THE ROLE OF CARBON IN RIVER BASINS

LOIS Working Note No. 7

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Contents

# The Role of Carbon in River Basins

1. Introduction

One of the main nutrients to be investigated within the NERC Land-Ocean Interaction Study (LOIS) RACS(R) is carbon [1]. This report aims to review the data that are currently available, the role of carbon in river basins and existing models of carbon flux. This report does not cover the role of carbon in micro-organics as this is covered elsewhere in RACS(R).

Carbon is almost ubiquitous, exists as a component of many molecules and all life on the planet is based on it. Carbon plays a role in many of the terrestrial and aquatic biogeochemical cycles [2, 3], ecosystem energetics [4] and as a pollutant [5]. More specifically carbon within a catchment ecosystem is important in its association with chemical speciation of metals and organic pollutants [6], particle surface and colloidal chemistry [7], ionic balance, pH [8], and colour [9]. For example, complexation with metals [38], trace elements and nutrients can affect biological availability and toxicity.

Carbon can be described in three main forms: particulate organic carbon (POC), dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC). Organic carbon refers to carbon bound up in organic molecules, many of which have complex chemical structures and have been derived from biota. Figure 1 shows the size range of particulate organic matter (POM) and dissolved organic matter (DOM) which are nearly always distinguished by passing through a 0.45 micron filter [10]. The terms organic carbon and organic matter are often, but not always, used interchangeably in the literature and refer to carbon bound in organic molecules. When organic matter and organic carbon are referred to as separate substances the former can be converted to the latter by multiplying by 0.6 and in this case organic carbon refers only to the carbon that is present in the organic molecule. As can be seen from figure 1 carbon is present in natural waters in many forms and the carbon cycle includes many organisms. POC, which consists of plant litter, algal debris, soil organic matter and invertebrates, can be subdivided into three further forms: coarse particulate organic matter (CPOM), fine particulate organic matter (FPOM) and very fine particulate organic matter (VPOM) [10]. The composition of DOC is usually dominated by the humic and fulvic acid fractions which consist of 50% to 75% of the total with colloidal matter comprising up to 20% of the total DOC [10]. DIC exists in ionic form as H_2CO_3, HCO_3^-, CO_3^{2-} and as $CO_{2(aq)}$ and is part of the carbonate system which describes the inorganic carbon reactions that take place in aqueous solution [11].

Stream flow and the route of water through a catchment inevitably play an important role in the amount of carbon in the stream and at the catchment outlet. Studies on a small North Pennine stream (Rough Sike) with a catchment area of 83 ha showed that at least 80% of the annual load from peat (g peat/l) was carried by spates of over 5.6 times the annual discharge [51]. Another study showed that 78% of the total particulate exports of a stream were discharged during storm events carrying only 9% of the annual flow [10]. These studies highlight the importance of storm events in the transport of carbon from catchments.

DOC loads in river water from various UK studies are in the range of 9.6 kg C/ha/yr to
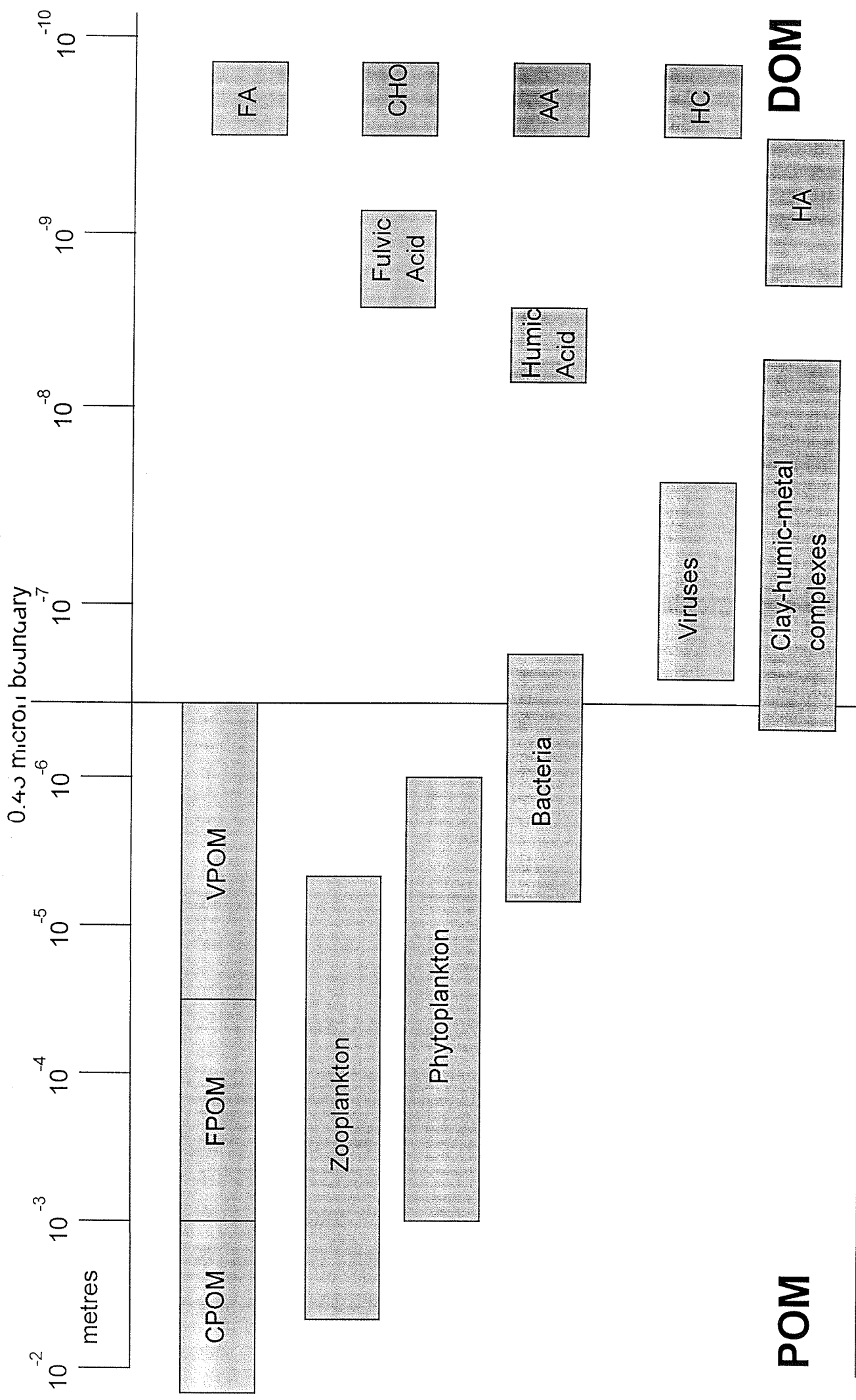
Size range of particulate and dissolved organic matter and carbon compounds in natural waters. AA, amino acids; CHO, carbohydrates; CPOM, coarse particulate organic matter; FA, fatty acids; FPOM, fine particulate organic matter; HA, hydrophilic acids; HC, hydrocarbons; VPOM, very fine particulate organic matter. Reproduced with kind permission from D. Hope.

Figure 1

90 kg C/ha/yr, while POC values vary between 2.3 kg C/ha/yr and 504.6 C/ha/yr depending upon many factors including land use, soil type and hydrology [10]. Values of $epCO_2$ between 1 and 15 times atmospheric partial pressure are common in the UK [8,10] as are loads of HCO_3^- between 5.0 kg C/ha/yr and 678 kg C/ha/yr [10].

2. Analysis of data

There are two main sources of carbon data for the LOIS study: the NRA and RPB datasets including the Harmonised Monitoring Dataset and the data collected within the LOIS programme. All of this data is accessible from the IH LOIS data centre [41].

2.1 NRA and RPB data

The NRA and RPB data are split up by region. At the time of writing (Oct 95) data up to 1993 for the Yorkshire region and the Tweed River Purification Board were available.

The only carbon determinand measured in the Tweed RPB region is hardness, measured as mg/l $CaCO_3$ which approximately equates with the amount of HCO_3^- and CO_3^{2-}. Figure 2 shows the distribution and mean concentration of total hardness at each site with an average concentration for all sites of 110.6 mg/l. Most of these sites have less than ten samples with the main three sites being the Whiteadder at Chesterfield with a mean of 145 mg/l and a range of 68 mg/l to 212 mg/l, the Tweed above Galafoot with a mean of 57.3 mg/l and a range of 30 mg/l to 82 mg/l and the Tweed at Northam bridge with a mean of 92.6 mg/l and a range of 48 mg/l to 140 mg/l [49].

Total organic carbon (TOC) in the NRA Yorkshire region is measured quite widely. However there are less than four samples available for many sites and the majority of sites only have a single value. Figure 3 shows the distribution and mean TOC concentration at sampling sites across the Yorkshire region. Values of TOC range between less than 0.1 mg C/l and 14 mg C/l.

The only trade discharge data currently available for TOC, e.g. discharges from chemical factories, are at a few sites across the Yorkshire region. Figure 4 shows mean TOC concentrations between 1 and 150 mg C/l.

Colour, in hazen units, is also measured in the Yorkshire region and is shown in figure 5. The colour data has been collected between 1986 and 1989 at a number of sites with the majority of samples taken on the river Calder where water is extracted for potable supplies [9]. Mean values range between 9 and 171 hazen with a mean across all sites of 45 hazen.

2.2 LOIS data

Along with a large number of other determinands DOC, POC, DIC (calculated from alkalinity, temperature and pH [42]) and stream flow are available at each of the eleven LOIS sites in the Yorkshire region and one in the Seven-Trent region. The twelve sites (figure 6) are Swale at Catterick Bridge, Swale at Thornton Manor, Nidd at Skip Bridge, Wharfe at Tadcaster, Ouse at Clifton Bridge, Derwent at Bubwith, Aire at Beal Bridge, Don at Sprotborough Bridge, Trent at Cromwell Lock, Calder at Methley Bridge, Ouse at Acaster

TOTAL HARDNESS (as CaCO3)mg/l (19)
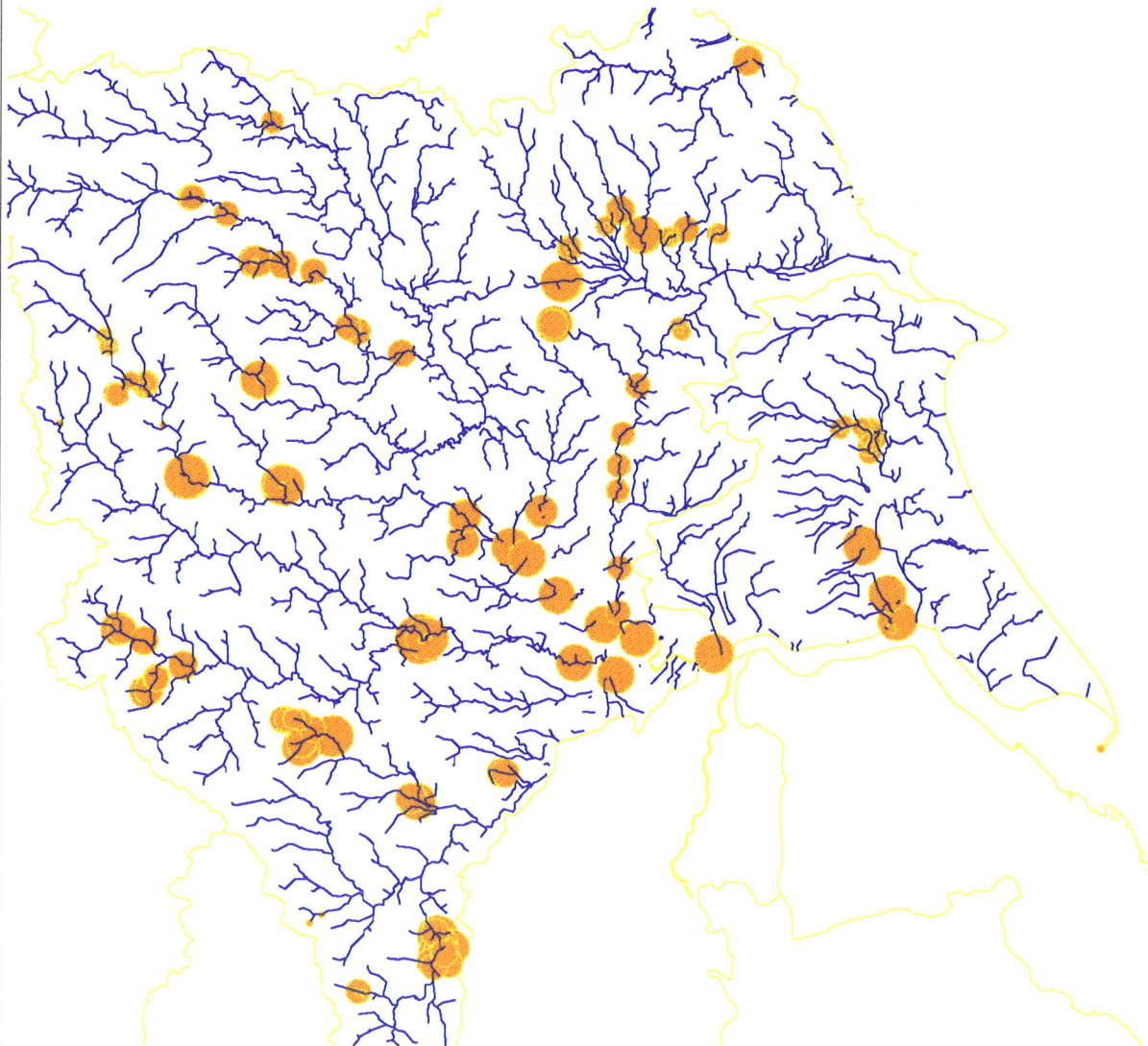
Mean Site Concentrations
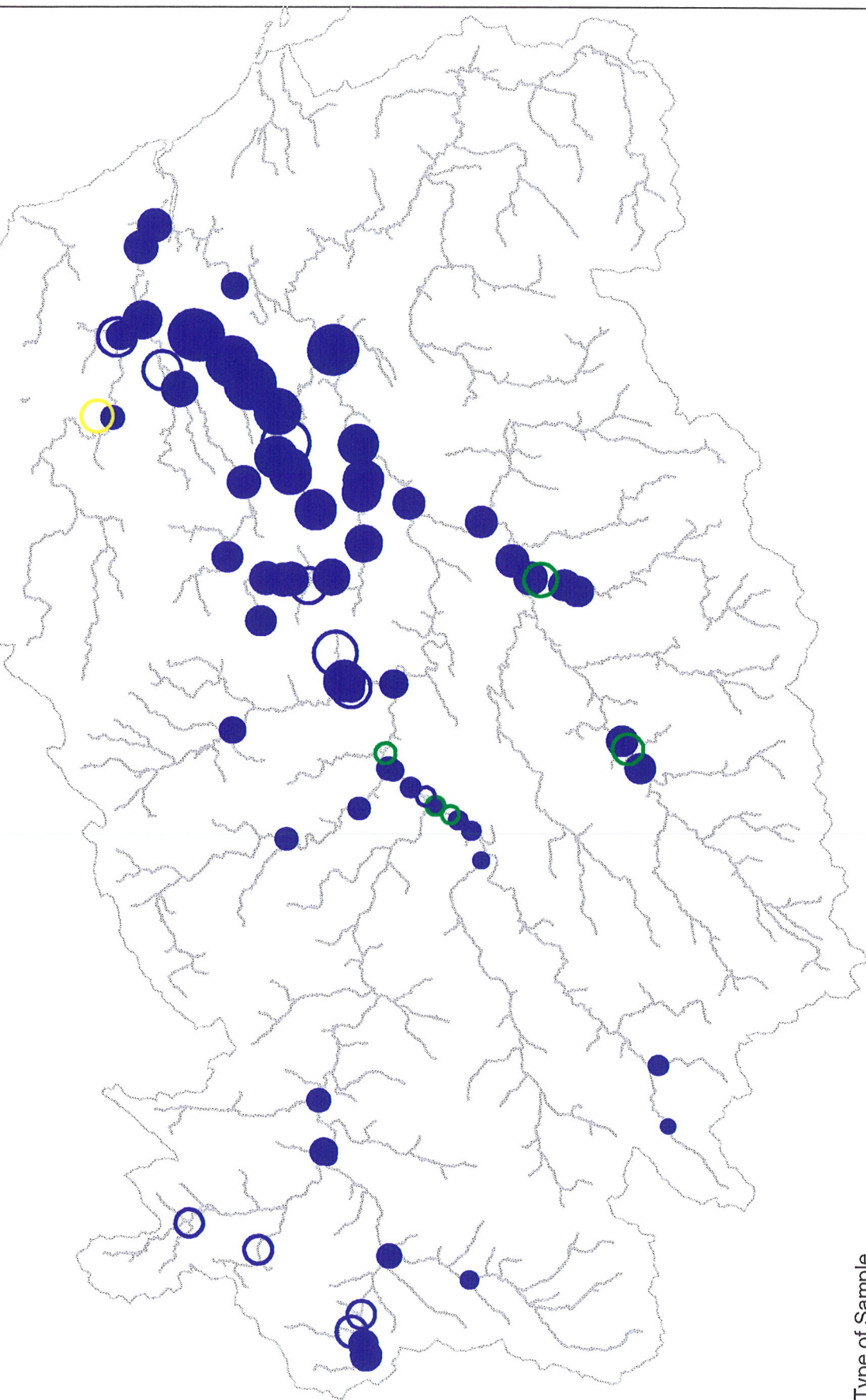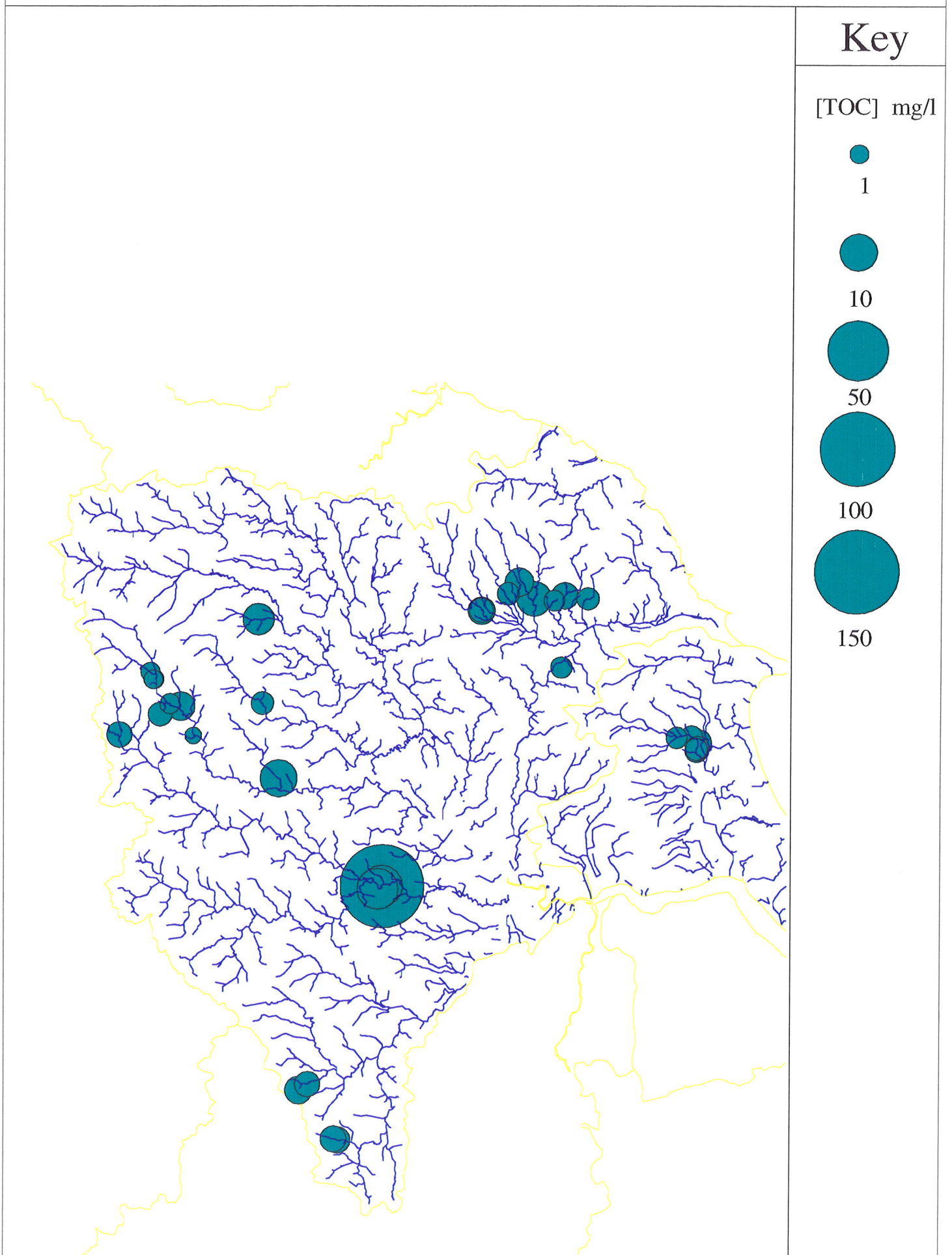

Figure 2

Figure 3

Average Total Organic Carbon in 1993

Key

- 0.1 mg/l
- 1.0 mg/l
- 5.0 mg/l
- 10.0 mg/l
- 14.0 mg/l

Figure 4

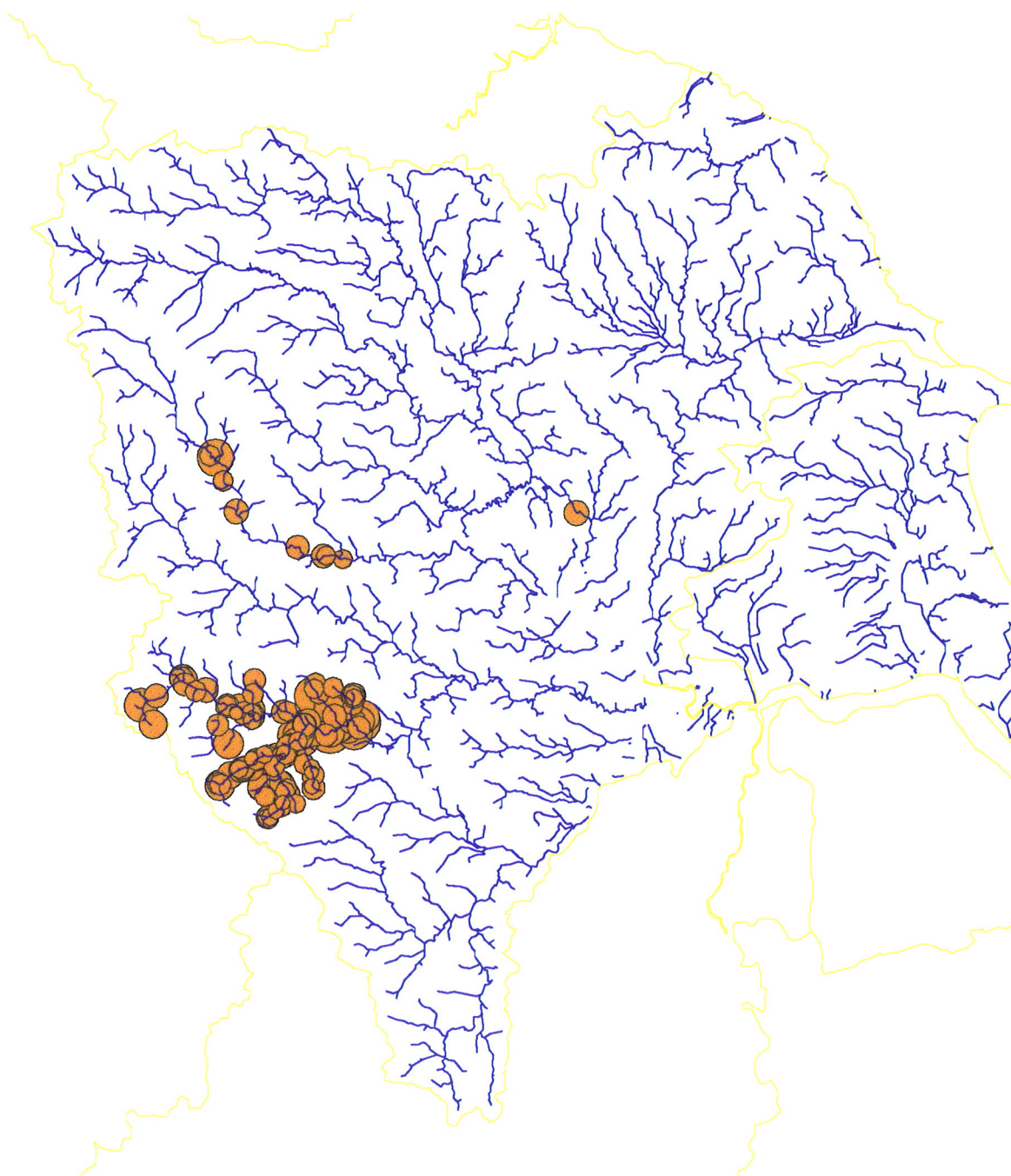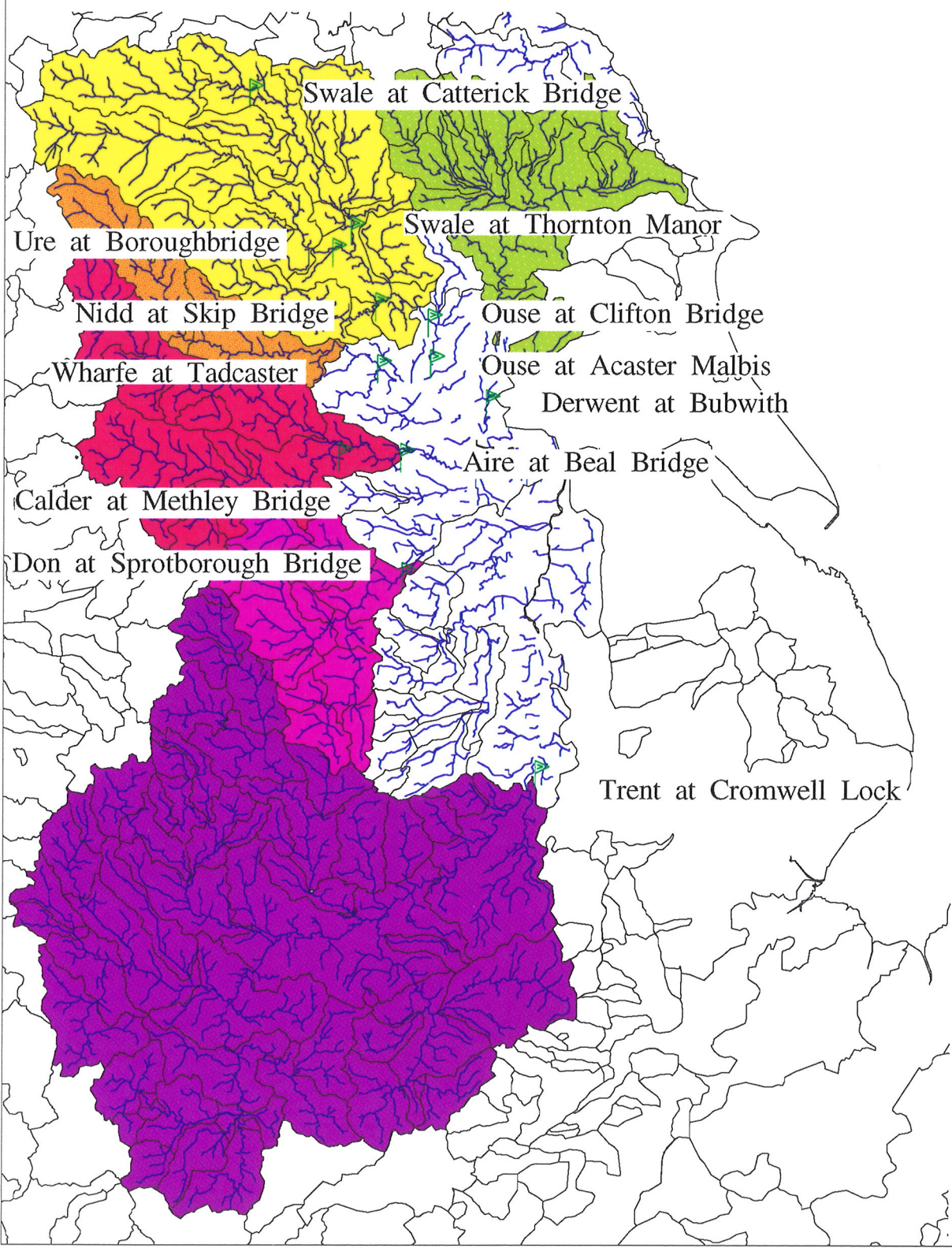# Mean TOC at Trade Discharge Sites for 1993

Key

[TOC] mg/l

1

10

50

100

150

Figure 5

Mean Colour

Figure 6

LOIS Monitoring Sites

Swale at Catterick Bridge

Swale at Thornton Manor

Ure at Boroughbridge

Nidd at Skip Bridge

Ouse at Clifton Bridge

Wharfe at Tadcaster

Ouse at Acaster Malbis

Derwent at Bubwith

Aire at Beal Bridge

Calder at Methley Bridge

Don at Sprotborough Bridge

Trent at Cromwell Lock

Malbis and the Ure at Boroughbridge. Sampling of these sites started in September 1993 on a weekly basis plus events, with the exception of the site at Acaster Malbis where sampling started in August 1994. The sampling is continuing until 1997 and the data shown here are those available from the LOIS IH data centre at the time of writing.

2.2.1 DOC

Figures 7a and b show time series of DOC at each of the twelve monitoring sites. DOC concentrations across all sites vary between approximately 1 and 15 mg C/l, with the exception of two very large peaks on the Wharfe and Derwent of 74 mg C/l and 64 mg C/l respectively which occurred on 24/1/94. Higher values of DOC can be seen between August 1994 and January 1995 on both river Swale sites, the Ouse at Clifton Bridge, the Ure and Nidd sites. On the Calder and Aire there are greater DOC concentrations occuring between September 1993 and December 1993 and again between April 1994 and December 1994. The higher winter concentrations are probably because of DOC leaching out of the soil as the ground saturates. Samples taken from both the Don and the Trent sites show little variation throughout the year with DOC concentrations varying around 5 mg C/l. With the exception of the two extreme points on the Wharfe and Derwent the river Calder has the highest DOC concentrations.

Figures 8a and b show the relationship between DOC concentrations and stream flow at each of the twelve LOIS monitoring sites. With the exception of samples taken from the Calder and Aire sites DOC was generally independent of stream flow with possibly some increase in DOC with flow. With the Calder and Aire there appears to be a tight relationship between DOC concentration and flow. On the river Calder the high DOC concentrations occur below a flow of 40 m³/s. As this flow is exceeded DOC concentrations fall to approximately 5 mg C/l or lower. The Calder drains into the Aire which shows a similar, but noisier relationship between DOC concentration and flow.
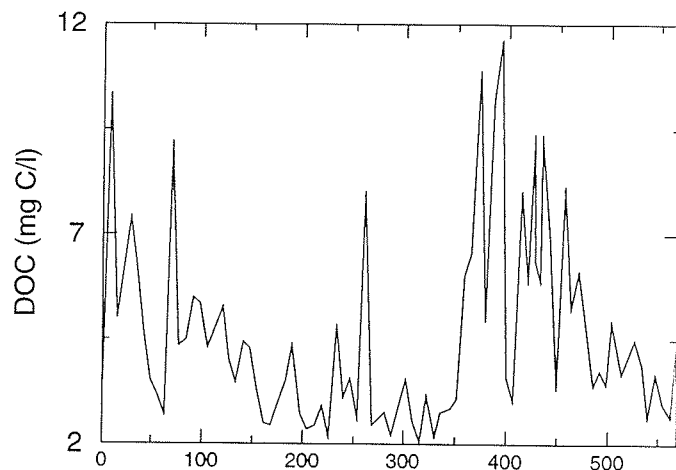
2.2.2 POC

Figures 9a and b show POC concentration against date of sample at the twelve LOIS monitoring sites. POC concentrations at all sites are a lot more variable in concentration with respect to time than DOC. POC concentrations vary between less than 1 mg C/l and 67 mg C/l with the majority of concentrations less than 10 mg C/l. The largest peak in concentration of POC occurred on the river Swale at Catterick Bridge during the late January 1995 flood event [43]. Generally the higher peaks in POC occur during the autumn and winter months. The peaks in POC concentration are higher in the Swale than in the Ouse, although there is only one large peak in the Swale at Catterick Bridge with the rest of the values below 5 mg C/l.

Graphs of POC against flow for each of the sites are plotted in figures 10a and b. At most of the sites POC increases with flow, particularly at high flows. The exception to this case is POC at the Trent site where flow either does not affect or has a very small affect on POC concentration.
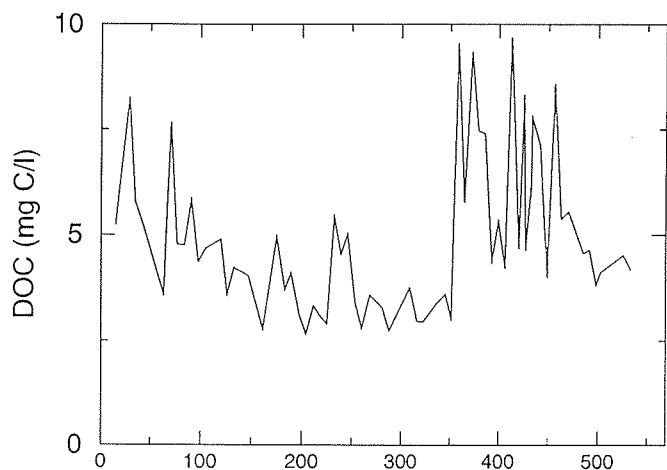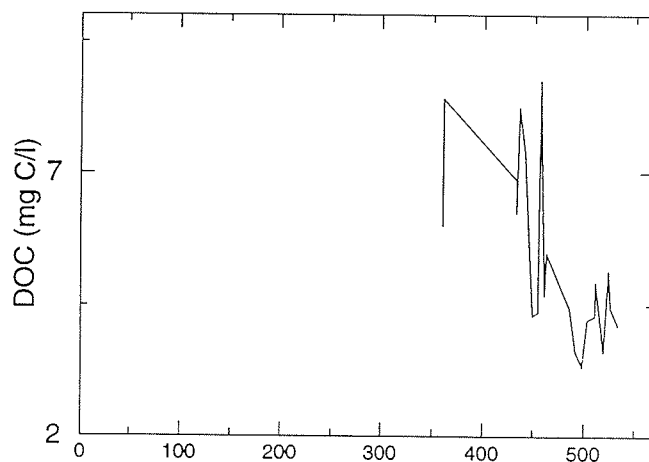
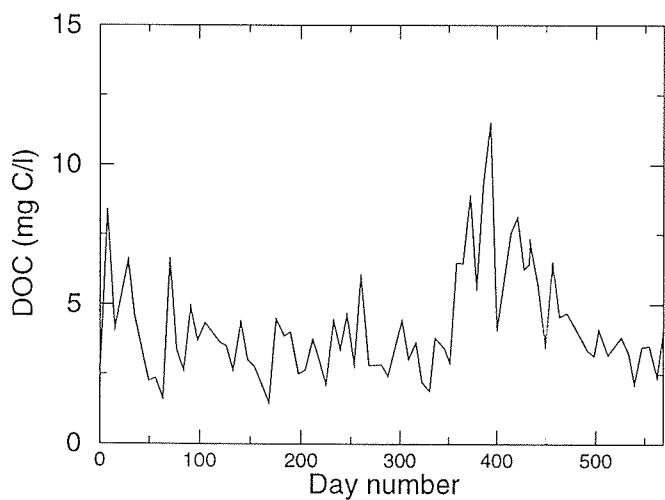## Swale at Catterick Bridge

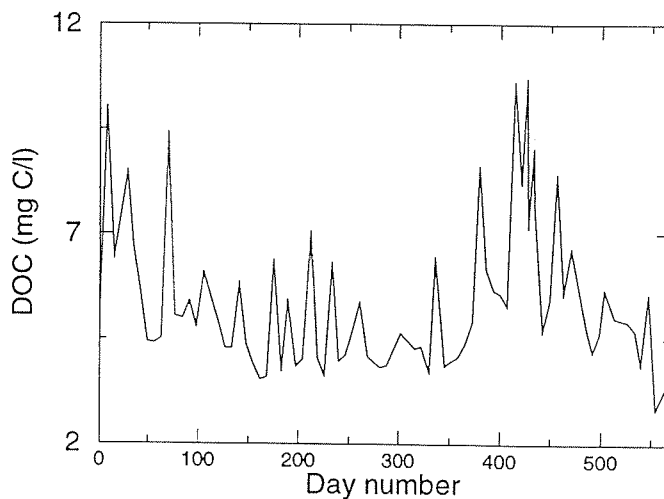## Swale at Thornton Manor

Ouse at Clifton Bridge

Ouse at Acaster Malbis
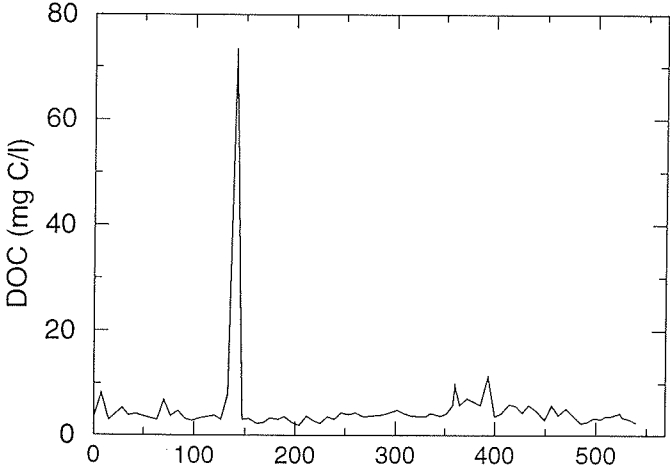
Ure at Boroughbridge
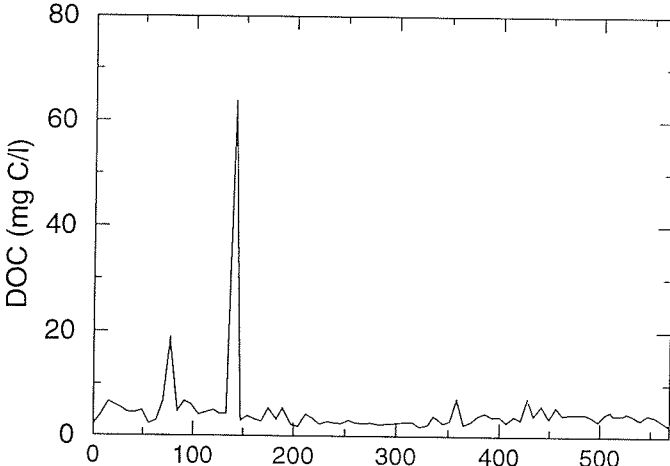
Nidd at Skip Bridge
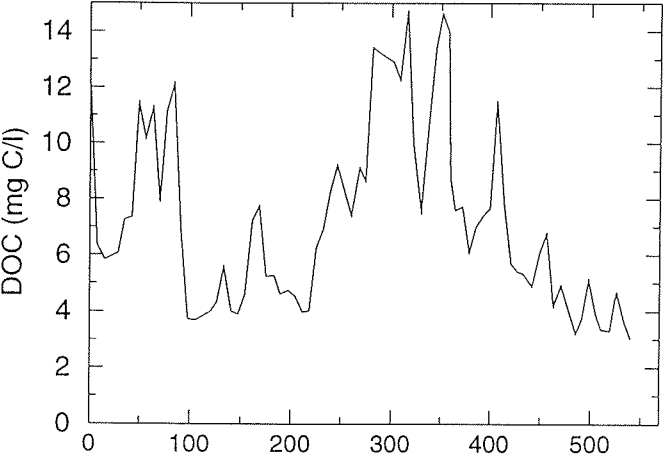

Day 1 = 7/9/1993
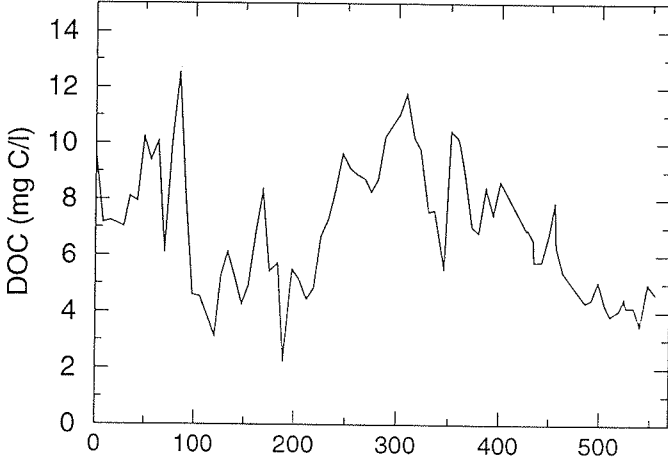
Day 1 = 7/9/1993

Wharfe at Tadcaster
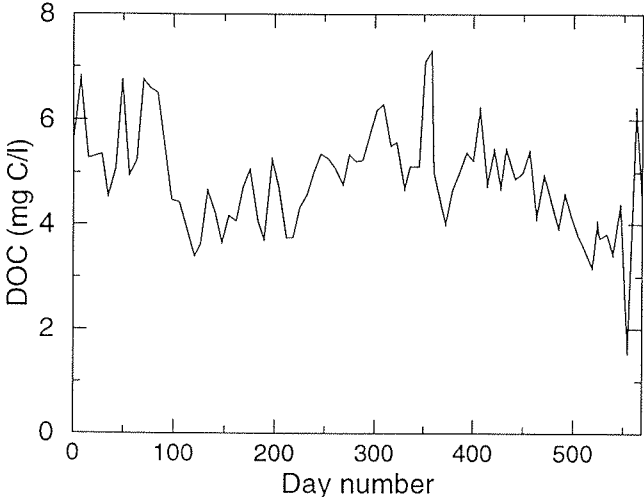
Derwent at Bubwith

Calder at Methley Bridge

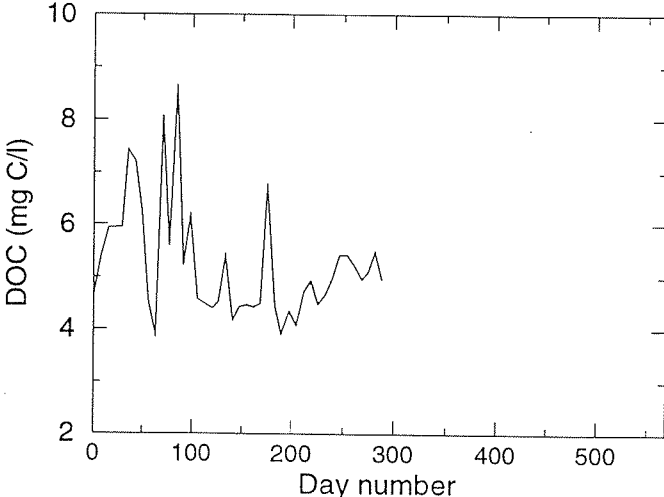## Aire at Beal Bridge

Don at Sprotborough Bridge

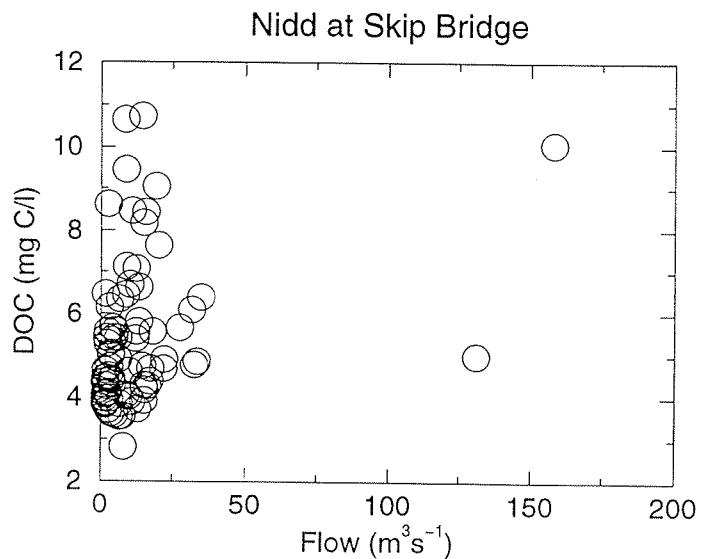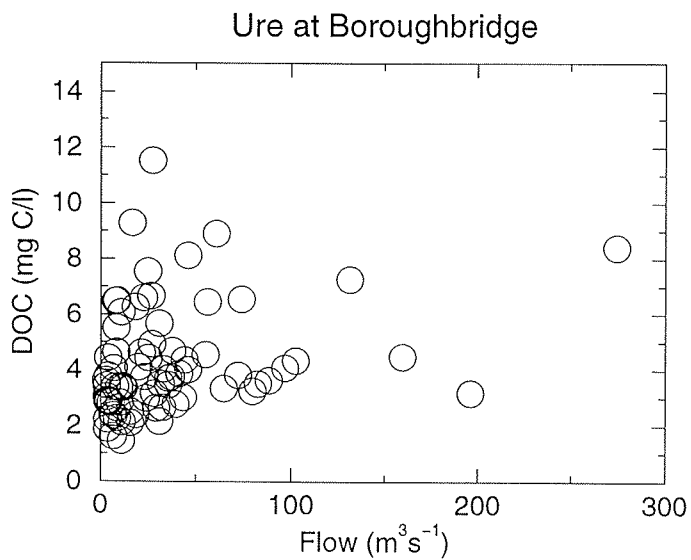## Trent at Cromwell Lock

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Day 1 = 7/9/1993

Swale at Catterick

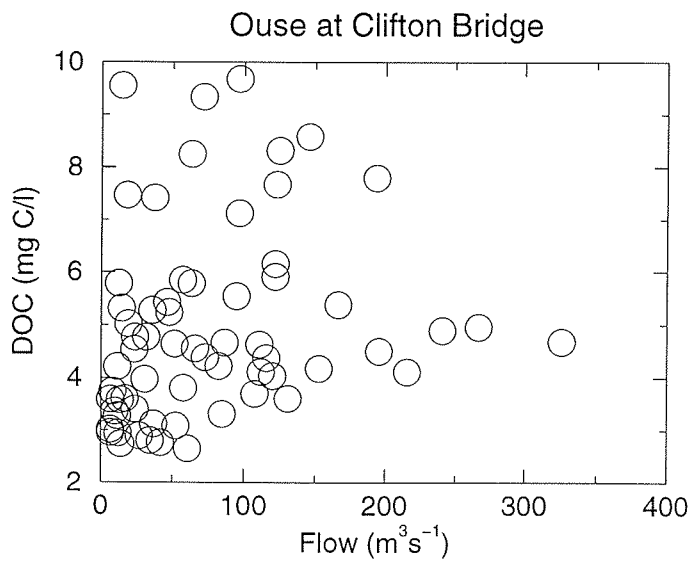# Swale at Thornton Manor

Ouse at Clifton Bridge

Ouse at Acaster Malbis

Ure at Boroughbridge

Nidd at Skip Bridge

Wharfe at Tadcaster

Derwent at Bubwith

Calder at Methley Bridge

Aire at Beal Bridge

Don at Sprotborough Bridge

Trent at Cromwell Lock

Swale at Catterick Bridge

Swale at Thornton Manor

Ouse at Clifton Bridge

Ouse at Acaster Malbis

Ure at Boroughbridge

Day 1 = 7/9/1993

Nidd at Skip Bridge

Day 1 = 7/9/1993

Wharfe at Tadcaster

Derwent at Bubwith

Calder at Methley Bridge

Aire at Beal Bridge

Don at Sprotborough Bridge

Trent at Cromwell Lock

Day 1 = 7/9/1993

Day 1 = 7/9/1993

Swale at Catterick

Swale at Thornton Manor

Ouse at Clifton Bridge

Ouse at Acaster Malbis

Ure at Boroughbridge

Nidd at Skip Bridge

Wharfe at Tadcaster

Derwent at Bubwith

Calder at Methley Bridge

Aire at Beal Bridge

Don at Sprotborough Bridge

Trent at Cromwell Lock
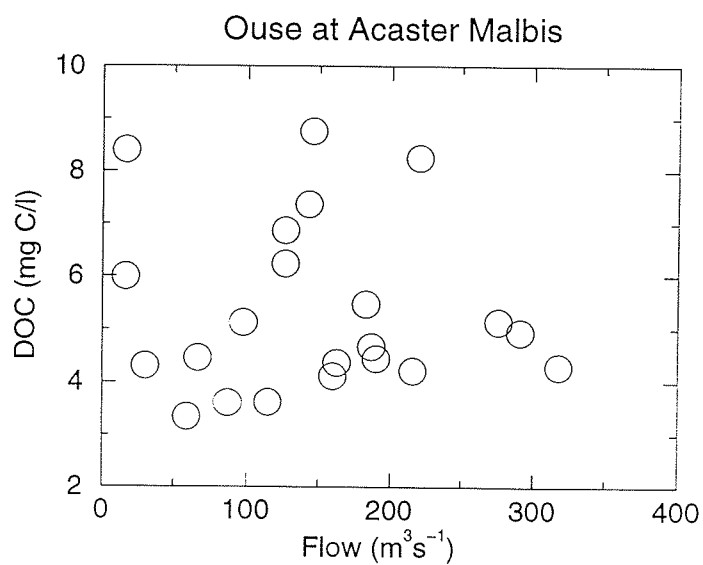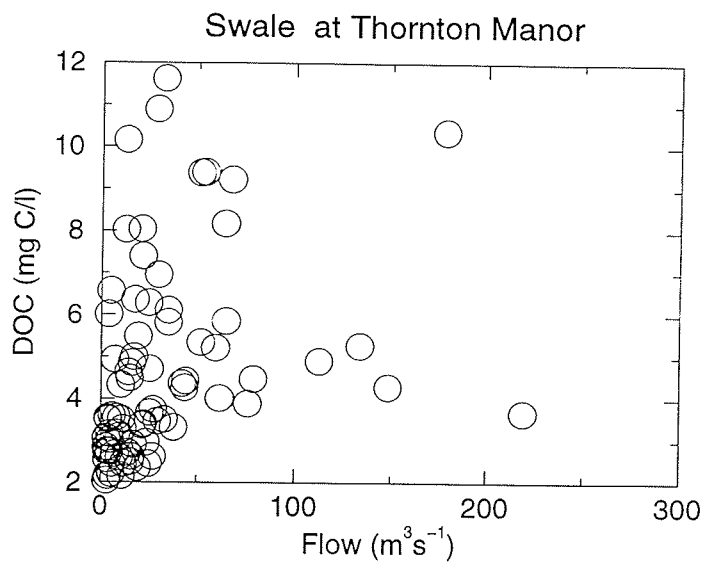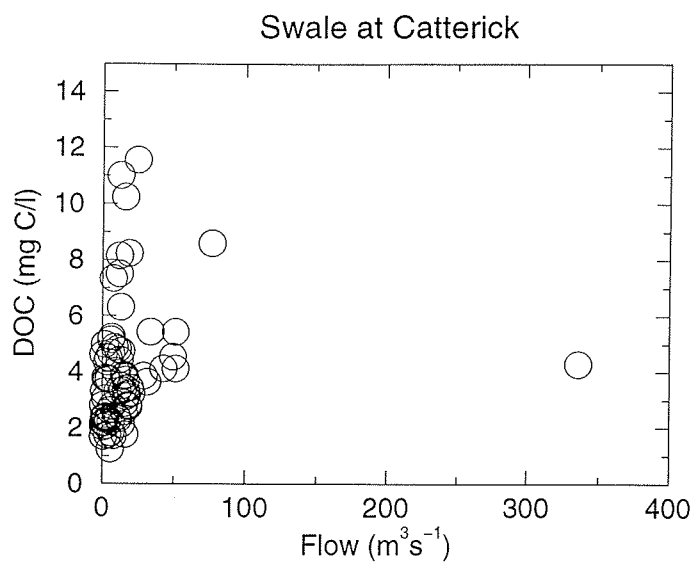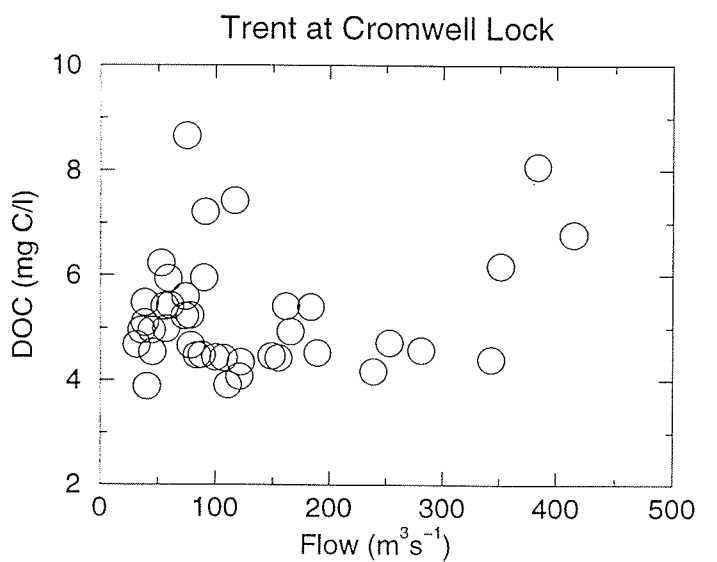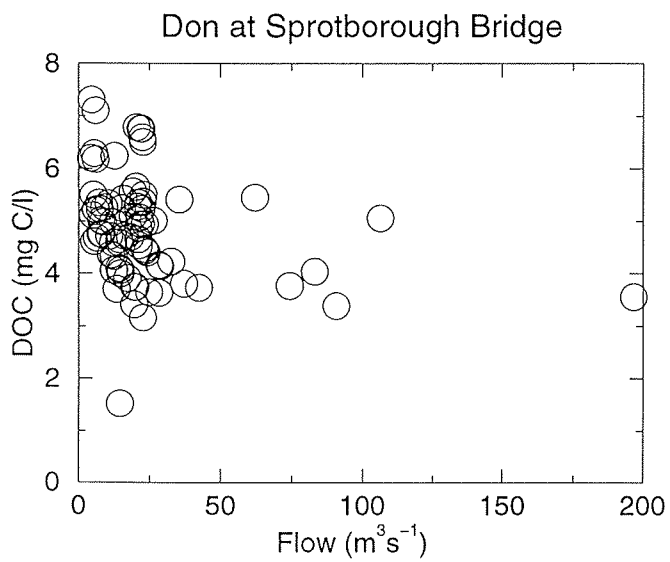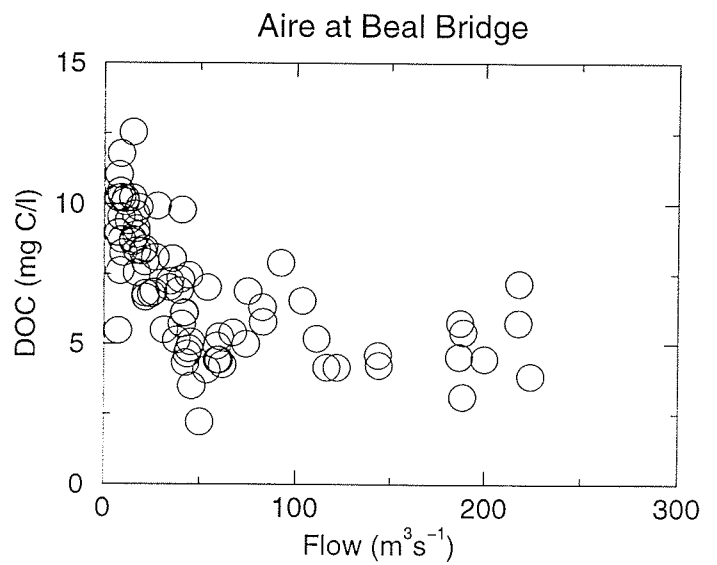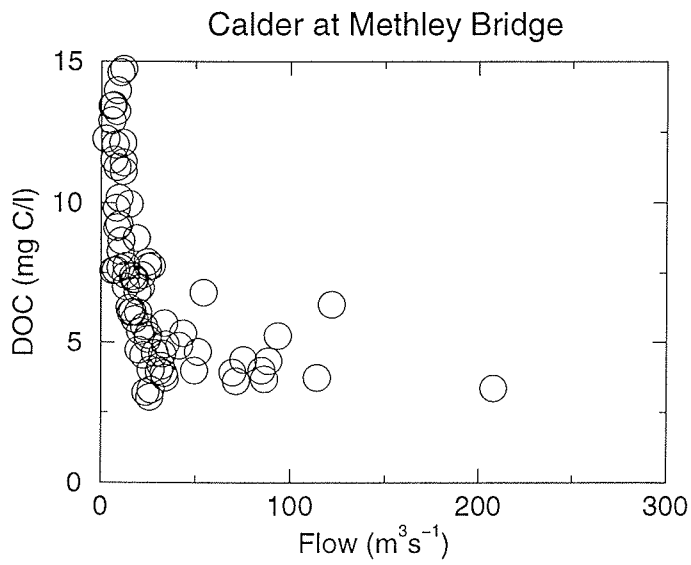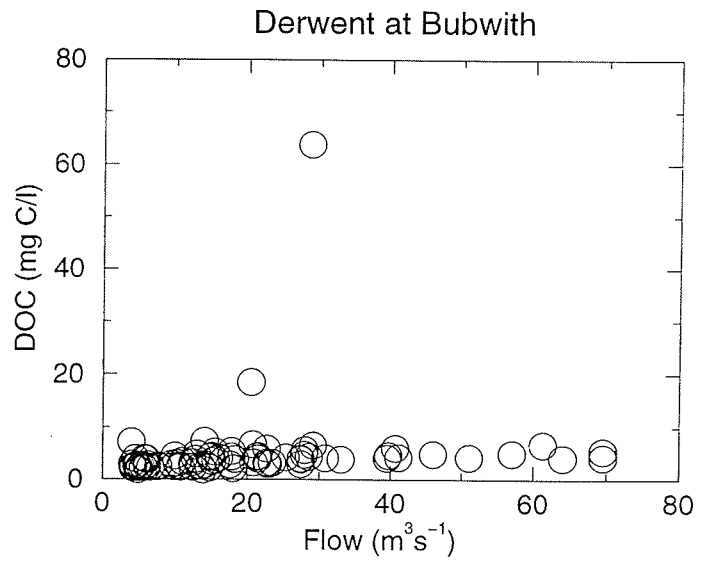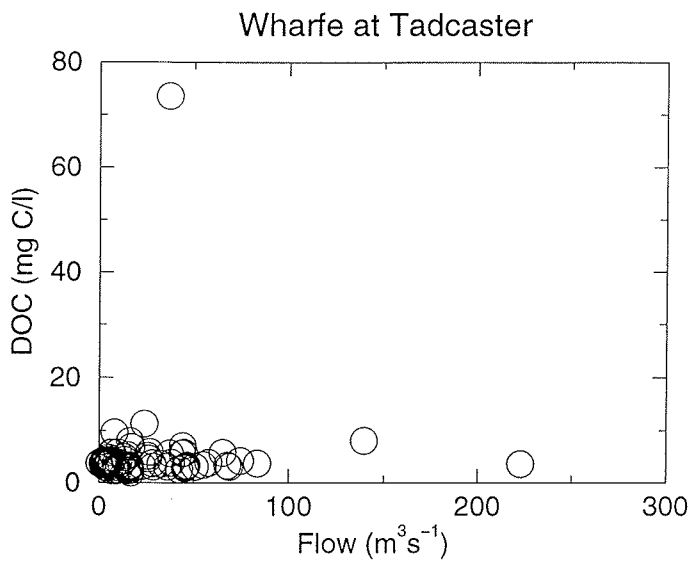
2.2.3 DIC, H_2CO_3, HCO_3^-, CO_3^{2-}, pCO_2 and $epCO_2$

DIC concentration against time is shown for each of the LOIS sites in figures 11a and b. These were calculated from alkalinity, pH and temperature using a methodology developed by Neal [42]. DIC concentrations are generally a lot higher in all the study rivers than DOC and POC. DIC is generally higher in the Swale at Thornton Manor, mean *c*. 30 mg C/l, than in the Swale at Catterick Bridge, mean *c*. 25 mg C/l, and returning to a mean of *c*. 25 mg C/l at Clifton Bridge on the Ouse. The Derwent and Trent rivers have the highest mean DIC concentrations of *c*. 40 mg C/l, with the Nidd and Calder with the lowest mean concentrations of *c*. 15 mg C/l. Generally the highest peaks in DIC occur during the summer months.

Figures 12a and b show DIC against flow for each of the LOIS sites. For most sites there is a general decrease in DIC with increasing flow, with the exception of the Trent where DIC is independent of flow. There is a large amount of noise around the general fall in DIC concentration with flow, particularly on the larger rivers with a wider range of flow values. There is observed a general fall in DIC concentrations down the Ouse river system, with maximum concentrations of 50 mg C/l on the Swale falling to 45 mg C/l on the Ouse at Clifton Bridge down to 35 mg C/l on the Ouse at Acaster Malbis. This suggests a dilution effect as the flows becomes larger down stream.

Figures 13a and b show the concentration of H_2CO_3 at each of the LOIS sampling sites from January 1994 through to February 1995 with a maximum value of 38.5 mg/l (Derwent) across all sites. There does not appear to be any increase in concentration from the top of the Swale down to the Ouse sampling point. The concentration of H_2CO_3 on the Calder, Aire and Don appears to be more variable with the Aire having generally higher peaks in concentration than the other rivers.

HCO_3^- concentration is shown in figures 14a and b at each of the LOIS sampling points. HCO_3^- at the Swale and Ouse sites show a large variation in concentration from *c*. 6 mg C/l up to *c*. 50 mg C/l. The Trent river generally shows the highest values of HCO_3^-, although the dataset is not for a full year.

Figures 15a and b show the concentration of CO_3^{2-} at each of the LOIS sampling sites. The largest concentration on the Swale at Catterick Bridge also occurs at the Ouse sampling site at Clifton Bridge and on the Ure at Boroughbridge on the same date (19/7/1994). However this peak does not appear at the Thornton Manor site on the river Swale. Generally the CO_3^{2-} concentrations are below 0.25 mg C/l at most sites with the exception of the Swale at Catterick Bridge which has a concentration of 0.15 mg C/l.

$epCO_2$ is shown in figures 16a and b and is expressed as the number of times the partial pressure of CO_2 in the stream exceeds the partial pressure of CO_2 in water at equilibrium with the atmosphere. The largest $epCO_2$ occurs at the Derwent sampling site with a value of 154 atm on 31/1/1994. Other high peaks occur on the Swale at Catterick (58 atm), the Ure (50 atm), the Calder (56 atm) the Don (51 atm), the Trent 101 atm and five on the Aire between 40 and 60 atmospheric.

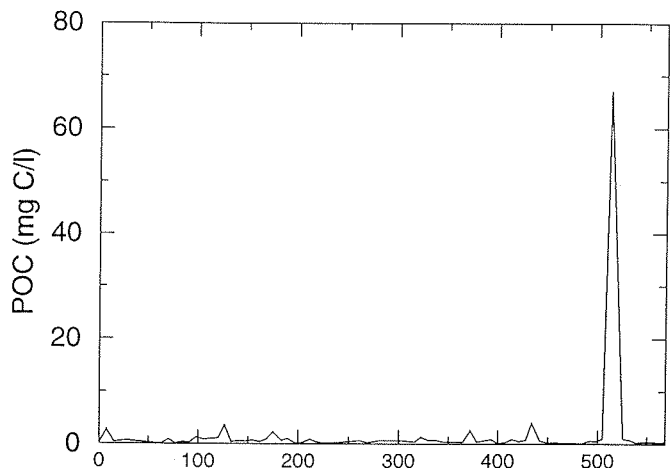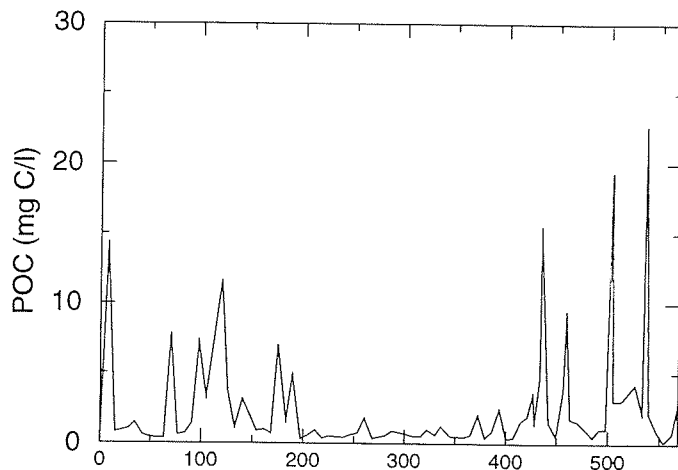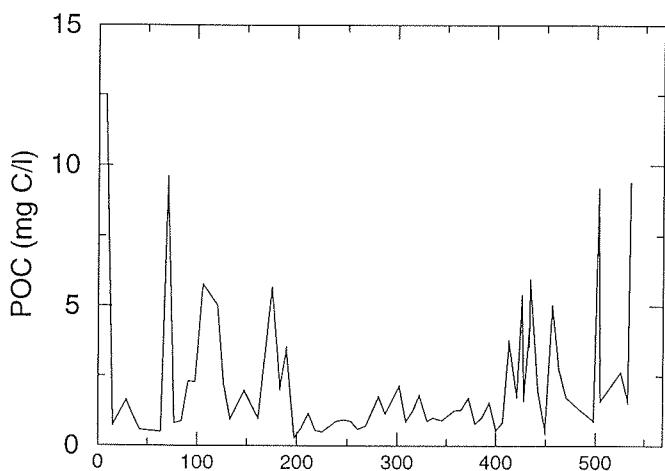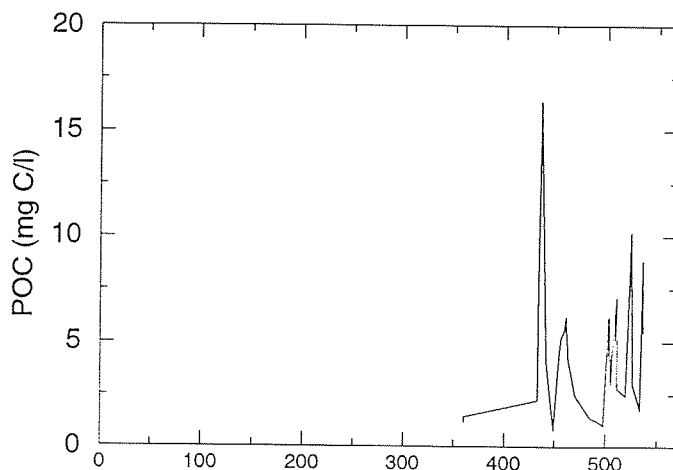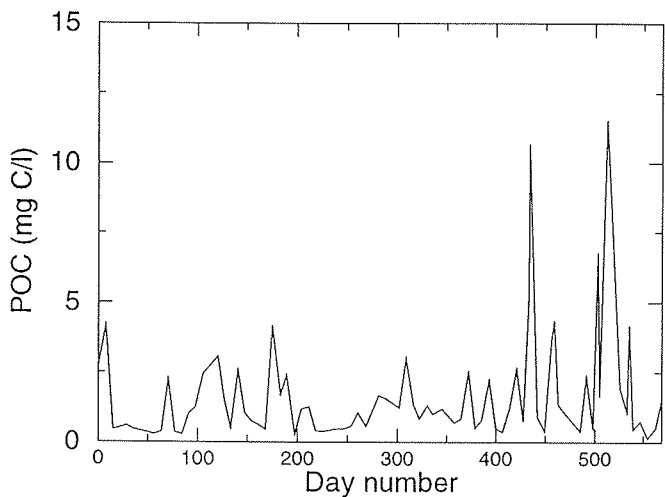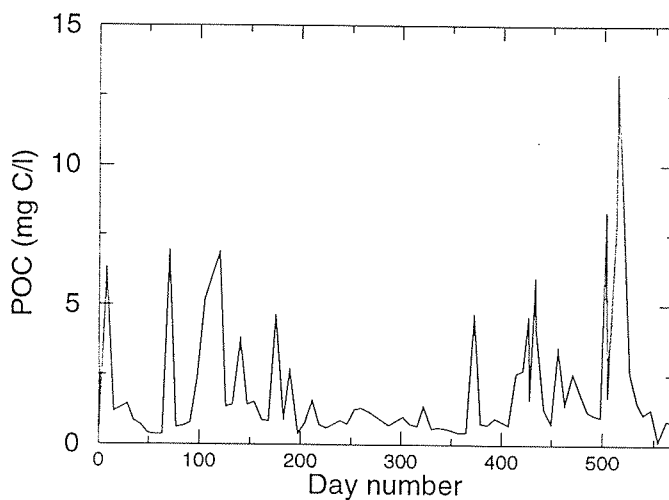## Swale at Catterick Bridge

Swale at Thornton Manor

Ouse at Clifton Bridge

Ouse at Acaster Malbis

Ure at Boroughbridge

Day 1 = 7/9/1993

Nidd at Skip Bridge
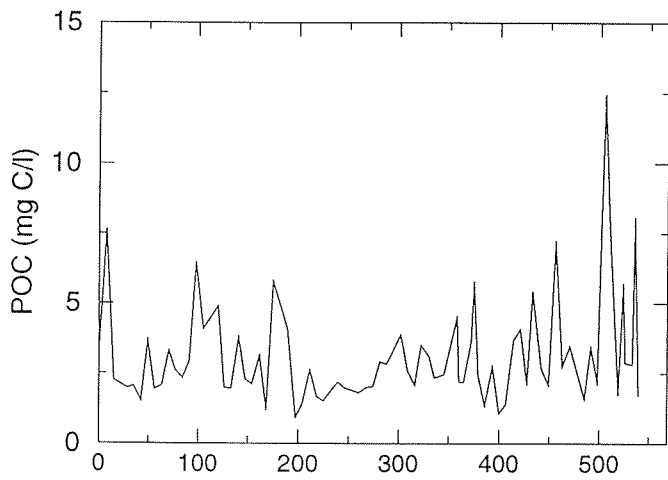

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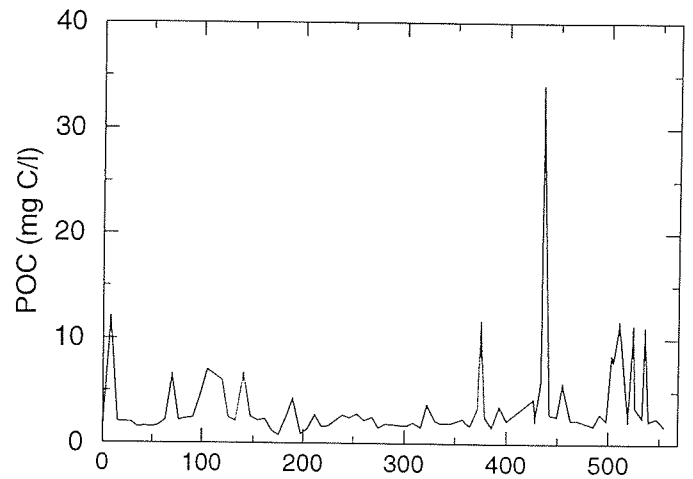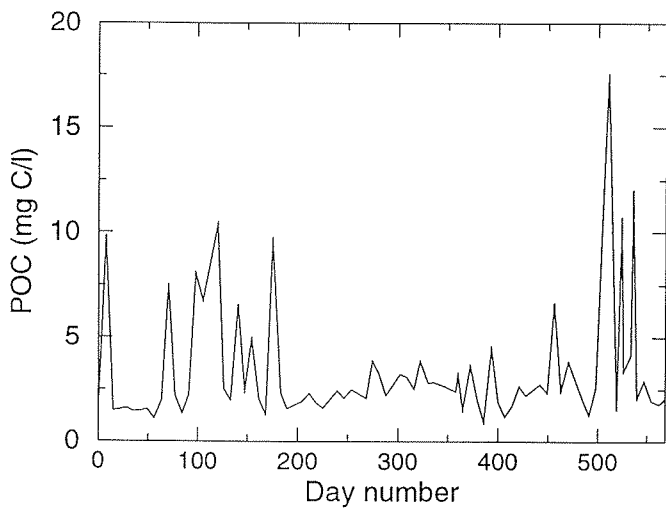## Wharfe at Tadcaster

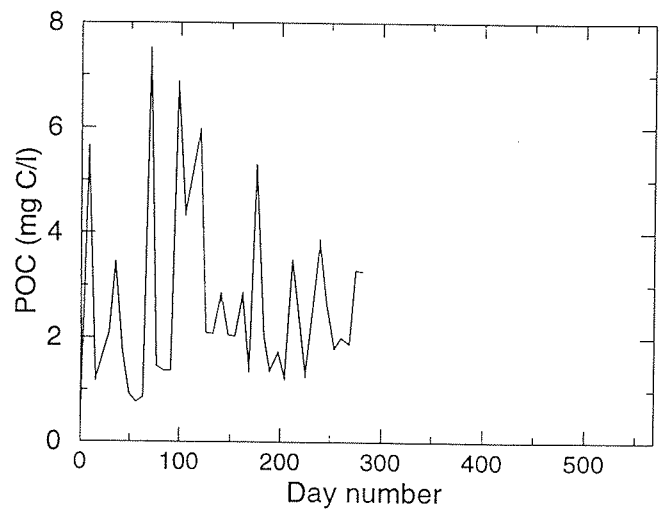## Derwent at Bubwith

Calder at Methley Bridge

Aire at Beal Bridge

Don at Sprotborough Bridge

Trent at Cromwell Lock
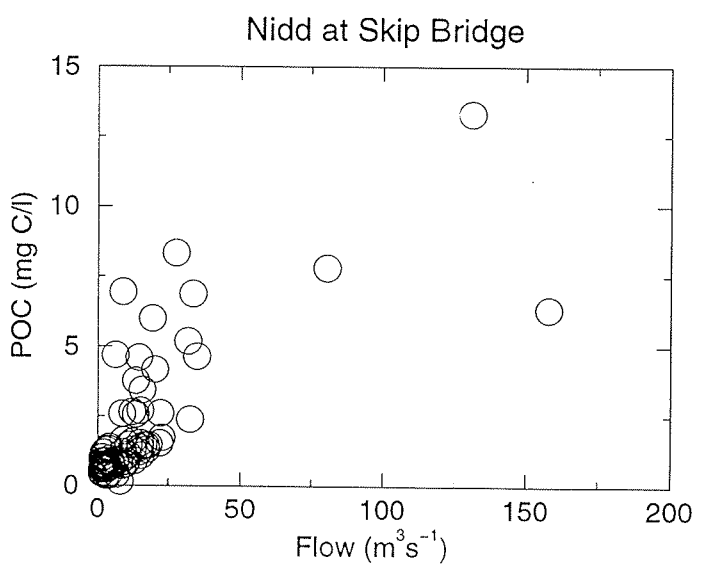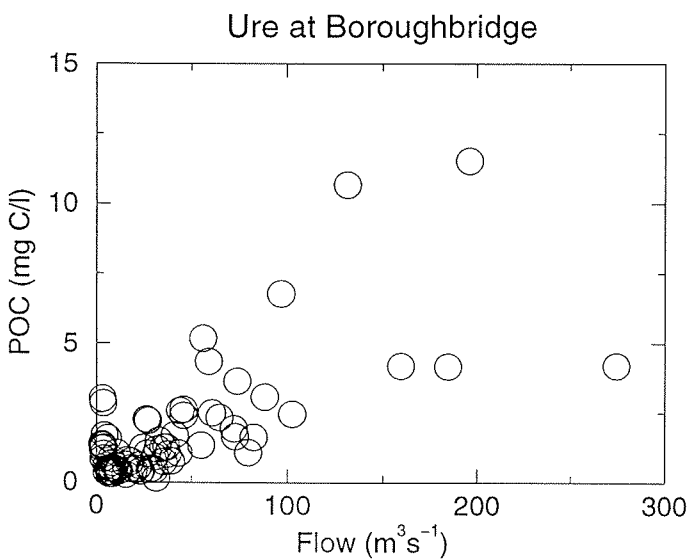

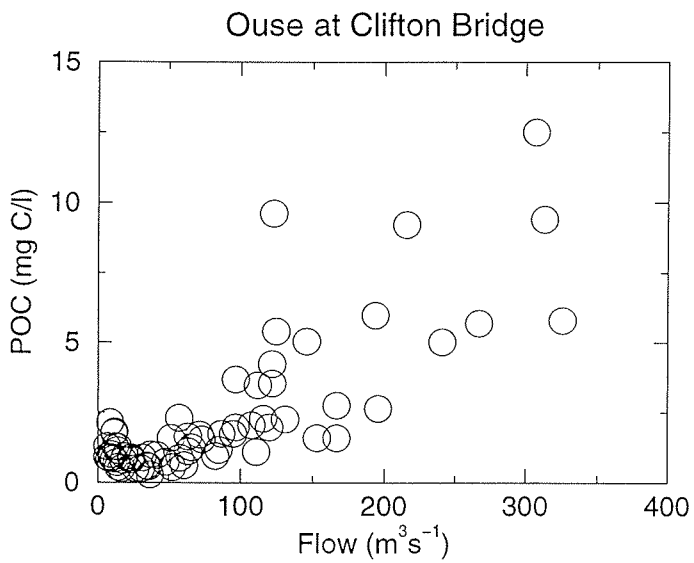Day 1 = 7/9/1993

Day 1 = 7/9/1993

Swale at Catterick

Swale at Thornton Manor

Ouse at Clifton Bridge

Ouse at Acaster Malbis

Ure at Boroughbridge

Nidd at Skip Bridge

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Day 1 = 7/9/1993

Wharfe at Tadcaster

Derwent at Bubwith

Calder at Methley Bridge

Aire at Beal Bridge

Don at Sprotborough Bridge

Day 1 = 7/9/1993

Trent at Cromwell Lock

Day 1 = 7/9/1993

Swale at Catterick Bridge

Swale at Thornton Manor

Ouse at Clifton Bridge

Ouse at Acaster Malbis

Ure at Boroughbridge

Day 1 = 7/9/1993

Nidd at Skip Bridge

Day 1 = 7/9/1993

Wharfe at Tadcaster

Derwent at Bubwith

Calder at Methley Bridge

Aire at Beal Bridge

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Trent at Cromwell Lock

Day 1 = 7/9/1993
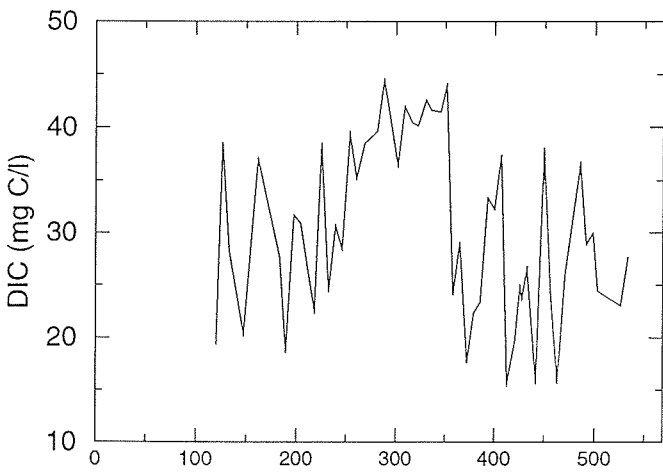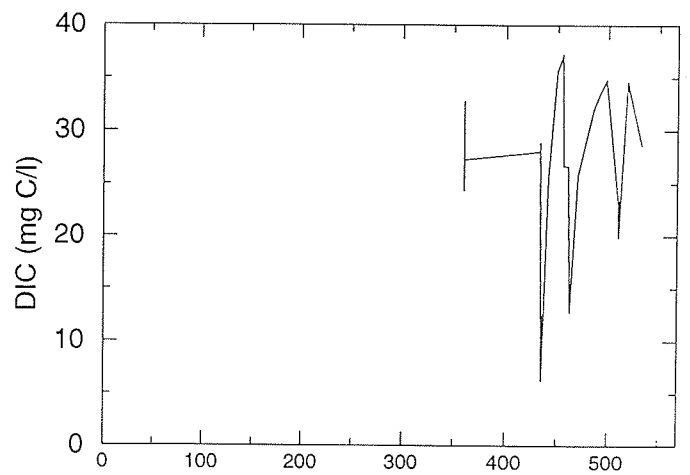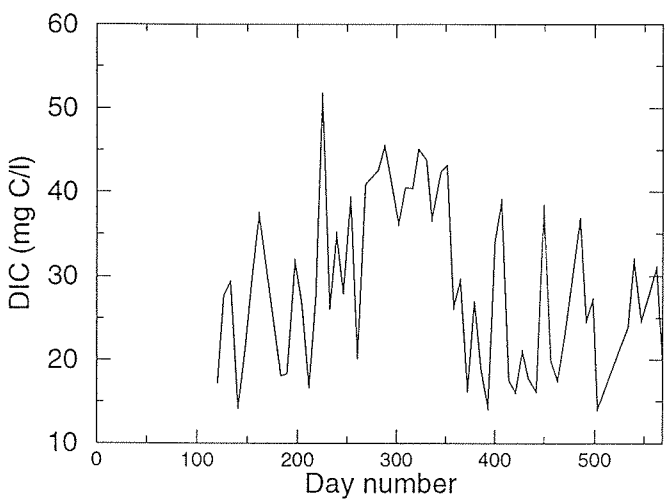
Swale at Catterick Bridge

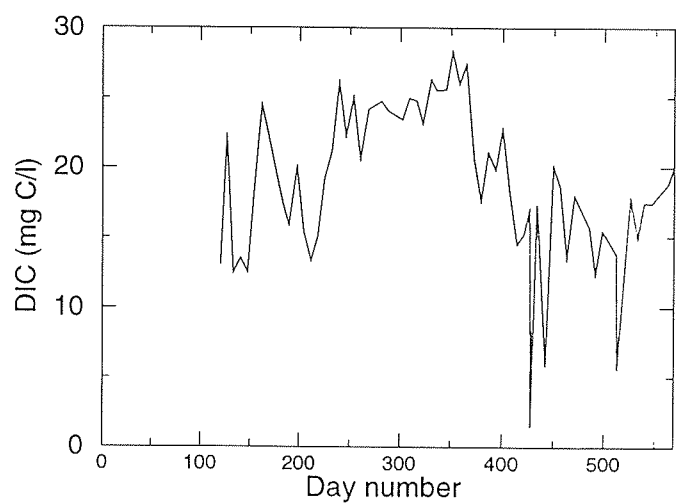Swale at Thornton Manor

Ouse at Clifton Bridge

Ouse at Acaster Malbis
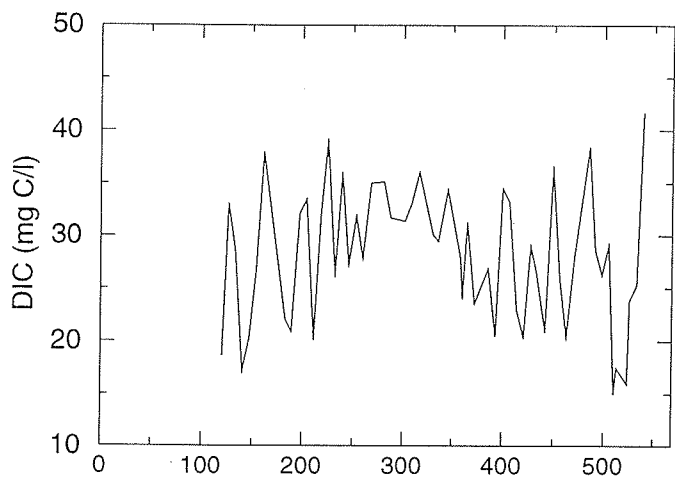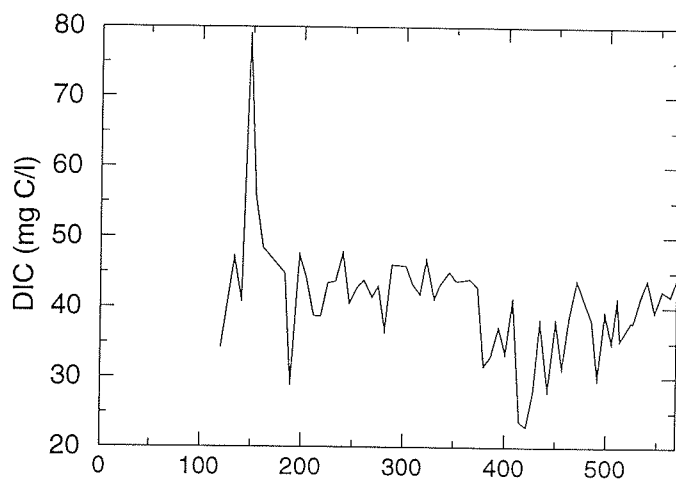
Ure at Boroughbridge

Nidd at Skip Bridge

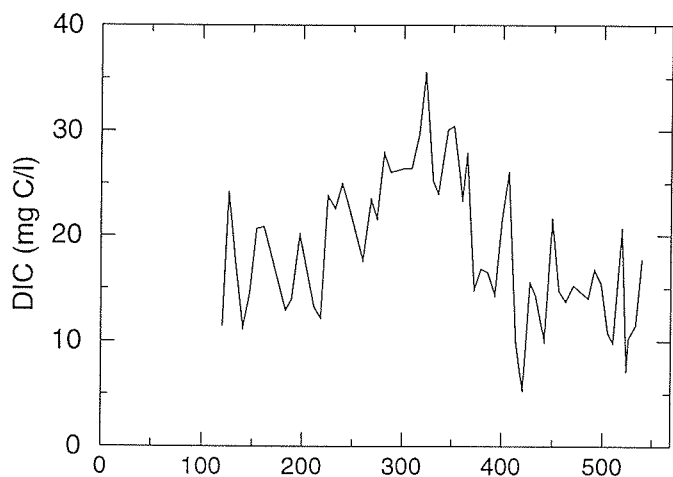Day 1 = 7/9/1993

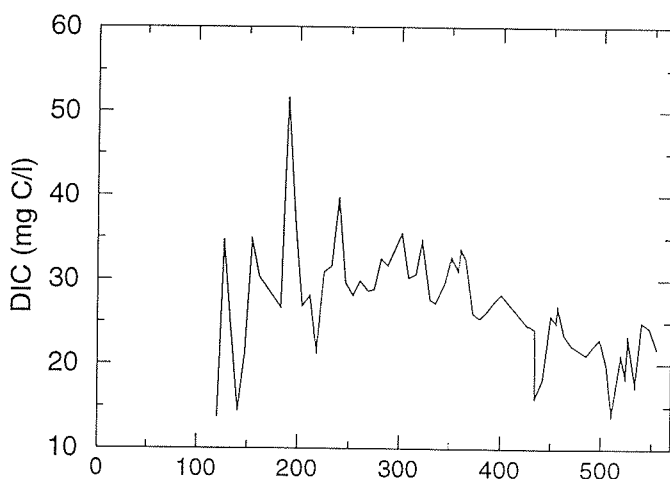Day 1 = 7/9/1993
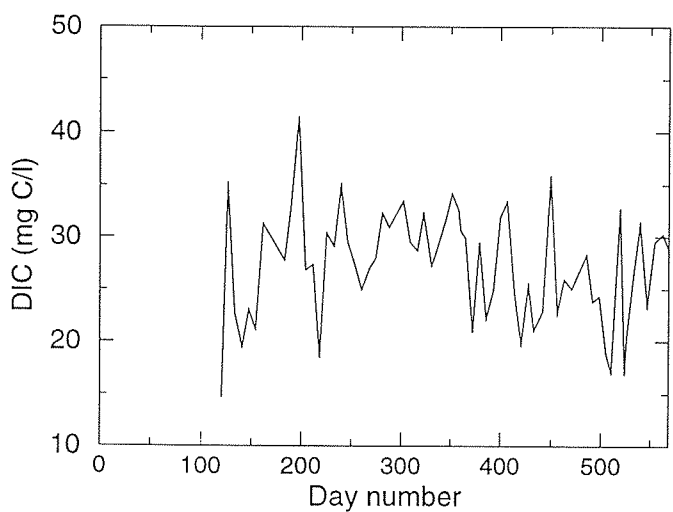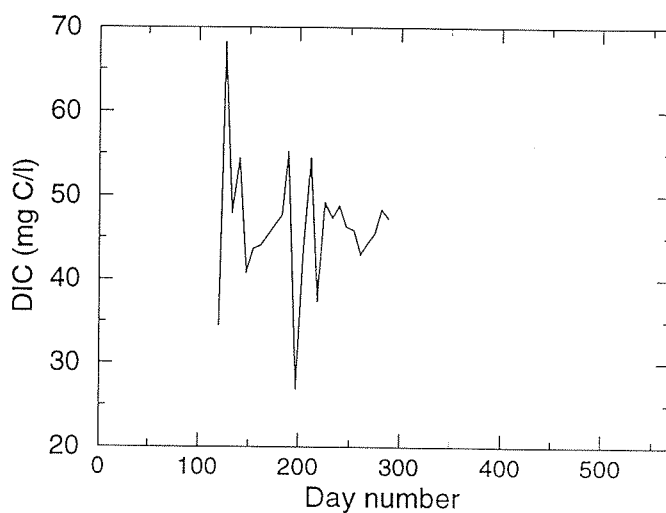
Wharfe at Tadcaster

Derwent at Bubwith

Calder at Methley Bridge

Aire at Beal Bridge

Don at Sprotborough Bridge

Trent at Cromwell Lock

Day number
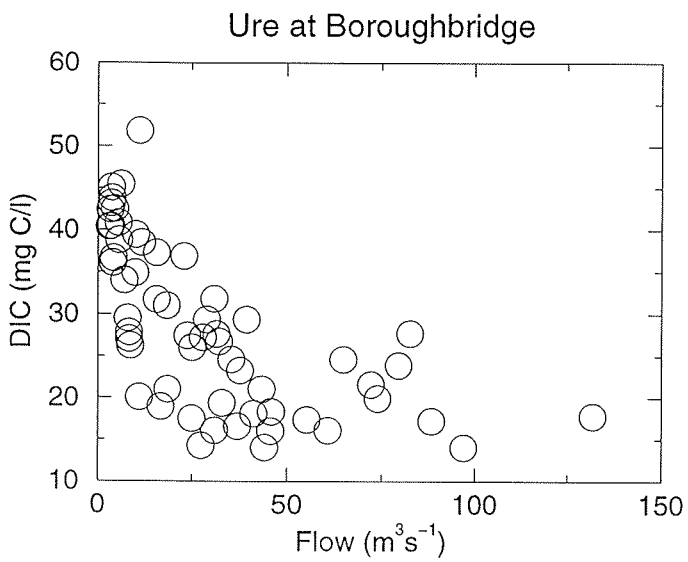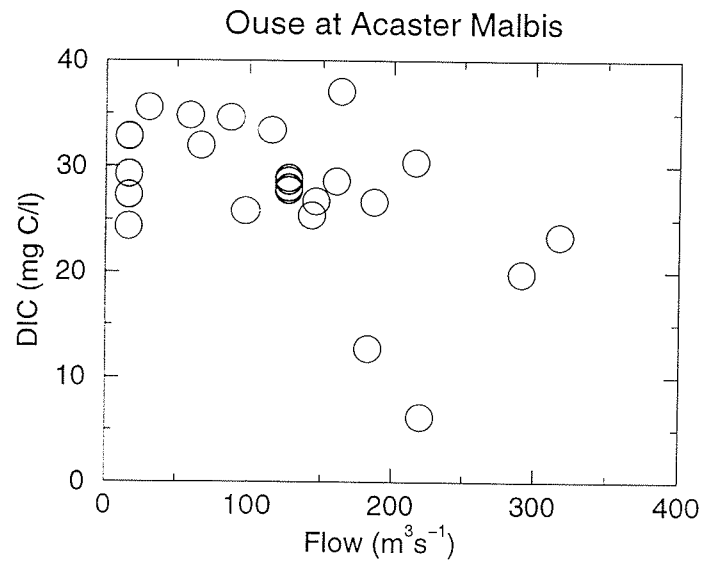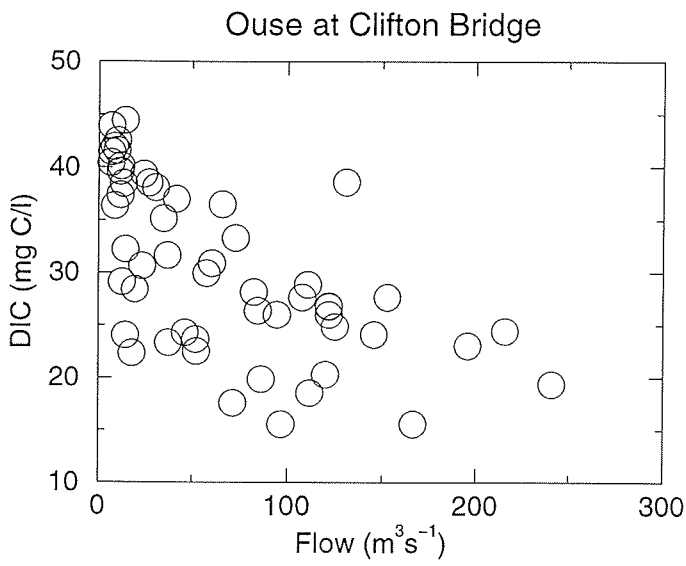
Day number

Day 1 = 7/9/1993

Day 1 = 7/9/1993

2.3 DOC, POC and DIC loads

Figures 17 and 18 show DOC, POC and DIC loads for each of the LOIS sites. The loads were calculated using a flow weighted methodology [44, 45] and are shown as kg/yr and kg/ha/yr.

It is acknowledged that this methodology may underestimate the loads passing down the rivers by up to 20% [44]. Further work in the estimation of loads is covered in a LOIS special topic [52]. The daily flow data were not available at the time of writing for a full year for the Swale at Catterick, Ouse at Clifton Bridge, Aire and Calder and so total flow was calculated from mean daily flow from the 1985-90 flow records [46].

The lowest DOC load is from the Swale at Catterick at 1.6 kt C/yr with the highest load at the Trent site of 16 kt C/yr and a mean load of 4.8 kt C/yr across all rivers. The total DOC load entering the Humber estuary (sum of loads at Ouse at Clifton Bridge, Wharfe, Aire, Derwent, Don and Trent) for 1994 was 41 kt C. The highest POC load across the LOIS sites was on the river Aire at 12 kt C/yr with the smallest value on the river Swale at Catterick of 0.4 kt C/yr and a mean value across all sites of 3.8 kt C/yr. The total POC entering the Humber estuary was 33 kt C/yr. The smallest DIC load measured was on the river Nidd of 4.8 kt C/yr and the largest on the river Trent of 156 kt C/yr with a mean DIC across all sites of 30 kt C/yr. The total amount of DIC entering the Humber estuary was 270 kt C/yr. The total carbon entering the Humber estuary in 1994 (sum of DOC, POC and DIC) was 343 kt, of which the river Trent contributed 53% (the Trent consists of c. 48% of the total contributing catchment area).

The graph of area weighted carbon loads (figure 18) shows that the Wharfe contributes the highest amount of DOC per unit area at 59 kg/ha/yr, with the Derwent contributing the smallest amount per unit area at 19 kg/ha/yr. The Derwent also contributed the lowest POC load per unit area at 6 kg/ha/yr and the river Aire contributed the highest POC load per unit area at 62 kg/ha/yr. The river Nidd contributes the smallest DIC load per unit area at 94 kg/ha/yr and the highest DIC load per unit area is contributed by the river Ure at 208 kg/ha/yr.

3. Sources and Sinks

The carbon present in river water can be divided up into three categories: allochthonous (terrestrial), anthropogenic (industrial, agricultural and domestic sources and sinks) and autochthonous (*in situ*).

3.1 Allochthonous sources and sinks

Precipitation falls onto the catchment canopy, onto the soil or directly into streams. The place where precipitation enters a catchment ecosystem can also directly affect its chemistry. Both DOC and POC can be found in precipitation, derived mainly from the combustion of carbon-based fuel, with DOC concentrations between 1 and 10 mg/l [10]. Concentrations of total particulate carbon, total suspended particulate ca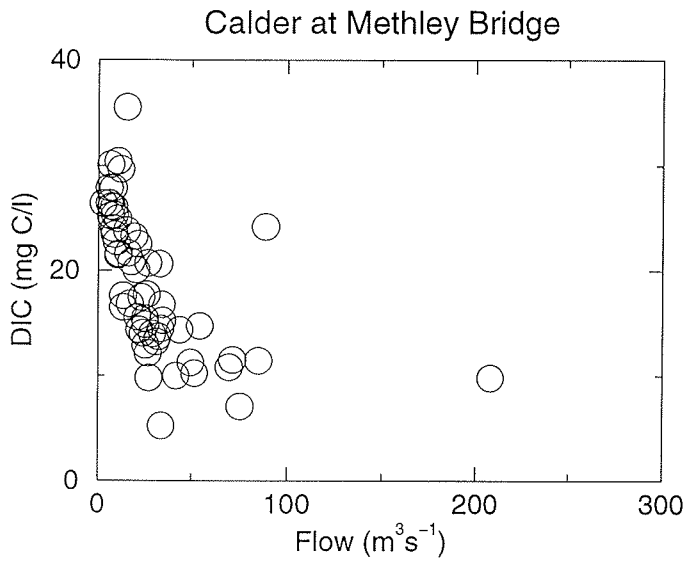rbon (TSP) and DOC were measured in the range 0.03-6.9 mg/l, 2.6-51.6 mg/l and 0.7-14 mg/l respectively in cloud water samples in southern Scotland [12]. The highest concentrations were found to occur during the winter

Carbon Loads at LOIS sites for 1994

Figure 17
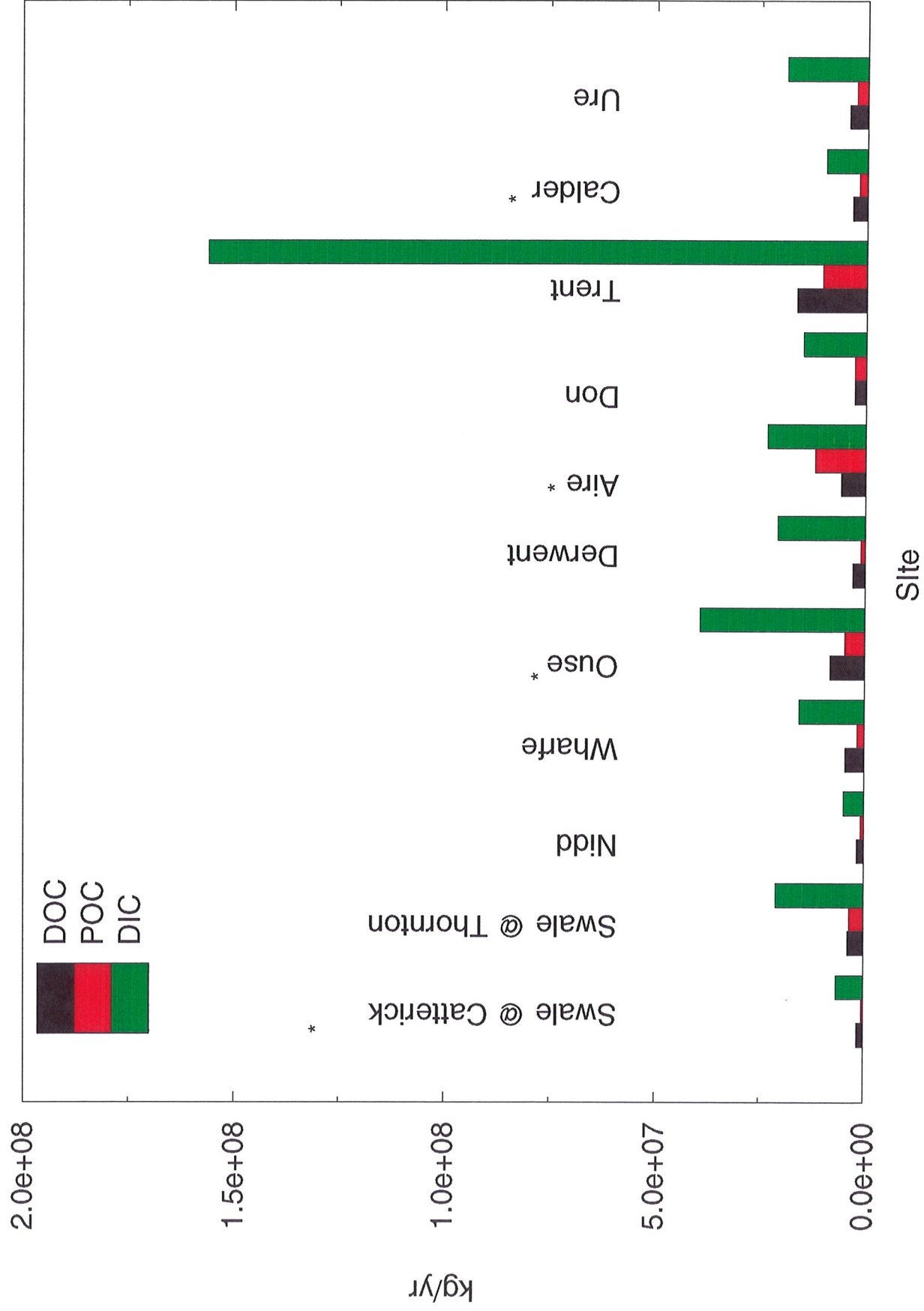
* 1994 total flow unavailable. total flow calculated from mean daily flow

Carbon Loads at LOIS sites for 1994

Site

Kg/ha/yr

Legend:
- DOC
- POC
- DIC

Sites: Swale @ Catterick *, Swale @ Thornton, Nidd, Wharfe, Ouse *, Derwent, Aire *, Don, Trent, Calder *, Ure

* 1994 total flow unavailable. total flow calculated from mean daily flow

Figure 18
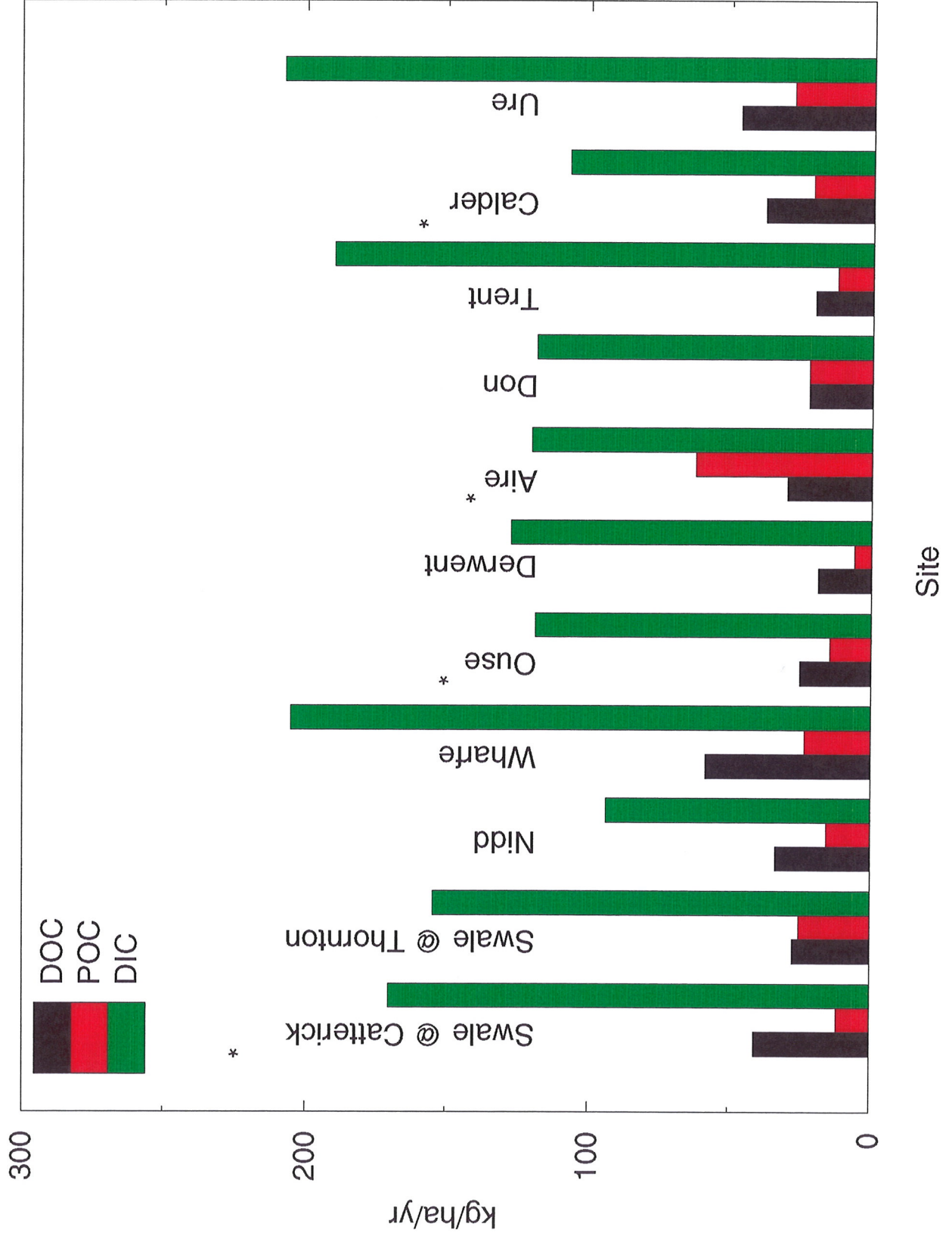
months, with TSP contributing up to 47% of the sample.

Vegetation plays an important role in the production of organic carbon within a catchment. A study in Olympic National Park, Washington, showed large additions of DOC from stemflow from Douglas-Fir, Western Hemlock and Western Redcedar trees [48]. Leaf litter from trees and other vegetation either falls onto the soil or falls directly into the stream from overhanging vegetation. The annual rate of litter return to the soil has been measured for some land uses. Cereals can contribute 1-2 t/ha organic carbon, compared with 2-4 t/ha for temperate grassland, 1.5-3 t/ha for coniferous forest and 1.5-4 t/ha for deciduous forest [13]. Root death and decay has also been estimated to be a third to a half of leaf fall contributions and timber fall to be at least equal to leaf fall contributions [13].

As well as vegetative sources, carbon can be added to the soil directly as fertiliser, e.g. farm yard manure (FYM), or as a by-product of cattle and sheep grazing the land, e.g. dairy cows grazing highly productive pastures can produce from 3.5 to 4.5 t FYM /ha/yr, equivalent to 2.1-2.7 t/ha/yr organic carbon [13]. FYM is widely used as an organic manure, e.g. over 1,003,000 ha of arable and grassland were treated in GB in 1993 [14], and it can be applied at a rate of 50 m³/ha [15]. As well as FYM, poultry manures, slurries and sewage sludge are also used as a source of organic matter, major nutrients and some trace elements [15]. DIC as ground limestone or ground chalk (collectively known as lime) is added to agricultural land where the soil pH falls below pH 6.2 for barley and 6.0 for other crops and grassland. Lime is added to bring the soil back up to pH 6.5 to a depth of 20 cm [15]. The amount of lime added and the extent is not known.

Organic and inorganic carbon entering the soil from precipitation, vegetation or agriculture is incorporated into the soil by the soil fauna and by the movement of water down the soil profile. The path taken by the water entering the soil and the antecedent condition of the soil affects the final carbon composition of the water as it enters the stream.

Organisms both on the surface and in the soil contribute to the turnover and amount of carbon entering the soil. In this study "living carbon", i.e. fauna, is not considered as part of the carbon pool, only the role played by fauna in the turnover of organic carbon. Earth worms play a large role in the decomposition of leaf litter in the soil. Estimates from feeding experiments have shown that a population of 120,000 adult worms per hectare can consume 25-30 t of cow dung annually [13]. Other mesofauna in the soil along with micro-organisms and macrofauna play an important role in the breakdown and turnover of organic matter and consequently the removal of DOC and POC from the soil in the soil water.

Organic matter entering the soil decomposes producing carbon dioxide and organic matter of a smaller molecular weight. Data from the Rothamsted classical field experiments, radiocarbon dating [22] and ^{14}C tracer experiments show the age of the different organic samples along with the gross turnover time of the organic matter for different plot studies. Organic matter in a sample taken in 1881 from an unmanured plot that had been growing wheat since 1843 showed small components of the soil to be up to 3700 years old (equivalent age) [21]. Other data indicate a gross turnover time for organic carbon of 16 years for plots using inorganic fertilisers and 22 years for unmanured plots [21]. A simple successful simulation of the organic carbon decay in the Rothamsted plots splits the decomposing carbon into five pools with half lives of 0.165, 1.69, 2.31, 49.5 and 1,980 years [21]. A map of the

current soil organic carbon stocks has been produced by the Soil Survey and Land Research Centre (SSLRC) and Macaulay Land Use Research Institute (MLURI) which estimates the total organic carbon content of the soil of GB at 21,784 million tonnes of carbon, with 87% of the total in Scottish soils and 75% of the total in Scottish peats [50].

Figure 19 shows the organic carbon content of each of the 1x1 km grid squares in the LOIS area. These data have been calculated from the SEISMIC soil series data [53] and the HOST classification system [54]. The total amount of organic carbon in the LOIS area is estimated to be 1,448 million tonnes, c. 52% of the total organic soil content (2773 million tonnes) of England and Wales [50].

One of the products from organic matter breakdown by microbes is the release of CO_2 into the soil water, soil air spaces and the atmosphere. Studies of two forested sites in the UK show that, as microbial activity increases during the summer months increased amounts of CO_2 are released to the atmosphere, with a maximum rate reported of 546 mg CO_2 /m^2/h. CO_2 release was also shown to be related to soil moisture conditions with low soil moisture limiting the breakdown of organic matter, thought to be restricting to the soil heterotrophs under severe drought and sandy soils [23].

Soil types can have a large affect on the distribution of DOC down the soil profile. In particular, DOC can bind to soil particles in mineral soils removing DOC from the soil water as it passes through the profile. In one study the adsorption of DOC was found to be pH dependent with a maximum occurring at pH 4.5 and the predominant mechanism of DOC retention being the physical adsorption on to the soil of hydrophobic organic solutes which in turn was dependent upon the iron minerals found in the soil [16]. An investigation at the Bear Brook site in Eastern Maine, USA, reports that mineral soils act as a buffer removing DOC from the soil water as it passes down through the soil horizon [17]. Water that bypasses the mineral soils during high flow conditions is shown to have higher DOC concentrations. Work at the Birkenes catchment in Norway demonstrates the removal of hydrophobic acids from the water as it passes through the E horizon. This differs from other studies where DOC is removed from association with the B horizon [18].

The presence of humic and fulvic acids in stream water cause a light to dark brown colouring of the water and is strongly associated with upland streams draining peatland moors [19]. Figure 20 shows the strong relationship between DOC, POC and the percentage of catchment covered by Winter Hill Peat, for some of the LOIS river monitoring sites. Although the consumption of coloured water is not harmful, aesthetically it is not pleasing and harmful substances can be produced when such water is chlorinated. One third of the drinking water in the UK is from upland sources and the periodic colour in these waters is an issue for water resources [9, 59]. Colour is thought to be produced from the aerobic decay of organic matter in peat which loses soil moisture during the summer months exposing organic matter previously in anaerobic conditions to the air. The decomposed organic matter dissolves into the soil water on rewetting and is subsequently leached to the stream. Decomposition of organic carbon also occurs under anaerobic conditions, but at a reduced rate. When peats become severely dried in the laboratory, loss of more than 35% of soil moisture, rewetting is prohibited because of macropore collapse and high suction-pressures found in micro-pores, which produce a delay in the leaching of DOC until the peat rewets [5].

Figure 19

1x1 km Soil Organic Carbon Dataset

Key

- 0 kt
- 15 kt
- 30 kt
- 45 kt
- 60 kt
- 75 kt
- 90 kt
- 105 kt
- 120 kt
- 135 kt
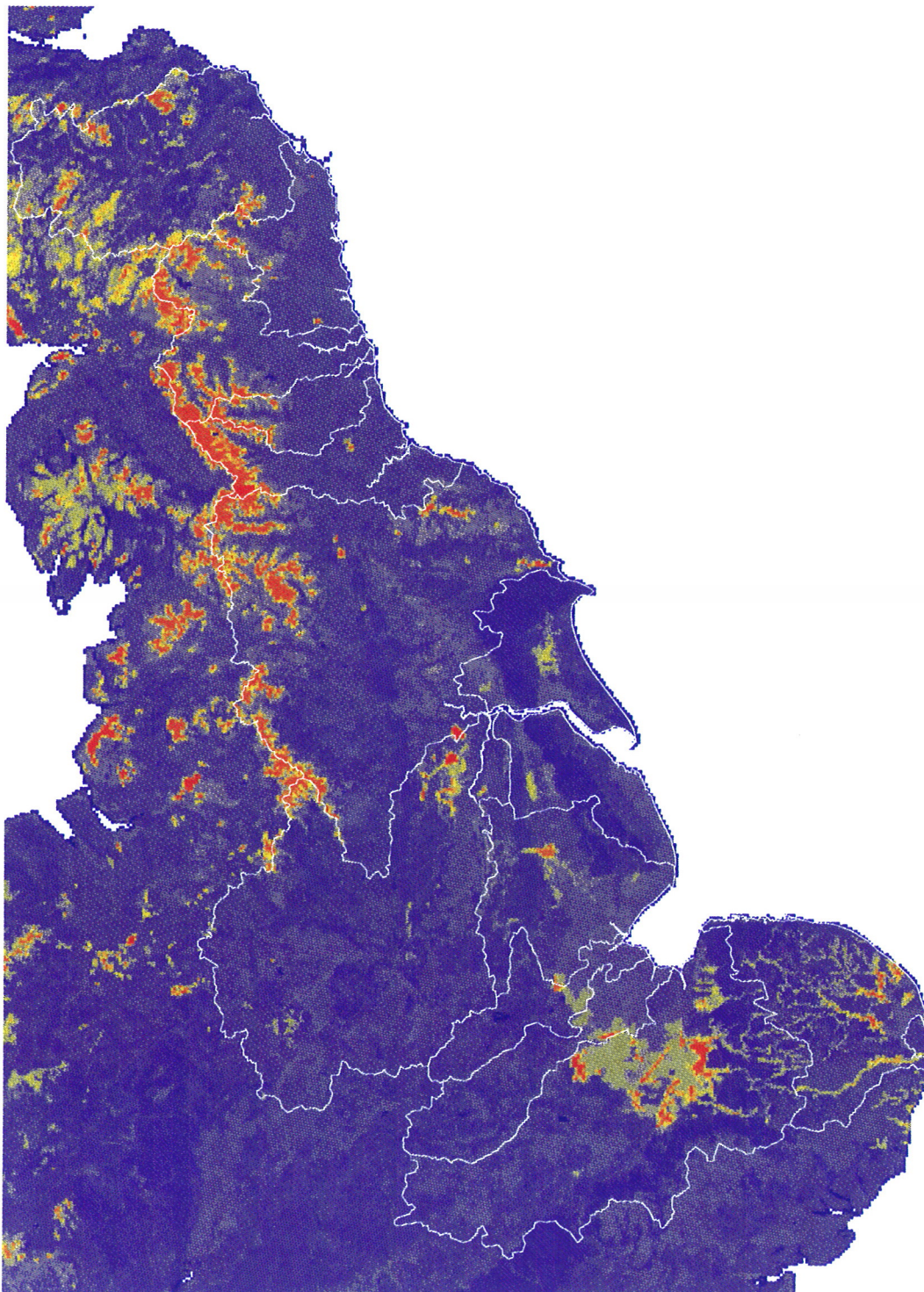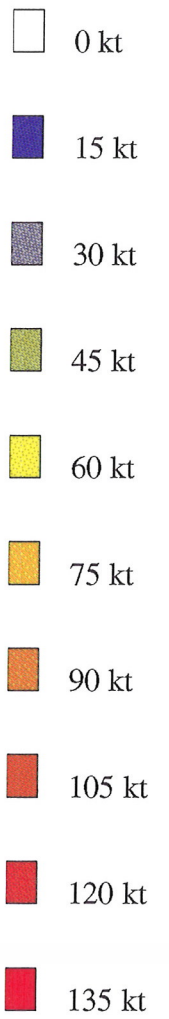
Load vs % Catchment Winterhill Peat

○ DOC   Correlation coefficient 0.89
□ POC   Correlation coefficient 0.74

Kg C/ha/yr

winterhill peat (%)
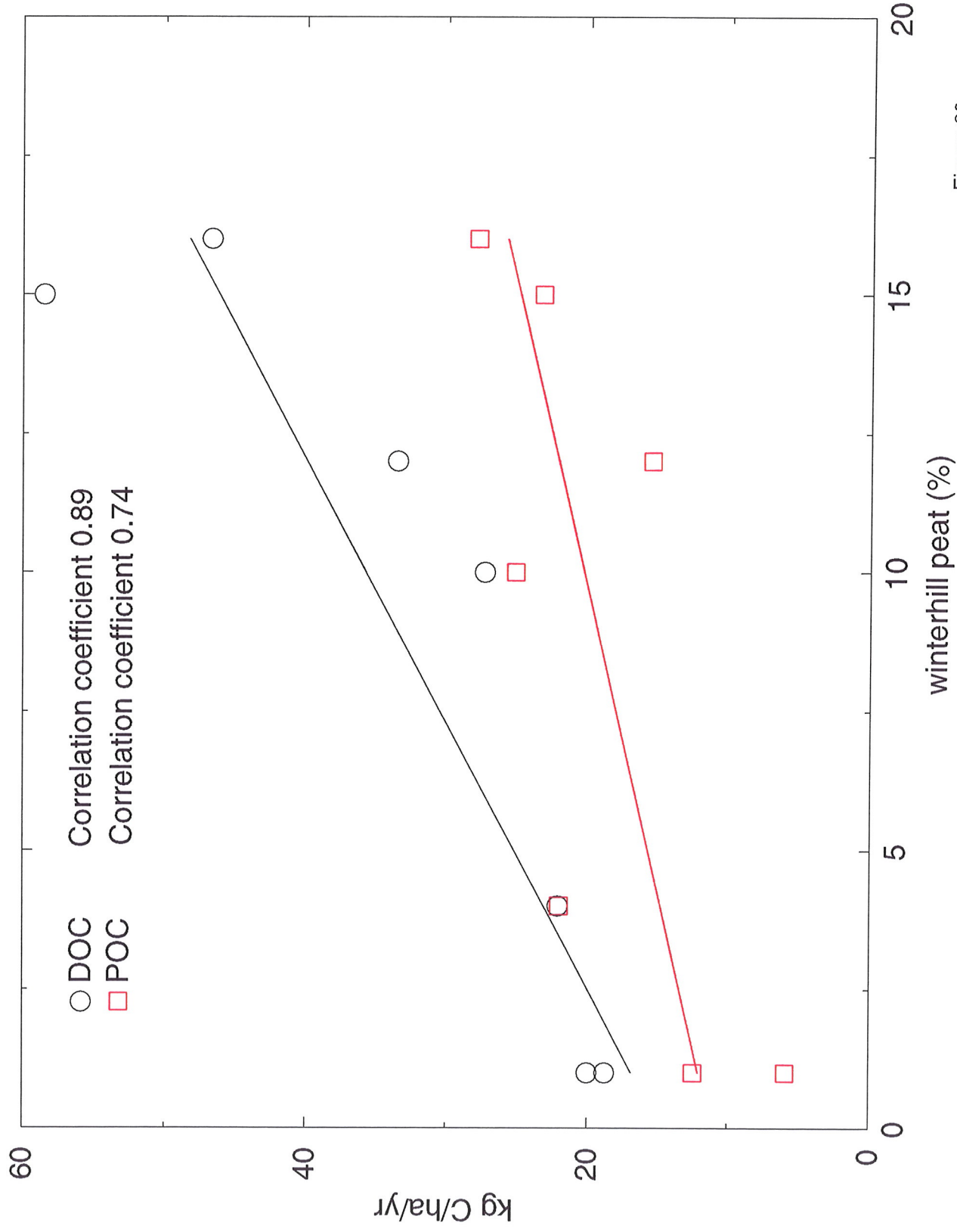
Figure 20

The bedrock, drift geology and soil of the LOIS region are undergoing continual erosion and weathering. This includes limestone weathering and the release of HCO_3^- into the aquifer, stream and soil water and can be found in the ground water in the region of the Triassic sandstone of the East Midlands and limestone in North Yorkshire. A short term (13 years) limestone weathering study in Australia showed erosion rates between 0.006 mm/yr and 0.013 mm/yr on exposure to subaerial erosion processes [28]. Another study, based in Scotland, using limestone tablets showed a mean erosional weight loss during the summer months of 0.503 g/yr and 0.055 g/yr during the winter months, with the difference attributed to the increased biological activity in the summer months [29]. Other work has demonstrated a strong correlation between soil pH and the degree of limestone weathering and shows rates of weathering at Tarn House, North Yorkshire of between 0.01 and 0.07 mm a^{-1} [47]. The limestone from the weathering and erosion processes will contribute carbonate to the stream water via the bedrock or soil, however the relative size of this carbon source compared to, say, liming is not at present clear.

3.2 Anthropogenic sources and sinks

Point sources from trade and sewage discharges are probably the largest sources of carbon entering the streams. Figure 21 shows the $c.1800$ trade (TDIS) and sewage (SDIS) point sources entering the rivers of the Yorkshire hydrometric area. There are very few data for carbon entering the streams either in the form of consents or as concentrations and flow. This is a serious omission and makes any mass balance or modelling study very difficult.

Water abstractions for potable, industrial or agricultural use occur within the LOIS area usually in terms of annual consents. These abstractions will remove water and carbon from the river system and act as sinks, perhaps returning the water to the river at a later stage with an altered chemistry. At present these data are not available.

3.3 Autochthonous sources and sinks

The carbon in the river in the form of DOC, POC or DIC is further modified as in-stream processes take effect. Radio-carbon studies, utilising the bomb effect (sharp increases in world ^{14}C concentrations because of nuclear bomb testing in the late 1950s early 1960s), have shown that the majority of carbon in streams is less than forty years old [22]. Biota play an important role in the uptake of DOC, the breakdown of POC to DOC and the breakdown of DOC to smaller molecular weights within a complex food web including the effect of bacteria, predators, shredders, gatherer-microbivores, gatherer-miners, scraper-gatherers and net-building filterers [20]. The net effect of the stream biota on carbon concentrations and loads is not clear and requires a great deal of further work.

The process of organic carbon degradation in the soil releases CO_2 into the surrounding air spaces and soil water. The soil water is unable to equilibrate with the atmosphere and large partial pressures of CO_2 are formed which move toward an equilibrium with the atmosphere resulting in CO_2 release from the stream. This process is known as degassing and is a sink for carbon in the stream. Excess pCO_2 ($epCO_2$) in stream waters have been recorded between 10 and 100 fold atmospheric pressure [30]. A study in a small upland headwater catchment in Scotland reported $epCO_2$ to fall from greater than ten times atmospheric at the source of the stream down to 1.5 atmospheric 2 km downstream, representing a carbon flux of free CO_2

Figure 21

Discharge Sites in LOIS Area

Key

△ — TDIS

○ — SDIS
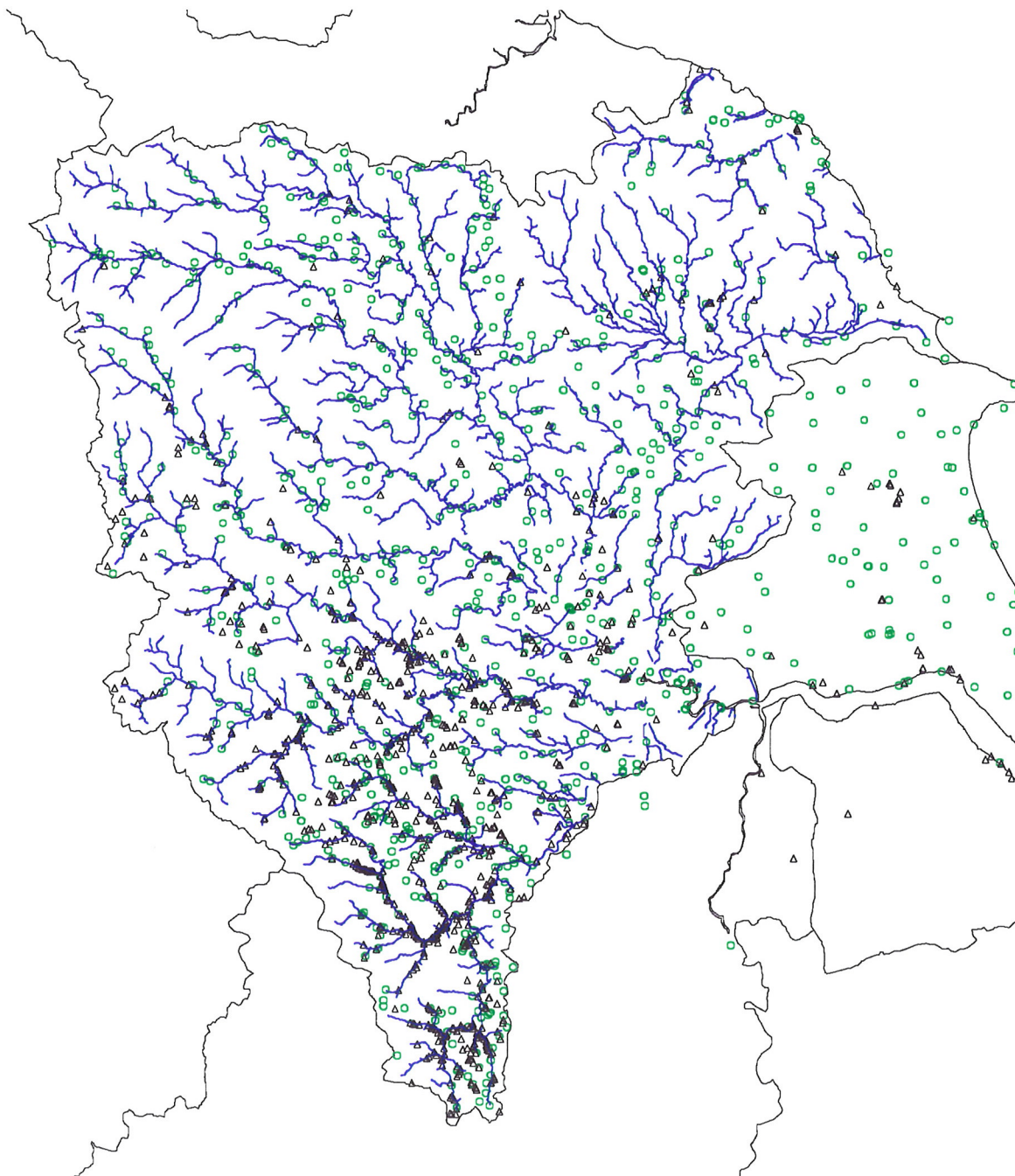
of 4.4 kg/ha/yr [30].

Degradation of DOC can occur on exposure to natural sunlight in rivers. There are two processes occuring, bleaching and the mineralization of DOC to smaller molecular weight compounds and CO_2. A study has shown up to 67% reduction in colour and 32% reduction in DOC concentration after a twelve day exposure to sunlight [27]. The study also showed that degradation was highest for high molecular weight compounds and when microbial activity was suppressed.

Groundwater is both a source and a sink for DOC and DIC in the LOIS area. There has not been an extensive study into the role carbon plays in groundwater quality, however some data are available. Triassic sandstone and chalk aquifers are present over much of the LOIS area. A study of 83 wells and boreholes in the Triassic sandstone aquifer of the Vale of York showed a mean HCO_3^- concentration of 348 mg/l, with a minimum of 189 mg/l and a maximum of 549 mg/l [24]. Spring discharges were estimated at 9.8 Ml/d without abstractions from the aquifer. An accurate measure of the ground water contributing to stream flow in the LOIS area is not known. However, there is a reasonable size base flow (table 1) to support flow in the main rivers over the summer period and this is reflected in the base flow index (BFI), which is the ratio of base flow to recorded hydrograph [60]. An estimate of the flow from East coast aquifers to the North Sea gave 1000 m³/d/km coast line [26]. Concentrations of DOC have been measured in the Triassic sandstone aquifer which contributes to the flow of the river Trent of between 0.1 and 1.25 mg/l with the highest concentrations found near the surface and a mean of c. 1 mg/l [25]. DOC concentrations from the Triassic limestone were between 0.8 and 1.5 mg/l [25].

In the stream POC is part of the suspended sediment transport system and associated benthic organic matter [39] and is not covered here.

Table 1
Base flow indices for the LOIS rivers

River	Gauging site number	BFI
Swale at Richmond	27024	0.35
Swale at Crakehill	27071	0.44
Nidd at Skip Bridge	27062	0.29
Wharfe at Flint Mill Wear	27002	0.39
Ouse at Skelton	27009	0.43
Derwent at Stamford Bridge	27015	0.69
Aire at Beal Weir	27003	0.53
Don at Doncaster	27021	0.58

Trent at North Muskham	28022	0.65
Calder at Newlands	27004	0.53
Ure at Westwick Lock	27007	0.4

4. Simulating carbon flux

Models of carbon in ecosystems vary from small scale simulations of the complexation properties of humic substances [31] to the large scale modelling of carbon budgets for assessing carbon emissions from a managed forest under differing management scenarios [32]. Exponential organic matter decay in soil models exist [21] along with statistical and process based simulations of water colour [9, 33, 57], highly complex models of soil dynamics [34] and carbon exchange between atmosphere, landuse and ecosystems applied on a world scale [35, 55], simulations of POM entrainment and deposition on river beds [39], models of the carbon cycling through the aquatic food web [39], end-member mixing models [37] and models of DOC dynamics in stream waters [36, 40].

The carbon model to be developed will be incorporated into an existing three-dimensional distributed flow model, referred to as a delivery model, and a river model, QUASAR [58]. The model required has to be process based and applicable at a regional scale and over a hundred year time period running on a daily time step. The simulation has to include both the terrestrial (delivery model) and in-stream processes (river model). None of the above simulations of carbon flux meet all of these requirements, however some of the them, e.g. the process based colour model [9], can be incorporated into the final integrated delivery model.

4.1 Mass balance calculations

The allochthonous, anthropogenic and autochthonous sources and sinks along with the various processes that involve carbon vary in magnitude [Section 3] and consequently vary in importance to the modelling process. Where data for sources are available it is possible to calculate an annual load entering and leaving a catchment and this has been done for the catchment area upstream of Thornton Manor on the river Swale. Table 2 below shows the loads that can be calculated using the data given in Section 3 above.

Table 2
Gains and Loses of Organic Carbon Upstream of Thornton Manor on the River Swale

Form	Source/Sink	Value
Gains of organic carbon		
POC	Precipitation[1]	4,025 t C/yr
DOC	Precipitation[2]	5,750 t C/yr
Organic C	Land use[3]	384,176 t C/yr

43

Organic C	Cattle manure[4]	277,632 t C/yr
Organic carbon in soil		
TOC	Organic matter[5]	42,987,000 t C
Losses of organic carbon		
CO_2	Decomposition from forest land use[6]	154,097 t C/yr
DOC	River load[7]	3,722 t C/yr
POC	River load[7]	3,429 t C/yr

[1] A mean POC concentration in precipitation of 3.5 mg/l [12] and a mean annual rainfall of 1.15×10^{12} l [46].

[2] A mean DOC concentration in precipitation of 5 mg/l [10] and a mean annual rainfall of 1.15×10^{12} l.

[3] The amount of carbon entering the soil was calculated from data about land use and litter fall [13] (see section 3.1).

[4] Data from the MAFF Small Area Statistics database shows that the area of land used for cattle was 115,680 ha [56]. This equates to an input of 277,632 t C/yr using 2.4 t C/ha/yr FYM from cattle [13].

[5] Calculated from map of soil carbon content (section 3.1).

[6] Mean carbon dioxide release, from forest soils during decomposition, can be estimated to be c. 350 mg/m²/h [23] over an area of 5026 ha.

[7] See section 2.3.

Using the data from table 2 the total organic carbon entering the catchment is 671,583 t C/yr. The total carbon leaving the catchment is 161,247 t C/yr, with a carbon store in the soil of 42,987,000 t C. These figures give a net increase in carbon of 510,336 t C/yr, however no allowance has been made for decomposition from land uses other than forest. If it is assumed that there is no net change in the catchment carbon content, i.e. the catchment is in equilibrium in terms of carbon, then the mean rate of decomposition for the other land classes in the catchment is c. 43 mg CO_2/m²/hr or 3.8 t C/ha/yr. This figure seems reasonable given that the lowest decomposition rate measured in a forested catchment was c. 100 mg CO_2/m²/hr [23] and other land uses are likely to have a rate lower than this.

The above estimates do not account for the application of FYM and slurries to the land, liming and livestock other than cattle. Once in the soil of there are many processes that occur that will affect the amount and type of carbon entering the river, however these are very difficult to quantify. Once the carbon enters the stream there are more processes that occur, but for which few quantifiable data are available, in particular the biotic processes. One process where data exists is the mechanism of degassing. Estimates in a Scottish stream put losses of CO_2 at 4.4 kg/ha/yr [section 3.3], however given the higher epCO_2 values found at the LOIS monitoring sites [section 2.2] these losses are likely to be higher. Another quantifiable autochthonous loss is the break down of DOC by sunlight, estimates of which show 32% losses within twelve days. However, given that the travel time for water in the LOIS rivers can be measured in hours, this is unlikely to be a major sink of DOC in rivers, but may be a significant loss for water stored in reservoirs. DIC is not included in these calculations as there are few data on the inputs and conversion of DIC, DOC and POC.

4.2 Modelling carbon in the catchment and river

In order to place carbon into the delivery and river models of LOIS it would seem to be best to start with a simple model for each of the three forms (DOC, POC and DIC) and build up the level of complexity as required to validate against the observed data in the river and as more data becomes available on the various processes involved.

4.2.1 Modelling DOC in the catchment

One starting point for the DOC delivery model is to group all of the sources, sinks and processes that occur in the soil together into a single reservoir of carbon. This pool of carbon decomposes releasing DOC in the soil water. Models of this nature have been shown to work for colour and DOC in upland catchments [20, 34, 58].

It is proposed that DOC should be modelled as a function of soil moisture and soil type in the delivery model. These functions are derived from studies on peat cores, at the University of Leeds, taken from Scar House, Yorkshire [59]. The rate of CO_2 evolution, from peat cores of 10 cm radius, after 200 hours and at differing soil moisture content was measured. It was assumed that the rate of CO_2 release was equal to the rate of production of DOC. The generation of DOC from Winter Hill peat (HOST class 29), which is the dominant soil type at Scar House, can be simulated as (Figure 22):

$$c = \exp(0.053s)-1 \ ; \ s<=71.4$$

$$c = 9253\exp(-0.07624s) \ ; \ s>71.4$$

Where, c - organic carbon (mg C/200 hours/0.031 m^2), s - percentage of maximum soil water (*i.e.* soil moisture/maximum soil moisture * 100). The units for organic carbon can be converted to kg/ha/day by multiplying by 0.038.

The resultant release of carbon (kg C/ha/day) is then scaled for the given HOST class of the soil using table 3 [54]. The scaling factor was derived from the amount of organic matter in each HOST class which in turn was calculated from the SEISMIC data set [53]. HOST class 29 is given a scaling factor of one. It was assumed the rate of release of DOC was similar for each soil HOST class.

The production of DOC for all HOST classes, except class 29, occurs in the top layer of the soil as represented in the delivery model. DOC is produced from HOST class 29 throughout the soil profile.

4.2.2 Modelling POC in the catchment

POC will be modelled as 10% of suspended sediment throughout the year, with the exception of 40 days representing the period of leaf fall for deciduous trees. On day 290, as used in MORECS [61], POC will be dependent upon day number as follows:

$$y=-0.05(x-310)^2+30 \ ; \ 290>=x<=330$$

45

Release of organic carbon from peat

Organic carbon
(mg C/200 hrs/0.031 m²)

Percentage of maximum soil water content
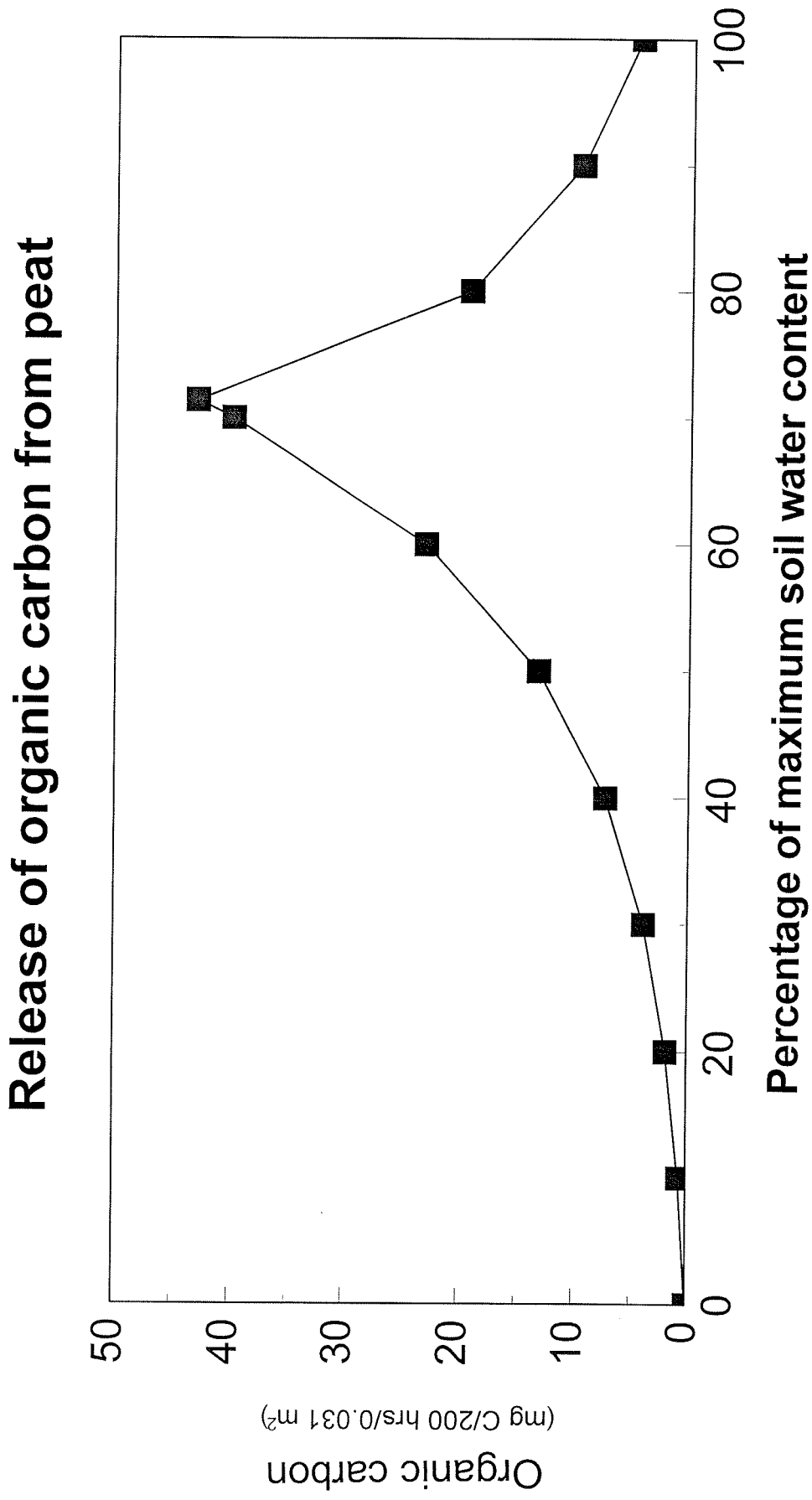
Figure 22

Where, y = POC (percentage of suspended sediment), x = day number (1st January is day 1).

This function describes a parabola passing through a maximum value of 30 on day 310. This means that on day 310 30% of the suspended sediment is in the form of POC.

Table 3

Scaling factor for DOC model based on HOST class.

HOST class	Scaling factor
1	0.114
2	0.259
3	0.153
4	0.173
5	0.184
6	0.111
7	0.194
8	0.13
9	0.21
10	0.279
11	1.089
12	0.966
13	0.157
14	0.096
15	0.33
16	0.084
17	0.153
18	0.097
19	0.278
20	0.132
21	0.186

22	0.433
23	0.144
24	0.138
25	0.128
26	0.187
27	0.519
28	0.0
29	1.0

4.2.3 Modelling DIC in the catchment

DIC will be generated in the basal layer of the delivery model at the rate of 1.6 kg/ha/day where the geology is classified in bands four and five. The rate of release was derived from an empirical relationship based on the geology of the river Swale and the calculated DIC load for the river (section 2.3). These represent geology such as Limestone, Durness Limestone and Upper Chalk [62].

4.2.4 Modelling carbon in the river

In the river model, because the majority of the processes are biotic, DOC should initially be modelled as conservative. Later as data become available, processes such as degassing and the breakdown of POC to DOC can be included. POC and DIC (main form HCO_3^-) are also initially modelled as conservative in the river model; riverine processes will be added as data becomes available.

5. References

[1] Natural Environmental Research Council, Land Ocean Interaction Study (LOIS), Implementation Plan for a Community Research Project, July 1994, Pubs. Natural Environment Research Council, ISBN 1 85531 121 6.

[2] Schindler, D.W., 1981, Interrelationships Between the Cycles of Elements in Freshwater Ecosystems. In: Some Perspectives of the Major Biogeochemical Cycles, Likens, G.E. (Ed), Pubs. SCOPE.

[3] Likens, G.E., Bormann, F.H. and Johnson, N.M., 1981, Interactions between Major Biogeochemical Cycles in Terrestrial Ecosystems. In: Some Perspectives of the Major Biogeochemical Cycles, Likens, G.E. (Ed), Pubs. SCOPE.

[4] Hall, R.O., 1995, Use of a stable isotope addition to trace bacterial carbon through a stream food web, J. N. Am. Benthol. Soc., 14(2), 269-277.

[5] Mitchell, G. and McDonald, A.T., 1992, Discolouration of water by peat following induced drought and rainfall simulation, Wat. Res., **26**(3), 321-326.

[6] Alberts, J.J., Griffin, C., Gwynne, K. and Leversee, G.J., 1994, Binding of natural humic matter to polycyclic aromatic hydrocarbons in rivers of the southeastern united states, Wat. Sci. Tech. **30**(10), 199-205.

[7] Tipping, E. and Hurley, M.A., 1988, A model of solid-solution interactions in acid organic soils, based on the complexation properties of humic substances, Journal of Soil Science, **39**, 505-519.

[8] Neal, C. and Hill, S., 1994, Dissolved inorganic and organic carbon in moorland and forest streams: Plynlimon, Mid-Wales, Journal of Hydrology, **153**, 231-243.

[9] Naden, P., 1992, Modelling water colour in upland catchments, Final report to Yorkshire Water plc. Institute of Hydrology Report.

[10] Hope, D., Billet, M.F. and Cresser, M.S., 1994, A review of the export of carbon in river water: fluxes and processes, Environmental Pollution **84**, 301-324.

[11] Cosby, B.J., Hornberger, G.M., Galloway, J.N. and Wright, R.F., 1985, Modelling the effects of acid deposition: assessment of a lumped parameter model of soil water and stream water chemistry, Water Resources Research, **21** (1), 51-63.

[12] Hadi, D.A., Crossley, A. and Cape, J.N., 1995, Particulate and dissolved organic carbon in cloud water in southern Scotland, Environmental Pollution, **88**, 299-306.

[13] White, R.E., 1979, In: Introduction to the principles and practice of soil science, p 24, Blackwell scientific publications, London.

[14] MAFF, FMA, SO, 1993, The British survey of fertiliser practice - fertiliser use on farm crops, HMSO.

[15] MAFF, 1994, Fertiliser recommendation for agricultural and horticultural crops, RB209, 6th edition, HMSO.

[16] Jardine, P.M., Weber, N.L. and McCarthy, J.F., 1989, Mechanisms of dissolved organic carbon adsorption on soil, Soil Sci. Soc. Am. J. **53**, 1378-1385.

[17] David, M.B., Vance, G.F. and Kahl, J.S., 1992, Chemistry of dissolved organic carbon and organic acids in two streams draining forested watersheds, Water Resources Research, **28**(2), 389-396.

[18] Easthouse, K.B., Mulder, J., Christophersen, N. and Seip, H.M., 1992, Dissolved organic carbon fractions in soil and stream water during variable hydrological conditions at Birkenes, Southern Norway, Water Resources Research, **28**(6), 1585-1596.

[19] Mitchell, G. and McDonald, A.T., 1992, Discolouration of water by peat following

induced drought and rainfall simulation, Wat. Res., 26(3), 321-326.

[20] Hall, R.O., 1995, Use of a stable carbon isotope addition to trace bacterial carbon through a stream food web, J. N. Am. Benthol. Soc., 14(2),269-277.

[21] Jenkinson, D.S., and Rayner, J.H., 1977, The turnover of soil organic matter in some of the Rothamsted classical experiments, Soil Science, 123, 298-305.

[22] Schiff, S.L., Aravena, R., Trumbore, S.E. and Dillon, P.J., 1990, Dissolved organic carbon cycling in forested watersheds: a carbon isotope approach, 26(12), 2949-2957.

[23] Anderson, J.M., 1973, Carbon dioxide evolution from two temperate, deciduous woodland soils, J. Applied Ecology, 10(2), 361-378.

[24] Reeves, M.J., Birtles, A.B., Courchee, R. and Aldrick, R.J., 1974, Groundwater resources of the Vale of York, Water Resources Board, HMSO.

[25] Burgess, W., 1995, Personal communication, UCL.

[26] Buckley, D.K., 1994, A review of the importance of coastal groundwater studies in the LOIS project, British Geological Survey technical report WD/94/50, NERC.

[27] Hongve, D, 1994, Sunlight degradation of aquatic humic substances, Acta hydrocim. hydrobiol. 22(3), 117-120.

[28] Smith, D.I., Greenaway, M.A., Moses, C. and Spate, A.P., 1995, Limestone weathering in eastern Australia, part 1: erosion rates, Earth surface processes and landforms, 20, 451-463.

[29] Trudgill, S.T., 1977, Problems in the estimation of short-term variations in limestone erosion processes, Earth surface processes, 2, 251-256.

[30] Dawson, J.J.C., Hope, D., Cresser, M.S. and Billet, M.F., 1995, Downstream changes in free carbon dioxide in an upland catchment from Northeastern Scotland, J. environ. qual., 24, 699-706.

[31] Tipping, E. and Hurley, M.A., 1988, A model of solid-solution interactions in acid organic soils, based on the complexation properties of humic substances, Journal of soil science, 39, 505-519.

[32] Karjalainen, T., Kellomäki, S. and Pussinen, A., 1995, Carbon balance in the forest sector in Finland during 1990-2039, Climatic change, 30, 451-478.

[33] Naden, P.S. and McDonald, A.T., 1989, Statistical modelling of water colour in the uplands: the upper Nidd catchment 1979-1987, Environmental pollution, 60, 141-163.

[34] Goto, N., Sakoda, A. and Suzuki, M., 1994, Modelling of soil carbon dynamics as a part of carbon cycle in terrestrial ecosystems, Ecological modelling, 74, 183-204.

50

[35] Suzuki, M., Goto, N. and Sakoda, A., 1993, Simplified dynamic model on carbon exchange between atmosphere and terrestrial ecosystems, Ecological modelling, **70**, 161-194.

[36] Grieve, I.C., 1991, A model of dissolved organic carbon concentrations in soil and stream waters, Hydrological processes, **5**, 301-307.

[37] Easthouse, K.B., Mulder, J, Christophersen, N., 1992, Dissolved organic carbon fractions in soil and stream water during variable hydrological conditions at Birkenes, Southern Norway, Water resources research, **28**(6), 1585-1596.

[38] Vogt, R.D., Seip, H.M. and Ranneklev, S., 1992, Soil and soil water studies at the HUMEX site, Environment international, **18**, 555-564.

[39] Webster, J.R., 1983, The role of benthic macroinvertebrates in detritus dynamics of streams: A computer simulation, Ecological monographs, **53**(4), 383-404.

[40] Kundzewicz, Z.W, Szpakowska, B. and Sibrecht. R., 1994, Modelling of chemicals dissolved in waters in an agricultural watershed, In: Hydrological, chemical and biological processes of transformation and transport of contaminants in aquatic environments, proceedings of the Rostov-on-don symposium, May 1993, IAHS Publ. no. 219.

[41] Watts, C. and Moore, R., 1994, WIS reference manual for LOIS data, IH internal document, unpublished.

[42] Neal, C., 1988, Bicarbonate estimation from alkalinity determinations for neutral to acidic low alkalinity natural waters: theoretical considerations, Hydrological sciences, **33** (6), 619 - 623.

[43] Marsh, T.J., 1995, Hydrological summary for Great Britain, January, National Water Archive, Institute of Hydrology, NERC.

[44] Littlewood, I.G., 1992, Estimating contaminant loads in rivers: review, Institute of Hydrology Report No. 117, NERC, ISBN 0 948540 38 9.

[45] Walling, D.A. and Webb, B.W., 1985, Estimating the discharge of contaminants to coastal waters by river: some cautionary comments, Marine Pollution Bulletin, **16** (12), 488-492.

[46] Marsh, T.J. and Lees, M.L. (eds), 1993, Hydrological data United Kingdom, Hydrometric Register and statistics 1986 -1990, Institute of Hydrology and British Geological Survey, NERC, ISBN 0 948540 44 3.

[47] Trudgill, S.T., 1985, Field observations of limestone weathering and erosion in the Malham district, North Yorkshire, Field Studies **6**, 201-236.

[48] Edmonds, R.L., Thomas, T.B. and Blew, R.D., 1995, Biogeochemistry of an old-growth forested watershed, olympic national park, washington, Water Resources Bulletin, **31**(3), 409-419.

51

[49] Robson, A.J., Neal, C., Currie, J.C., Virtue, W.A., Ringrose, A., 196, The water quality of the Tweed and its tributaries, Institute of Hydrology Report No. 128, NERC.

[50] Howard, P.J.A., Loveland, P.J., Bradley, R.I., Dry, F.T., Howard, D.M. and Howard, D.C., 1995, The carbon content of soil and its geographical distribution in Great Britain, Soil Use and Management 11, 9-15.

[51] Crisp, D.T. and Robson, S., 1979, Some effects of discharge upon transport of animals and peat in a north Penine headstream, Journal of Applied Ecology, 116, 721-736.

[52] Webb, B.W., Phillips, J.M., Walling, D.E., Littlewood, I.G., Watts, C. and Leeks, G., 1996, Load estimation methodologies for British rivers and their relevance to the LOIS RACS(R) programme, Special Volume Science and the Total Environment (in press).

[53] Hallett, S.H., Jones, R.J.A. and Keay, C.A., 1993, SEISMIC: A spatial environmental information system for modelling the impact of chemicals. In: Environmental modelling: the next 10 years, A report of a symposium held on 16 December 1992 at the Society of Chemical Industry, London, eds Stebbing, A,R.D., Travis, K. and Matthiessen, P., SETAC - Europe, UK branch, pp40-49.

[54] Boorman, D.B., Hollis, J.M. and Lilly, A., 1996, Hydrology of soil types: a hydrologically-based classification of the soils of the United Kingdom, Institute of Hydrology, Report No. 126, NERC.

[55] Esser, G. and Kohlmaier, G.H., 1991, Modelling terrestrial sources of nitrogen, phosphorus, sulphur and organic carbon to rivers, In: biogeochemistry of major world rivers, Degens, E.T., Kempe, S. and Richey, J.E. (Eds), SCOPE, Pubs. John Wiley and Sons Ltd.

[56] MAFF, 1992, Agricultural and horticultural census: 1 June 1992, Ministry of Agriculture, Fisheries and Food, Government buildings, Epsom Rd., Guilford, Surrey.

[57] Boyer, E.W., Hornberger, G.M., Bencala, K.E. and McKnight, D., 1996, Overview of a simple model describing variation of dissolved organic carbon in an upland catchment, Ecological Modelling, 86, 183-188.

[58] Lewis, D.R., 1995, Application of QUASAR to the Yorkshire Ouse, LOIS working note No. 4. Institute of Hydrology, UK.

[59] McDonald, A.T., Mitchell, G.N., Naden, P.S. and Martin, D.S.J, 1991, Discoloured water investigations: final report to Yorkshire Water Plc., University of Leeds, School of geography.

[60] Gustard, A, Bullock, A. and Dixon, J.M., 1992, Low flow estimation in the United Kingdom, Report No. 108, Institute of Hydrology, NERC.

[61] Thompson, N., Barrie, I.A. and Ayles, M., 1982, The meteorological office rainfall and evaporation calculation system (MORECS) (July 1981), Meteorological office, Hydrological memorandum No. 45, H.M.S.O.

[62] British Geological Survey, 1977, Hydrogeological map of England and Wales.