1	Method 2	Method 4	Method 5
Min	94.909944	98.778957	99.787349	103.85519	197.69626	216.3632	203.82251	223.0679
Max	2286.6127	4395.3863	2252.187	4329.2123	1215.5578	2306.0355	1233.3078	2339.709
Range	2191.7027	4296.6073	2152.3997	4225.3572	1017.8615	2089.6723	1029.4852	2116.6411
Actual Load = 551.8 kg								
Table 4: Summary of flux calculations for every data set produced from the intensive 14 day field campaign. Once daily samples were taken once every 24 hours, twice daily every 12 hours. Methods used correspond to methods investigated in Walling and Web (1985)								

As mentioned above, ‘Actual Load’ (that which these figures are compared with), were calculated using an adaptation of Method 3 from Walling and Webb (1985). From these results it is clear that accuracy of flux calculation is improved by increased sample number. The results also suggest that during this period, DOC flux can be more accurately predicted with fewer samples than POC. This is due to the smaller range of results for interpolation methods predicting DOC loads (e.g. ranges of up to ~ 100 kg for 12 hourly samples

compared to over 2000 kg for POC). Looking at the POC results, both under and overestimates of flux are clear. These wide ranges of results are caused when sampling times either completely miss or coincide with a peak of sediment flux. If missed, the interpolation method cannot include any portion of this peak of sediment flux. Conversely, if sampling occurs during this peak, extrapolation of this concentration and discharge occurs over a much longer period than is true in the field, due to the flashy regime of these systems. As such, massive overestimates are also possible. Figure 7 plots the hydrograph, POC and DOC concentrations for the full data set over the period. This once again highlights the episodic nature of POC flux from these upland systems and underlines the importance of careful, high resolution sampling regimes.



During this period a total of 1938.43 kg OC export is measured. Of this POC contributes 28.5 %. In terms of wider scale carbon budgets, it is difficult to compare these results with existing work that considers annual flux loads. This is because the variability of both DOC and POC flux is likely to change with season and effects on antecedent conditions, water

table, sediment availability and linkage to the channel etc. Although this period of sampling includes a range of hydrological situations (e.g. a prolonged low discharge followed by a storm event and subsequent fluctuations of discharge), it is still unsuitable to extrapolate these results over longer timescales than this study. Instead this study identifies the episodic nature POC flux and the potential for POC to be of much greater significance in peatland carbon budgets than previously reported by highlighting the significant increases and variability of flux during high discharge events.

5.0 Conclusions

In conclusion, this research project has found several interesting key points which should be considered when investigating fluvial OC fluxes from the peatland carbon store. These can be summarised as:

1. OC rich sediments (POC) may provide an active in-channel source of DOC as experimental results show increases of DOC as a function of sediment concentration, time and agitation of different sediment-water mixes.
2. Deposition of POC in flood plain settings may provide a link between fluvial export and the atmosphere, as mass balance experiments show losses of up to ~ 40 % of OC rich peat sediments in controlled natural settings, inferred as loss through oxidation
3. POC contents of upland systems are consistent during low discharge regimes and decline during high discharge periods due to increased mobility of inorganic mineral matter. POC concentrations average ~ 47 % of SSC over extensive annual sampling.
4. During storm periods, POC can be proportionally much more significant than DOC export, with results showing a 70/30 % split respectively.
5. Intensive field monitoring has highlighted the episodic nature of POC flux and modelling of sampling regimes has identified potential inaccuracies with interpolation of these fluxes.

Overall these findings emphasise the potentially important role that particulate carbon plays in the carbon balance of peatland systems. For regions such as the Peak District where peat

erosion is severe particulate carbon loss has the potential to be the largest single carbon loss from the system. The work reported here is some of the first to address these issues. A more detailed assessment of the role of particulate carbon in Peak District carbon budgets is required and is ongoing in this project. The potential scale of particulate carbon losses represents a threat but, in the light of current and future planned work on erosion control, may also represent an opportunity to manage carbon losses from Peak District Moorlands

6.0 Acknowledgements

We would like to thank Moors for the Future for the provision of a Small Project Grant and the School of Environment and Development, The University of Manchester, for fieldwork funding. The authors are also grateful to The National Trust for allowing work to be carried out in the Upper North Grain catchment.

7.0 REFERENCES

Aguilar L. and Thibodeaux L.J. (2005), Kinetics of peat soil dissolved organic carbon release from bed sediment to water. Part 1. Laboratory simulation, *Chemosphere*, **58** 1309-1318

Blodau C., Basiliko N and Moore T.R. (2004) Carbon turnover in peatland mesocosms exposed to different water table levels, *Biogeochemistry* **67** 331-351

Charman D. (2002) *Peatlands and Environmental Change* Wiley, Chichester

Dawson J.J.C., Billet M.F., Neil C. and Hill S., (2002), A Comparison of particulate, dissolved and gaseous carbon in two contrasting upland streams in the UK, *Journal of Hydrology*, **257** 226-246

Holden J. and Burt T.P. (2003), Hydrological studies on blanket peat: the significance of the acrotelm-catotelm model, *Journal of Ecology*, **91** 86-102

Hope D., Billet M.F. and Cresser M.S., (1997a), Exports of organic carbon from two river systems in NE Scotland, *Journal of Hydrology*, **193** 61-82

Hope, D., Billett, M.F., Milne, R. and Brown, T.A.W., (1997b). Exports of organic carbon in British rivers, *Hydrological Processes*, **11**, 325–344.

Koelmans A.A. and Prevo L. (2003), Production of dissolved organic carbon in aquatic sediment suspensions, *Water Research*, **37** 2217-2222

Lindsay, R.A., Charman, D.J., Everingham, F, O'Reilly, R.M., Palmer, M.A., Rowell, T.A. and Stroud, D.A. (1988), The Flow Country: The peatlands of Caithness and Sutherland. Peterborough, *Nature Conservancy Council*

Rothwell J.J., Robinson S.G., Evans M.G, Yang J. and Allott T.E.H Heavy metal release by peat erosion in the Peak District, Southern Pennines, UK, *Hydrological Processes*, **19**, 2973-2989

Schlesinger W.H. and Melack J.M. (1981) Transport of organic carbon in the world's rivers, *Tellus*, **33**

Tipping E., Marker A.F.H., Butterwick C., Collett G.D., Cranwell P.A. Ingram J.K.G., Leach D.V., Lishman J.P., Pinder A.C., Rigg E. and Simon B.M., (1997), Organic carbon in the Humber rivers, *Science of the Total Environment*, **194/195** 345-355

Wetzel R. (1983). *Limnology*, Saunders, Philadelphia

Worrall F., Reed M., Warburton J. and Burt T.P. (2003a), Carbon budget for a British upland peat catchment. *The Science of the Total Environment*, **312** 133-146

Worrall F., Burt T. and Sheddon R., (2003b) Long Term records of riverine carbon flux, *Biogeochemistry*, **64** 165-178

Worrall F., Burt T. and Adamson J., (2004) Can climate change explain the increases in DOC flux from upland peat catchments, *Science of the Total Environment*, **326** 95-112

Worrall F. and Burt T. (2004b) Predicting the future DOC flux from upland peat catchments, *Journal of Hydrology*, **300** 126–139