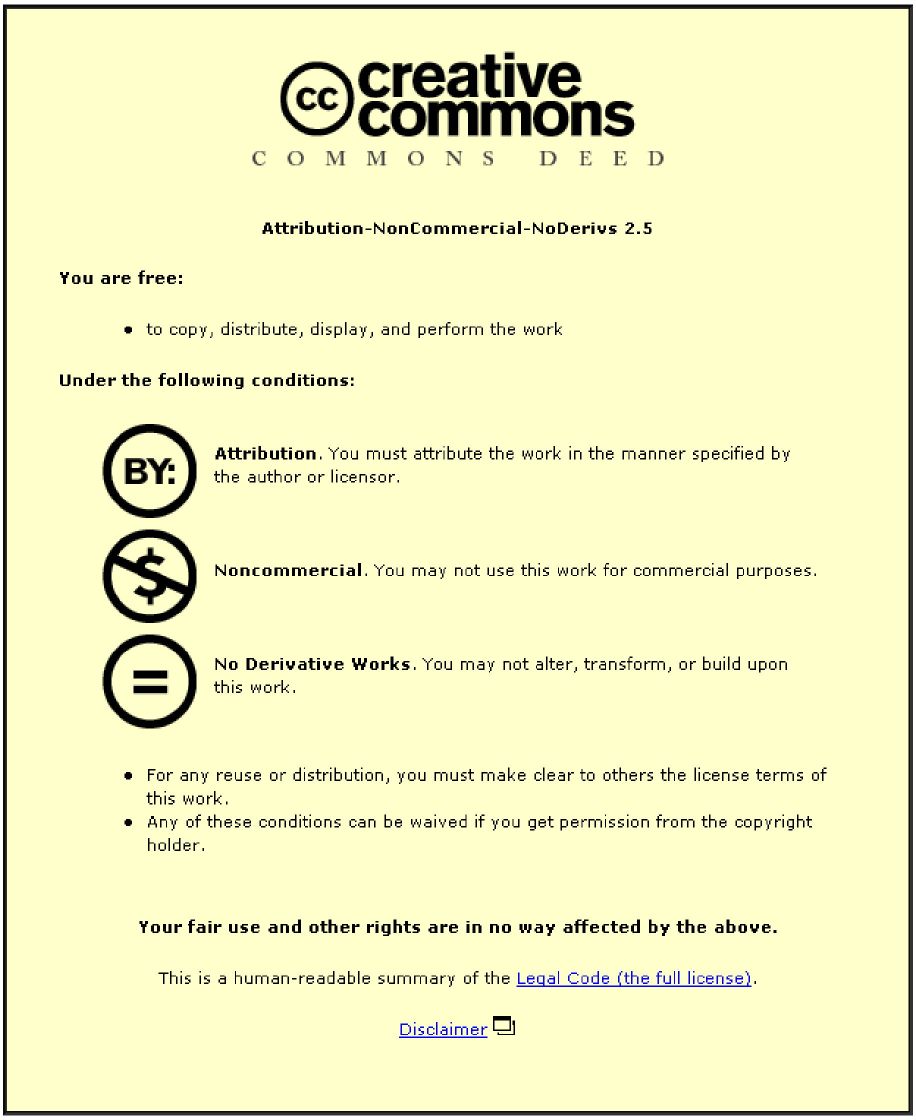

WATER CHEMISTRY VARIATIONS BELOW REGULATING RESERVOIRS IN GREAT BRITAIN.

by

TIMOTHY ROBERT FOULGER.

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ABSTRACT.

The downstream influence of storage reservoirs upon river water chemistry is an area largely devoid of literature. Yet approximately fifty per cent of such reservoirs in Great Britain significantly regulate flow, both by flood control, and increasingly through irregular but discrete large-volume releases. Natural patterns of stream water chemistry are shown to be disturbed by the effects of Man, through changing land-use and effluent discharge. Moreover, the establishment of a reservoir in the head waters of a major river, can change the water quality regime for a considerable distance below the dam. Changing patterns of river water chemistry, resulting from upstream impoundment, take place over different time scales. Two contrasting scales of impact are identified, namely annual or seasonal patterns, and short term variations associated with rapid, artificial flow fluctuations. In order to examine these impacts, different reservoir/river systems were studied. (1) To ascertain the seasonal reservoir influence, data were analysed for the River Derwent, Derbyshire, for the period 1977-1984. (2) To assess the instantaneous effects of large volume releases, three regulated rivers were investigated; the Afon Tryweryn in North Wales, the River Washburn in North Yorkshire and the River Tyne in Northumberland.

Monthly intensive spatial surveys of selected water quality parameters, namely, nitrate, calcium, pH and conductivity, together with Water Authority data are used to model the seasonal influence of the Derwent reservoir system. River regulation is shown to have changed the chemical nature of the river for approximately fifty kilometres below Ladybower Reservoir. Seasonal changes are related to the artificial control of the relative contributions to stream flow, from gritstone and limestone sources, and to discharge independent chemical patterns.

Water quality changes along short reaches, of up to fifteen kilometres, were monitored for thirty controlled reservoir releases on the Tryweryn, Washburn, and North Tyne, in order to examine the effects of rapid artificial short-term flow fluctuation. In each case, marked water quality changes were recorded. These are characterised by an initial rise in conductivity - and reflected by calcium concentration, associated with the onset of discharge increase, followed by steady dilution to a constant low sometime after the attainment of maximum stage. This pattern is demonstrated to relate not only to the routing of released water, but also to the dispersion of solutes from in-channel sources. Standard kinematic routing models were found to be inapplicable to reservoir release waves in the rough boundary boulder bed, upland channels.

Finally, the modelling of water quality variations in regulated rivers are shown to require an improved understanding of in-channel biogeochemical processes, associated with extended residence times, and dead zone storage, and for upland, boulder bed channels at least, of the relationship between wave routing and water movement. The effects of such water movement on downstream quality are found to be dependent upon regulation policy, and the relative contribution to flow from tributary inputs. Tributary flood solutes may be stored in the main channel to be released, and hence depleted rapidly by reservoir releases. The implications of this are suggested; regulation strategy must consider not only hydrological and river form aspects, but also the significant water chemistry changes that can be induced by such management policies.

INTRODUCTION.

"...for the rivers could now be regarded
as aqueducts, provided as it were free of
charge." T. Margerison, 1976.

Margerison (1976) promotes the view of rivers as inert features of landscape - natural aqueducts for the distribution of water. Another popular view is of rivers as natural sewers for the transport, and removal, of the waste products from natural and anthropogenic processes (Petts, 1985). In reality, these two views are intimately linked. Water supply management is as much to do with quality considerations as it is with quantities and river regulation strategies must consider the full range of consequences. Rivers are geomorphologically and ecologically dynamic components of the Biosphere and river regulation strategies must show some sympathy for these issues not least to enhance the broader resource potential in terms of recreation, amenity and education. This thesis investigates the effects of river regulation by large dams on downstream water chemistry for selected British upland rivers.

i. River Regulation: The significance.

River regulation has become a common operational procedure for water resources management, replacing direct-supply methods in many countries. The number of reservoirs constructed has doubled since 1950 (Beaumont, 1978), in response to the demand for water and for the use of floodplain land, and over fifteen percent of the river runoff in Europe is now regulated (Lvovitch, 1973). Increasingly, reservoir releases to meet hydro-electric power demands in particular, are becoming a prominent characteristic of regulated rivers. Furthermore, in Great Britain at least, considerable interest is being given to a 'national grid' water distribution network, based on regulating the flow of rivers by means of reservoirs and groundwater pumping schemes. In this way, even in the driest year, the average amount of available water could be at least twice the amount required (Margerison, 1976). Such regulation not only alters the flow regime of a river, through the suppression of high flows and the augmentation of low flows, but significantly influences channel water chemistry. Even without this grandiose national water supply network scheme, regulating reservoirs and the associated river systems are increasingly being utilised for major water resources development projects.

ii. Water quality of river-reservoir systems.

Rivers, lakes and reservoirs are fundamentally related in terms of water quality to the catchment ecosystems from which their waters are derived (Petts and Foster, 1985), but hydrodynamic and biogeochemical processes within water bodies are also important.

iia. The importance of river water quality.

River water quality implies different things to different people, nevertheless whatever the criteria adopted, two phenomena for users are universally objectionable. Firstly, a gradual yet preventable decline in quality e.g the acidification of upland water bodies (Almer,1974; Wright, 1984), or the nitrification of groundwater supplies (Tomlinson, 1970; Garnett, 1975). Secondly, rapid large changes in water chemistry induced through accidental pollution spillages (Critchley, 1981), or sudden hydrologic events e.g natural and artificial floodwaves, and storm sewage overflow. Regulation can alter water quality in both cases due to potential changes being induced in the impounded water body itself, and in the river which it is regulating.

iib. The river system.

The dominant factors controlling the transport of solutes in stream systems can be divided into three groups:- 1) those that are primarily physical, such as advection and dispersion, 2) chemical reactions between dissolved constituents or between dissolved materials and stream solids, and 3) reactions between dissolved solids and the stream biota (Douglas al, 1972). Reservoir regulation of streams will influence each of these factors. Physically through the nature of flow regulation, chemically through the nature of the water released, and ecologically according to both the volume and the nature of the artifical flow. Thus, regulation influences upon stream water quality may be due to either hydrological factors or the changing chemical nature of the river, brought about by impoundment.

iic. The reservoir system.

A reservoir must be considered as a dynamic trophic system in which natural and regulated flow dynamics interact with thermal stratification and community metabolism to control the chemical dynamics within the impoundment, and chemical composition of the outflow (Hannan, 1980). The chemical composition of stream water entering a reservoir is likely to undergo important chemical changes associated typically with thermal stratification, density currents, overturn, and biological activities. In temperate climates these processes are linked very much to air temperature changes, and hence display a seasonal pattern. Thus releases made at different times of the year are likely to have different solute loads, and hence a different effect on downstream water chemistry.

iii. Objectives.

This thesis seeks to investigate water quantity - quality relationships within regulated rivers. Specifically, the thesis aims to evaluate the impact of flow regulation on river water chemistry downstream from dams over two time-scales: (1) annual, related to the alteration of seasonal flow variations (Chapters 5 and 6), and (2) short-term, related to the imposition of rapid flow-fluctuations (Chapters 7 and 8). The context for this thesis is established by reviewing the nature of river water chemistry, with particular reference to the significance of human impacts (Chapters 1 and 2), and assessing the nature of river regulation in England (Chapter 3).

iiia. The field study areas.

Primarily the study aims to identify the effect of regulation on the chemistry of rivers, both spatially and temporally. Rivers were chosen for study in order to fulfill these objectives. The major study rivers were the River Derwent, Derbyshire, England, and the River Tryweryn, Clywd, Wales. The former catchment was chosen in order to establish the long-term and seasonal modification of water chemistry induced by impoundment, and the latter in order to assess the effects of relatively instantaneous 'pulse' releases on water chemistry. To supplement data collected from the River Tryweryn, further reservoir releases were also monitored on two other upland rivers, namely, the River Washburn, Yorkshire, England, and the River North Tyne, Northumberland, England.

iiib. Summary of Approach.

Each study area is located in upland Britain, and is associated with coal/scremeston group geologies, acidic soils, and moorland scenery. Natural solute loads are predominantly low, necessitating extremely sensitive methods of analysis, together with suitable collection and storage techniques, in order to avoid the contamination of samples. The isolated situation of the study rivers meant that major fieldwork problems associated with the portability and durability of equipment were encountered. Many automatic and supposedly portable water quantity and quality monitoring systems e.g stage, pH, dissolved oxygen, and conductivity meters, which were designed for, and tested in lowland river surveys, under mild stable weather conditions, did not prove to be robust enough for use in this study. The extremely low winter temperatures caused batteries to be drained of charge too quickly, and heavy and prolonged rainfall, soon penetrated the 'water proof' cases of many of the solid state meters, rendering them unusable. Equipment more solidly constructed was not portable enough to be of use, due to the inaccessibility of many of the sampling sites.

The use of easily transportable, simple and reliable equipment was also advocated by the short warning period given before reservoir releases. Although authorities controlling the study reservoirs usually had advanced release planning, amendments are constantly made, according to catchment conditions, and user demand. Often there was as little as forty eight hours notice before a reservoir release. Consequently, little time was available to transport, and establish complex sampling and recording equipment. Thus, a methodology was adopted using simple staff stage poles, 250ml sampling containers, and sufficient manpower to collect enough samples to give a genuine representation of the water chemistry variation below the regulating reservoir. On average some 300 samples were collected during each reservoir release.

The spatial surveys of water chemistry on the River Derwent required the as-near-as possible synchronous sampling of sites throughout the catchment to avoid problems of hydrological variability. Each survey of twenty one sites was completed within five hours. The hydrological identity of each site was estimated by extrapolation between Severn Trent Water Authority gauging stations. Monthly surveys were undertaken between Ambergate and the River Derwent immediately above its impoundment. The data were used as a control for hydrological variability, so as to isolate the background pattern of seasonal water chemistry change.

Apart from the relatively simple problems of water sample collection, contamination, and storage (e.g Rainwater and Thatcher, 1960), chemical analyses led to considerable interesting difficulties. The chem lab continuous flow automatic analyser used as the key tool in the study was maintained and operated entirely by the author, and during the three year research period an extensive trouble shooting guide was compiled (APPENDIX B.1)Nevertheless, the accuracy and consistency of the results were found to be satisfactory (Chapter 4). The analysis on samples began within one days return to the laboratory. In order to achieve the desired intensity of field sampling it was decided to restrict the research programme to selected water quality parameters.

Parameters for analyses were chosen in order to (1) give a view of the effect of reservoir releases on the three major cycles determining stream water quality, namely, the sedimentary cycle (through the measurement of calcium and conductivity), the nutrient cycle (through the analysis of nitrate and phosphate concentrations), and the hydrological cycle (by considering chloride and pH levels). (2) Those naturally occurring streamwater solutes most likely, according to the literature (e.g Edwards, 1973b) to give the most easily identifiable response to the changing hydrological and chemical conditions created by a reservoir release.

iv. Significance of chemical response in context.

The literature review of this study (Chapters 1 and 2) aims not only to present work already carried out on the impacts of regulation on river water chemistry, but also to put the magnitude and extent of changes in context with other man-induced and naturally occurring events within a basin. Equivalent natural events are catchment floods, solute flushing after periods of drought, and seasonal variations. According to Douglas (1972), man influences water quality basically in four ways:- (1) forest clearance (2) irrigation (3) application of fertilizers, and 4) industrial and domestic pollution. By quantifying these natural and man induced changes, a datum level against which changes that occur in water chemistry as a result of regulation either seasonally, or during releases may be produced.

v. Extent of downstream impact.

Most studies considering the effect of regulation on stream water quality have usually only been interested in change immediately below the outfall, and a short way downstream - less than one kilometre (e.g Lavis and Smith, 1972; Crisp, 1977; and Soltero et al, 1973). However, a few authors (e.g Roux, 1984), have discovered that large scale reservoir releases, can affect water quality as far downstream as 160 kilometres. The reaches considered in this study varied between two kilometres on the River Washburn, and fifty kilometres on the River Derwent. Although the extreme distances as considered by Roux (1984) were not examined, it was felt that the majority of chemical changes created by the extent and type of regulation on each study river, would have been achieved by the lowest downstream sampling site - except perhaps with releases on the River Tryweryn, however, changes could not be translated beyond the basal sampling site, since the river is diverted into Bala Lake.

In the literature the effects of releases on sediment movement downstream (e.g Haidel, 1956; and Beschta et al, 1981) has been linked to the hydraulic relationships of wave and water movement. Attempts to relate solute variation to hydraulic processes, have been less successful (e.g Hamill, 1983). Such studies have often considered the time of travel of pollutant inputs (e.g Brady and Johnson, 1981; and Hermann et al, 1981), by linking them with dye tracer surveys, of the nature pursued by Warner and Smith (1978) for example. Few efforts have been made to use naturally occurring solutes as surrogate tracers, and interest has largely focused on a lag effect between stage change and tracer arrival (e.g Glover and Johnson, 1974). In order to predict how a pulse release will affect downstream water chemistry, and to establish a cause-effect relationship between changing water chemistry and river regulation, detailed hydrological data are required. This study was very careful to link the response of solutes at-a-station, to stage change, thereby giving each sample a hydrological identity. In this way, not only may relationships be established between release wave/water movement and local stream water chemistry (Chapter 7), but also the accuracy of relevant flood routing models may be assessed (Chapter 8).

vi. Time scale of response.

The significance of river regulation on water quality is dependent to a large extent, upon the time scale of enquiry. Thus two temporal perspectives were considered in depth. The seasonal scale and the instantaneous scale. Although a longer time scale was considered very briefly, as water quality data for the River Derwent catchment prior to impoundment could be calculated from the chemical nature of present day tributary inputs, and [illegible] archival flows [illegible]. This theoretical water chemistry could then be compared to the present day water chemistry of the River Derwent. The seasonal time scale of response, was also investigated with data collected from the River Derwent catchment, where data from routine monthly chemical surveys carried out by Severn Trent Water Authority, coupled with more spatially intensive sampling by the author, were amalgamated to give the seasonal pattern of chemical change in the Derwent catchment. The effect of varying reservoir discharge volumes upon this pattern was then modelled (Chapter 6).

At the instantaneous time scale, the rate of chemical change created by reservoir releases, was examined. This was undertaken primarily on the River Tryweryn, where regular releases are made for water supply and to meet recreational demands, although findings were verified through releases on the River Washburn and River North Tyne. The response can be linked to wave and water dynamics of the release itself, leading to a knowledge of the likely water chemistry response within the channel to different sized releases, made onto varying compensation flow volumes. Furthermore, the chemical response was used to give an indication of the relationship between wave and water movement; naturally occurring solutes were used as tracing agents.

In the final analysis, when considering water chemistry variations below regulating reservoirs it is necessary to approach the problem from both varying timescales and spatial perspectives. Furthermore, in order to establish cause-effect relationships it is important to link water movement, wave movement, and at-a-station chemograph response.

CHAPTER 1.

THE CHEMICAL NATURE OF STREAM WATER.

The chemical nature of stream water is complex, being a function of drainage basin characteristics and their dynamic interactions. A range of biogeochemical processes produce variations of water chemistry over a range of temporal and spatial scales. The quality of stream water is an important control on water resource utilisation for supply and is also markedly affected by the influence of man in the catchment; as such the chemical composition of stream water has attracted much interest, especially in the past 20 years. In Britain, the study of water quality by geographers has been stimulated by the work of Walling (e.g Walling, 1974, 1975, 1977, 1980). River solute concentration has been used as a measure of catchment denudation (Finlayson,1980); as an indicator of contributions from different hydrological source areas (Brady and Johnson, 1981); and as a monitor of agricultural (Tomlinson 1970, Edwards 1973a), domestic (Wehr, Say, and Whitton, 1981) and industrial (Biesecker+George, 1966.) pollution. The chemistry of large rivers such as the Nile or the Amazon has been documented (Gibbs, 1967), as have moderate sized rivers such as the River Exe (Walling and Webb, 1975), but smaller first order channels have been studied most intensively (e.g Foster, 1978a) often as field experiments (e.g Burt, 1979b). The natural seasonal variation of solute concentrations has been investigated (Casey, 1977; Edwards, 1975) and the significance of geology and soil type has been demonstrated in studies of spatial patterns (Hem, 1970; Walling+Webb,1975).Short term variations have been studied during both flood (Johnson and East, 1982) and drought (Foster and Walling, 1978) conditions. However, characteristically, these studies demonstrate that the chemical nature of a river is complex and often unique to each drainage system.

1.1 River Water Chemistry and the Hydrological Cycle.

Walling (1980) has demonstrated that the water chemical cycle is intimately associated with the hydrological cycle, his graphic representation (Fig 1.1a&b) succinctly summarizes the pertinent factors influencing river water chemistry. Importantly, this demonstrates that river water quality is determined by the modification of atmospheric inputs by biotic

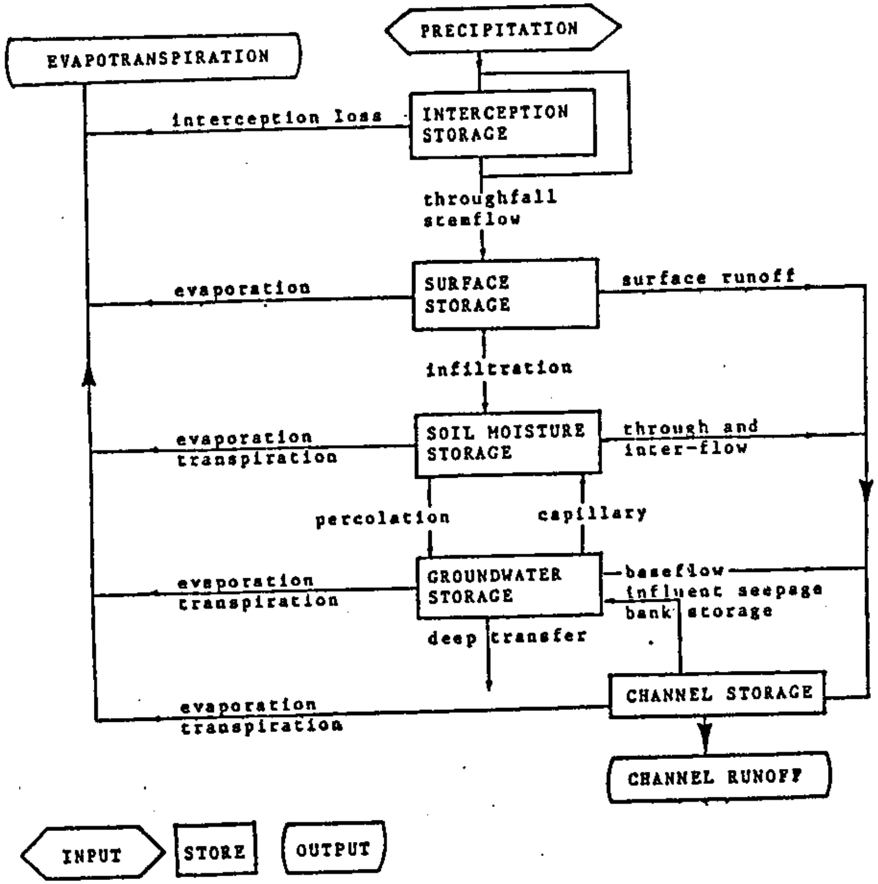


Fig.1.1a. Hydrological processes operating in the catchment (Walling, 1980).

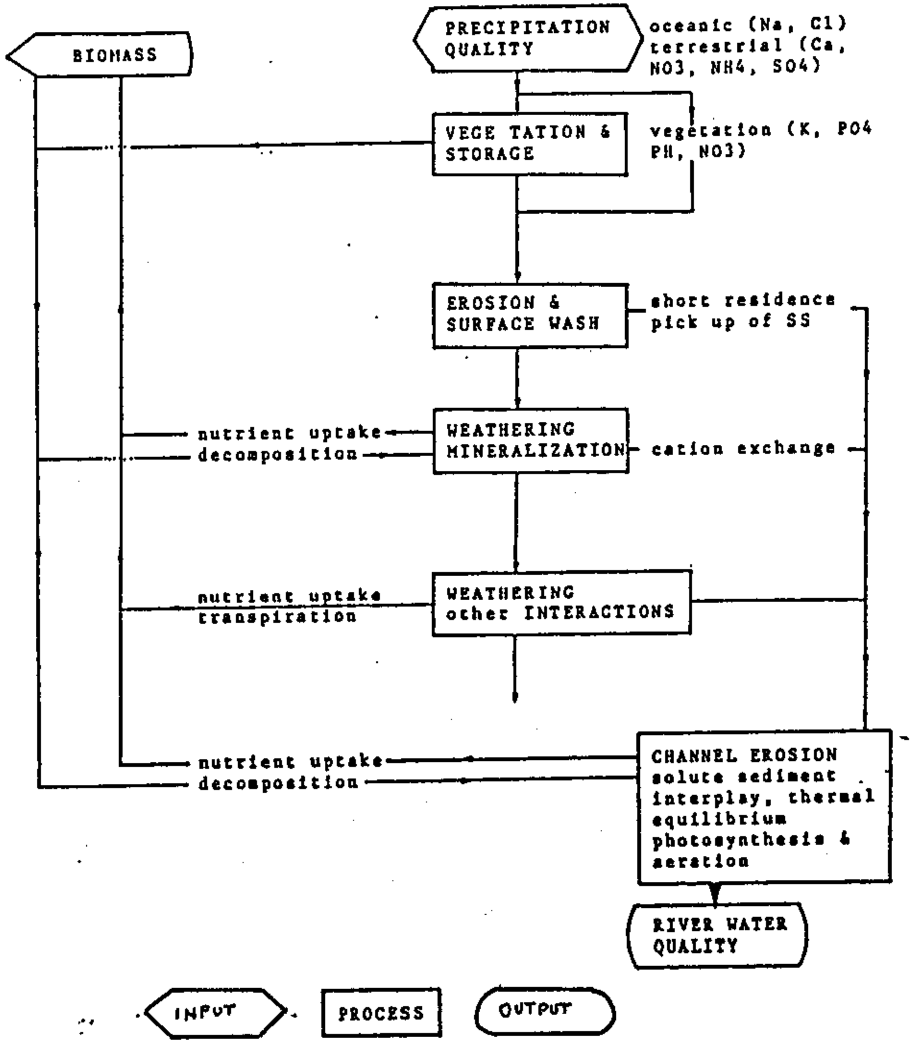


Fig.1.1b. Major influences within the catchment on water quality (adapted from Walling, 1980).

and geologic processes and at any point in time, is a reflection of the relative contributions of the different hydrological pathways through the drainage basin (Pilgrim et al, 1979).

Precipitation quality is the product of two mechanisms: rainout and washout. In the first instance, dust particles are used as condensation centres for the raindrops. The source of these particles is twofold: namely oceanic or terrestrial. An oceanic origin, gives precipitation dominated by sodium/chloride ions (Na^+ /Cl^-). In contrast, a terrestrial origin is characterised by calcium (Ca^{2+}), nitrate (NO_3^-), ammonia (NH_4^+), and sulphate (SO_4^{2-}) ions in abundance. In the second instance, that of 'washout', chemicals within the atmosphere are physically removed; a process which may cause flushes of precipitation with very high chemical concentrations at the onset of storms (Dethier, 1979). Precipitation quality is highly variable, both temporally and spatially, and will vary with wind direction, storm intensity and duration (Walling, 1980). Nevertheless, precipitation is relatively dilute in comparison to river water.

The chemical nature of precipitation is changed by reactions with vegetation, soils, surface deposits, and solid geology.The extent of this change is dependent upon the intensity and duration of the precipitation, ground infiltration capacity, amount of water in the soil at field capacity, and the permeability of the substrata (Walling, 1980). The concentration of solutes in precipitation, except for inorganic nitrogen, which is taken up by plant tissue, is likely to be increased through contact with vegetation, due to the leaching of metabolites from the plant tissue, and the washing of chemicals deposited on plant surfaces. Foster (1979) accounted for a substantial increase in potassium (K^+)in stream water during the early part of a storm event by relating it to such plant washing. Carlise *et al* (1967) noted increases of potassium, calcium, magnesium, and sodium as a result of storm flow, and an increase of acidity in water draining Oak forest, from pH 4.1-4.6 of incident precipitation, to pH 3.5-3.9 for throughfall.

On reaching the soil surface two main changes occur to the content of precipitation water. First, the incorporation of soluble material, and secondly, the entrainment of sediment particles. The first mechanism is relatively unimportant due to the short residence time of surface water, although naturally the solubility of the material with which the surface water is in contact is important (Walling,1980). The entrainment of sediment particles however, is vital and will be closely related to the process of sheet and rill erosion which, in turn, depend on the energy associated with raindrop impact, with surface runoff, and on the erodibility of the soil.

Once surface water has infiltrated into the soil many interesting changes can happen to the water chemistry. These will be the result of one or more of five types of reaction (Walling, 1980):

i. solution
ii. colloid formation
iii. ion exchange
iv. hydration and hydrolysis
v. oxidation and reduction.

The presence of bacteria and benthic organisms, which are usually confined to these upper layers of the so called sediment column, act as catalytic agents in the reactions (Gasser, 1980). Ion exchange mechanisms are primarily concerned with cations and are of considerable importance in influencing soil water quality (Walling, 1980). Anion exchange mechanisms are a minor factor since the adsorption capacity of the soil for anions is small. Calcium, magnesium, hydrogen, potassium, and ammonia are the dominant cations in the exchange mechanisms. Of particular importance is the H^+ ion, as this may be removed from solution and replaced by exchangable cations. Colloids provide the major source of exchange sites and cation exchange capacity generally increases with fine textured soils. In addition to adsorption associated with ion exchange, which is reversible, "specific adsorption" may occur, which is non-reversible, involving chemical, not electrostatic attraction. Adsorption of phosphate ions by clay is a classic example of this mechanism (Walling, 1980).

Perhaps the most significant influence on soil water quality is the role of water as an agent of chemical weathering. Of critical importance here is the residence time of the water in the soil. Essentially the products of chemical weathering are; dissociated silica, sodium, potassium, magnesium and bicarbonate ions. An ionic concentration gradient within the soil may be established (Pierce et al, 197) with soil salts passing rapidly into solution and toward the area of lower salt content. The closer ionic concentrations are between resident and infiltration water, the slower the rate of ion exchange. Eventually a chemical equilibrium is attained. However, this is not likely to occur until infiltration water has reached the bedrock stores.

The significance of geology on solute concentration is illustrated in Tables 1.1a, 1.1b and 1.2. These show that local variations in water chemistry from a similar rock type, are insignificant in comparison with water from different geological source areas. The small local variations, relate to areas of high groundwater transmissibility, associated with lines of geologic weakness, such as faults and joints within the structure. Even possible effects from coastal, or for that matter industrial or agricultural inputs, at low flow, at least, are not comparable with the dominance of rock type on river water quality. Thus, studies of the water quality of rivers at low flow, show remarkably consistent water chemistries over time (e.g East, 1978; Foster,1979; Davies, 1971; Gardiner,1980; and Webb, 1980), due to the predominance of groundwater in a state of chemical equilibrium.

Channel processes can have an effect on water quality, although these are usually associated with high flow. Of particular significance is the control of suspended sediment concentrations, since interactions between the sediment and the solution phase may occur not least, with calcium, magnesium, potassium and phosphate which can be absorbed to a considerable degree by stream sediments (e.g. Bedient, 1980; Foster, 1979; and Shih, 1969). As a result sediments can buffer changes in the concentration of these ions within stream water.

1.2 The seasonal patterns of water chemistry within a channel.

Much work has been carried out into the characteristics of seasonal variation in river water chemistry, and this has been reviewed by Walling and Webb (1975) and, more recently by Petts and Foster (1985). Most studies emphasise the importance of catchment controls. In one example, Feller (1977), studied nutrient movement through Red Cedar ecosystems in Southwestern British Columbia, and showed that pH values fall in late summer, and rise to a maximum during the winter months. Feller suggested that this pattern is due to increased biological activity in the warm months, producing carbon dioxide which dissociates in water yielding an acidic solution. Large fluctuations may be related to climate in this way, although in so doing the potential hydrological significance is ignored.

Conductivity measurements from the same study, also exhibited a marked seasonal pattern with maximum values in autumn and minimum values in late winter. This seasonal behaviour reflects

KARSTIC	(Ca^{2+})mg l^{-1}	NON KARSTIC	(Ca^{2+})mg l^{-1}
Groom & Williams* (1965), S Wales	51-90	Rodda (1976) Scotland- granite	1.3
Pitty (1968) Derbyshire	76	Cryer* (1980) Wales- Ordovician shales	1.2
Gorham (1961) Malham	80		
Sweeting (1960) Mendips	100-250		

* referenced in Carling (1983).

TABLE 1.1a. Comparison of calcium concentration in surface waters of Karstic and Non-Karstic areas. (From Carling, 1983).

ROCK TYPE	(Ca^{2+}) mg l^{-1}	(Cl^{-}) mg l^{-1}
Phyllite	5.7	4.9
Granite	7.7	4.2
Mica schist	9.3	5.4
Basalt	68.3	5.7
Cretaceous	133.4	17.3

TABLE 1.1b. Comparison of calcium and chloride concentrations in surface waters draining single rock types. (From Clarke, 1924).

(ION) $mg\,l^{-1}$	SIERRA NEVADA Feth (1961)	SANGRE de CRISTO Miller (1961)	VERMONT Johnson (1977)
Calcium	4.4	3.6	2.1
Magnesium	1.5	0.9	0.6
Sodium	2.4	1.8	0.9
Potassium	0.5	0.3	0.3
Bicarbonate	6.9	5.1	1.8
Sulphate	0.9	1.4	3.5
Chloride	0.8	1.0	0.5
Nitrate	0.07	0.04	0.1
Silicon	0.2	0.2	0.1

All studies carried out in mountainous areas of granitic bedrock, under autumnal baseflow conditions.

TABLE 1.2. Comparison of average solute concentrations in streams draining mountainous areas of the USA.

an accumulation of decomposed and weathered products during the summer, followed by a flushing of this debris through the system by autumnal rains. The seasonal pattern of calcium concentrations, for example - with calcium usually the dominant cation - mirrors the conductivity pattern with highest concentrations in autumn and lowest in winter or early spring, with occasional peaks in late spring.

Of the anions nitrate, phosphate, and chloride concentrations, Feller discovered, were all highest in autumn or late summer, and lowest in winter or spring, thus paralleling cation concentration patterns. Chlorides are leached from forest litter, and dry fallout is washed into solution. As this solution passes down through the soil, the concentration of chloride and nitrate is reduced due to adsorption reactions in which the anions are immobilized because the cations with which they are associated become adsorbed to the soil exchange complex. For example, phosphate concentration is reduced due to the fixation of iron and aluminium. Other researchers including Edwards (1975), Sutcliffe (1983), and Tomlinson (1970), also report that ionic concentrations in small river catchments demonstrate a strongly seasonal pattern, which is particularly well illustrated by nitrate drainage water, having highest concentrations in the autumn and lowest values in summer, attributed to the autumnal washout of nitrates that had accumulated in the fallow soil during summer.

The summer storage of nitrate is explained by Tomlinson (1970) as a result of summer evaporation and the transpiration from plants preventing downward movement of water in the soil, whilst the high temperature favours nitrification of organic reserves. At the same time, active plant growth uses nitrate as it becomes available and converts it to living plant material. Toward the end of summer, plant growth slows the nitrification process and free nitrates accumulate in the soil, so that when evaporation slows and downward movement of water begins, nitrate in the soil is washed out thereby causing a rise in the nitrate content of streamwater. During winter, drainage continues, but as soil temperature falls, nitrification slows and the rate of loss of nitrate in drainage water declines. Edwards (1975) however, from work on the nitrate and non carbonate hardness records of the River Stour, Essex concludes rather differently, suggesting that the annual cycle of nitrate and non carbonate hardness in drainage water is a phenomenon of leaching rather than biological depletion of storage, and that concentrations of nitrate and non carbonate hardness are greatest in rivers when the drainage network is at its maximum extent through the soil. A conclusion supported by Sutcliffe (1983), who found clear seasonal patterns of nitrate, with highest concentrations occurring in winter.

In complete contrast to the above examples, Casey and Newton (1973) showed from work on the River Frome, Dorset, that nitrate concentrations varied little throughout the year, and any slight increase was thought to be due to the in-washing of fertilizers; for example a peak of 2 milligrammes per litre of nitrate above background levels in February was noticed (Casey and Clarke, 1979). Oborne et al (1980) substantiate these findings with results from the River Wye. Neither nitrate nor phoshate exhibited any marked seasonal pattern. However, calcium concentrations were generally lowest during winter periods and highest during summer periods. MacCrimmon and Kelso (1970) also document seasonal trends for calcium and total alkalinity with a similar pattern to that descibed by Oborne et al (1980). This manifestation correlated to discharge values. Nitrate levels were extremely variable and showed no obvious cyclical tendency during the year. The cyclic pattern of alkalinity and calcium hardness, MacCrimmon and Kelso attribute to the utilization of carbonate forms during periods of greatest biological activity in spring and early summer, and the subsequent return of carbonate to solution during reduced activity in response to the lower temperatures of fall and winter. It is clear from the above that the seasonal behaviour of nutrients in natural systems is highly variable. The solute concentration of a given discharge varies seasonally, partly because the quickflow and the delayed flow proportions differ, and partly because of seasonal biological influences. Smaller streams draining relatively homogeneous rock- and vegetation- types, and with a water source dominated by a particular flow path, will tend to demonstrate patterns much more clearly than large rivers. In such large scale channels water quality represents the sum total of numerous different rock types, soil types, and flow routes. Consequently there is a buffering of the trends so dominant at the small drainage channel scale. Solute dynamics thus reflect nutrient cycling processes, with separate nutrients behaving uniquely both seasonally and in storm periods, so that the total solute concentration is a complex summation of these separate ionic variations.

1.3 The effect of discharge on background water chemistry.

The variation in discharge has been widely recognized as a dominant factor determining background water quality at a given time (e.g Hem, 1970; Toler, 1965; Johnson and Glover, 1974), with background water quality usually defined as the average water quality at a given location during the year. Various forms of inverse relationships have been presented: including hyperbolic (Durum, 1953) and logarithmic (Gunnerson, 1967; Pionke and Nicks, 1970). In some cases, the consideration of antecedent flow conditions has improved the relationship (Ledbetter and Gloyna, 1964; Hall, 1971). However, inclusion of inter-flow, in addition to surface and baseflow has been suggested to provide a more realistic basis of analysis (Hart et al, 1964), indeed several studies have shown that the combination of routes of water particles through bedrock, soil, vegetation, and the minor drainage network of a catchment area, determine the form of the discharge hydrograph, and is also a major influence upon the solute load variations (Hendrickson and Krieger, 1964; Toler 1965; Johnson and Glover, 1974). The availability of solutes along varying routes will differ substantially, so the solute content of the total discharge will vary with differing quantities of flow from different catchment sources. This gives rise over time to the hysteretic looped response of mainstream water quality during a catchment flood. Such loops, which maybe either clockwise or anti clockwise, have been explained by differing catchment water sources, having different water chemistries, becoming dominant during a flood event.

Hendrickson and Krieger (1964) studied the relationship between specific conductance and water discharge for streams in Kentucky, USA. In each basin studied, a fundamental cyclic pattern emerged, which the experimenters divided into three phases. First, the decrease in specific conductance was slow due to the washing into the stream of immediately available and readily soluble material, derived from the soil, from the stream bed, and from shallow groundwater. In addition, 'old' water in pools and in storage within the channel may constitute an appreciable portion of the water in the initial stage rise. These materials tend to retard the rate of decrease in the dissolved mineral matter of the stream, even though discharge is rising rapidly. Secondly, since most of the readily soluble material has been flushed from the surface stores, water entering the main channel is almost devoid of solute load. Moreover, at high channel flow, a hydraulic gradient exists from the channel to the floodplain, enabling water to move from the stream into the channel bank sediments, thereby preventing groundwater from entering the stream. As a result, the water in the stream channel decreases greatly in specific conductance without much change in discharge.

During the third and final phase of discharge recession, the relative contribution of ground water increases, raising solute concentrations toward pre-flood levels. Toler (1965)reports a clockwise cyclic relationship of concentration to discharge in Spring Creek, Southwestern Georgia, USA. The changing contribution of groundwater flow, is thought to be the dominant control of inchannel water quality for the majority of the flow regime. However, at extremely high discharges, surface runoff is much more effective in controlling the water chemistry. In this instance, initial solute values are quickly reduced by the rapid increase of low solute load surface runoff, when discharge has reached the recessional turning point (the hydrograph peak), the relative contribution of high solute load groundwater to low solute load surface runoff begins to increase. Thus on the recessional limb of the hydrograph solute load increases as discharge decreases, giving rise to a clockwise hysteresis.

To predict the form of such cyclical patterns, Johnson and East (1982) used a chemical mass balance approach, in conjunction with a knowledge of the relative magnitudes of chemical concentrations in flow from different catchment sources. The chemical mass balance equation is presented below:

$$QTCT = QSR * CSR + QI * CI + QG * CG \qquad (Eq.1.1)$$

Where :- QTCT is the total flow of chemical concentration, CT
QSR is the surface runoff, CSR is the surface runoff chemical content;
QI is the interflow, CI is the interflow chemical content;
QG is the groundflow, and CG is the groundflow chemical content.

The character of the cycle during unsteady conditions, on the rising and falling limb of the hydrograph, is due to:

1. Variations in the quantity of flow from the various geochemically distict sources.

2. Variations in the accumulation of solids in these sources and their contribution to the chemical concentrations of flow components.

3. The effect of routing these discharges and chemical variations through the channel network.

Results from a study on Bicknoller Combe, Quantock, Somerset by Burt (1979b) confirms the importance of differing catchment water sources, with unique chemical blueprints determining water chemistry in the major river during a storm. Fig 1.2a gives an approximate summary of findings, with AB representing the flushing in of readily available soluble salts from the catchment surface, and from easily accessible soils stores during the relatively rapid hydrograph rise. BC represents a reduction of discharge as initial surface runoff abates, but a substantial rise in the water conductivity can occur, due to the input of solutes from throughflow and interflow - both comparatively rich in solutes. Line CD represents the recession of the storm, with groundwater being the major contributor to both discharge and solute load. Main flow conductivity is higher at the end of the storm than at the beginning, due to the displacement of highly concentrated basal groundwater by the influx of storm water.

In contrast to Burt's example a more typical pattern is shown in Fig 1.2b, where initial flushing flows are absent. AB represents dilution of background water quality by low solute load precipitation and rapid overland flow, BC shows solute concentration rising quickly in comparison with discharge, as more concentrated throughflow and soil derived water reaches the channel. CD illustrates the recessional curve, when chemical concentration is still rising due to the input of ground water, and water from the far extremes of the catchment, rich in solutes (Petts and Foster, 1985).

1.4. Water Solute load change through the catchment.

In order to really appreciate and understand the cyclic hysteresis described in the previous sections, some knowledge of chemical dynamics must be gained. The relative contributions of solutes from varying catchment sources has often been oversimplified. For example, Livingstone (1963), considered that groundwater, because of its longstanding close contact with rocks and mineral soil, would always be chemically more concentrated than surface runoff. Conversely, Weisel and Newell (1970), considered that surface runoff was always more concentrated than main flow stream water, due to the rapid entrainment and deposition of solutes and sediments in the surface flow. Such statements were made purely on observational

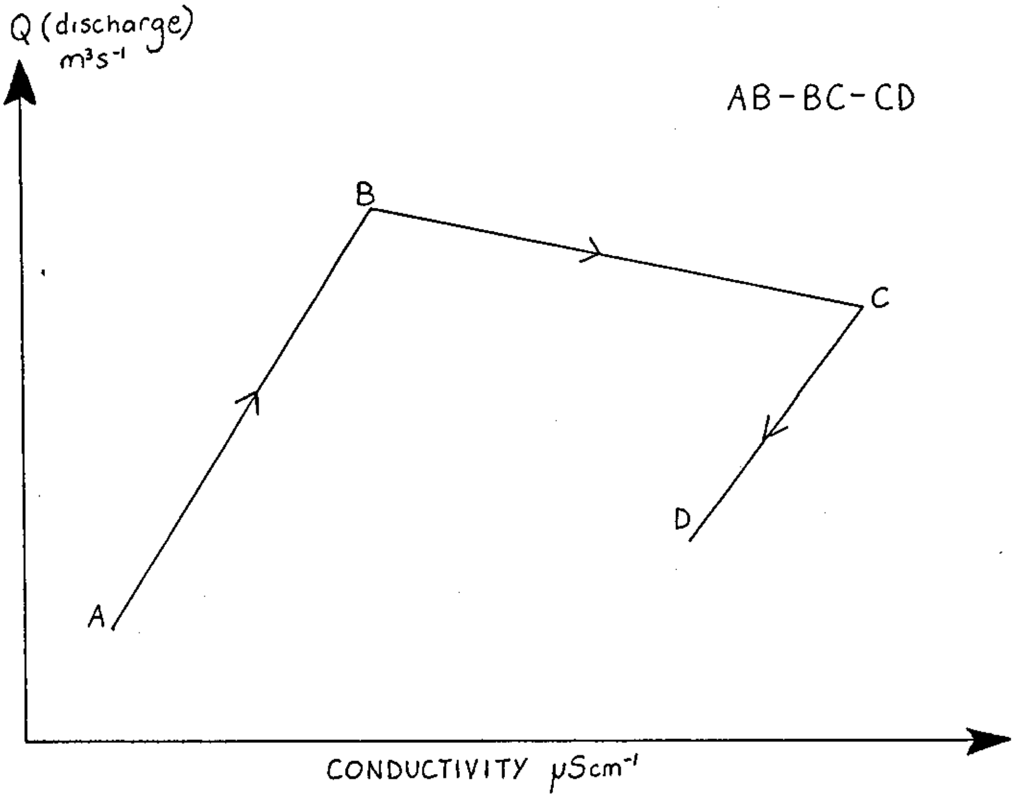


Fig. 1.2a. The 'flushing' response of conductivity during a natural flood.

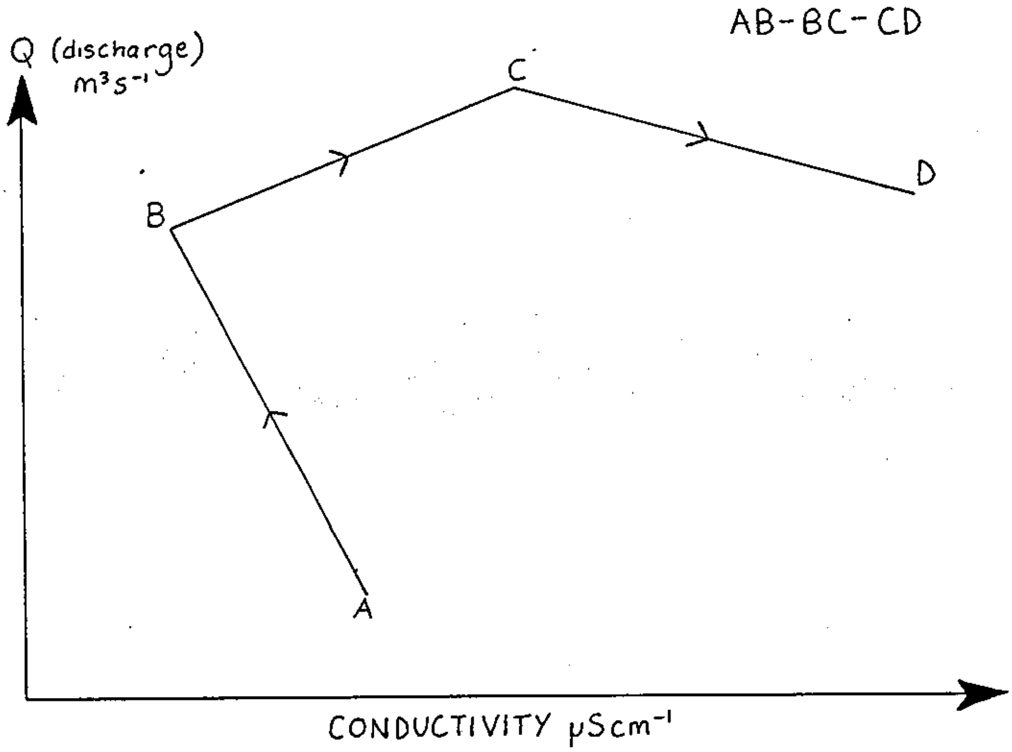


Fig. 1.2b. The typical cyclical response of river conductivity values during a natural flood event.

evidence.

A more theoretical knowledge of soil solution chemistry can help to explain differing responses of apparently alike systems to similar events. The major anions of solution are not stored to any extent within the soil matrix, but tend to remain in solution. Cations, which are stored in the matrix, are required to maintain electro-neutrality and thus leaching of cations through the soil depends to a great extent upon the amount of anions present. This in turn depends on a complex series of equilibrium, adsorption, displacement, immobilization, weathering, and decomposition reactions. Physical removal of ions will then depend on leaching susceptibility, which is a function of biological decomposition, and mineral weathering. Thus in a soil matrix highly susceptible to leaching, it is likely that soil water concentration will be greater than groundwater. However, in soils less threatened by leaching, surface runoff and soil water are likely to contain fewer solutes than the groundwater source. The former situation is documented by Feller (1977) where groundwater was found to be less concentrated than streamflow water, and the latter situation (the more usual occurrence) expressed by, for example, Gorham (1961), Livingstone (1963) and Steele (1968). The contrasting nature of these studies together with the above brief explanation of soil water chemistry, show that water from given hydrological pathways within a catchment, will not always have a unique chemical quality. A detailed discussion of soil-water chemistry is provided by Foster (1979), Garrels and Christ (1965) and Bolt et al (1976).

1.5. Response of individual ions to changing discharge.

Some studies (e.g Edwards, 1973a; Walling, 1974) have demonstrated that the response of river water chemistry to discharge depends largely on the solute under consideration, and that the standard discharge/chemistry equation, as used by Uryvageu (1968) in North Eastern USSR, Jaworska (1968) in Poland, Iorns et al (1965) in USA, and Douglas (1967) for streams in Australia, Malaysia and Singapore, (Eq 1.2) is not applicable to all substances.

$$\mathrm{Log}\ C_{ij} = \log a - b \log Q_j \qquad \text{(Eq. 1.2)}$$

C_i is the concentration of each constituent at sampling time j,

Q is discharge.
a and b are constants.

Potassium has actually been shown to exhibit positive relationships with discharge as indeed has total phosphorus (Verhoff and Melfi, 1978). These are suggested to be due to either the input of phosphate from river banks and bed, or from catchment runoff from an area rich in soluble phosphates.

On the River Wye, Oborne et al (1980) observed the concentration of total dissolved solids, bicarbonate, phosphate, calcium, magnesium, sodium, potassium and alkalinity to be diluted, and suspended sediments and nitrate to be concentrated by increased flow. Foster (1978a) from experimentation on a small agricultural catchment (1.6 km^2) in East Devon, with a river water sampling interval of thirty minutes, in comparison with most other study sampling intervals of one hour or more, confirmed earlier observations that with the exception of potassium, all solute measures were inversely related to stream discharge.

White et al (1971) from work in the Lake District, also found significant inverse relationships between most solutes and flow rate. In the case of the bicarbonate and calcium ions, 75% and 55% respectively of the variability in concentration could be related to flow. However, with chloride, sodium, and sulphate, a little more than 10% in the variation of concentration was related to flow. Edwards (1973a&b) presents data from some Norfolk rivers indicating that individual ions behave differently in response to increasing discharge. However, patterns of solute variation were found to relate to storm size. Large storms appeared to have little or no effect on mainstream calcium concentrations. On the River Yar, between 19th and 26th January 1971, calcium concentration fell by some 20 mg l^{-1}, and bicarbonate by 70 mg l^{-1}. On other occasions the effects of dilution, if present, were of the same order as analytical precision. The explanation of this variable relationship between calcium and discharge, is thought to be due to the existence of two sources of calcium in the basin, namely calcium sulphate and calcium carbonate. Whereas carbonate in the form of the bicarbonate ion shows a distinct inverse correlation with discharge, sulphate displays a positive one. Thus according to runoff source, calcium may increase within the river with discharge, or decrease.

Attempts have been made to categorize the different behavioural patterns of ions during unsteady flow conditions. In particular, studies by Edwards (1973a and 1975) and Louis and Grant (1979) demonstrate the difficulty of generalising in this context.

Edwards (1973b) recognises four classes of solute according to their response to increases in river discharge;

(1) Nitrate and sulphate increase in concentration.
(2) Magnesium, bicarbonate & phosphorous are usually diluted.
(3) Sodium and potassium, probably derived mainly from chlorides, fall into an intermediate category although potassium concentrations increase at the beginning of most storm events.
(4) Calcium and silicon show little relationship to discharge. Such responses are tentatively explained by a combination of two observed factors: the solubility of minerals dissolved, and their location in the vertical profile of the catchment deposits.

In contrast to the work by Edwards (1973a, 1975), Louis and Grant (1979) studying the dependence of concentration and yield of dissolved substances on water discharge over a 150 week period in the water shed of Corno Creek, Colorado, USA, discovered from weekly sampling that substances could be divided into three distinct groups (with no need for an intermediate fourth group, unlike the Edwards study) on the basis of relationship between discharge and concentration:

(1) substances whose concentrations decrease with increasing discharge (bicarbonate, nitrate, calcium, magnesium, and sodium)
(2) substances whose concentrations show no trend with discharge (ammonia, dissolved organic phosphorus and nitrogen, potassium and sulphate)
(3) substances whose concentration increase with increasing discharge (dissolved organic carbon, hydrogen, and phosphate)

If a comparison is made with the results from Edwards (1973a. 1975), then for common parameters, apart from the bicarbonate and magnesium ions, which are both diluted with increasing discharge, there is little similarity in response. Edwards reports the increase of nitrate with discharge, whereas Louis and Grant show nitrate being diluted. Louis and Grant indicate a dilution in calcium and sodium, and no change in potassium, sulphate and phosphorus however, Edwards documents no response for calcium and sodium, an increase in potassium and sulphate, and a dilution of phosphorus; clearly results are hardly comparable.

Furthermore, Louis and Grant (1979) identify three categories of solute yield in response to increasing discharge. Firstly, where yield increases more slowly than discharge (bicarbonate, nitrate, calcium, magnesium, and sodium) secondly, where yield increases at the same rate as discharge (ammonia), and finally, where yield increases faster than discharge (potassium, sulphate, hydrogen, and phosphate). It is concluded, that simple groundwater, precipitation, throughflow, mixing models, such as those presentd by Toler (1965), Hendrikson and Krieger (1964), and Johnson and East (1982) are not adequate, but that account must also be taken of the chemical reaction of incoming precipitation with soil and soil water, and the intensity of biological demands for the substances. Such demand interrupts the recycling pattern of ions, and may create periods of sudden release of solute to the river. Such a phenomena is termed "flushing".

1.6. Flushing.

An additional characteristic of some chemographs relating to particular storm events and usually requiring certain antecedent conditions, is a pulse of relatively highly concentrated solutes on the rising limb of the hydrograph.

When rainwater infiltrates the soil during the beginning of a storm, salts that have accumulated in this area are quickly dissolved and removed as the water drains downslope toward the main stream, producing an initial increase in main channel salinity with the onset of a flood (Miller and Drever, 1977). Such a phenomenon is likely to be easily identifiable because discharge at the start of a storm is still comparatively low, and therefore, even small volumes of solutes flushed out will produce a significant rise in river water concentration values. Once these available salts have been removed, relatively dilute runoff will reduce concentrations in the main stream.

Observations on initial flushing have been made by Anderson and Burt (1978), Brookes (1974), Buckney (1977), Casey and Ladle (1976), Claridge (1970), Cordery (1977), Feller and Krimmons (1979), Foster (1980), Gunnerson (1967), Hendrickson and Krieger

(1964), Overton and Meadows (1976), Oxley (1974), Steele (1968), and Walling (1974). Each study attributes the early flushing to the leaching of ions from various catchment sources. Leaves and litter (Claridge ,1970), stormwater drains (Cordery, 1977), different geologic strata (Anderson and Burt, 1978), soil sources (Foster and Walling, 1978;Cooke+Williams 1970; Miller and Drever, 1977), ground water inputs (Casey and Ladle, 1976), and the sudden extension of the drainage network removing accumulated weathered and organic deposits (Edwards, 1973a). A number of authors have also found different timing of major yearly flushes; for example, Overton and Meadows (1976) state that the first flush effect is most noticeable during the low flow summer months, whereas Cooke+Williams (1970) document flushes associated with the intense microbiological activity within the soil during spring, and to a lesser extent during autumn. Foster and Walling (1978), and Anderson and Burt (1978) from independent work during the 1976 drought, conclude that the flushing process was most noticeable with the first storms of late summer. It is suggested that this peak is related to a throughflow storm runoff component (i.e the lateral movement of water through the soil) and that the source of high solute levels is from the solution of readily soluble residues, which had accumulated in the soil during the drought.

Not only has the flushing process been shown to be seasonally biased, but also it has been demonstrated that some solutes are more susceptible to flushing than others. Walling (1974), found that the dominant ion in this process was calcium, increasing in value by as much as 10 times, in contrast to this Casey and Ladle (1976) found nitrate to be the major ion involved in flushing, with concentrations within the main channel increasing by up to 4 times pre-storm values. Foster and Walling (1978), from work on the River Yendacott, S. Devon, observed specific electrical conductance to increase two fold, calcium three fold and nitrate over twelve fold in main channel water at the immediate end of the 1976 drought, other determinands were not as sensitive to the change of soil moisture content.

Thus, the degree of solute flushing at the onset of storm runoff, reflected by a pulse of relatively solute rich water, has been explained by seasonal and short term changes in the soil water store, associated with vegetational and microbiological processes, together with drainage network dynamics. Individual solutes display unique responses in terms of flushing, with nitrate and calcium the most responsive.

1.7. Man's influence on river water chemistry.

Man's influence on river water chemistry may be viewed over three different time scales. First, from the long term perspective; long term in this case being more than ten years e.g the effect of reservoir storage on outflowing water solute load once the reservoir has established its own micro- system of conditions (see Crisp, 1977 and Petts, 1985); trend in nitrate concentration in rivers and ground water as a result of fertiliser application (see Tomlinson, 1970); and the alteration of the 'geo-hydro-chemo-system' by established urbanisation (see Lewis, 1981; and Koch, 1970).

Secondly, man's influence is at a yearly or seasonal time scale. Man has tended to exaggerate natural seasonal fluctuations(Angino et al, 1972; Monke et al, 1981) particularly through advanced agricultural techniques. Ploughing releases soil particles and their associated ions for leaching and wash off, fertilizer application makes nitrates and phosphates readily available for flushing during heavy spring and autumn storms, intensive cultivation and vegetation grounds during summer reduces chemical imput to streams; and harvesting suddenly reveals soil and nutrient rich stores to be depleted by runoff. Timber plantations particularly illustrate these trends (see Feller & Krimmons, 1979; Feller, 1977; Pierce et al, 1970; Sopper, 1975).

Thirdly, man's influence on background water quality can be viewed from an instantaneous time scale, whereby this average chemical nature is disturbed by sudden inputs of solute rich water e.g. the effects of urban floods on water quality (Cordery, 1977; Bryan, 1972); the immediate effects of development e.g. Crippen (1967), Walling (1974); the effects of irrigation e.g Mrowka (1974), Sylvester and Seabloom (1963); the effects of clearcutting e.g. Pierce et at (1970); and the effect of reservoir releases e.g. Beschta et al (1981), Brady and Johnson (1981), Heidel (1956).

The next three sections discuss the magnitude of change associated with man's activites at these three time scales.

1.7.1. Short Term fluctuations in water chemistry.

Cordery (1977) for urban storm drains in Sydney Australia, has found that the concentration of pollutants increases rapidly at the beginning of flood flow. A typical first flush of phosphate would be as much as 1 mg l^{-1}, approximately doubling dry weather flow values. After the initial flush, values tend to fall off rapidly to values well below that of dry weather discharge. Data from three storm drains from Cordery's study are given in Table 1.3. High values for nitrate, phosphate, ammonia, and low pH during flood, are initial flush products, and lower values indicate dilution effects of the storm. In general the effects of the 'urban storm' is to cause initial rise in nitrate by about 1.3 times, and then reduce values by about 4 times the initial value. Similarly, phosphate may rise by up to 2.5 times initially, but then during the course of the flood be diluted by up to 3 times below that of dry weather flow concentrations.

A comprehensive study by Bedient [illegible] (1980), of water quality variation in a concrete lined urban channel, confirmed the Cordery (1977) study. The major effect of stormwater is to reduce nutrient concentrations 3-4 times, simply due to dilution.

Crippen (1967) investigated the immediate effects of suburban development on river load in a small basin in the coastal region of central California, USA. The total load of dissolved solids carried from the basin in streamflow increased 10 times, due to leaching of freshly exposed material and flushing brought about by domestic and municipal irrigation. Solute rich water is also produced by irrigation practices documented by Mrowka (1974) and Sylvester and Seabloom (1963). Return flow is greatly increased in salinity due to evapotranspiration, ionic exchange, filtration, soil erosion, and the solution of any additional chemicals applied to the fields, in particular pesticides and fertilizers. From table 1.4 it can be seen that irrigation has caused conductivity in drainage water to increase 5 times, chloride 12 times, nitrate 10 times, phosphate 3 times, and calcium 4 times. Such increases are highly significant particularly in terms of algal blooms, and their related problem of deoxygenation of stream water.

1.7.2. Intermediate fluctuations in water chemistry.

Angino et al (1972) considered the effects of urbanisation on stormwater runoff quality by weekly sampling of flow in a representative channel - Naismith ditch, Lawrence, Kansas. The yearly range of values within the ditch were exceptionally high; 6.2-10.1 pH, 2.2-14.8 mg l^{-1} nitrate, and 0-513 mg l^{-1} chloride. Such values were attributed to the wash-in of pollutants from road maintenance, municipal gardening, and some sewage. The

	MUSGRAVE AVENUE DRAIN		POWELLS CREEK		BUNNERONG STORM WATER COURSE	
	DRY	FLOOD	DRY	FLOOD	DRY	FLOOD
Nitrate mg l^{-1}	1.0-2.5	0.14-1.9	0.98	0.5-1.6	0.1-1.0	0.2-0.9
Phosphate mg l^{-1}	0.8-3.2	0.8-7.6	0.7-4.9	0.7-5.4	0.8-2.0	0.6-4.3
pH units	6.7-7.8	5.8-7.6	7.2-7.7	6.6-7.5	6.9-7.9	6.1-6.8
Ammonia mg l^{-1}	0.3-4.9	0.4-13.3	0.4-2.1	0.4-14.0	0.3-2.6	1.2-4.1

TABLE 1.3. Comparison of water quality of storm drains in Sydney, Australia in dry and flood conditions. (From Cordery, 1977).

	IRRIGATION WATER	DRAINAGE WATER
Temperature °C	16	13.3
pH units	8.1	7.7
Conductivity $\mu S\ cm^{-1}$	82	420
Chloride $mg\ l^{-1}$	1.0	2.5
Nitrate $mg\ l^{-1}$	0.25	2.5
Phosphate $mg\ l^{-1}$	0.21	0.66
Calcium $mg\ l^{-1}$	10.0	44.0

TABLE 1.4. Comparison of irrigation water quality and surface drainage quality in the Yakima River Valley, Washington, USA. (From Sylvester and Seabloom, 1963).

range reported exceeds expected natural fluctuations, normally in the range of 2 pH units, 3mg l^{-1} nitrate and 5-10 mg l^{-1} chloride (see Sutcliffe, 1983), although in some natural channels the response to individual storms can give a suprisingly high degree of change. For example Edwards (1973b), from work on the rivers Yare, Tud and Wenson reports that calcium spanned 20 mg l^{-1}, nitrate ranged from 8.5-14 mg l^{-1} and sulphate from 33-49 mg l^{-1}. Foster and Walling (1978) document the following values for the Yendacot rural stream in Devon, after the prolonged 1976 drought. Values of conductivity rose from an average of 500 to 1000 μS cm^{-1}, calcium from 25 to 75 mg l^{-1} and nitrate from 5 to 75 mg l. These high values however dominate water chemistry for a matter of days in natural channels, whereas urban channels have more consistently high concentrations, occasionally drastically reduced by stormwater discharge (Cordery,1977). Furthermore, it has been shown e.g. Bryan (1982), that input from some urban areas of organic matter, gives higher values than those obtained by the discharge of raw sewage from an area of the equivalent size.

Sewage itself has a serious impact on intermediate fluctuations of drainage water quality (Scorer, 1974), by tending to introduce chemicals not produced in a natural basin in any significant quantity e.g. chlorine and inorganic ammonia. Both of these substances are known to be highly lethal to fish communities (Lewis, 1981). The influence of such chemicals may extend some distance below the sewage outfall, although this depends very much upon the speed of flow of the receiving stream, with faster moving water bodies being affected further downstream, than those moving sluggishly (Lewis, 1981).

Seasonal fluctuations of nitrate in ditches draining heavily fertilized agricultural land, is well recognised although it has been measurered consistently at only a very few places in Britain. One of these is the Saxmundham experimental station, where clear peaks in concentration of nitrate are displayed during May, June and July, brought about by the leaching of nitrogen applied as fertilizer and liberated by mineralization. Flows that contain most nitrate occur during the summer, and invariably follow heavy rain (20mm or more in 24 hours). Values may reach 30-90 mg l^{-1} which is primarily due to a rapid expansion of drainage area (Cooke and Williams, 1970). Despite these extremely high nitrate values, the receiving river, the River Alde, rarely has nitrate values above 2 mg l^{-1} (Cooke & Williams, 1970), owing to the fact that much of the water in the Alde is from non-arable farming land.

The influence of farming types on drainage water chemistry is very important, and is shown by Table 1.5. It would seem that intensive cattle rearing or milk production, can have a very serious, detrimental effect on local drainage water; however, Cooke and Williams (1970) conclude from their study that the suprising feature of the small drainage ditches is not that they are polluted, but that the lower reaches of the rivers receiving such dirty water, should contain as little nitrate and phosphate as they do. Such a feature must be the result of three processes: oxidation of ammonia to nitrate by naturally occurring bacteria, a process well used in the sewage disposal industry; uptake and adsorption of nitrates and phosphates by diatoms, algae and mosses, all found in abundance in the natural channels; and dilution by rainwater and drainage water from less intensively farmed areas of the catchment.

Variation in the nutrient discharge for two sub watersheds with different land use in response to storms, was compared by Monke et al (1981), and Table 1.6 illustrates the importance of arable land use on stream nutrient level. In particular, results indicate that nitrate concentrations are higher in the channel draining the sub watershed, which encompasses a larger percentage of agricultural land, and that amounts of nutrients in both areas were greatly affected by rainfall. Interestingly, the concentration of nutrients contained in sediments is extremely high, particularly during small storm events. This shows how the preparation of the soil for arable crops, makes nutrients readily available for "wash off", and such sediment bound nutrients may remain in temporary channel storage within the stream, only to be removed from the sediment during the violent first phase of a storm, adding to the flushing process of readily soluble nutrients. The significance of such inchannel storage potentially can be most important to the resultant chemographs during storm events, and should not be overlooked as a contributary factor.

Controlled experiments at the catchment scale altering land use totally, gives a very clear appreciation of the seasonal/yearly nutrient variations that occur in rivers as a result of such change. The quality of water flowing from undisturbed watersheds is usually regarded as high (e.g see Omernick, 1976), albeit somewhat acidic (Sopper 1975); for example, pH in the range of 4-5 is not uncommon from waters draining oak forests.

	Ammonia	Nitrate	Phosphate	Chloride
	(concentrations in mg l^{-1})			
Effluent farm poultry manure	2.5	0.0	5.0	280
Stream flowing by manure heap	0.2	4.5	0.4	74
Stream flowing by intensive cow unit	30	1.5	2.6	375

TABLE 1.5. The significance of farming types on surface drainage water quality. (From Cooke and Williams, 1970).

	Baseflow (1)	Small events (2)	Big events (3)
Total soluble phosphate mg l^{-1}	0.05 (0.12)	0.10 (0.22)	0.08 (0.13)
Sediment phosphate mg l^{-1}	0.11 (0.38)	1.3 (1.6)	3.7 (2.9)
Soluble nitrate mg l^{-1}	2.1 (3.6)	7.4 (4.5)	5.2 (4.0)
Sediment nitrate	0.4 (1.1)	5.6 (6.8)	2.5 (2.0)

Values in brackets for DREISHBACK DRAIN, catchment containing 74% gently rolling, 26% level topography (35% of the drainage area is arable, 2% is occupied by town of Harlan, the remaining 63% is grassland). Values not in brackets for SMITH FRY DRAIN, catchment containing 29% gently rolling, 71% level topography (63% of the darinage area is arable, and the remainder is grassland)
(1) Baseflow - long time steady in nature - largely groundwater inputs (2) small events - in between (1) and (3) (3) big events - producing more than 2.5 cm of runoff from an entire drainage area.

TABLE 1.6. Chemical response of two different landuse types to storm water input. (From Monke et al, 1981).

When forests are removed by clear cutting, this quality is almost invariably affected (Feller and Krimmins, 1979). Early studies indicate that once roads are built and the protective influence of the forest removed, then significant increases occur in streamflow(Hibbert+Cunningham, 1967) sediment levels (Reinhart and Eschner, 1962), maximum stream temperature (Brown and Krugier, 1970) and dissolved nutrient levels (Likens et al, 1967). Although this latter may decline when rapid leaching removes available sources.

From the classic Hubbard Brook experiment (literature summarised in Likens et al, 1977), in which a complete sub catchment in the White Mountains, Utah, USA, was deforested, and vegetation regrowth restrained for two years by the application of herbicide, it was reported that changes in water quality of the stream draining the cleared water shed, did not appear until about 5 months after the clearing. Despite the lack of overhead canopy, factors such as non disturbance of the humus layer, normal deposition of leaves from the previous autumn and the presence of a snow cover on the ground, at the time of cutting, and subsequent snow accumulation for the remainder of the winter, all apparently maintained the water shed in a dormant winter condition, similar to the forested watersheds. Immediately after snow melt runoff however, marked changes in stream water chemistry occurred.

In the summer months, June to September, nitrate levels in the stream water of the Hubbard Brook, normally occurred in concentrations of less than 0.1 mg/1^{-1}. In the autumn, available nitrate is leached through the soil and ultimately contributes to increased concentrations in stream water, rising to a peak of 2 mg/1^{-1} in March or early April, only to decrease to low levels again in May or June. After forest clearance nitrate levels increased dramatically in May to as much as 80 mg/1^{-1}, with an overall increase of about 50 fold for the period of total deforestation.

Other than nitrate, calcium levels rose 2 - 6 times above concentrations in undisturbed watersheds. Chloride concentrations increased from about 0.5 - 1.0 mg/1^{-1}, although this gradually diminished to pre-treatment levels. pH fell from 5.1 - 4.3 units, probably due to the production of hydrogen ions during nitrification of soil organics (Pierce et al, 1970).

In sharp contrast to these large nutrient losses reported for the Hubbard Brook Watersheds in New Hampshire, data presented from other parts of the US, report little nutrient depletion after clearcutting (Sopper, 1975). For example, Aubertin and Patric (1972), found that nutrient release, increased only slightly after a carefully planned economic clearcut, where the top soil is disturbed as little as possible, vegetation regrowth encouraged, and harvesting is carried out after spring snowmelt, but before the summer time growth spurt. Table 1.7 from Sopper (1975) shows relatively little variation in nutrient loss from forest and clearcut watersheds.

Studies by Reinhart and Eschner (1962), and Fredrickson (1971, 1972) reiterate the findings of Aubertin and Patric (1972), that nutrient loss from clear cutting is not a serious input to drainage water. The Hubbard Brook experiment in fact, appears to be atypical, and perhaps too much emphasis has been placed on the results from this single, albeit comprehensive, experiment. The experimental procedures bear little or no resemblance to commercial clearcut forestry practices, primarily in two respects. Firstly, during industrial logging large volumes of forest litter are not left lying to decay, and secondly, re-vegetation is rapid,(indeed virtually an immediate regrowth of the disturbed flora) certainly there is no hampering of restablishment by massive doses of herbicide.

At the intermediate or seasonal time scale, man can have a significant effect on river water quality, either directly through the input of sewage, storm water drainage, and irrigation, or indirectly through urbanisation, fertilizer application and other agricultural practices. However, it would seem from the majority of studies, that much of the initial rapid changes due to man's activities, are absorbed by natural responses at this intermediate time level; unfortunately, long term trends are not so easily buffered.

1.7.3. Man's long term impacts on river water quality.

Every new suburban development, every new industrial plant, and every change in fertilizer use, alters the hydro-chemical balance of a river (Douglas 1983). The long term consequences of such alteration, although perhaps appearing to be insignificant in comparison with some dramatic changes in water chemistry e.g the polluting effects of untreated sewage released into a river system, or an accidental spillage of hazardous waste - are none the less insidious, despite the fact that other parts of the catchment system may have time to adapt to the new constraints

	GROWING SEASON May - Oct		DORMANT SEASON Nov - April	
NUTRIENT ($mg\ l^{-1}$)	CLEARCUT	FOREST	CLEARCUT	FOREST
Nitrate	0.8	0.32	0.49	0.10
Calcium	0.99	1.07	0.73	0.78
Phosphate	0.07	0.04	0.04	0.02

TABLE 1.7. Average nutrient concentration in streamwater from forested and clearcut Fernow watersheds, USA. From Aubertin and Patric, in Sopper (1975).

placed upon them. The reason for this insidiousness is that the solutions to the problems of the long term changes in water chemistry - e.g the problems of acid rain, high nitrate levels in groundwater or deoxygenation of estuaries - require major changes in our own life style.

Long term effects of man's activities on river water quality are often difficult to assess, due to natural cyclical variations, poor data base, and isolation of critical factors e.g is defoliation in the Scandinavian forests due to acid rain, resulting from coalfired power stations, or is it due to hydro carbon pollutants from traffic exhaust, or indeed is it in response to a tree disease? Nevertheless inspite of these problems there is little doubt that long term changes are occurring in river water chemistry. A way of demonstrating this without a long data base, is presented by Koch (1970), who compares natural and man affected river water quality (Table 1.8).

Figures presented in Table 1.8, have been averaged over one year, however it is clear that there is a significant difference between urban and rural water quality. Assuming the streams are comparable, nitrates have risen by about 13-14 times, chloride and conductivity by about 4 times, and phosphate concentration is actually lower in urban streams. These changes are associated with industrial and domestic sewage inputs, stormwater drains, and change in catchment surface permeability - from woodland and pasture, to concrete and tarmac.

In agricultural areas, the threat of slowly increasing stream nitrate levels, due to fertilizer leaching (Troake etal,1976) has caused much concern, and also given much scope for research. Essentially, because nitrate is the major nutrient for plant growth, too much in rivers may give rise to excessive weed growth, leading to eutrophication, and hence dramatic deoxygenation of the waters. Furthermore, recent research suggests that drinking water containing nitrate concentrations of more than 25 $mg \cdot l^{-1}$ can cause brain damage (Goodman, 1980). Obviously the significant upward trend of nitrate concentration is undesirable in British rivers.

The blame for this upward trend of nutrients in our rivers is not only to be taken by the increasing amount of nitrogenous fertilizers applied per acre of land, but also by the actual management of that land, such as fertilizer application rate (Owens 1970), and landuse. Williams (1976) found that drainage

STATE OF RIVER	NAME	Ca^{2+} mg/l^{-1}	Cl^{-} mg l^{-1}	NO_3^{-} mg l^{-1}	PO_4^{-} mg l^{-1}	Cond μScm^{-1}	pH units
NATURAL	Carmans River						
May 1966	at Yaphank	6.2	8.2	1.7	-	86	6.9
June 1968		6.2	7.0	1.2	0.09	86	6.7
NATURAL	Connetquot River						
May 1966	at North Great	4.2	7.9	1.5	-	71	6.8
June 1968	River	4.0	6.5	1.7	0.15	65	6.8
URBAN	Massapequa Creek						
May 1966	at Massapequa	13	20	12	-	211	6.2
June 1968		20	27	28	0.1	301	6.5
URBAN	East Meadows						
May 1966	Brook, at East	18	47	22	-	326	5.9
June 1968	Meadows	23	64	20	0.08	411	6.8
URBAN	Millburn Creek						
May 1966	at Baldwin	-	17	10	-	239	6.4
June 1968		-	25	26	0.04	350	6.7

TABLE 1.8. The Water Quality of Streams in Southern Nassau County. From Koch (1970). A comparison of urban and natural streams under equivalent flow conditions.

water from arable land at Rothamsted (1970-74) contained an average of 9.8 mg l^{-1} nitrate. At Saxmundham (1972-74) he found 19.3 mg l^{-1} from arable land, and 4.1 mg l^{-1} from grass and lucerne. Webber and Wadsworth (1976) found that streams fed by upland pasture drainage, contained little nitrate. At Pwllperion, Dyfed, North Wales, the mean was 0.25 mg l^{-1}, and at Redesdale, the means of six sampling points were in the range of 0.47 - 0.76 mg l^{-1}. In comparison with these values, at Rossendale, Lancashire, where grassland receives about 190 kg ha^{-1} of fertilizer nitrogen, and about 94 kg ha^{-1} nitrogen in manure and slurry each year, drainage water had levels in the range 2.2-7.4 mg l^{-1} (in 1971-73). Hood (1976) from work at Jealotts Hill, Berkshire, noted that very heavy application of nitrogen to partly grazed grassland, resulted in substantial losses to drainage. Runoff from grassland treated with 250 kg ha^{-1} of fertilizer nitrogen, contained annual average nitrate concentrations of 9.4-10.7 mg l^{-1}, whilst treatment with 750 kg ha^{-1} of the same fertilizer, resulted in averages of 18.8.-35.5 mg l^{-1}, a three fold increase in fertilizer creating an approximate 2-4 times increase in nitrate in drainage water.

As with natural river systems, nitrate concentrations in agricultural drainage ditches, have been shown to be greatest when the extent of drainage is greatest, usually in winter and spring (Gostick and Dermott, 1975). Such patterns are consistent from year to year, and thus a new "natural" background water quality has been established. The great concern is however, that the general trend of nitrate concentration is upward, although Tomlinson (1970) investigating trends in nitrate concentration in English Rivers in relation to fertilizer use, found that there was little change in nitrate levels e.g The River Dee at Chester had an increase of 1.1 - 1.6 mg l^{-1} nitrate (1961-67); the River Derwent at Hathersage an increase of 0.8 - 1.7 mg l^{-1} nitrate (1953 - 67); the River Tyne at Wylam an increase of 0.3 - 0.9 mg l^{-1} nitrate (1953 -67). Tomlinson concluded from this survey that there was no general increase of nitrate concentration in English Rivers during the 15 year period considered. Such a static situation is not due to the better adsorption of the increasing use of fertilizers, and better land management, but rather due to the buffering capabilities of natural waterways.

1.8. Chapter Summary.

When all time scales of channel response to catchment change are considered (and of course in reality they are not isolated responses), an approximate table of comparison can be produced, using data restricted to authors who actually present a range of figures (table 1.9). The most comprehensive set of values is for nitrate, and change is somewhat dramatic. This is to be expected, since disturbing the catchment, either naturally or by an extension of runoff, or by ploughing or building, previously unexposed soil sources of nitrate become immediately available for solution, eventually leading to a rise in stream nitrate levels. Interestingly, natural events can cause at least as much, if not more, increase in nitrate concentrations than man induced catchment change events; however, such "natural" events are freak occurrences, not everyday happenings.

Other ionic responses to the effect of urban and agricultural development are certainly important, although from Table 1.9, it would seem that changes are no more than those expected in a natural system, except in the case of urbanisation on chloride levels. This huge increase is due to the input of treated domestic sewage, which contains a high concentration of bleach, that is sodium hypochloride. It must be said that in the literature, examples only with spectacular natural change are likely to be reported, whereas no change in water chemistry, as a result of dramatic catchment development, is more likely to be reported than significant change. Despite this, Table 1.9 does provide a useful ready reckoner against which to measure any changes in water chemistry reported in this and other studies.

The studies discussed in this chapter, highlight the significant areas of research, when considering water quality in the natural or man effected riverine system. In particular, it emphasises the importance of identifying a time scale at which to direct inquiry. Such a scale may be short term, intermediate (seasonal) or long term. In the assessment of the impact of reservoirs on downstream water quality, some study has been made on the long term impacts by considering the effects of reservoir eutrophication (Mortimer 1971; Battarbee, 1977; Gower, 1980), although the real effects of this process on the nature of the river water downstream, has only been considered at best for under a kilometre below the outfall and at worst, hypothetically. Little research has been directed to the effects of reservoirs on the seasonal or short term water quality fluctuations in regulated rivers, and yet it is clear from works already mentioned that at these time scales, change can be significant.

DOMINANT FACTOR	AUTHORS	Cond. $\mu S\ cm^{-1}$	PO_4^{2-} $mg\ l^{-1}$	Ca^{2+} $mg\ l^{-1}$	NO_3^- $mg\ l^{-1}$	Cl^- $mg\ l^{-1}$	pH units
FIRST FLUSH	Foster & Walling'78	x2	-	x3	x15	-	-
SEASONAL	Sutcliffe '83	-	-	x2	x3	x2	+-2
	Feller & Krimmons '79	x3	-	-	-	-	+-0.8
URBANISATION	Koch'70	x4	x0.6	x1.5	x13	x4.5	+-0.4
	Angino et al '72	-	-	-	x6	x500	+-3.9
AGRICULTURAL (fertilizer)	Williams '76	-	-	-	x4.7	-	-
	Webber & Wadsworth ' 76	-	-	-	x5.5	-	-
	Hood'76	-	-	-	x2.7	-	-
	Monke et al '81	x0.9	x2.0	-	x1.5	-	-
VEGETATION REMOVAL							
	Sopper'75	x1.8	-	x0.9	x1.6	-	-
	Pierce et al '67	-	-	x2.6	x50	x2	+-0.8
IRRIGATION	Sylvester & Seabloom '63	x5	x3	x4	x10	x12	+-0.4
FLOODS							
South Tyne	Johnson & Glover '74	-	-	x4	-	-	-
Hodge Beck	" "	-	-	x5	-	-	-
Dunton Beck	" "	-	-	x2	-	-	-
Catchwater	Imeson'70	-	-	x1.5	-	-	-
Maesmant	Lewin' et al '74	-	-	x4	-	-	-
R Cynan	Edwards '73b	-	-	x8	-	-	-
R Yare	" "	-	-	x1.5	-	-	-
R Tud	" "	-	-	x1.5	-	-	-
R Wensum	" "	-	-	x1.5	-	-	-
R.Hooke	" "	-	-	x2	-	-	-

TABLE 1.9. River water chemistry changes induced by a variety of catchment events.

The literature also portrays the extreme difficulty of comparing data on a temporal or spatial basis in identifying water quality changes due to a specific impact. Using controlled reservoir releases at the short time scale, the dominant factors can be isolated, and specific impacts identified. Furthermore, these impacts can be traced downstream for as far as they remain identifiable. Both at this scale and the seasonal scale, it has been shown, that of prime importance to the chemical content of river water, is the effect of flushing. Since this phenomenon (which can disrupt the inverse discharge/solute load relationship), has been demonstrated to be primarily dependent upon hydrological drainage paths, removing readily soluble deposits that have accumulated in the catchment, this process should certainly be manifest at the seasonal time scale. At the immediate time scale however, during a controlled reservoir release, the phenomenon of flushing should be missing, since the majority of water flowing in the channel is derived from the reservoir, and not from catchment sources, and therefore will be devoid of extra solutes, from storage sources within the catchment. Unless, as has been mentioned only in passing by other research workers, inchannel stored solutes are significant to the chemistry/discharge relationship. .

In summary, workers in the past have identified relationships between drainage and solute load variation for natural floods (short term), and seasonal patterns of water quality, relating to changing catchment water source areas and vegetational conditions. However, specific process/response impacts have proved difficult to identify, particularly at the major river scale. This is the result, not least, of the failure by many workers to link successfully water quality models with hydrological/flow routing models. This study seeks to isolate the impacts of reservoirs on major rivers, both at the intermediate and instantaneous time scales, and particularly asks the question - are chemical changes within the river system during varying discharge conditions real changes, or simply hydrological manifestations?

CHAPTER 2.

THE WATER QUALITY OF REGULATED RIVERS.

The regulation of rivers may involve any number of structural or diversionary tactics. However, in the context of this thesis, the only regulation being considered is that produced by reservoir construction. This chapter examines the chemical importance of controlling a river in such a fashion. Three areas of change are considered: the chemical variation of inflowing water, the chemical change of outflowing water, and the dominance of these alterations downstream. The significance of lateral and vertical patterns of reservoir water quality, and this influence on inflowing water, become crucial when assessing this downstream impact of releasing reservoir water.

2.1. Reservoir impact downstream - non U.K literature.

Work on reservoirs in countries other than the U.K have shown limnological controls to be of prime importance when considering the reservoir effects on downstream quality. In particular, the time of year and the depth of release have been shown to be critical factors. Patterns of change in calcium, bicarbonate, hydrogen, manganese, iron, and oxygen concentrations in release water from Canyon Reservoir, Texas (Hannan and Young, 1974)- a deep storage, basal outflow reservoir - were related to flow dynamics within the water body. Such dynamics were a result of the interaction of natural inflow, regulated outflow, thermal stratification, the pattern of hypolimnetic dissolved oxygen depletion, overturn and community metabolism. In particular, calcium levels decreased with distance down reservoir, which was attributed to the precipitation of calcium carbonate. At overturn, the lower concentration of calcium in the epilimnion at the dam end of the reservoir diluted the higher concentration that occurred in the hypolimnion during anoxia. The result was progressive down-reservoir decrease in calcium concentration during the winter months, hence a reduction of calcium concentration in outflowing water, leading to dilution of this species downstream.

Somewhat in contrast to this, it has been documented that throughout the year Slapy Reservoir, Czechoslovakia (Hrbacek, 1969) does little to change the actual nature of inflowing solute load. The concentration of dissolved and suspended chemical substances within the surface layer of this reservoir, showed a more or less close relationship to the concentration of these substances in inflowing water. However, although the basic nature of water quality remained unchanged by the reservoir, solute concentration was reduced, which led to a downstream dilution effect.

An improvement in water quality, resulting from river regulation is presented by Simmons and Voshell (1978). When examining the North Anna River Basin, USA, before and after reservoir construction, they found that downstream water chemistry had improved and that the new reservoir acted as a sink for anions and harmful cations; in particular, heavy metals released by upstream mine workings.

It is not always the case that the reservoir releases higher quality, lower solute load water, into its impounded river. Discharges of water of high salinity from Lake Mead into the Colorado River, and from Bighorn Lake Reservoir into the Bighorn River, as a result of deep water withdrawal, have a marked effect on downstream biological production (Soltero et al, 1973). The clear, nutrient rich release water is abundantly more fertile than the receiving stream water, leading to an increased productivity downstream.

It would seem then that the effects of release water on downstream water quality may be divided into two categories, according to the depth of outflow, a dilution effect if surface water is released, and an enriching effect if basal water is released. Martin and Arneson (1978) set out to study this hypothesis, first proposed by Wright (1967). The study areas were: Hebgen Lake, Montana, USA, which is a deep bottom draining reservoir and Quake Lake, also in Montana, which is a natural deep lake, with surface discharge. Both water bodies demonstrated epilimnetic depletion and hypolimnetic accumulation of nitrate as summer progressed. This seasonal pattern was directly related to thermal stratification and fall overturn. Salinity also increased in the hypolimnion of both lakes during this time. During the thermal stratification period, Quake Lake (surface outlet) discharged low nutrient and low salinity water, whereas Hebgen Lake (basal outlet) discharged high nutrient and high salinity water. At other periods of the year increases of nutrients and other salts, usually trapped in the hypolimnion, would mix with the epilimnion, particularly during overturn, giving a more homogeneous water chemistry, hence increasing solute content at the outflow for the surface draining lake, and lowering it for the basal draining reservoir. These trends reported by Martin and Arneson (1978) are substantiated by other workers (see Hannan, 1980), and it must be concluded that reservoirs often act as sinks for many organic and inorganic substances, the result being lower concentrations of these chemicals at the outflow regardless of release depth.

2.2. Average water chemistry of a regulated river.

Average water chemistry in rivers downstream of regulating reservoirs is the product of a combination of natural catchment processes, and reservoir water chemistry, which is in itself a product of natural limnological processes within the impounded water body (Truesdale, 1973). If tributary inflow is low in comparison with the contribution of reservoir release water, then the riverine system will reflect the limnological ecosystem processes and phases. However, if the tributary inflow is high in comparison with release water, the the effect of the reservoir will be negligible. A summary of water chemistry changes below dams is given in table 2.1 (adapted from Petts 1984). This table gives an indication of the lack of work that has been done on the water chemistry of regulated rivers in this country in comparison with that in the USA. Apart from the consideration of temperature variations (e.g. Smith and Lavis, 1975), Crisp (1977) is the only author to examine systematically reservoir effects on water quality immediately downstream of the outflow, and then for only one reservoir-river system, namely the Tees below Cow Green Reservoir.

Fig 2.1, attempts to outline the pertinent factors for the consideration of the effects of river regulation. Essentially it may be divided into two parts, namely; river water processes and reservoir water processes. These two integrated sets of controls, in regulated rivers are united and combine to create a unique river water chemistry.

It has been established in the literature, that for natural water chemistry as a whole, geology is the dominant factor determining solute load (e.g Gregory and Walling, 1976; Douglas, 1972; Feth ., 1961; Hem, 1970). Rock composition influences water solute load directly, via chemical weathering and indirectly via the provision of parent material for soils and nutrients for plants, which can then be washed into the riverine system. Hence there is a significant relationship between background water chemistry, vegetation, soil type, and

River, reservoir location	Water quality change	Source
Missouri River, Fort Randall Dam USA	normal high salinity of river discharge was delayed	Neel, 1963
Brazos River, Morris Shephard Dam, Texas, USA	solute loads reduced to between 10 and 80% of of influent flow levels	Stanford and Ward, 1979
Bighorn River, Bighorn Lake, USA	total nitrogen and total phosphorus reduced to 75% and 14% respectively	Soltero et al 1973
Niger River, Kainji Reservoir Nigeria	natural river low in chemical nutrients; bicarbonate, calcium and sodium increased in reservoir outflow	Imevbore, 1970
River Tees, Cow Green, Reservoir, UK	mean calcium concentrations reduced by 50% but annual maxima reduced by 75%, from 37.2mg l^{-1} to 8.9mg l^{-1}; and minima increased by nearly 100%	Crisp, 1977
Guadalupe River, Canyon Reservoir USA	mean specific conductance reduced by 34% but concs of ferrous iron may be increased by up to 1800% during periods of stratification	Hannan and Broz, 1976

TABLE 2.1 Some observations of water chemistry changes below dams.

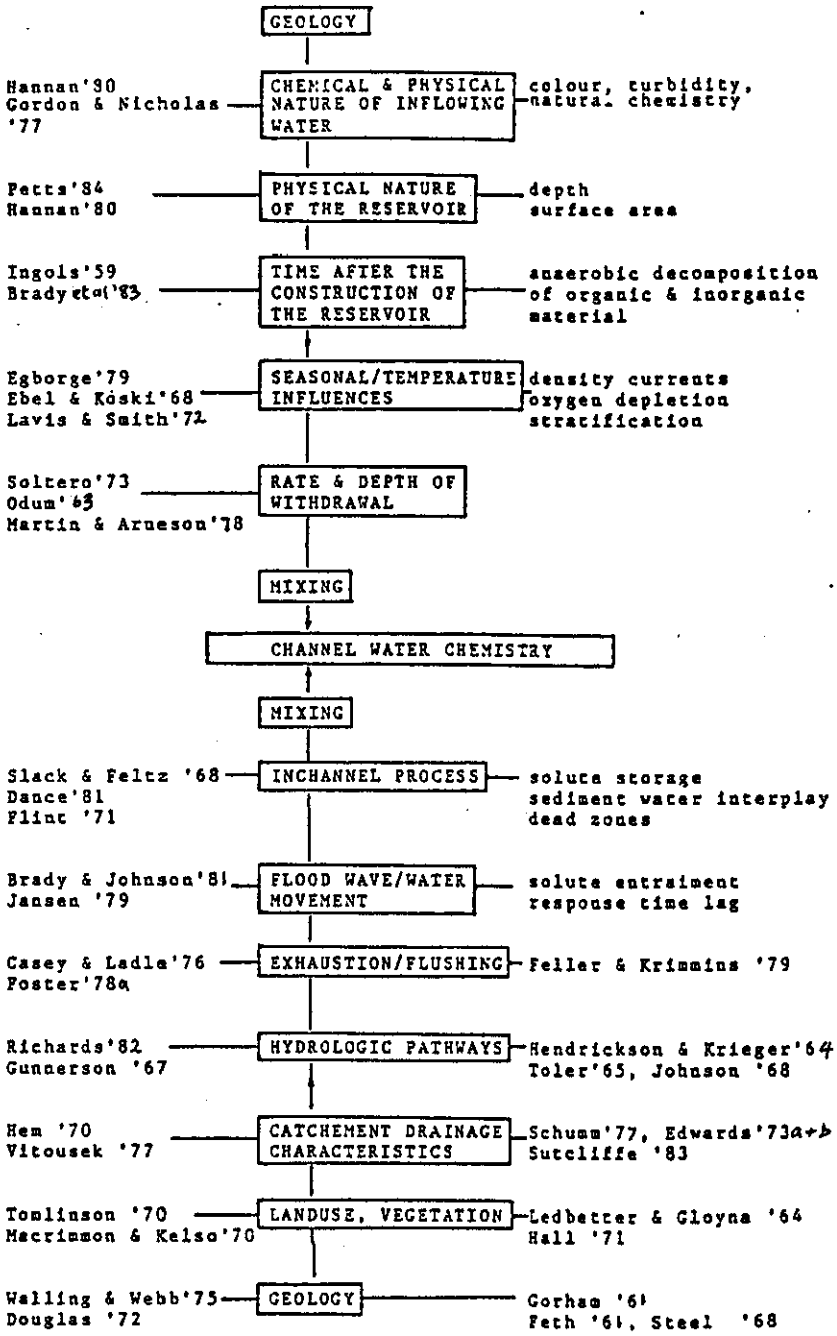


Fig.2.1. Factors influencing inchannel natural water chemistry.

landuse, governed by the basic geology (e.g Walling and Webb, 1975).

Catchment drainage characteristics are, in turn, dependent upon those four factors (see Leopold et al, 1964; and Schumm, 1977, 1979). Water chemistry from varying catchment hydrological zones, has been shown to have particular solute characteristics according to the given transmission route (Hendrickson and Krieger, 1964; Toler, 1965; Johnson , 1968; O'Connor, 1976; and Burt, 1979a). This factor, together with the effects of natural solute flushing and exhaustion, plus inchannel processes are the major catchment determinants of background river water quality and have been discussed in Chapter 1.

The water chemistry of large storage reservoirs, in contrast to stream water chemistry, is relatively simple, and may be considered as a dynamic trophic system, in which natural and regulated flow dynamics interact with thermal stratification and community metabolism, to control the chemical dynamics within the impoundment and chemical composition of the outflow (Hannan, 1980). Therefore, water released from a reservoir to a river is likely to be of predictable quality (assuming the depth of release is known) and will be relatively consistent in its chemical nature. This composition is now examined.

2.3 The chemical nature of reservoir water.

River water that is impounded undergoes a series of changes in its solute load, due to physical, thermal, and biochemical effects. These three semi-dependent groups of processes, although influencing the background river water chemistry, take on different, and in some cases more significant roles when the low volume, rapidly moving river water is retained behind a dam to create a large volume, slow moving water body. The most important factor influencing the chemical nature of an impounded lake, once maturity is reached, is thermal stratification (Petts, 1984).

2.3.1 Thermal Stratification.

In summer, within temperate regions, intense surface heating causes three well defined layers to develop in a large lake: an upper level, the epilimnion; a lower level, the hypolimnion; and a distinct zone of downward decreasing temperature (thermocline) between these, termed as the metalimnion (Smalley and Novak, 1978). The development of these layers depends not only upon surface heating, but also upon such physical constraints as water depth, surface area, exposure to wind, the retention time of water, colour and turbidity. Thermal stratification will occur, in temperate zones, if the water body is 15-20 metres in depth (Ridley and Steel, 1975), any shallower than this and radiation, coupled with convective processes, will keep temperature homogenity. Furthermore, any slight stratification that might develop, can be quickly dissipated by physical disturbance of the water.

2.3.2 Physical constraints on stratification.

If the lake has a large surface area, then it is subject to physical disturbance by wind, leading to wave action, which can create a mixing of layers and destruction of any stratification (Lackey, 1972; Canter, 1983). If the rate of inflow and outflow is high, that is, the water retention time is short, then again, layers are disturbed; although if stratification is well established, then inflow water of a distinct thermal and chemical nature, may not mix at all and simply flow as a 'stream' through the reservoir, that is, as a density current. The importance of such currents is illustrated by Harding et al (1981).

Dark coloured water, or water with a high turbidity is more susceptible to thermal stratification than clean water, as sunlight cannot penetrate very deeply, and heat is well absorbed by the dark surface body. The ideal reservoir then, for thermal sratification would be deep (15 metres or more), of small surface area, well protected from the wind, and with a small but steady input of debris laden, highly coloured water.

An almost perfect example of such a reservoir is the Alminke Reservoir, Crimea, USSR. It has a surface area of only 25 ha, a depth of 15m, and receives sediment rich inflowing water. The thermal stratification is impressive, with a summer temperature gradient from 23°C at the surface, to a basal temperature of 15.6°C. In complete contrast to this is the Rybinsk Reservoir, on the Upper Volga, USSR. It has a surface area of 450,000 ha and an average depth of 5.5m; as a consequence thermal stratification does not develop (Zh adin and Gerd, 1963).

2.3.3 Overturn.

In temperate regions, during the autumn, there is a progressive cooling of surface water, which sinks and is replaced by warmer upward-moving water; a phase termed overturn. Eventually isothermal conditions will establish. As with the establishment of summer thermal stratification, the rate of overturn is determined by physical controls (Petts, 1984). In the winter, intense thermal stratification may occur again, as in high latitude and high altitude lakes, with surface freezing and a gradual warming with depth to a maximum of 4°C. The spring will see the surface water warming, creating once again a period of overturn and for a relatively short time interval, isothermal conditions.

2.3.4. Thermal environmental effects on water chemistry.

The thermal environment within an impounded water body is critical in determining water chemistry in two ways. Firstly its effect on water density may inhibit the cyclical movement of ions, which in summer will result in a nutrient poor, upper water stratum, where planktonic organisms abound, and a nutrient rich lower stratum that is deficient in living planktonic organisms (Brylinsky and Man, 1973; Denny, 1972; Ganf, 1974; Proszynska 1966; Talling, 1966; Thomas and Ratcliffe, 1973). In short, the thermal regime creates layers of unique chemical character. Secondly, the cold dense water is often depleted in dissolved oxygen, a fact exaggerated by the oxygen consumption within this layer by heterotrophic bacteria and decaying phytoplankton (Petts, 1984), leading to anaerobic conditions within the hypolimnion during summer, which in turn leads to the chemical reduction of nitrogen compounds, and the release of manganese, iron, and hydrogen sulphide together with other reduced compounds from basal sediments (Ebel and Koski, 1968; Egborge, 1979; Hannan, 1980; Martin and Arneson, 1978;). It is important to realize that seasonal variations in the reduction potential of basal sediments is not solely due to the temperature cycle, but is due also to the rate of removal of reduced substances, and to the accumulation of organic debris. For example, Mortimer (1971) inferred that the seasonal variation in the denitrification potential in the sediments of Lake Arreso, USA, was a response to increased sedimentation of organic materials, and not due to temperature variations.

2.3.5. Spatial pattern of water quality.

A thermally induced pattern of water quality within large water bodies has been described by many authors; for example, Egborge (1979) shows from work on Lake Asejire, Nigeria, stratified patterns of pH, conductivity, and phosphate, to be in phase with thermal stratifications. During phase one, October-December, thermal gradients exist without stratification. Phase 2, December-January, is characterised by a period of isothermy induced by the cold hamattan wind. Between February and May (phase 3), the Lake is permanently stratified, and during phase 4, June-September, destratification of the water mass results from the floods of the rainy season. However, many reservoirs also display a spatial pattern of water quality development.

Ebel and Koski (1968) from work on Brownlee Reservoir, Oregon, USA and Gorden and Nicholas (1977) from a study of the Cherokee Reservoir, Tennessee, USA, illustrate the horizontal pattern of water quality in reservoirs. Brownlee reservoir, a deep storage impoundment with an outlet approximately one third of the depth below the surface, showed oxygen depletion up-reservoir in early spring. This depletion spread towards the dam during the summer months. Planktonic productivity was high during the summertime, as indicated by a high pH, high phenolphthalien alkalinity, and low bicarbonate alkalinity. These conditions, together with anoxia in the hypolimnion, caused typical vertical stratification characteristics of eutrophic conditions. Physiochemical conditions varied at the outlet, according to surface and subsurface currents, which were governed by the rate of inflow and outflow. Cherokee reservoir however, whilst being a deep storage reservoir, unlike Brownlee, has a deep outlet. Hypolimnetic dissolved oxygen depletion was observed to occur firstly upreservoir, and then to develop down-reservoir to the dam as the summer progressed. Periodic heavy inflows of well aerated water destroyed much of the anaerobic conditions up-reservoir, however, soon after thermal stratification had established a denser hypolimnion, the dissolved oxygen depletion rate increased, masking the influence of such inflows.

In complete contrast to the above two examples, Norris Reservoir, Tennessee, USA (Weibe, 1938), a deep storage, deep outflow reservoir, was found to have little or no lateral variation in dissolved oxygen or solute load. A strong vertical stratification totally dominated the spatial pattern throughout the year. These examples indicate the problems of predicting release water quality at a given time and from a given strata within the water mass.

2.4. River regulation, and reservoir function.

It has been suggested that dams represent perhaps the greatest point-source of hydrological interference by man (Petts, 1984). Mean annual discharge has been reduced by as much as 80% as a consequence of river impoundment. Water is lost through evaporation, seepage into groundwater, or to industrial and domestic users. High flows have also been reduced, and the timing of annual extremes of flow has been altered. The changes brought about by river impoundment in some instances are likely to be transmitted considerable distances downstream from the dam, so that even the delta or estuary are not excluded from modification. Due to these changes the biological components of the lotic ecosystem, which are adapted not only to average flows, but also to the extremes of flow, are put under considerable stress.

The primary aim of river impoundment is to regulate discharge fluctuations within the river downstream of the dam. Seasonal variations can be controlled by storage of wet season runoff for subsequent release during periods of low flow or drought. Short term discharge fluctuations can be regulated by the storage, and the subsequent gradual release of flood water. Impoundment then, can provide both regular water supplies and relief from flood damage caused by floodplain inundation.

2.4.1. Flood regulation.

Rutter and Engstrom (1964) stated that the basic concept of flood regulation was 'empty space'. That is, the effect of a reservoir upon individual flood discharges is related to the content of the reservoir prior to the arrival of the flood wave. The amount of storage available within the reservoir, depends on the time interval between successive high flows and the volume of those flows in relation to the flood storage capacity of the reservoir, together with the rate of water release and the operational procedures of the given reservoir.

Flood control reservoirs can be divided into two categories, namely, detention basins and retarding reservoirs (Knappen et al, 1952). Detention basins have one or more controlled outlets to allow the planned management of the reservoir storage volume. In contrast to this retarding reservoirs are simple flood storage areas which release water through uncontrolled outlets. The flow-rate through these outlets is proportional to the square root of the head of the water above the outlet. In reality then it is only the detention basin that can be classified as a regulating reservoir, since downstream floods can be effectively managed by the controlled release of water as the reservoir fills in response to the arrival of the flood discharge.

2.4.2. Discharge time lag.

Changes will occur in the timing and rate of flow as a flood wave passes through a reservoir. The flood discharge moving along a channel manifests both translation and attenuation. As the flood water flows into a detention basin it is stored, the water level of the lake is raised and the potential outflow increases; but because of storage changes this potential peak of discharge will not be as high for the outflow as for the inflow. When the inflow ceases, or decreases to a level such that outflow is greater than inflow, the relatively slow drainage from the reservoir causes the flood duration to be increased, and the peak attenuated. This attenuation is obviously dependent upon reservoir management and the rate of flood inflow.

2.4.3. Effectiveness of flood control.

Many of the controls on the hydrological characteristics of a river are altered by river impoundment, so that the direct comparison of inflow and outflow hydrographs may be rendered problematical (Petts, 1984). Precipitation onto the reservoir surface may be important where the reservoir inundates more than 5% of the catchment area (I.C.E, 1975). The effective shortening of stream lengths, following the drowning of tributaries by the reservoir, may also be important. Both these factors serve to increase the rate of water level rise within the reservoir, in comparison with that expected from hydrological records obtained for the natural river at the dam site.

For major floodplain rivers, some impoundments have actually been found to increase flood peaks. Under natural conditions the floodplain may act as a temporary storage of flood water. The construction of the reservoir will reduce this store, and despite attenuation of flood peaks and high retention times, the water released from the impoundment is likely to give a greater peak downstream than before construction (Rutter and Engstrom, 1964).

The containing effect of reservoir storage is independent of the size of the inflow events. In other words, the same volume of a large or small flood will be retained. Therefore, downstream of the dam, floods of moderate frequency may be considerably lower in magnitude than the inflow flood, but rarer floods may be altered only to a negligible degree (Lauterbach and Leder, 1969). Thus, Warner (1981) reported that subsequent to the closure of the Warragamba Dam, Australia, floods with a recurrence interval of less than 2.33 years were reduced in magnitude by more than half, but rarer events were less significantly affected, and the magnitude of the 50 years flood was virtually the same as that of pre-dam event.

Downstream the effects of the impoundment become less and less important, as the contribution of regulated to unregulated water input decreases. However the lag of main stream peak discharges routed through the reservoir may desynchronize the main stream and tributary peaks, although under certain conditions and for particular situations, the opposite effect can occur. The superimposition of hydrographs may result where alteration of the timing of an event causes the main stream and tributary peaks to coincide. Nevertheless, the frequency of tributary confluences below the dam, and the relative magnitude of the tributary streams will determine the length of river affected by impoundment.

2.4.4. Water supply structures.

Although solid-wall conservation dams have been constructed for several thousand years in western Europe they became common only during the eighteenth and nineteenth centuries. Today, over 60% of the dams in Britain impound lakes with a surface area of less than one square kilometre, and 80% have areas of less than 4 square kilometres. Such dams are designed to provide a reliable water supply for industrial and domestic users. Excess water is allowed to discharge freely over a high spillweir, while controlled releases are made to provide a compensation flow, maintaining minimum water levels within the river downstream.

Once the basins are full, the structures exert an immediate effect upon the river discharges downstream. During the time of year that the reservoir is filling, only compensation water is released; once this has been achieved, releases will be made on top of the compensation flow according to downstream requirements and the storage volume left within the reservoir. Thus, the seasonal variation in runoff yield is much less apparent for regulated than natural rivers. In particular the dams almost eliminate extreme low flow, and reduce the frequency of high flows. Separation of the inflow and outflow flood frequency distribution, based upon the annual exceedance series (Chow, 1964), for Stocks Reservoir, River Hodder, England, demonstrates that the frequency distributions for the winter data are closely comparable, but that the magnitudes of summmer-flow frequencies differ considerably. The magnitude of the 5 year returnperiod winter flood is reduced by only 8%, whilst the 5 year summer flood is halved. Also, the small storage reservoirs tend to have a significant effect on the reduction of small and medium sized flood peaks downstream, but little or no effect on rarer, high magnitude events.

2.4.5. Multi purpose reservoirs.

The recent trend in reservoir construction has been toward structures that are multi purpose e.g hydro-electric power, navigation, water supply and flood prevention schemes good examples of such structures are; the Murray Darling system in Australia, in which the river is regulated by nine principal storage reservoirs which supply water for irrigation, hydro-electric power, flood control, and domestic and industrial users (Cadwallader, 1978); the Colorado River, USA, which is arguably the most controlled river system in the world (Dolan et al, 1974), not only is the main stream regulated but also the majority of its major tributaries, it is controlled to such an extent that less than 1% of the Colorado's virgin flow reaches the rivermouth; the Bighorn Lake, USA (Soltero et al, 1973) is designed to meet recreational needs, but the operational pattern is flexible allowing it to meet a changing set of demands. In essence multi purpose reservoirs are monolithic structures, that impose a set of conditions downstream of their outlet almost entirely according to the operational procedure.

2.5 Reservoir releases.

A wide range of operational procedures can produce sudden fluctuations in discharge. Often the rate of water release is in excess of even the largest natural flood rate of rise. Such discharges are usually for hydro-electric power, and irrigation demand, although peak discharge waves have been utilized for navigational purposes (Jansen , 1979), and to meet recreational needs. Furthermore, pulse releases have been made to remove sediment accumulations in the main channel downstream (e.g Graf,1980). Such sediment has usually been deposited by uncontrolled tributary inflows, as documented by Hey (1975), Grimshaw and Lewin (1980), and Petts (1979, 1980, 1984). Below Granby Dam, flushing flows caused marked discharge pulses on the Colorado River (Eustis and Hillen, 1954). These flow fluctuations,(from 0.57 m^3s^{-1} to 7 m^3s^{-1}, over periods of 15 minutes) successfully scoured sediment and algae from below the dam. However, little is known about the the effects of these unnatural surges on the inchannel flora and fauna. Often the rates of stage change, together with the associated changes in water quality, may be more important than the actual magnitude of the release itself. Neel (1963) recognized that daily fluctuations brought about by reservoir releases can discourage littoral stream-life, and may adversely affect the stream's carrying capacity for many life forms. Subsequently, several researchers have examined the impact of rapid flow fluctuations on benthic invertebrate populations (Petts and Greenwood, 1981).

2.6. Dam overspill.

Dam overspill as the term suggests is an occurrence, which although planned for in the design of the dam, is largely uncontrollable. The effect of such releases downstream, from a hydrological viewpoint could be disastrous. Unplanned overspill will only occur in times of long duration, intense precipitation, leading to rapid filling of the reservoir, and consequent spill over the dam. This sudden surge of reservoir water, will place additional strain on the waterway already in flood, possibly leading to bank collapse, and extensive flooding. The effect on the water chemistry however, is likely to be much less significant, because solute levels in the river and the reservoir, will both be at a much diluted level, that is assuming that overspill will occur toward the end of a storm, when natural catchment nutrients and other solute sources, are much depleted. Furthermore, due to the large volume of water involved, local sources of pollution - detectable at low and medium flow - will be washed out with the advent of a catchment event of sufficient magnitude to induce dam overspill.

It could be argued that dam overspill might occur when the downstream river is actually in a state of low flow, at the end of catchment flooding. A localised reservoir catchment storm, might be sufficient to raise water levels enough to induce overspill. Solutes and sediments deposited in the main channel during the large scale catchment flood, will be flushed out by the dilute reservoir water, producing a significant initial rise in the chemograph, followed by rapid dilution down to low solute concentration, approaching that of the reservoir water. In essence, the effect of dam overtopping on downstream water quality depends not so much on the volume of escape water, but rather on the time, in relation to the catchment flood at which the event occurs. Thus, although the chemistry of reservoir water during the flood remains constant, the same is not true for the natural stream water, and the timing of overspill becomes critical.

Discharge control resulting from reservoir impoundment involves the redistribution of discharge in time. The reservoir reduces short and long term flow variability within the river downstream, filling when the inflow exceeds outflow, and emptying when the dam releases exceed the inflow. Many factors determine the precise effects of an impoundment upon the flow regime of a river, and these are summarised in Fig.2.2. The two key influences illustrated here in relation to water chemistry are increased flow fluctuation, and the reduced seasonal variability, together with altered timing of extreme flows. It could be suggested that the pure hydrological significance of these factors alone, (regardless of any chemical change in water quality due to the storage of large volumes of water within a reservoir) will have a major effect upon downstream water chemistry. Furthermore, the changes in water quality vary according to the scale of inquiry (as outlined in Chapter 1). Thus, the immediate variations in water solute load associated with increased flow fluctuations over a period of hours, will be different to water quality changes due to reduced seasonal variability of the flow. In the long term however, the summation of effects, may be to create a river water quality entirely due to pure hydrological regulation. In this study, these two crucial levels of investigation were followed, using the River Derwent, Derbyshire to assess the hydrological impact of river regulation at the seasonal time scale, and the Rivers Tryweryn, Washburn and North Tyne, located in North Wales, North Yorkshire, and Northumberland respectively, to assess the hydrological impact of impoundment on downstream water quality at the hourly (immediate) time scale.

2.7. Chapter Summary.

Most research on the water quality of regulated rivers has been carried out overseas, findings made are directly applicable to reservoirs in this country. Three factors

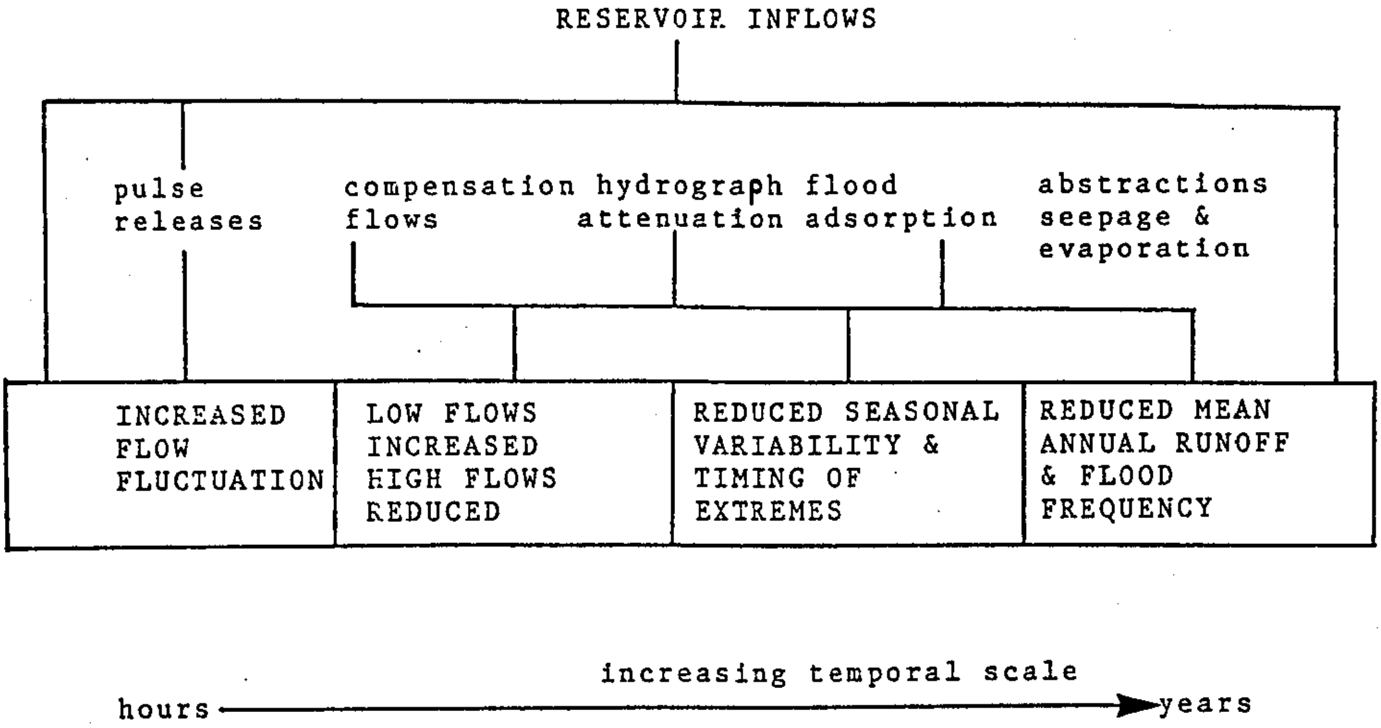


Fig. 2.2. The hydrological effects of river regulation. (Adapted from Petts, 1985).

of impoundment documented in the literature of particular significance in determining the quality of reservoir releases are:-

i) The thermal stratification and the development of density currents, determining the three-dimensional water quality within the impoundment.

ii) The 'sink effect' of the storage of flowing water. Fundamentally, research has shown the 'natural' solute concentrations of water flowing into a reservoir to be diluted by that storage. Although in some instances, metals in particular, not usually found in the unoxidised or dissociated state naturally, can be increased significantly in outflowing water, by retentional processes.

iii) The limnological control factor has been shown to dominate downstream water chemistry. Depth and time of year of release are of particular significance. However, if downstream tributary input is high, then the chemical effects of regulation is likely to be obscured.

Fig.2.2 gives a summary of the factors affecting inchannel water chemistry of regulated rivers. The impact of dams, which are arguably the greatest point-source hydrological interference by man, can be transferred considerable distances below the outfall, essentially due to hydrological control. Thus, flood magnitudes are reduced; discharge in the regulated channel becomes out of phase with its tributary inflows; low flow discharge is carefully controlled; and instant releases down the channel may be made at any time of the year. All these factors are shown to be important to the water chemistry of the channel. The next chapter discusses the problem of linking hydrological changes with water chemistry variations.

CHAPTER 3.

RELEASE MODELLING.

"To develop an understanding of the hydrochemical lag phenomenon occurring in rivers, a knowledge of the behaviour of a flood wave travelling down a channel is necessary"- Glover and Johnson (1974). This statement identifies the importance of linking hydraulics with water chemistry, a concept that may be acheived by determining relationships between wave movement (a hydraulic function) and water particle movement (essentially a chemical function). Unfortunately, often within the literature, there is no clear distinction made between flood wave movement, and flood water movement, and yet results from surveys of changing water quality with natural floods e.g East, 1978; Foster, 1977; Heidel, 1956; Hem, 1970; and Johnson, 1968, all point to the necessity of distinguishing between wave and water movement. Heidel (1956) shows flood water can lag behind its associated wave by up to 12 hours. To accurately follow water movement downstream requires complicated, labour intensive, tracer surveys; such techniques have been applied to the time of travel of both natural solutes (e.g Melfi and Verhoff, 1979) and pollutants (e.g Critchley, 1981; Stall and Hiestand, 1969; White et al, 1979). However, to monitor flood-wave movement simply requires the installation of robust stage recorders. Consequently, research has concentrated on predicting flood-water translation theoretically from observations of flood-wave movement. To produce a satisfactory process based on theory linking the two, firstly requires accurate knowledge as to how the flood-wave itself moves down the channel, and which factors influence this movement. Prediction of flood-water translation alone is complex (Valentine and Wood, 1977), and most attempts use models which necessarily include empirical coefficients. Models of this type, applicable to the analysis of artifical reservoir release waves are of the "flood routing family" and are primarily designed to track flood waves as they move down a river (Weinmann and Laurenson, 1979). These models will be reviewed briefly in order to identify particular simulations applicable to the nature of releases in this study.

3.1. Mathematical flood routing models.

The mathematical flood routing models currently available fall into two broad classes: process-type models, often called hydraulic methods, and models using a conceptual or systems approach, sometimes referred to as the 'black box' approach, but most commonly termed 'hydrologic methods'. The first category adopt complete equations of motion for unsteady flow in open channels, whereas the second category use principles of continuity and the temporary storage of excess volumes of water during the flood period. For natural channels, unfortunately this distinction is fallacious, as the complex physical properties of natural river systems defy exact representation, and therefore, any form of modelling necessarily involves conceptual elements (Weinmann and Laurenson, 1979). Indeed, when attempting to predict the modification of a flood hydrograph in its passage through a river reach, any routing model will involve a number of assumptions and simplifications.

Usually the first step in the development of a mathematical model for flood routing computations is to simplify flow to being purely one dimensional, and to represent all processes that contribute to the loss of energy or momentum by a single lumped parameter, sometimes called the 'frictional resistance coefficient'. This then leads to the Saint Venant system of equations for one dimensional, gradually varied flow. Two groups of models can be identified, models that attempt to solve the complete suite of equations, which are termed complete dynamic models, and those that simplify the equations down, and are called approximate models.

3.1.1. Complete dynamic models.

The Saint Venant equations for gradually varied, unsteady, open channel flow are written (Weinmann and Laurenson, 1979):

$$B\frac{\partial y}{\partial t} + \frac{\partial (Av)}{\partial x} - q = 0 \qquad \text{(Eq.3.1)}$$

and

$$\frac{1}{g}\frac{\partial v}{\partial t} + \frac{v\partial u}{g\partial x} + \frac{\partial y}{\partial x} + S_f - S_o + \frac{q}{gA}(v - u_x) = 0 \qquad \text{(Eq.3.2)}$$

in which t = time; x = distance along the channel; y, v, A, and B = depth, velocity, cross-sectional area, and surface width of flow respectively; g = acceleration due to gravity; q = lateral inflow per unit length of river; ux = x component of the velocity of lateral inflow; S_f = friction slope; S_o = the bedslope.

Equation (3.1) is the continuity equation and describes the conservation of mass. The momentum or dynamic equation, (Eq.3.2) is derived by applying Newtons second law of motion and expresses the conservation of momentum. The grouped terms from left to right are dimensionless measures of: local and convective acceleration, pressure force of the fluid, friction and gravity forces, and the acceleration of any lateral inflow. This non linear system of equations has no known analytical solution, but may be solved numerically given one initial and two boundary conditions.

Such numerical methods convert Eq.3.1 and Eq.3.2 into algebraic equations that can be solved for y and v (depth and velocity) at finite incremental values of x and t (distance and time). The solution methods available can be grouped into two categories:

(i) Explicit finite difference schemes.
(ii) Implicit finite difference schemes.

The former solutions use explicit equations for y and v (depth and velocity) at a given point x, t, whilst implicit schemes use sets of simultaneous equations to find y and v at several x values simultaneously for a given t value. The simplest form of solution of the Saint Venant celerity equation for a solitary wave is given in an explicit form by Hamill (1983):

$$c = (2g(y + h)^2 / \sqrt{(2y + h))} \qquad \text{(Eq.3.3)}$$

where h = wave amplitude above the normal water surface; y = the water depth prior to the arrival of the wave; and c = wave celerity. The relationship beween wave celerity and wave velocity in this instance is given below:

$$V_W = c + V_1 \qquad \text{(Eq.3.4)}$$

where V_W = wave velocity; V_1 = mean baseflow velocity.

Hamill (1983) used this equation for routing mine water waste along a small channel, a maximum of 8 metres wide, in East Durham, England. Predicted values were between 3 and 5 times faster than observed values, dependent on the degree of inchannel vegetation.

In natural channels the presence of dynamic waves if at all, are usually very short lived (Jansen, 1979). The full suite of

Saint Venant equations represent a wave that will attenuate very quickly . Wooding (1965) quantifies this phenomena in terms of the Froude number:

$$F = \sqrt{v/(gy)} \qquad \text{(Eq.3.5)}$$

where F = froude number; v = mean velocity of flow.

If F is less than 1, dynamic waves will decay exponentially with time constant v/(gS(1 - F/2)) where S = channel slope. If F is greater than 1 but less than 2, there maybe a period of dynamic wave growth, depending upon the initial conditions within the channel, but this will quickly lead to the formation of a bore which decays exponentially with time. Therefore, it is clear that conditions to allow the growth of a dynamic wave within a natural channel are very specific, and the waves formed are themselves highly transitory in nature. Thus, as Ponce et al (1978) explain, the full dynamic models are not really applicable to natural rivers, because of the non-permanent nature of dynamic disturbances in open channel flow. Furthermore, given all the irregularities present in a natural channel, flow tends to resemble uniform and not dynamic movement (Ponce et al, 1978). Therefore, so called approximate models based on parts of the full Saint Venant equation of continuity of discharge, although deigned "approximate", may in reality be a more precise measure of wave movement down a channel.

3.2. Approximate Models.

All mathematical flood routing models in some form or another, use the equations of continuity. However, different groups of models consider different numbers of terms in these fundemental equations (Eqs.3.1 and 3.2). Most commonly the terms in equation (3.2) which consider acceleration factors other than those related to bedslope are ignored, because the bedslope factor is dominant in determining acceleration, at least that is in long reaches, or if all the effects of channel irregularities are included in the empirical roughness coefficient (Weinmann and Laurenson, 1979). Thus ignoring all acceleration terms:

$$y/x + S_f - S_o = 0 \qquad \text{(Eq.3.6)}$$

Such models are either called approximate dynamic models (e.g Weinmann and Laurenson, 1979), diffusion analogy models (e.g Jones and Moore, 1980), or kinematic models corrected for dynamic effects (e.g Brady and Johnson, 1981), depending upon the form in which the equations are expressed.

If long reaches are studied, and all the effects of channel irregularities including bank reaction forces are lumped together with the roughness coefficient (S_f), then the effect of the pressure force term becomes negligible, typically being an order of magnitude less than S_o. Therefore, in terms of an approximation it may be neglected, leading to the simplest form of the momentum equation:

$S_f = S_o$ i.e friction slope = bed slope (Eq.3.7)

which forms the basis of kinematic wave models.

3.2.1. Approximate Dynamic models.

These models are based on the continuity equation in the following form:

$$\frac{\partial A}{\partial t} + \frac{\partial Q}{\partial x} = q$$ (Eq.3.8)(Weinmann and Laurenson, 1979)

This equation is then solved numerically, in a similar way to that of the full dynamic equations at finite incremental values of x and t. This is performed either: explicitly with governing equations so arranged to update dependent variables in terms of previously known values; or implicitly with equations placed so as to obtain solutions for dependent variables at different grid points, these values are dependent not only on known values but also on unknown neighbouring values at surrounding grid points. Either way, the solutions for this equation are extremely complicated in themselves.

Price (1973, 1974) compared four numerical methods based on approximate models for the flood routing of a monoclinal wave: leapfrog explicit method; fixed mesh characteristic method; two step Lax-Wendroff method; and the four point implicit method. The basic conclusion from this comparison was that there was little to choose between the models, except that the implicit method was computationally faster, and had an advantage if the flood wave speed was high.

3.2.2. Diffusion Analogy Models.

Convective diffusion models are in the form shown below (Weinmann and Laurenson, 1979; Jansen, 1979).

$$\frac{\partial Q}{\partial t} + \frac{c\partial Q}{\partial x} = \frac{D\partial^2 Q}{\partial x^2} + cq \qquad \text{(Eq.3.9a)}$$

Here, the coefficient 'c' describes the translatory characteristics of the wave, and coefficient D the attenuation effects. For regular channels the coefficients have been evaluated as:

$$c = \frac{1}{B}\frac{dQ}{dy} \quad \text{and} \quad D = \frac{Q}{2BS_0} \qquad \text{(Eq.3.9b)}$$

where B is surface width and So is bedslope.

Jones and Moore (1980) present a routing model of the diffusion analogy type, which was chosen to model flows from Bala Reservoir, down the River Dee, North Wales. Both time and space are divided into discrete intervals, denoted t and n, respectively, and the flow Q(n,t) at different time and space points are represented by the equation:

$$Q_t^n = \theta Q_{t-1}^{n-1} + (1-\theta)Q_{t-1}^n + \theta q_t^n \qquad \text{(Eq.3.10a)}$$

where the quantities q denote tributary and other lateral inflows and θ is an empirical coefficient (for the River Dee this was found to equal 0.65).

The problem with the above model is that the single empirical factor controls both the translation (speed) and the attenuation of the hydrograph. Thus for a fixed θ , the travel speed resulting from the above formulation is constant. In order to represent observed values of times of travel, has been adapted to vary with flow, thus θ is replaced by θ_t^n , and can be different at each time and space node:

$$Q_t^n = \theta_t^n Q_{t-1}^{n-1} + (1-\theta_t^n)Q_{t-1}^n + \theta_t^n q_t^n \qquad \text{(Eq.3.10b)}$$

Such a model then requires a considerable amount of empirical data in order to make it 'fit' reality. However, from a conceptual point of view, the model is useful in that at least it allows for the possibility of both attenuation and translation of the flood wave in different reaches.

3.3. Kinematic Models.

These are undoubtedly the simplest and most popular routing models and take the form:

$$\frac{1}{c}\frac{\partial Q}{\partial t} + \frac{\partial Q}{\partial x} = q \qquad \text{(Eq.3.11)}$$

Where 1/c is the kinematic wave speed, and q is lateral inflow per unit area of river. 1/c maybe kept constant, or varied, leading respectively to linear and non linear models (see Goring, 1984). This factor maybe evaluated at a given cross section by the Kleitz-Seddon Law, which in its simplest form is:

$$c = \frac{dQ}{dA} \qquad \text{(Eq.3.12)}$$

therefore,

$$c = \frac{1}{B}\,\frac{dQ}{dy} \qquad \text{(Eq.3.13)}$$

Kinematic models are so called because they are based on concepts of water movement alone, and neglect consideration of forces causing this movement. This idea was first presented by Lighthill and Whitham (1955), although the Kleitz-Seddon principal itself dates back to 1900 (Seddon, 1900).

The model in its simplest form has been variously applied to natural floods (Wiltshire and Novak, 1984; Beven, 1979; Wooding, 1965), channel surges (Rantz, 1961), catastrophic dam failure (Hunt, 1982), drainage water release (Hamill, 1983), and reservoir releases (Brady and Johnson, 1981). Levels of success of fitting the model to reality, have usually been good after the inclusion of an empirical correction factor. However, in most cases, the stringent theoretical conditions under which the kinematic model is applicable, have either been forgotten or deliberately ignored. This has led to confusion as to what the added correction factor is actually allowing for. According to theory, the Kleitz-Seddon Law for kinematic waves, is only applicable under the following conditions:

i) When the disturbance created is a monoclinal wave i.e a single peaked wave, that remains permanently in this form down channel (Wiltshire and Novak, 1984).
ii) when this monoclinal wave moves into an initially steady flow (Wiltshire and Novak, 1984).
iii) when any dynamic (acceleration) effects within the wave, are negligibe (Wiltshire and Novak, 1984).
iv) when discharge is a single function of flow depth (Beven, 1979).
v) when the increase in discharge and flow area are slow (Hamill, 1983).
vi) if the wave front itself is extremely flat (Rantz,

1961).
vii) when the wave peak has a constant velocity (Brady and Johnson, 1981).
viii) when the wave does not lengthen, disperse, or subside. However, the theory is still applicable if distortion of the wave occurs, which will happen because dQ/dA increases with y (depth) - see Fig. 3.1a (Henderson, 1963).

These laws lead to the following, more practical observations and limitations of the model:

i) the larger the increment in Q the greater the error in the calculation of wave velocity (Rantz, 1961).
ii)initial disturbances on a larger baseflow will travel faster than the initial disturbance on a lower baseflow, see Fig.3.1b (Rantz, 1961).
iii) for dam failure problems, Hunt (1982) argues that the conditions for kinematic wave movement are not fulfilled until the flood wave has advanced approximately four reservoir lengths downstream.

In view of these theoretical and practical constraints, it is necessary to question the applicabilty of kinematic wave theory to instantaneous reservoir releases. Brady and Johnson (1981), Rantz (1961), and Hamill (1983) use the Kleitz Seddon law to derive times of travel of approximately instantaneous releases of water into natural channels. The channel in each case is divided into a number of sub-reaches and the change in area and change in discharge between low and high flow for the differing reaches are measured. Observed wave speeds are then related to theoretical wave speeds. Brady and Johnson (1981) proposed the following relationship:

$$V_{ob} = k(dQ/dA) \qquad \text{(Eq.3.14)}$$

Where V_{ob} = observed velocity of the wave, and k = correction factor.
(k = V_{ob}/Vtheoretical)

This vital k value, according to Brady and Johnson, is an index of roughness within the reach and assumes a constant value. Rantz (1961) however, points out that since the k value of any change in area at any given gauging site is related to the shape of the rating curve at that site, (which already integrates the effects of channel properties such as slope, geometry and

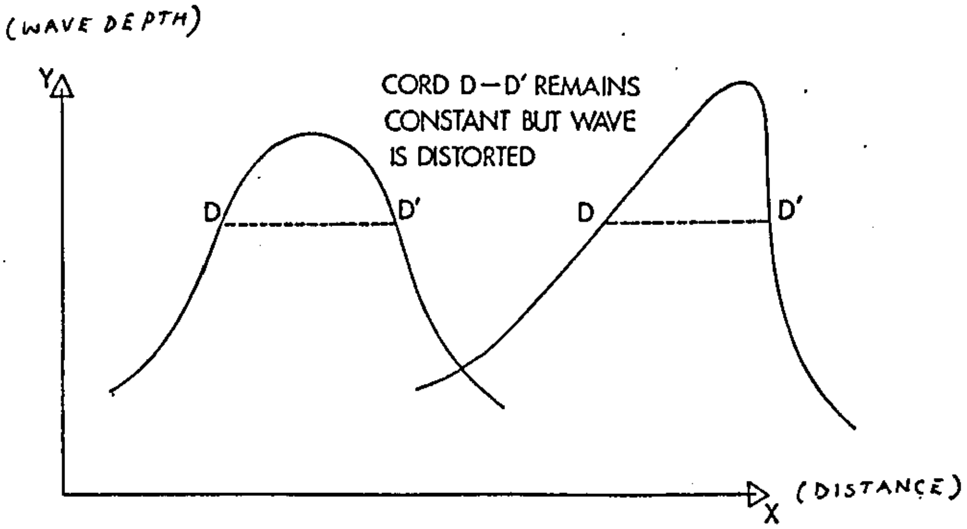


Fig. 3.1a. Typical release wave movement downstream (Henderson, 1963). The wave does not lengthen or disperse, however it does distort because dQ/dA increases with y (depth).

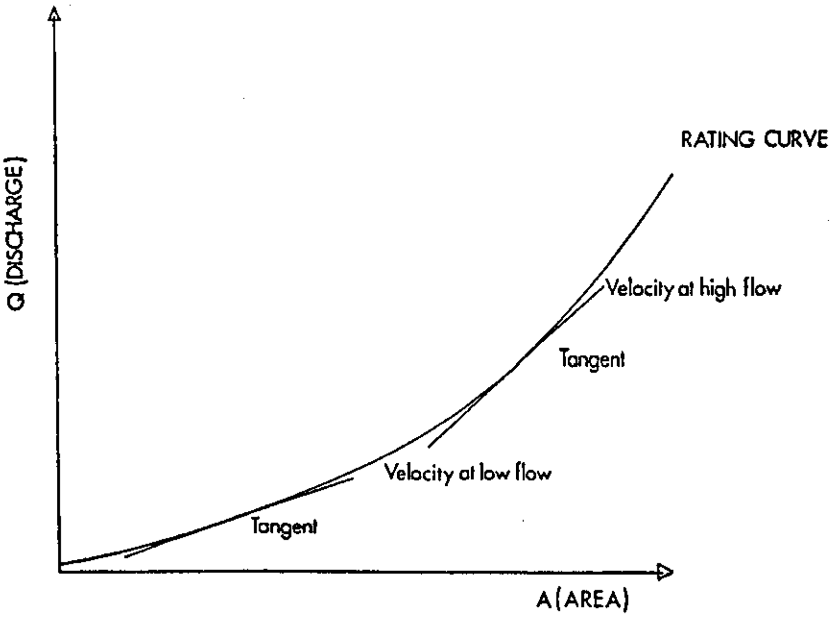


Fig. 3.1b. Changing velocity of release waves made onto different existing channel discharges (Rantz, 1961).

roughness in the adjacent subreach) it is essentially a function of all channel properties and not simply roughness. Furthermore, Hamill (1983) argues that k, if used, should not be constant, because channel roughness effects themselves are not constant. In Hamill's study the change in density of aquatic vegetation within the channel during the year, seriously altered wave travel time; therefore it was a nonsense to have one constant k value for one reach. Also from theory already outlined, kinematic wave velocity is dependent very much upon the discharge already within the reach. Therefore, the Brady and Johnson (1981) constant k value idea, at best is a correction factor allowing for channel irregularities and channel storage, for a given floodwave on a given baseflow. It certainly is not purely and simply a roughness coefficient for the channel, determining the rate of movement of all floods. The above studies illustrate the pitfalls and problems of attempting to fit theoretical models by the use of inflexible coefficients.

A different approach to the use of kinematic theory in flood routing problems is the method based on an explicit-finite difference scheme proposed by Cunge (1969). This scheme works with discrete time intervals, and introduces a weighting coefficient in the finite representation of the time derivative, which is shown below in the finite difference form of the kinematic equation (Eq.11) (Weinmann and Laurenson, 1979):

$$\left\langle\frac{1}{c}\right\rangle \frac{\theta(I_2 - I_1) + (1-\theta)(Q_2 - Q_1)}{\Delta t} + \frac{Q_1 + Q_2 - I_1 - I_2}{2\Delta x} \qquad \text{(Eq.3.15)}$$

Where $\left\langle\frac{1}{c}\right\rangle$ = an average value for the kinematic wave speed in the reach; Q_1 and I_1 are outflow and inflow upstream; Q_2 and I_2 are the outflow and inflow downstream; t = time; x = distance, and θ = dimensionless weighting coefficient. Introducing the travel time parameter: $m = \Delta x/\langle c\rangle$ gives the solution Q_2:

$$Q_2 = C_1 I_1 + C_2 I_2 + C_3 Q_1 \qquad \text{(Eq.3.16)}$$

where $C_1 = \dfrac{m\theta + \Delta t/2}{m(1-\theta) + \Delta t/2}$ $\qquad C_2 = \dfrac{-m\theta + \Delta t/2}{m(1-\theta) + \Delta t/2}$

$C_3 = \dfrac{m(1-\theta) - \Delta t/2}{m(1-\theta) + \Delta t/2}$ $\qquad$ and $C_1 + C_2 + C_3 = 1$

Eq.3.16 is identical to the classical Muskingum coefficient equation by McCarthy (1957: in Chow,1964). This generalized kinematic routing model has been updated and improved, for example by Nash (1959), and Koussis (1976). However, regardless of the version applied, the success of the model is totally dependent upon the selection of parameters x, t, and (c), which in turn are dependent upon results from accurate field tracer studies. These data negate any necessity to know exactly the effects of channel non-conformities, (such as roughness or slope) as all of these factors are explicit in the movement of the tracer downstream.

3.4. Instant Release Models.

An instantaneous reservoir release is a special case in flood routing studies, and although routing models designed to accomodate varying flows from varying sources at varying time intervals can be reasonably applied, as illustrated by Hunt (1982) and Brady and Johnson (1981), theory specific to the problem should be more appropriate.

Early theoretical treatment of instant release waves was made by Ritter (1892). However, the assumption of frictionless flow in Ritter's work made his solution unrealistic as the behaviour of waves is affected greatly by channel resistance. Dressler (1952), extended this work to include a 'dam break' function, allowing for the resistance effect of a channel of infinite width, (Tun-Shi-Su and Barnes,1970) then confined this resistance effect to take into account the true cross sectional influence of shape and resistance on flood wave movement.

Using the full dynamic equations as fundamental building blocks (Eqs.3.1 and 3.2), and solving Sf (friction slope) from the Chezy formulae where:

$$Sf = U^2 / C^2 R \qquad \text{(Eq.3.17)}$$

C is the Chezy resistance coefficient. Equations (3.1) and (3.2) may be approximately solved to give:

$$dx/dt = u \pm c \qquad \text{(Eq.3.18)}$$

Where c is wave celerity; u is water speed; $d(u \pm W)/dt = 0$ and $d/dt(u \pm w) = 0$, (Eq.3.19)
in which $c = a(gy)^{\frac{1}{2}}$ and $w = 2/a(gy)^{\frac{1}{2}}$ and $a = (A/By)^{\frac{1}{2}}$
Where A = wetted area; B= water width; y = water depth.

These equations may then be transformed into dimensionless form, and solved with respect to wave and water speed:

$$C = a(\alpha - \beta X/t) \qquad \text{(Eq.3.20)}$$

$$U = 2\beta + \alpha X/t \qquad \text{(Eq.3.21)}$$

Approximate values for α, β, and for different channel shapes are given in tabular form (see Tun-Shi-Su and Barnes, 1970; p2190). Eqs.3.20 and 3.21 make no account of resistance within the channel, a Dressler dam break function may be applied (see Tun.-Shi-Su and Barnes, 1970); however in so doing, more approximate indefinable coefficients are introduced, which although perhaps giving a more accurate solution, do not improve the theoretical understanding of wave movement downstream.

A simpler and conceptually more rewarding approach to the problem, is to consider a release wave to behave in a purely translatory fashion. Dynamics of movement are still based on the continuity of flow equations, but the major difference between this approach and the kinematic approach is that unlike the latter theory, the forces of propogation are considered. From Fig. 3.2 it is assumed that the wave illustrated has been produced instantaneously by the release of water from a reservoir, through gate G. Discharge is increased from Q_1 to Q_2, the depth D_1 being increased to D_2. Between the gate and the wave, frictional loss and channel slope effects, are assumed to be negligible, and each cross section has the same area - a_2, and same velocity V_2.

The wave which travels with a velocity of V_W, is at the end of one second, a distance V_W below the gate (V_{Wm}/s x 1s = V_{Wm}). The volume of water entering the channel in one second is $Q_2 = a_2V_2$. The increase in volume is thus given:

$$Q_2 - Q_1 = V_W(a_2 - a_1) \qquad \text{(Eq.3.22)}$$

Substituting a_2V_2 and a_1V_1, respectively for Q_2 and Q_1;

$$V_2 = (a_1V_1 + a_2V_W - a_1V_W)(1/a_2) \qquad \text{(Eq.3.23)}$$

The mass of water behind the wave has had its velocity increased from V_1 to V_2, and therefore its momentum must also have increased (since F = mV).
If m is the mass and w the unit weight of water;

$$F = m(V_2 - V_1) = \frac{(V_W - V_2)\ a_{2W}\ (V_2 - V_1)}{g} \qquad \text{(Eq.3.24)}$$

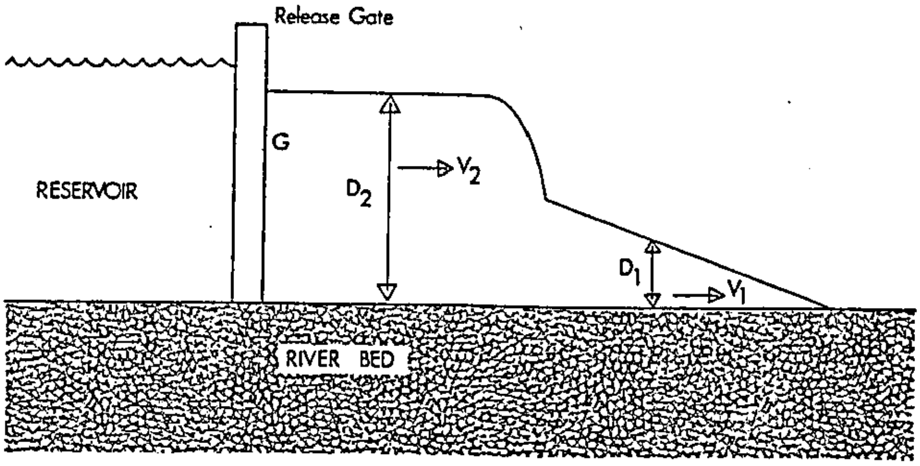


Fig. 3.2 TRANSLATORY STEPPED FLOW (King, 1954). The simple case of instantaneous flow change.

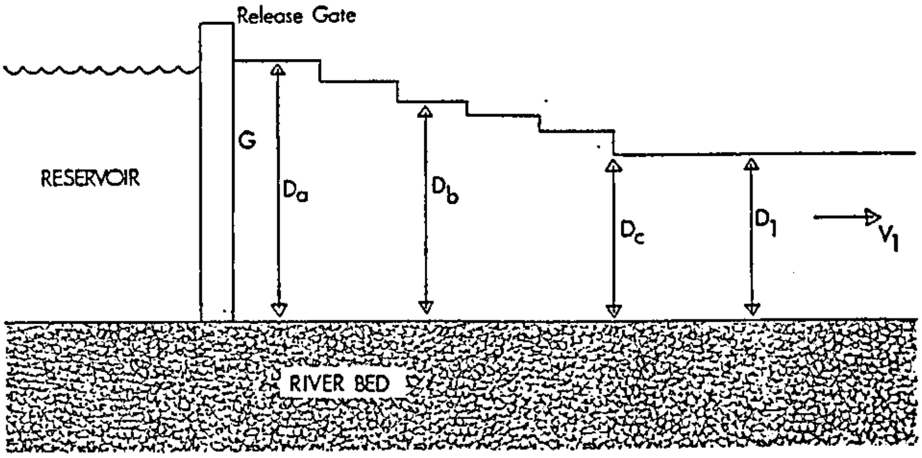


Fig. 3.3. TRANSLATORY STEPPED FLOW (King, 1954). The complex case of realistic change in flow.

This force is equal to the difference in hydrostatic pressures corresponding to the areas a2 and a1, or;

$$F = wa_2 y_2 - wa_1 y_1 \qquad \text{(Eq.3.25)}$$

Where y_2 and y_1 are depths to the centre of gravity of cross sections, whose areas are respectively a and a . Thus:

$$(V_W - V_2)(V_2 - V_1) = (g/a_2)(V_2\ y_2 - a_1\ y_1) \qquad \text{(Eq.3.26)}$$

Substituting the value of V_2 given by Eq.3.23 into the above equation:

$$(V_W - V_1)^2 = g\ \frac{a_2 y_2 - a_1\ y_1}{a_1\ (1 - a_1/a_2)} \qquad \text{(Eq.3.27)}$$

This is a general equation and applies to all cases of the abrupt wave in channels of any form: $V_W - V_1$ being the velocity of the wave with respect to the water in the shallower portion of the stream (King, 1954).
The solution of Eq.3.27 gives:

$$V_W = \sqrt{g\ \frac{a_2 y_2 - a_1 y_1}{a_1\ (1 - a_1/a_2)} + V} \qquad \text{(Eq.3.28)}$$

For very low waves a is approximately equal to a_2, and equation (3.28) simplifies to:

$$V_W = \sqrt{(gD_M) + V} \qquad \text{(Eq.3.29)}$$

Where D_m is the mean depth at a station, and V is the velocity of the water.

Equations (3.22) to (3.29) assume an instaneous change in flow, but in reality this is never possible to accomplish.

Conditions resulting from increasing discharge at a comparatively rapid rate as shown in Fig.3.3. The added water passes downstream in a series of shock waves:a, b, c, d etc, with depths D_a, D_b, D_c respectively. An inspection of Eq.3.29 reveals that the waves at greater depths have greater velocities, and that each wave is being gradually overtaken by the wave behind it. The tendency, therefore, is for the waves to combine and eventually to form a simple large wave. The net result then becomes practically the same as it would have been if an equal change in depth had been produced instantaneously

(King, 1954). Thus the velocity for the bottom wave from diagram Fig. 3.5 (using Eq.3.29):

$$V_a = \sqrt{(gD_1)} + V_1 \qquad \text{(Eq.3.30)}$$

and the velocity of the top wave will be:

$$V_b = \sqrt{(gD_2)} + V_2 \qquad \text{(Eq.3.31)}$$

Assuming a straight line variation between V_a and V_b, which is justifiable because it has been shown that the net result is as if the change had occurred instantaneously (eq.3.29), the mean velocity of the wave is:

$$V_m = \tfrac{1}{2}(V_a + V_b) \qquad \text{(Eq.3.32)}$$

As reach length increases or intial depth decreases, so the effect of slope and loss of head due to friction become important. In summary, as D_1 increases, the effect of frictional loss decreases allowing the waves to move rapidly downstream. Conversley when a high wave is produced in relatively shallow water, both the height and velocity of the wave are modified significantly by frictional loss. As D_1 (initial depth) decreases so V_2 (release water velocity) approaches Vw (release wave velocity) that is, the velocity of the release water approaches the velocity of the release wave.

3.5. The Resistance problem.

The effect of roughness on the rate of water-travel down a channel is particularly critical when considering reservoir release water movement, because more often than not, such releases are made on compensation flow i.e a high wave is produced in shallow water, which according to theory (equations 3.30, 3.31,and 3.32) will mean that the significance of energy lost in overcoming the friction created by inchannel roughness, will be extremely high. In practical terms, given similar volume reservoir releases, this means that the lag between wave arrival at a station and water arrival, will vary according to the roughness of the channel at the time of the reservoir release - the "rougher" the channel, the smaller the lag. This would mean that the Brady and Johnson (1981) equation for wave travel could be applicable as it essentially defines lag time through a constant 'k' roughness value. Unfortunately, as already stressed (Hamill, 1983), roughness is not temporally constant, it certainly is not spatially constant and also, as flow characteristics vary, so the relative importance of form and skin roughness change. Bathurst (1978) from theoretical work, showed that for different discharges at the same site, roughness can change by 70% or more. Furthermore, from tracer tests over the whole of the mainstream lengths of the River Wye and River Severn, experimental catchments at Plynlimnon, Central Wales, (Newson and Harrison, 1978), it has been shown that the overall velocities of flow of water through the network were non-linear at low to medium flow, but approached a slowly increasing or constant value at high discharges. It was suggested that at low discharges, the average velocities over a reasonable length of stream, are controlled by slow tranquil flow through numerous sections of pools. As flow increases many of the controls and major form roughness elements maintaining such pools become drowned out and, ultimately, the velocities are controlled by overfall and major riffle sections for which the overall slope of the stream (a constant) may be a suitable surrogate of these controlling variables (Beven, 1979). Basically, Beven suggests that there are two levels of water velocity: velocity at low flow, and velocity at high flow. The value of the former being determined by local resistance caused by the roughness of the channel boundary, and the latter determined by the geometrical properties of the channel. However, according to Bathurst (1978, p64) it is the local resistance that is the only resistance to flow, with gross resistance involving not so much a physical hampering, as a change in the form of the velocity profile caused initially by boundary resistance.

In detail, skin and form roughness or local and gross resistance, can be subdivided (Bathurst 1978, p64):

Skin/local resistance:
  i) Boundary roughness, dependent on size, spacing, shape and grading of sediment. This affects the bed shear stress.
  ii) Large scale roughness, defined by the relative roughness and spacing of the sediment. This disrupts the logarithmic velocity profile and changes the bed resistance from a shear stress to a form drag.

Form/Gross resistance:
  i) Non uniform longitudinal slope of the water surface.
  ii) Non uniform longitudinal slope of the bed, possibly producing back water conditions which affect the shear velocity profile.

iii) Non uniform longitudinal plan of the channel - inducing secondary currents, which cause non uniform distribution of bed shear.
iv) Cross-sectional shape of the channel, determining the distribution of the bed shear at a station.
v) Froude number effects associated with surface waves. These are unlikely to be important at Froude numbers less than 0.5 and values higher than this are rarely encountered in rivers (Leopold and Wolman, 1960).

In essence, gross resistance factors are a resultant of non uniform conditions at a section, and non uniform conditions along the channel. It is clear then, that during a reservoir release, resistance to flow within the channel will vary as flow increases. If the release is made into a boulder bed river, with the majority of boulders uncovered at low flow, then wetted frontal cross-section will increase with discharge, causing roughness to increase; however, as boulders are not all the same size, some will be completely covered at a given depth, whilst others are still exposed. Once a roughness element is completely covered, its resistance effect is drastically reduced (Bathurst , 1978). As flow depth rises, some boulders are contributory to increased resistance, while the resistance effects of others are being rapidly drowned out. Therefore, at a given cross section on a boulder bedded river, the degree of roughness change with depth, is dependent upon the rate of 'coverage' of the boulders. Once the majority of individual skin roughness elements are covered, a quasi-smooth flow is reached, where the fluid skims over their crests.

Some reaches in boulder bed channels have all large scale roughness elements completely covered at a given flow, whereas other reaches do not. Therefore in order to assess the resistance effect on flow within that river, two different approaches must be made to determining the resistance. When all boulders are covered, boundary layer theory may be applied, with bed roughness elements behaving collectively as one surface, applying a frictional shear on flow, translated into a velocity profile. However, when some large scale roughness elements are not completely covered, the velocity profile is completely disrupted, since those elements act individually and total resistance is the sum of each individual boulder drag force. In short, except for extreme conditions drowning out all boulders, local channel roughness and not general channel form is the critical resistance factor influencing flow.

In order to model roughness effects on flow, detailed and extensive field work is called for, measuring individual boulder drag forces. However, by studying reservoir releases of constant volume onto different low flow discharges, and hence different local roughness, the significance of varying local and general resistance on water velocity can be assessed, without studying individual roughness elements.

3.6. Reservoir releases in Great Britain.

Regulation policy of surface water reservoirs can be summarised into three categories: i) compensation flow ii) unregulated overspill (or dam failure) and iii) controlled releases. In Great Britain, compensation flow is usually equivalent to average spring flow conditions throughout the year; however, this policy does vary slightly between individual reservoir systems. Compensation flow according to government legislation - must be sufficient to keep pollution levels in the stream at an acceptable level (guidelines for acceptable levels as suggested by the EEC; Goodman 1981). Furthermore, particularly in upland areas, fisheries requirements may cause the procedure to be modified.

Unregulated overspill may be considered as an unintentional release, and as such cannot be legislated for, although it is possible to control this discharge by planned valve releases. The effect of this spillage upon the receiving river water is very difficult to measure accurately due to the problems of forecasting the timings of such events. Lavis and Smith (1972) observed daily mean temperatures below Grassholme Reservoir, River Lune, UK, and even with the occasional overspill, variation of water temperature was less than 10% of that of the natural stream. The unimpounded river section exhibited a temperature range of about 4 °C in winter, and about 12 ° C in summer. Below the reservoir however, there was a span of less than 0.5°C. The daily temperature sequences for the reservoir, reflected the general trend of water temperature for that month. On the rare occasion that a diurnal temperature fluctuation did occur in summer, the maximum range observed had a magnitude of 1.3°C and this fluctuation probably reflected the internal circulation of water within the reservoir.

Apart from the Lavis and Smith study (1972) shown above and work by Crisp (1977) on Cow Green Reservoir - little research has been published on the effects of reservoir releases on downstream water quality in the UK. There are, however

Water Authority internal reports documenting the effects of releases on the receiving river, and the findings from a selection of these are now presented.

3.6.1. River Derwent, Derbyshire, test releases September 1980-September 1981, Severn Trent Water Authority. (1981)

In the period from September 1980 to September 1981, three independent test releases were made from Ladybower Reservoir into the River Derwent, Derbyshire, at a time of extreme low flow. On the 24-25/9/80, a release of 280 Ml d^{-1} was made, on the 31/7-2/8/80, 144Ml d was released, and on 9-10/9/81, 186 Ml d^{-1} was discharged. All releases were in the form of a single pulse.

The objective of these experiments was to ascertain the wave speed of large releases on very low flows in order to be able to apply the catchment water routing model FLOUT, in which the most significant parameter is that of wave speed (Pirt, 1983). Monitoring sites were established as far downstream as Derby (approximately 75km below the outfall). Large variations in wave speed between sites were found, which were explained by the variation of channel morphology, with rougher upland reaches retarding wave movement, and canalised/ponded sections inducing unexpectedly high wave velocities.

The overall wave speeds of the releases from Ladybower to Longbridge Weir, Derby, were 2.34 km h^{-1}, 3.56 km h^{-1} and 2.55 km h^{-1} respectively. In each instance the compensation flow volume upon which the release was made, varied significantly. Therefore, release velocities cannot reliably be compared. It is worth noting, however, that the lowest wave velocity was for the largest release made onto the highest compensation flow, and that the highest wave velocity was for the smallest release made on the second highest compensation flow. With only three data points it is impossible to draw any firm conclusions about the relationship between; low flow, release volume and wave velocity - particularly when the study reach is long and significantly affected by major tributaries. Nevertheless, the study does illustrate the influence of low flow discharge and channel morphology on release wave speed. Also, in terms of water quality, the test releases showed that a wave was identifiable even as far downstream as Derby, indicating a potentially rapid alteration in water chemistry.

3.6.2. Llyn Clywedog Test Releases, 24-28 June 1975. Severn

Trent Water Authority. (1978)

The tests were made in order to obtain information on operating procedures and the effects of large scale releases of regulation water, as would occur if a Craig Goch project was developed. A stepped release involving increases to 1100 Ml d^{-1} during a six hour period, 2200 Ml d^{-1} during the next six hours, and to 2425 Ml d^{-1} during the next six hours, was made on a compensation flow of 180 Ml d^{-1}.

Measurements made during the release showed that some bed load and gravel movement took place during the test. The threshold to movement was calculated to be 1100 Ml d^{-1} (which was well inside the proposed maximum releases from the Craig Goch scheme). Water quality variation during the release showed an initial rise in manganese and iron, associated with incorporation of these substances within the scour valve water, 74% of which made up the total release volume; within 24 hours the concentrations of these substances was much reduced. The dissolved oxygen concentration was shown to rise by as much as 100% during the release, due to the mechanical aeration effects; temperature, however, fell by as much as 4 ° C. pH values were reduced by upto 1.5 units, and conductivity fell by 44%. These water quality changes lagged behind the hydrological changes, but not by as much as had been expected.

After the release, fish catches improved to above original levels, however during the release fishing was exceptionally poor. No significant movement of the salmon spawning gravels occurred, and the release had a dramatic but short term effect upon the availability of bottom living organisms.

Essentially, this report showed that apart from superficial flushing of deposits from within the reservoir and from the channel itself, the release had little or no effect upon the natural ecosystem. Subsequent fisheries reports have tended to question this finding, since they have claimed that all game fish were washed out of the reach of the river for at least 2 kilometres below the dam (Cowxs, 1981).

3.6.3. Stocks Reservoir Releases, Cumbria. North West Water Authority. (1973)

Releases of 15mgd, 50mgd, and 80mgd were made in August 1972 from Stocks Reservoir, on compensation flow of 4mgd. The releases were graduated and took 24 hours to reach the specified release discharge. The object of the exercise was to observe the effects of such artifical freshets upon fish migration in the River Hodder, since it had been suggested by Banks (1969) that such practice could be of benefit to the stimulation of salmonid movement. Unfortunately, very little fish migration occurred during the freshets, and it was concluded that the water released from a freshet flow from a reservoir does not have the same influence upon fish and their migratory habits as a natural freshet - no attempt was made in the report to explain this finding.

3.6.4.Thirlmere Reservoir Releases, Northumbria. Northumbrian Water Authority. (1974)

A series of test releases were made from Thirlmere(between 1972 and 1973),in order to study the effects of such releases upon the River Derwent, particularly in respect of water losses. Only comparatively small releases of 0.75 m^3 s^{-1}were made and results are presented of time of travel of this water to various downstream points. The overall conclusion was one of surprise at the high rate of release water movement. Although the use of automatic stage recorders limited the accuracy of the results to plus or minus one hour, nevertheless, the water quality implications are significant; a release as small as 0.75 m^3 s^{-1} can be identified approximately 30 km below the reservoir outfall, therefore there is a potential for water chemistry change as well.

These studies show the importance of channel morphology, and tributary inflow on the velocity of the release wave, with rougher sections retarding flow. Furthermore, they show that water authorities are aware of the possible significance of release water on downstream ecology and quality, and that this effect may be translated a considerable distance. Not only is water chemistry rapidly changed - sometimes for the worse, with the input of scour valve water - but also invertebrates are in danger of being swept away, together with fish and their spawning gravels. Unfortunately, the approach to ascertaining the extent of these effects is somewhat haphazard, to say the least. Although problems of collectingreliable data are exaggerated by;the lack of extreme low flow days throughout the year on which to make the releases; and of course, by the interests of other river users.

3.7. Water Authority Questionnaire Survey.

In order to establish the extent and significance of river regulation in Great Britain, a questionaire survey was written (along guidelines proposed by Dixon and Leach, 1978) and sent to all the major water authorities. The survey was designed to establish the locations of the major regulating reservoirs in the country, how often they made releases the operational procedures of the release, and the purpose for such releases. The proforma (see APPENDIX A) asked for information on each authority's 5 major reservoirs. Information was received from: Northumbrian, Northwest, Severn Trent, South West, Southern, Anglian, and Thames Water Authorities. Anglian and Thames do not have any regulating reservoirs as such within their area, therefore the results in Table 3.1. are from only 5 water authorities, and represent only the five largest regulating reservoirs from each authority.

Of the 28 reservoirs for which data were received, eight make significant releases frequently throughout the year (more than 3 releases per season), and a further six, make releases occasionally (less than 3 releases per season). If these statistics are representative of reservoirs throughout the country, then of the major reservoir systems about 50% make significant discrete releases of water into the impounded river downstream, other than compensation flow. All releases - apart from those made from Draycote Water, and the Derwent Valley system - are stepped and are made from water throughout all strata within the reservoir. Theoretically, the impact on river water chemistry of such releases, should create a smaller stress level than a singlestep, single strata, release. Obviously, some thought has been given by the operational engineers of the Water Authorities to the problem of downstream scour.

According to the questionnaire, most releases are made for one or all of the following reasons:i) domestic supply ii)industrial supply iii) recreational requirements, iv) and to reduce the chance of overspill. Domestic releases usually are simply the transference of water via the river to an abstraction point downstream. Such releases are more prevalent in the summer months, and because of this are likely to have a dramatic effect on the low flow river water quality. Although it could be argued that, due to compensation flow, water level in the summer is kept artificially high, and consequently, the river water quality will tend to reflect that of the reservoir.

Reservoir Name	Water Authority	Maximum capacity (cubic metres)	Compensation flow m^3d^{-1}	Frequency of releases	Type of release	Purpose
Kielder Water	Northumbrian	200,000,000	114,000	F	Stepped	D, I, R
Lake Vrynwry	Severn-Trent	59,670,000	45,000	F	Stepped	D, I, O
Llyn Clwedog	Severn-Trent	50,000,000	18,000	F	Stepped	D, I, R, P, O
Derwent Valley*	Severn-Trent	46,347,000	92,763	Oc	Single	I, O
Cow Green	Northumbrian	40,915,000	38,600	F	Stepped	D, I, O
Thirlmere	North West	38,678,000	14,000	Oc	Stepped	I
Bewl Bridge	Southern	31,367,000	3,410	F	Stepped	D, I, P
Wimbleball	South West	21,540,000	9,100	F	Stepped	D, I, R
Draycote Water	Severn Trent	20,370,000	1,100	F	Single	D, I, P
Balderhead	Northumbrian	19,670,000	15,200	Oc	Stepped	D, I, O
Selset	Northumbrian	15,320,000	28,400	Oc	Stepped	D, I, O
Stocks	North West	12,000,000	14,000	Oc	Stepped	R
Ardingly	Southern	4,770,000	800	Oc	Stepped	D, I, P
Siblyback	South West	3,360,000	3,090	F	Stepped	D, I

Notes:
* complete system
Welsh Water, Yorkshire Water and Wessex Water did not reply to the survey. Anglian and Thames Water contain no regulating reservoirs as such within their region.

R = recreation (usually fisheries)
D = domestic supplies
I = industrial uses (includind HEP)
O = overspill
P = releases to reduce downstream pollution

F = more than 3 releases/seaso
Oc = less than 3 releases/seas

TABLE 3.1 The frequency and purpose of reservoir releases in England. Results from a Questionnaire Survey (see Appendix A1).

Industrial releases are made in a similar way to the domestic releases, although this category also includes hydro-electric power releases. With such regular releases, it is likely that the system is so release dominated that the effect of any single release upon the downstream water quality will be negligible. Recreational releases are usually made for fisheries, but sometimes are designed to meet white water canoeing demands. In general, releases for fisheries are made in an attempt to induce upstream migration, to clean spawning gravels of silt, to reduce pollutant concentration, and to reoxygenate downstream riverwater. The success of these ventures depends upon: a) the size of the release b) the nature of the release and c) the quality of release water. Below Clywedog Reservoir, releases of such magnitude have been made (Cowxs, 1981) as to completely wash away fishery ecosystems. Salmon spawning gravels, aquatic flora and the fish themselves were all 'transported' downstream, and the delicate balance of chemistry/bacteria/ecology was destroyed.

For most upland reservoirs, the water released is significantly lower in organic and solute load than the natural receiving water. This creates a dilution of organic material, nutrients and other solutes, which together with the potential change of pH, can result in an environment unsuitable to the natural aquatic life forms, leading to deaths and/or migration. Furthermore, the potential for disturbing inchannel sediment and solute sources, which are deposited in the main channel by tributary floods, may lead to an initial concentrating effect of solute and sediment load as the release wave arrives, again leading to ecological stress.

3.8. Chapter summmary.

The water quality of regulated rivers is a function of reservoir processes, regulation strategy, and downstream adaptation to this policy. Reservoir releases in Great Britain are common, with about 50% of all major reservoirs making regular instantaneous large scale discharges. These inputs are made for either/or industrial, domestic, recreational or dam overspill reasons.

The impacts of such releases on downstream water chemistry in both the long/intermediate, and short term, have largely been overlooked in the published literature. Water Authority reports on such occurrences tend to be produced haphazardly and are

MODEL NAME	DATA REQUIREMENTS	EXAMPLES OF APPLICATION	MAJOR LIMITATIONS
Complete Dynamic	Local and convective acceleration Pressure force of fluid friction and gravity forces acceleration of lateral inflows hydraulic geometry	velocity of mine discharges (Hamill, 1983); wave bore movement (Wooding, 1965); flood routing with dynamic effects (Jansen, 1979)	no analytical solution of equation only applicable when dynamic (acceleration) effects on rivers are significant
Diffusion Analogy	Chezy coefficient translatory wave coefficient acceleration due to bedslope hydraulic geometry lateral inflow	reservoir release routing (Jones and Moore, 1980)	single empirical factor controlling attenuation and translation
Kinematic (e.g Kleitz-Seddon)	kinematic wave speed observed flood wave velocity hydraulic radius	flood routing(e.g Wiltshire & Novak, 1983); channel surges (e.g Rantz, 1961); dam failure (Hunt, 1982); reservoir releases (Brady and Johnson, 1981); tracer movement (Glover & Johnson, 1974)	neglect forces causing movement; only applicable when stringent theoretical conditions for for kinematic waves exist; does not allow for physical attenuation
Inflow-outflow models e.g Muskingum	reach kinematic wave speeds inflow to a reach outflow from the reach realistic reach length	natural flood forecasting e.g Price, 1973;	not process based; prediction only as good as initial data for reaches, inflow and outflow upstream
Instant release	Chezy coefficient wave celerity water velocity hydraulic geometry	dam failure (Dressler, 1952) flood wave movement (Tun-Shia Su and Barnes, 1970)	no account of resistance forces; complexity of initial equations
Translatory	low flow depth high flow depth acceleration due to gravity low flow velocity low flow width high flow width	reservoir releases (King, 1954) flood bores (Jansen, 1979) breaking waves (Jansen, 1979)	no consideration of frictional forces; no consideration of kinematic or accel eration effects

TABLE 3.2 General Characteristics of flood routing models - a summary.

usually simple desciptions, offerring little explanation of the findings. This study attempts to fill this void, by assessing the impact of release policy on downstream water quality at the long/intermediate time scale (by looking at the effects on downstream seasonal patterns of river water chemistry), and at the short/intermediate timescale (by considering instantaneous releases and their immediate effect on the receiving river water chemistry). In order to predict the influence of release water downstream at this immediate time scale, the actual rate of water movement must be considered, which involves the use of routing models.

Such routing models are all essentially variants of either the kinematic wave or diffusion analogy models (Weinmann and Laurenson, 1979). The success of any such model depends upon appropriate selection of a number of empirical parameters to fit its idealization to the real river reach, together with appropriate selection of model which describes the water movement under consideration (a summary of such models, together with their application is given in Table 3.2.). If the release wave created is dynamic, then kinematic models are not applicable, and vice-versa. Routing models do not explain the effect of irregularities within the channel upon flow, they simply attempt to accommodate the sum total of the effects, and then produce a realistic approximate of the rate of water movement downstream. However, unless the dynamic significance of such effects is appreciated, the chance of producing a realistic approximate of water velocity is small. Of the models presented in the literature, the Kleitz-Seddon approach is the most suitable for water quality applications, since it identifies the difference between wave and water movement. Furthermore the necessary field measurements render it reasonably practical to the upland river environment. Therefore, it was this approach that was selected for use in determining the possible effects of releases on the downstream inchannel environment (see Chapter 8).

CHAPTER 4.

SAMPLING AND CHEMICAL ANALYSES.

The discussion presented in chapters 1 and 2 has shown that the water quality of regulated rivers must be examined over two time scales, namely a seasonal time-scale related to changes in the annual flow regime, and a short-term scale related to individual hydrographs. Thus, two sampling procedures were adopted. First, a monthly spatial survey of a single river system over two years. The River Derwent, Derbyshire, (see Fig. 7.1 for the location of this river) and its major tributaries from Ambergate to the headwaters was selected for this study, not least because important tributary inputs have contrasting solute loadings to the headwaters of the main stream. Furthermore, the sixty kilometre reach of the river between Ladybower Dam and Ambergate, was chosen because it may be used as a routeway for Ladybower Reservoir water, being transferred via the Ambergate tunnel to Carsington Reservoir. Discussion of this study is presented in chapters 5 and 6. Monitoring sites were chosen according to accessibility and to where change in the chemistry and/or flow occurs. These latter were determined from pilot spatial surveys of the whole Derwent catchment above Ambergate. Secondly, a programme of intensive monitoring was undertaken on three regulated rivers, during reservoir releases, in order, to investigate water quality changes during artificial flow fluctuations. These rivers were: the River Tryweryn in North Wales, the River Washburn in North Yorkshire, and the River North Tyne in Northumberland. They are all situated in upland Britain, and are associated with Celyn Reservoir, Thruscross Reservoir and Kielder Water respectively (see Fig. 7.1 for locations). The hydrology of the rivers, at least until the first major tributary input, is entirely dominated by the reservoir operational procedures, and flow may vary between a compensation discharge and a regulated flood, within a matter of minutes. The consequences and implications of these dramatic flow changes on water chemistry are examined in chapters 7 and 8.

4.1. Water Quality Parameters.

"River quality is the physical, chemical and biological character of a river with regard to its suitability for a specified purpose" Rickert et al (1975). A sound understanding of such river quality provides a starting point for systematic evaluation of socioeconomic and political options. The specific impact of man on water quality is through a combination of inputs, ranging from sewage to acid rain. Any study pertaining to assess the significance of reservoirs on river water quality, must be aware of such impacts. Therefore, a brief summary of these factors is now presented :

i) Organic wastes include agricutural, and domestic sewage, and also 'natural vegetation debris'. Essentially this input creates a depletion of dissolved oxygen in the water, leading to ecological stress and the reduction of nutrients (Lewis ., 1981; Paller et al, 1983). Natural organic input via catchment runoff e.g peat derived drainage water, often leads to serious colouring of the water (Dance, 1981), which can be problematic for industrial and domestic consumers.

ii) Bacteria are the single most important indicator of water quality, and coliform bacteria are often used to measure fecal contamination of water. When the water is for human consumption bacteria become a critical consideration due to the transmission of diseases (Overton and Meadows, 1976).

iii) Sediments - which are generally a function of; rock and soil type, state of the drainage network, and the nature, extent and intensity of land use practice (Nilsson, 1976; Rooseboom and Harmse, 1979) - are important because they may be dense enough to cover Benthal communities, whereby leading to their destruction. Gills of fish can also become clogged, their spawning gravels covered, and they have been shown to be a major vector of pesticides, inorganics, and fertilizers - particularly phosphates (Gardiner, 1980).

iv) Nutrients not derived from natural stores within rocks and soils, primarily enter the riverine system via point sources of waste input, or diffuse sources resulting from agricultural practice (Taylor et al, 1971).

In particular, nitrate from organic wastes and fertilizers, and phosphates from fertilizers and sediments (Brezonik, 1973; Beniot, 1973; Burwell et al, 1974). Excess of nutrients within the stream can lead to excessive algae growth, and the associated problems relating to deoxygenation (Dugan and McGauhey, 1974; Bachman, 1978).

v) Metals primarily cause problems due to biological magnification in the food chain. Metals also inhibit bacterial activities in decomposing organic wastes. In natural waters metal concentrations are usually insignificant (Walling, 1974). However, if the catchment is disturbed, for example through mining (Wehr et al, 1981; Corbett, 1977; Perhac, 1972), or urbanisation (Cordery, 1976), then these levels can increase to such an extent, as to become toxic to all users of the water. Furthermore, it is the presence of certain metal cations (e.g calcium carbonate), that determine the hardness of the water, which is an important consideration for industrial consumers.

vi) Oil and petroleum products entering a river system, will disrupt the natural re-aeration process. This in turn will lead to increases in COD (chemical oxygen demand) which in some instances, can exceed BOD (biological oxygen demand)(Overton and Meadows, 1976), leading to severe ecological stress.

vii) Pesticides derived from agricultural practices, on entering a river may decompose, and these products are often more dangerous and carcinogenic than the parent compounds (Logan, 1977).

viii) pH and alkalinity usually reflect the geological water source from which they are derived, which usually includes metal anions based on the bicarbonate cation. This natural balance can be serously upset by the input of acid rain and landuse change, in particular afforestation (Packer, 1967). This disruption of the natural acidity of surface waters, has been shown to be particularly insidious to the ecology of that environment (Gorham, 1976; Almer, 1974).

ix) Temperature is obviously important to the life within the stream. Thermal pollution is usually associated in rivers, with the input from cooling towers, although evidently workers have found virtually nothing that they could attribute to a rise in temperature associated with cooling towers (Ross, 1971; Howells, 1983).

The parameters analysed in this study did not span this list, due mainly to practical reasons. However, within these constraints solutes were selected to allow rapid and relatively simple analysis to be completed within seven days of collection. In order to achieve the desired intensity of field sampling further restrictions were made as to the selection of water quality parameters. Six determinands were monitored: calcium and conductivity as an indication of the response of the sedimentary cycle to reservoir releases, nitrate and phosphate indicating the response of the nutrient cycle, and chloride and pH indicating the response of the hydrological cycle. These parameters have been documented to respond to changing hydrological conditions in rivers (e.g. Edwards, 1975). Thus, components selected were considered to be representative of water quality response.

Furthermore, organic wastes come primarily from industrial and domestic sewage and for the majority of the rivers studied the input from sewage works was negligible. River regulation effects upon bacteria have been considered (Straskrabova et al, 1973), and only marginal changes in concentration of bacteria through the reservoir were found. The effects of releases upon downstream bacteria, were therefore considered to be of only minor importance, particularly due to the lack of sewage input to either reservoirs or rivers under examination. Sediment and the effect of releases, has been documented by Beschta et al, 1981), and is being further analysed on the rivers in this study by Gilvear (pers.comm.).

The response of major nutrients and metals within the streamwater, to instantaneous releases was considered to be important, not least because of the potential concentration effects of agriculturally derived nutrients (Cooke and Williams, 1970; Tomlinson, 1970) within the channels during long periods of compensation discharge. From studies by Edwards (1973a) and Lovis and Grant (1979) it has been shown (paragraph 1.5), that important indicators of discharge variation in the river are nitrate, bicarbonate and magnesium, and usually calcium. Therefore, of the nutrients nitrate was measured (the response of phosphate and chloride were also monitored, but found to be erratic during reservoir releases). Of the metals, calcium was selected in preference to magnesium, because calcium concentrations in the streamwater were consistently greater, and thus changes during releases easier to identify. Bicarbonate was found primarily in the form of calcium bicarbonate, and was therefore indirectly measured through the examination of calcium. Other metals such as sodium, potassium, and phosphorus, which are shown in the literature (Edwards, 1973a and Lovis and Grant, 1979), to display little response to changing discharge, were not therefore, measured. Trace metals, particularly iron and manganese, which could be introduced into downstream water chemistry, due to disturbance of these substances in reservoir basal sediments (Nakata, 1977), were not found in significant quantities during pilot surveys, to warrant consistent monitoring.

Since most reservoir regulated rivers are situated in upland Britain (paragraph 3.5), the problem of deteriorating water quality due to the accidental input of oil and petroleum products rarely occurs, therefore no consideration of this quality parameter was made. The behaviour of pesticides in upland reservoir/river systems is a phenomenon that also was not examined, because inputs of pesticides into the drainage system are associated with runoff from areas of extensive arable zones. Since the catchments in this study are basically moorland, with only limited cereal crop areas, pesticide input is likely to be minimal. The response of pH in the regulated rivers was considered to be too important not to monitor, due to the recent concern of acidification of upland water bodies (Gorham, 1976). No direct analysis was made as to the ecological stress created by regulation, although this has received documentation, amongst others by: Simmons and Voshell,(1978) and Petts and Greenwood (1981). Nor was the response of temperature monitored because this has been examined by numerous authors e.g Crisp (1977), Lavis and Smith (1972), Wright (1967), and has been shown to have little significance.

4.2.1 Sampling.

The suitability of different types of sampling containers for river water have been considered and described in detail by Rainwater and Thatcher (1960), and the pertinent factors include resistance to solution, adsorption (Laterell et al, 1974), breakage, weight, size, efficiency of closure, and cost. In this study, 250ml polythene screw top containers were used, similar to the type recommended by Foster (1977) and Webb (1980). The advantages of using polythene bottles, was that they fitted all the prerequistes laid down above by Rainwater and Thatcher (1960). 250ml samples were taken in preference to litre samples - which have been said to be representative of the river water chemistry, at the given point in time (Walling, 1975) - because, from comparative studies they were found to give just as good a representation of river quality, and yet took up one quarter of the space and weight of litre samples. Consequently, as transport space to the laboratory for samples was limited, 250ml containers were more practical. Cleanliness of these sample bottles was ensured by washing them in the laboratory, firstly with a very weak solution of quadralene (1 drop per four litres of tap water) - a solution stronger than this was found to lead to contamination of samples, particularly with respect to nitrate (see section 4.4). Secondly, they were thoroughly rinsed with tap water, and finally with deionised water. Bottles when not in use, were stored capless, but neck down (to avoid dust contamination), dry, and in the dark. In this way the possibility of any organic staleness (bacterial film) and sample contamination (algal growth) was avoided. Immediately prior to sampling, as a final precaution, bottles were well rinsed in the sample water.

4.2.2. Spatial surveys.

All spatial surveys were made, where possible, when rainfall in the catchment during the previous seven days had been negligible, in order to assess maximum contrasts in solute levels. At high flow many dissolved constituents may be diluted toward common low values, which are typical of incoming precipitation (Hem, 1970; Webb,1980; Walling and Webb, 1975), although of course this is reliant on the nature of the river chemograph to rising discharge (paragraph 1.3). Sampling at low flow, that is when the concentration of the dissolved load, approaches that of ground or surface reservoirs feeding the stream (ASCE Task Committee, 1980) creates problems, since it is possible that solute parameters may not be homogeneous throughout the cross-section. Furthermore, the longitudinal location of sampling point is important, since it is not the case that at low flow, water qualities are uniformly poorer, because improved performance of biological oxidation by plants, a high quota of good quality groundwater, and increased retention time - leading to an increase in deposition and biological oxidation - will produce contracted, but worsened polluted stretches (Flint, 1971). Regular monitoring sites, were therefore chosen very carefully, according to downstream change in chemistry and/or flow, and obvious accessibility. These were determined from pilot spatial surveys of the whole of the Derwent catchment above Ambergate (Fig 5.2a and paragraph 5.3).

Since channels with irregular profiles, and deep stationary pools are more likely to develop inhomogenities than in steady regular flowing streams (Johnson, 1971), due to poor lateral and vertical mixing (Hem, 1970), an assessment was made as to the importance of such factors on the solute parameters under consideration in this study. A pilot survey was made at low flow on two reaches of the Afon Tryweryn; a regular stretch and a step/pool reach. The results of which are presented in Fig. 4.1a&b. From the results of this pilot survey it was found that the range of percentage variance at low flow on the Tryweryn for phosphate, nitrate, calcium and chloride was low, varying between 0 and 12%. Lateral variation at high flow was also considered (see Fig 8.13a&b and Fig 8.14a&b). This lack of lateral variation in water chemistry, even at extreme low flow is shown very clearly in Fig 4.1a&b. Nevertheless, samples were taken at least 0.5 metres away from the banks in order to be sure not to disturb any bank solute stores, or unique local bank chemical circulations. Also samples were taken within the main thread of flow, with the collection bottle totally immersed in the river, and the opening pointing downstream - to exclude air and local drift deposits, as recommended by, Ineson (1970) and Hem (1970), Webb (1980). The time of sampling itself, was designed to avoid any catchment hydrological events.

4.2.3. Release sampling strategy.

During a release samples of surface water were taken, at a frequency of every 3 min on the rising limb, every 4 min for the first 2 hours of constant dicharge, reduced to 30 min after this

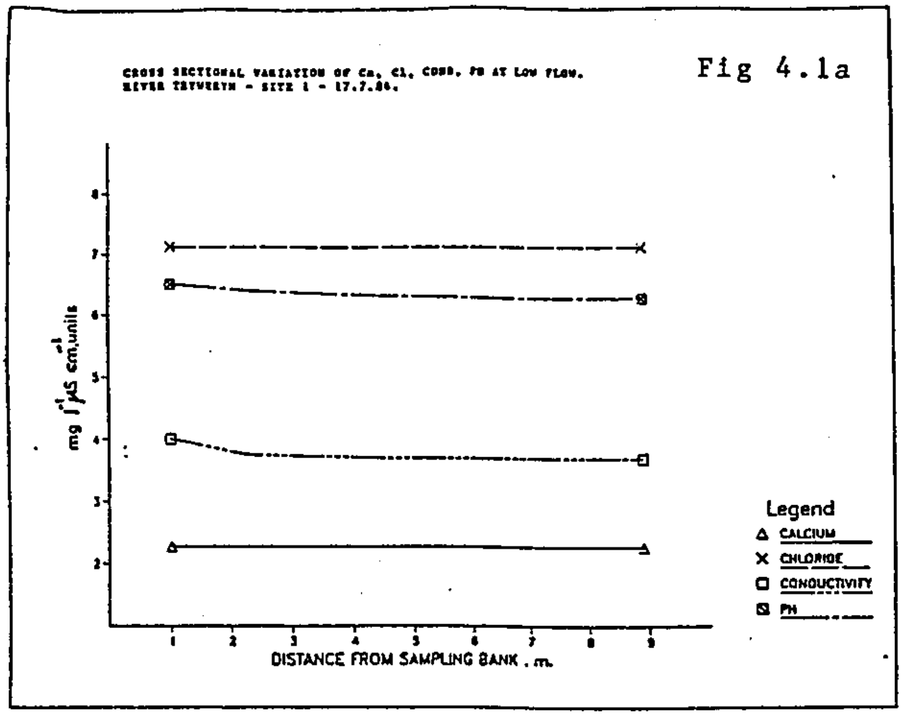


Fig 4.1a

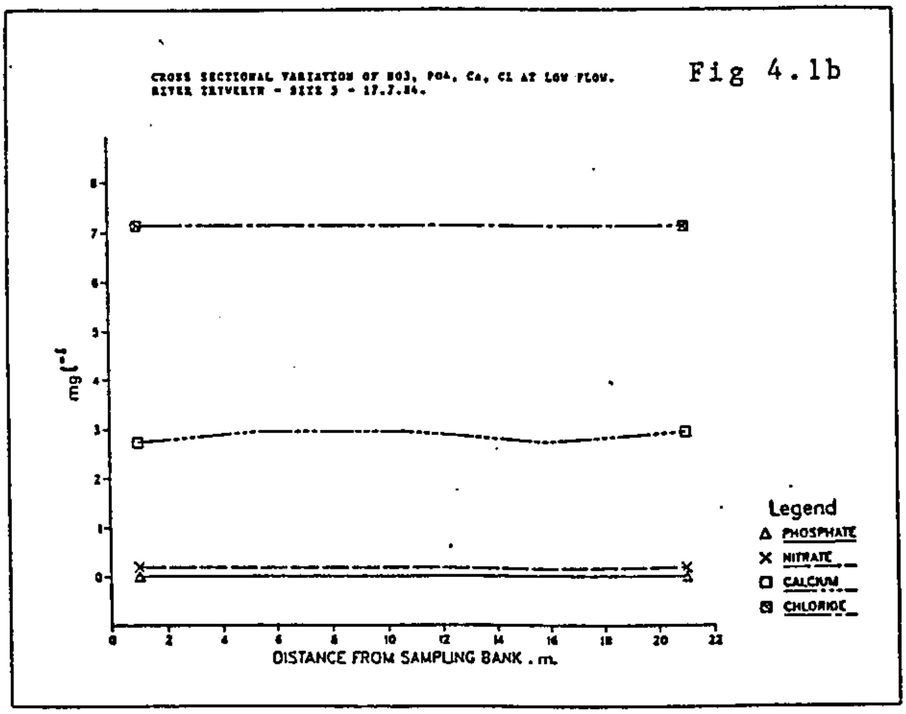


Fig 4.1b

FIG. 4.1 Lateral variation of solute concentration at low flow: River Tryweryn Site 1 (a) site 5 (b). Five data points were obtained on each transect (see section 4.2.2 and Appendix A4).

period, and increased to 5 min on the falling stage. This strategy was adopted after pilot surveys of the water quality change during two releases on the River Tryweryn, when samples were taken every minute from 3 hours prior to hydrograph rise, to 5 hours after the attainment of peak stage. These results indicated that when considering the effects of the release wave/water front only, the sampling frequency outlined was adequate, starting a minimum of 1 hour before the release, and continuing for a minimum of two hours after peak stage. After two hours water quality reflected a relatively stable balance between reservoir and channel water. This frequency of sampling enabled water quality response to be related to water quantity response, thus enabling cause-effect relationships, so lacking in water quality models (Rickert et al, 1975), to be quantified.

Samples of surface water were taken at arms length from the bank, a procedure found to remove any bank effects of poor mixing after numerous vertical and lateral mixing surveys carried out on the Afon Tryweryn (results shown in Table 4.1 & 2). Water samples of different depths were obtained by using a portable vacuum bottle sampler. This method was adapted from vacuum pump sampler machines, simply by fitting a suitable valve and nozzle to a pump sampler bottle. Once the sample had been collected, it was immediately transferred to a polythene bottle, in order to ensure that the chemistry of the water was not in any way affected by contact with the toughened glass (Rainwater and Thatcher, 1960). Samples from different positions across the channel, were obtained either with the aid of a white-water specification canoe, or by using synchronized strategically placed pump samplers. Table 4.1 & 4.2 show the results of mixing surveys at site 5 and site 6 during releases on the River Tryweryn. The mean values for determinands during a release obviously are only statistical summaries, and do not refer to any particular time during the release when these values were attained. This is also true for both the standard deviation and the % variance values. However, the results are meaningful for a comparative exercise between: sampling positions across the channel, sampling sites down the channel, and different releases. Also, if percentage variance at a site is compared with the real change in concentration, then degree of irregularity of determinand response during the rising stage and toward a steady dilution, can be quantified.

Thus for conductivity at site 6 on 23.4.83, across the channel the variation between mean values is only 1.76 μS cm^{-1}

		MEAN	SD	%VAR between samples	Change during a release (max)
SITE 6: 25/10/82; n=20					
Cond	NR*	61.53	5.70	4.9	16 μS cm^{-1}
	MID*	62.18	2.81	4.5	10
pH	NR	6.92	0.16	2.0	0.60 units
	MID	6.93	0.07	1.0	0.59
NO_3^-	NR	0.56	0.17	30	0.47 mg l^{-1}
	MID	0.73	0.09	12	0.40
Cl^-	NR	8.26	0.67	8	1.5 mg l^{-1}
	MID	9.01	0.32	4	1.5
Ca^{2+}	NR	4.5	1.70	3.8	3.8 mg l^{-1}
	MID	6.2	0.19	3.0	0.6
SITE 6 24/4/83; n=25					
Cond	NR	53.60	9.15	17	22 μS cm^{-1}
	FAR*	51.55	8.34	16	21
pH	NR	6.77	0.20	3	0.46 units
	FAR	6.55	0.28	4	0.77
NO_3^-	NR	0.48	0.10	21	0.28 mg l^{-1}
	FAR	0.42	0.08	19	0.25
Cl^-	NR	No change			
	FAR	No change			
Ca^{2+}	NR	6.19	1.83	30	4.64 mg l^{-1}
	FAR	5.97	1.62	27	4.35

TABLE 4.1 Cross channel mean solute variation for two 12.252m s^{-1} releases on the River Tryweryn.

* NR :- near bank (east side)
* FAR :- far bank (west side)
* MID :- mid channel

		MEAN	SD	%VAR between samples	Change during a release (max)
SITE 6: 23/4/83; n=26					
Cond	NR*	54.57	7.26	13	22 μS cm^{-1}
	MID*	56.24	6.9	12	18
	FAR*	54.00	7.66	14	26
pH	NR	6.88	0.04	0.5	0.13 units
	MID	6.58	0.10	1.0	0.30
	FAR	6.47	0.22	3.0	0.49
NO_3^-	NR	0.58	0.06	10	0.26 mg l^{-1}
	MID	0.58	0.06	10	0.30
	FAR	0.54	0.07	13	0.31
Cl^-	NR	14.7	2.6	18	5.0 mg l^{-1}
	MID	19.0	1.07	6	2.0
	FAR	17.0	1.05	6	2.0
Ca^{2+}	NR	5.23	0.92	18	2.53 mg l^{-1}
	MID	6.15	1.61	26	2.86
	FAR	6.36	1.82	29	2.35
SITE 5 25/10/82; n=25					
Cond	NR	43.8	8.5	19	22 μS cm^{-1}
	MID	44.9	10.0	22	26
	FAR	44.4	9.6	22	23
pH	NR	6.76	0.22	3	0.7 units
	MID	6.70	0.17	2	0.46
	FAR	6.73	0.18	3	0.48
NO_3^-	NR	0.35	0.15	43	0.38 mg l^{-1}
	MID	0.31	0.14	45	0.40
	FAR	0.34	0.14	41	0.34
Cl^-	NR	7.4	0.33	4.5	0.9 mg l^{-1}
	MID	7.13	0.66	9	2.1
	FAR	7.86	0.67	9	1.8
Ca^{2+}	NR	3.36	1.2	36	3.2 mg l^{-1}
	MID	3.29	1.13	34	3.2
	FAR	3.56	1.27	36	3.2

TABLE 4.2 Cross channel mean solute variation for two sites on the River Tryweryn during a 12.252m s^{-1}release.

* NR :- near bank (east)
* FAR :- far bank (west)
* MID :- mid channel

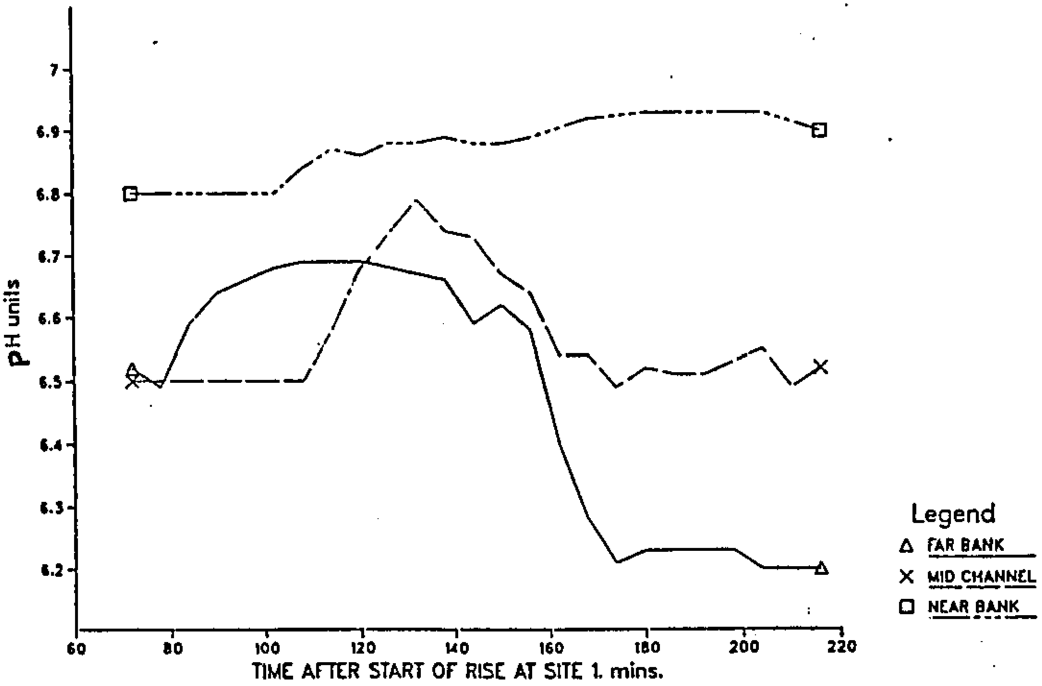
indicating a similar overall response to the release at each cross channel site. % variance and standard deviations are also very close, and the latter is less than a third of the actual change, indicating a lack of very rapid local flushing or dilution. A very similar response is portrayed by conductivity at site 5, 5.10.82; by nitrate for both releases; and calcium at site 5, with variation across the channel being consistent, with little evidence of local significant changes.

pH at site 6, shows considerable standard deviation variance between sampling positions, there is also considerable difference betweeen % variance and actual change. This is because the range of change at each point is different, with the greatest change at the near position , followed by mid, and then far. A similar response occurs with pH at site 5, having a larger range of change at the near bank, in comparison with the other two sampling positions. These patterns do suggest that with respect to pH, the spatial location for sampling could be important.

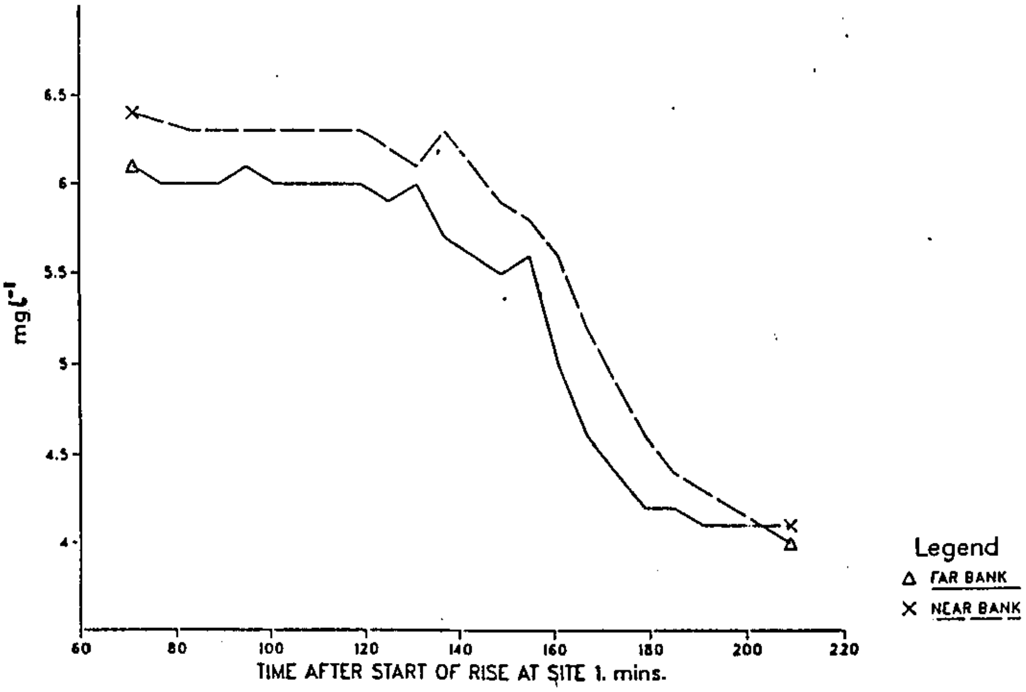
The chloride response at sites 5 and 6 is interesting in that, both mid and far sampling positions present very similar results, indicating uniform mixing, and a steady attainment of maximum dilution however, results from the near sampling point at both sites are erratic. At this position, the standard deviation and % variance are over twice as large as those from the other two locations, and the amount of change almost three times greater, yet the mean value is almost 5 mg l^{-1} less. This suggests a very unsteady dilution, with pulses of chloride, from local sources being rapidly flushed out. At site 5, the % variance between samples, is at the near location, half that of the other two, as is the degree of change, indicating that in this instance, the pattern of change at the near site is both reduced in magnitude and less erratic, than the response to the release wave front at the other two sites. Finally, the calcium response at site 6, is very similar to the chloride response at site 5, with a conservative reaction at the near bank, in comparison with that at the other two locations.

Figs. 4.2 a-d show the graphical representation of pH, calcium, and nitrate change during releases, at the furthest downstream, widest and least turbulent site on the River Tryweryn. The possibility of uneven distribution of solutes in the water body is high (e.g Anderson, 1963). However, graphical representation of results show that for calcium at least change is consistent - a maximum variation of 20% - although not quite

MIXING SURVEY. SITE 6 ; pH .23.4.83. Fig 4.2a



MIXING SURVEY . SITE 6 ; CALCIUM . 23.4.83. Fig 4.2b



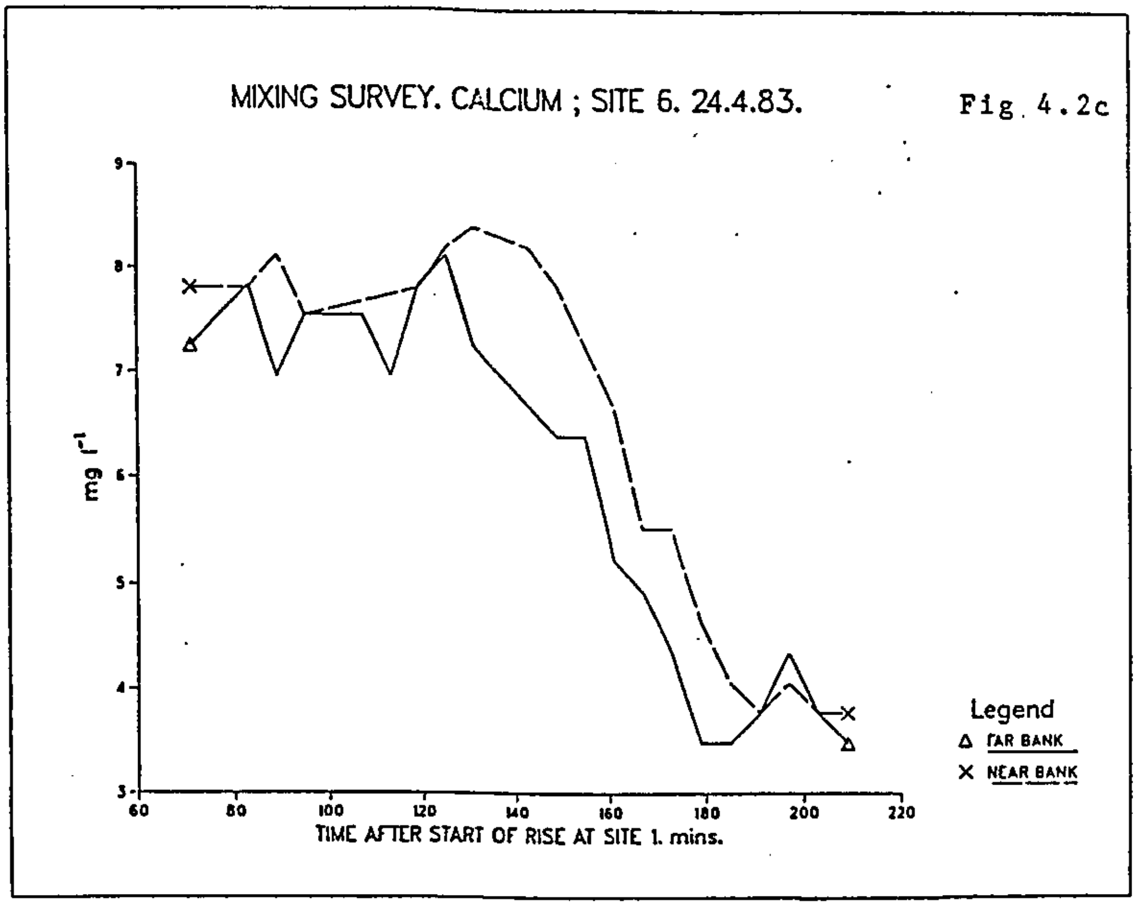


Fig. 4.2c

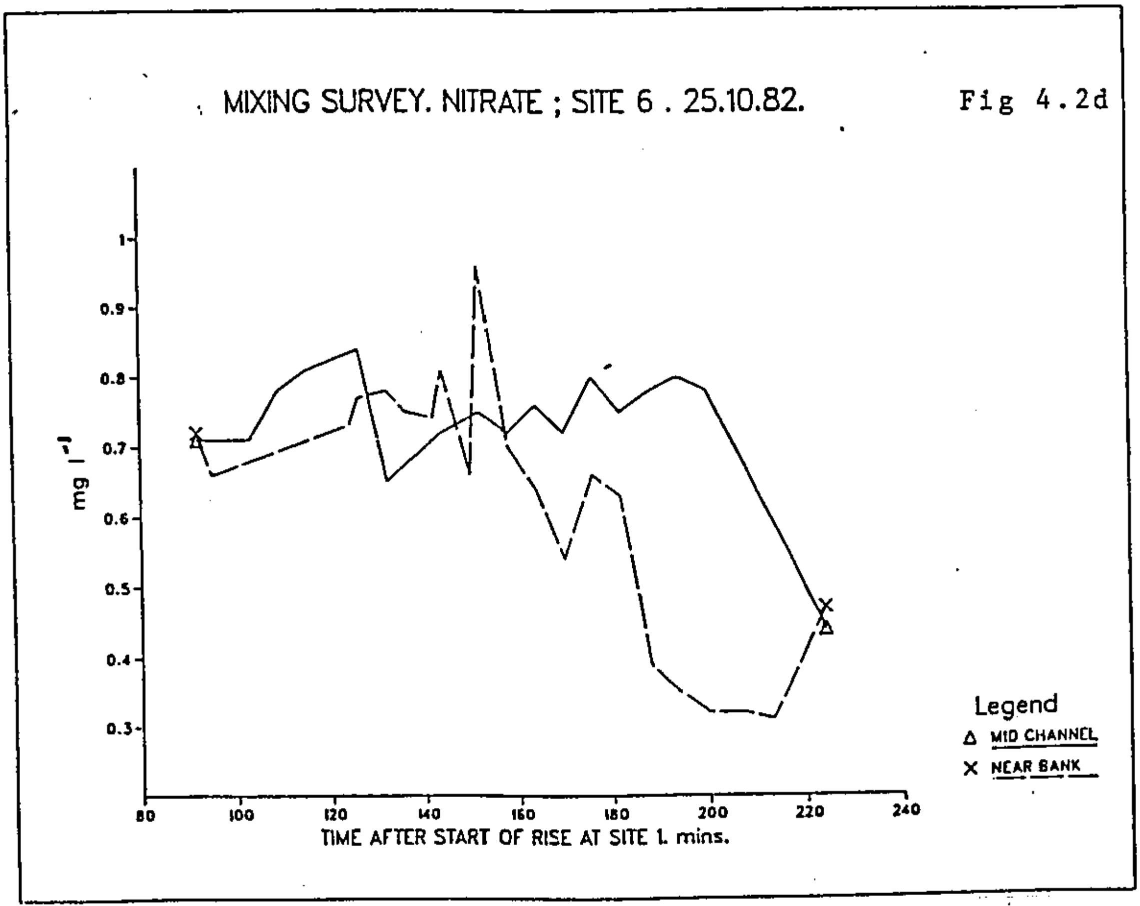


Fig 4.2d

FIG. 4.2 Lateral variation of solute concentration during a 12.252 m^3s^{-1} release on the River Tryweryn at site 6: pH on 23/4/83 (a), calcium on 23/4/83 (b), calcium on 24/4/83 (c), and nitrate on 25/10/82 (d). Each graph is series of 65 data points (see section 4.2.3).

as uniform as results presented by Johnson (1971), who recorded only a 5% deviation across the channel. The response of both nitrate and pH do show cross channel differences, with as much as 50% variation for nitrate, and nearly 1 unit for pH. Although the response of nitrate is irregular, the general trend at all sampling locations, during a release, is toward dilution. For pH however, there is no general response, with the far and mid sampling points exhibiting a decrease in pH, whilst the near bank values remain relatively constant, during a release.

These results indicate that there is variation in the mixing process across the channel, with this variation being different for individual determinands. However, the overall timing and response of all parameters considered (apart from pH) is similar, and final steady concentrations at high flow are consistent, indicating a very localised mixing pattern. Therefore, although sampling a single point across the channel, at a given time, may not give a precise representation of the exact magnitude of response of a given determinand, it does nevertheless, over the period of the release, show the pattern of response. The reaction of pH is somewhat unique however, since pH is notoriously difficult to measure accurately (paragraph 4.6.6), it is possible that this response is due to instrument error.

4.3. Sample Storage.

Success in analytical chemistry depends on analytical technique, treatment and storage (Jenkins,1968). In essence the maxim of "shorter the better" for storage time, proposed by the American Public Health association (1955 - in Rainwater and Thatcher, 1960), is as good a criterion as any, particularly for samples containing much organic material. Various workers however, propose various maximum limits to storage time, which vary from substance to substance. Johnson (1971) for example, suggests that conductivity should be determined immediately upon return to the laboratory, whereas other determinands should be analysed within two or three days. Whittel (1977) noted a 1.60 unit increase in pH of river water samples after 10 days storage in small plastic bottles. The American Waterworks Association (1966 - in Mackereth et al, 1978) stipulate that unpolluted samples should be analysed within 32 hours. In contrast Foster (1977), found that 10 days storage did not significantly affect specific conductance, calcium, magnesium, potassium, nitrate, or chloride values. For example, Foster shows that for a range of 2.7-16.9 mg 1^{-1} of nitrate, average results from 30 samples, subjected to 17 analyses over a period of 10 days, have a maximum change within the first few hours. After a further period of two weeks, samples were reanalysed and it was found that certain samples varied by as much as 22% from their previous values (Foster, 1977). In opposition to this Brookes (1974), and Rainwater and Thatcher (1960) state that stable dissolved constituents may survive unaltered in storage for periods of up to three months.

Since changes in the sample during storage must be due to: i) interaction of water with materials within the container ii) biochemical or iii) chemical reactions with entrapped sediment, not only is the length of storage time critical but also important is the treatment of the sample prior to storage and indeed, the actual nature of storage. Filtering will remove most inorganic sediment, however it does not remove colloids which are capable of adsorbing a high proportion of dissolved chemicals (Webb, 1980). Furthermore, nitrogen, phosphorus and organics concentration may actually increase on the passage through a glass fibre filter, due to the leaching of these chemicals from the fibres of the filter (Golterman and Clymo, 1969). In this study filtering was shown to increase nitrate values consistently, by as much as 10%; phosphate values by 15%; and calcium by 8%. This is due not only (if at all) to leaching from the glass fibre filter, but rather to the washing of organic, and in particular inorganic deposits, trapped on the filter paper. Consequently, it was decided not to filter samples prior to analysis. However, this meant that an amount of sediment was left in the sample bottle and the effects of this on the sample were examined.

4.4. Effects of sample sediments on water chemistry.

The influence of inorganic sediment and organics on water samples, could be significant, since they have been shown to be important in the transport of river solutes (Shi Chia Shun, 1969). Therefore they were examined by taking amounts of silts, fines and moss from the study river channel (in this instance the Afon Tryweryn) at five different locations downstream. In the laboratory, in order to ascertain the maximum possible handling effects, 10g of each substance was added to 100ml of deionized water, and shaken vigourously for exactly two minutes, in the standard 250ml polythene collecting vessels. Aliquots were then analysed, as usual, for nitrate, chloride, calcium, conductivity, and pH. The samples were then left to stand for 24 hours, and reanalysed. Data are shown in table 4.3. These results demonstrate that physically disturbing the sediments is

			SITE 1			SITE 3			SITE 4			SITE 5			SITE 6		CONTROL		
		MOSS	SILT	FINES	MOSS	SILTS	FINES	MOSS	SILTS	FINES	MOSS	SILTS	FINES	MOSS	SILTS	FINES	–	–	–
CHLORIDE (mgl^{-1})	Shaken	1.5	1.5	0	1.5	1.0	0	0	5	2.5	0	2.5	1.0	0.5	2.5	1.5	0	0	0
	24hrs	1.5	1.5	0	1.5	1.0	0	0	5	2.5	0	2.5	1.0	0.5	2.5	1.5	0	0	0
			9.0			9.0			10			10			11				river values
NITRATE (mgl^{-1})	Shaken	0	0.4	0.34	0	0.22	0.19	0	1.04	0.44	0	0.34	0.38	0	0.36	0.21	0.44	0.32	0.32
	24hrs	0	0.3	0.3	0	0.2	0.19	0	1.0	0.4	0	0.34	0.4	0	0.36	0.24	0.44	0.32	0.32
			0.05			0.05			0.05			0.05			0.05				river values
CALCIUM (mgl^{-1})	Shaken	0	2.31	0	0	2.31	0	0	2.31	0	0	2.31	0	0	2.31	0	0	0	0
	24hrs	0	3.4	1.0	0	2.4	1.0	0	2.5	0.5	0	3.1	0	0	2.5	0	0	0	0
			3.3			3.3			2.31			3.5			2.97				river values
COND (μScm^{-1})	Shaken	30	9	9	30	9	9	19	9.6	9.8	18	7.8	11.0	20	10	6	7.5	6.1	9.0
	24hrs	29	10	10	29	10	10	18	8.9	10	18	8	12	15	8	5	8	7	10
			45			42			40			48			47				river values
PH (units)	Shaken	5.88	6.20	6.29	5.98	6.01	6.0	6.21	5.82	5.59	5.57	5.73	5.66	6.00	5.81	5.87	5.11	5.17	5.00
	24hrs	5.7	6.1	6.2	5.8	5.9	6.0	6.2	5.7	5.4	5.4	5.8	5.7	5.9	5.8	5.9	5.09	5.2	5.10
			6.98			6.73			6.3			6.9			7.0				river values

TABLE 4.3. Effect of handling upon solute concentrations in river water samples.

more significant in releasing solutes, than the time factor of leaving the samples to stand overnight. It is interesting to note that the contribution to sample change from the relatively large amounts of moss, silts, and fines added to the deionized water, in comparison to the chemical concentration of river water itself is minimal, except in the case of silt and calcium, and moss with nitrate and conductivity. Incidentally, the high nitrate values recorded are due to high nitrate values in the deionized water as shown in the control samples. These high values were traced to be the result of the leaching of detergent products from the deionized water containers. However, despite these problems, the sediment shaking experiment results, do show clearly the effect of keeping in storage a large amount of vegetable matter, which uses up available nitrates, whereas non-organic silts and fines do not affect nitrate values.

In terms of analyses of river water samples these findings were applied, so that samples were not disturbed prior to testing, and measurement for nitrate, calcium, chloride and phosphate was begun on return to the laboratory, and completed within five days. Similarly pH and conductivity testing, were completed within two days after returning to the laboratory. These tests show importantly that the handling of water samples is more important than the immediate time factor in producing an accurate representation of river water quality.

4.5.CHEM LAB - continuous flow autoanalyser.

The water chemistry analytical system used in this study, was similar to that described by Davies (1971), and Foster (1977). It comprises five major modules: a sampler, proportioning pump, time pac modules, colorimeter, and chart recorder.

4.5.1. The sampler.

The sampler supplies standard solutions, water samples and wash water to the autoanalyser, at a rate controlled by a cam, and cam follower. The sampling tray holds forty, 4ml cups, into which a pickup probe is inserted at regular intervals. Once in position the cups are protected from foriegn bodies entering the samples, by means of a perspex plate.

4.5.2. The proportioning pump.

This is the central part of the system, bringing samples and chemicals together at a constant rate. It comprises a pair of roller chains, five stainless steel rollers, and a platen plate. A peristaltic pumping action is induced by the steel rollers pressing flexible tubing against the platen. The actual rate of flow is controlled by the internal diameter of the tubes and can vary from 0.019 to 3.9 ml min^{-1}. Reagents and samples are held in separate tubes until reaching the time pac module.

4.5.3. The time pac module.

The design of this part of the system depends entirely upon the chemical being analysed. However, in general it consists of four integral parts:

i) tubing introducing air bubbles into the sample line to separate the flow. The bubble pattern is absolutely crucial to the operation of all autoanalyser systems, as the bubbles not only delimit samples, but also the surface tension created by the bubble passing through the tubing, scrubbing the walls minimizing contamination between samples and increasing the efficiency of analysis by reducing the wash time with deionised water between samples.

ii) mixing coils play two roles in the analysis, firstly they ensure a thorough mixing of all chemicals concerned, and secondly they create a delay before reaching the colorimeter, which enables sufficient colour development to take place.

iii) dialyser; this is the clarification stage in the analytical process, which removes suspended materials and colloidal matter. It consists of two plates on each of which is engraved a spiral groove, these are mirror images of each other. Between these plates is placed a cellophane membrane. The sample is pumped along the groove of one plate, and the ions dialyze across the membrane into the recipient groove of the plate below.

iv) heating coil, which may or maynot be necessary to bring chemicals to the optimum reaction temperature.

4.5.4. The colorimeter.

Comprises of a single light source split into two separate beams. One beam passes through a flow cell into

RIVERS' TRYWERYN, WASHBURN, NORTH TYNE

Calcium	1, 2, 4, 8, 16 mg l^{-1}	GAIN 7
Nitrate	0.05, 0.1, 0.2, 0.4, 0.8 mg l^{-1}	"
Phosphate	0.025, 0.05, 0.10, 0.20, 0.40 mg l^{-1}	"
Chloride	2.5, 5, 10, 20, 40 mg l^{-1}	"
Conductance	10, 20, 30, 40, 50 μS cm^{-1}	
pH	Buffer 7.0 units	

RIVER DERWENT

Calcium	10, 20, 40, 80, 160 mg l^{-1}	GAIN 3
Nitrate	0.5, 1, 2, 4, 8 mg l^{-1}	GAIN 5
Phosphate	0.25, 0.5, 1.0, 2.0, 4.0 mg l^{-1}	GAIN 7
Chloride	5, 10, 20, 40, 80 mg l^{-1}	GAIN 5
Conductance	50, 100, 200, 400, 800 μS cm^{-1}	
pH	Buffer 7.0 units	

TABLE 4.4 Standard Values of calibration curves for calcium, nitrate, phosphate, chloride and conductivity, together with gain (sensitivity) setting for the Chem Lab autoanalyser.

which the sample flows and is detected by a photosensitive cell. The second passes through an identical one which acts as a reference. Light filters are inserted between the light sources and the photosensitive cells, to isolate the correct wave length required for analysis.

4.5.5. The Recorder.

The response of the balanced photocells is measured and recorded continuously by means of a pen and chart recorder. The sensitivity can be altered to some extent by the varying dilution of the sample. In general however, samples from the River Derwent were analysed at a sensitivity of; 0-250mg $l^{-1}$for chloride, 0-50mg $l^{-1}$for nitrate, 0-50mg $l^{-1}$for phosphate, and 0-400mg $l^{-1}$for calcium. For samples collected from the River Tryweryn, Washburn and North Tyne the sensitivity was increased to; 0-250mg $l^{-1}$for chloride, 0-1mg $l^{-1}$for nitrate, 0-1mg $l^{-1}$for phosphate, and 0-400mg $l^{-1}$for calcium.

Operation of the Chem Lab autoanalyser, in common with most other chemical analytical methods, requires the preparation of standard solutions. Stock 1000mg l^{-1} solutions were prepared for nitrate, phosphate and chloride, a 400mg l^{-1}calcium standard was obtained direct from a chemical supplier. These stock solutions were then diluted to the appropriate range for each river sampled (see Table 4.4). Great care was taken to ensure that these standards were consistent and accurate. Fresh stock solutions were made up every two months, and compared against the old solutions, to ensure continuity, and to minimize contamination and deterioration through time. Nitrate solutions were further preserved by the addition of 1ml l^{-1} of chloroform (this destoys any living water borne organisms that might thrive on the nitrate).

The use of the autoanalyser system, which is primarily designed as a clinical tool, and as such to be run continuously, requires extreme precision and care. Great patience is needed by the experimentor, to ensure that the system is initially working satisfactorily. The Loughborough University, Geography departmental system, was assembled and operated entirely by the author. During this three year research period, an extensive trouble shooting guide was developed, which has proved invaluable to subsequent users, a copy of which is presented in the APPENDIX B1. Essentially, before accurate analysis could be undertaken on the CHEMLAB, two prerequistes were necessary i) an even spacing of reagent to air bubbles flowing through the timepac module, and ii) a steady and even baseline on the chart recorder. Problems in these two areas usually related to the degree of surfactant in the reagents, age and tension of pump tubing, dirt in the dialyser membrane or flow cell, temperature and age of reagents, and the type of pump tubing connectors used. The lack of irregularities and steadiness of the baseline was also dependent on the level of sensitivity of the analysis, with more noise for a greater sensitivity. Providing this noise was not excessive - 15% or less of peak height - analysis was possible. During the testing of samples for a given solute, little interference from other solutes, or organic colouring was found, the only problems related to mechanical faults of the sampler and the colorimeter.

4.6. Individual parameter analysis. (Table 4.5)

4.6.1. Chloride.

Chloride is present in all natural waters, but mostly concentrations are low, less than a few tens of milligrams per litre (Hem, 1970). It is assumed that this small amount of chloride in unpolluted streams is derived from rainwater, although it may also be derived from sedimentary rocks, and sea spray. Chloride is unaffected by biological processes, little adsorbed onto sediments, and not utilized by bacteria and plants, therefore should be the ideal natural tracer, however its low concentration is likely to make identification of reservoir and river water on this basis problematic. The automatic flow determination of this substance is based on the property of chloride to release thiocynate ions stoichiometrically when reacted with mercuric thiocyanate. These are then estimated colorimetrically as the red ferric thiocyanate (see APPENDIX B3).

Range: Derwent = 10.0 - 50.0 mg l^{-1}
Range: others (Tryweryn, Washburn and North Tyne)= 5.0 - 25 mg l^{-1}

4.6.2. Phosphate.

Most soils contain large reservoirs of phosphates (Davies, 1971), but they are strongly adsorbed and complexed, and therefore, are not readily released. Phosphate fertilizers are insoluble, and superphosphate fertilizers form insoluble compounds with iron and aluminium. It is only at very low levels

	DERWENT	TRYWERYN	WASHBURN	N TYNE
COND (μScm^{-1})	50-500	30-70	80-150	50-150
pH (units)	3.8-8.5	5.9-7.4	6.3-7.8	6.0-7.5
NITRATE (mgl^{-1})	0.1-5.0	0.02-0.80	0.2-1.5	0.05-2.5
CHLORIDE (mgl^{-1})	10-50	5-20	10-20	5-25
CALCIUM (mgl^{-1})	3-150	2-10	6-20	2-20
PHOSPHATE (mgl^{-1})	0.01-0.50	0.01-0.05	0.02-0.05	0.01-0.03

TABLE 4.5 Measurement Ranges of solutes on the Study Rivers.

of pH, that such aluminium-phosphate compounds can dissociate into free ions, and be washed into stream water. Phosphate concentration is measured in mg l^{-1} and analysed by a method based on the reaction of ammonium molybdate in acid solution with orthophosphates to form molybdo-phosphoric acid, which is reduced to molybedenum blue by ascorbic acid, the strength of which is then measured colorimetrically (APPENDIX B2).

Range: Derwent = 0.01 to 0.50mgl^{-1} Range: others = 0.01 to 0.05mgl^{-1}

4.6.3. Calcium.

Calcium is found in waters associated with calcite, and dolomite (Weyl, 1958), and indeed is one of the most abundant metals in natural water (Walling and Webb, 1978). Therefore, determination can be made at a level of analysis, which is relatively insensitive to experimental error. Thus, it is an important solute, in identifying the response of river water quality to flow regulation. Furthermore, hardness and alkalinity are related to this ion - temporary hardness, when calcium exists as a bicarbonate, and permanent hardness if calcium occurs in the form of sulphate and chloride salts (Davies, 1971). Its concentration is measured in mg l^{-1} and analysed by a method based on the emergence of a highly coloured complex, produced by the formation of chelate by cresolphalien complexone in the presence of calcium ions. This is then converted to a highly coloured complex by the addition of a base. The addition of acidic 8-hydroxyquinoline, reduces the interference by magnesium, and releases calcium, and the use of cyanides mask any effect of transition metals (see APPENDIX for detailed methodology).

Range: Derwent = 3 to 150mgl^{-1} Range: others = 2 to 20mgl^{-1}

4.6.4. Nitrate.

A detailed explanation of the nitrogen cycle is presented by Brezonik (1973). In essence however, nitrates in stream water will have come from one of three areas: natural nitrate sinks in the soil; nitrogenous fertilizers; or oxidation of ammonia produced by aerobic or anaerobic decomposition of nitrogenous matter. Because its concentration is associated with these factors, the values in regulated rivers and their associated reservoirs, are likely to be very different, and therefore, releases of reservoir water down the channel may create significant changes in streamwater nitrate levels. As with other solutes the concentration measurement unit is mg l^{-1}. The basis of the titration that occurs during automatic flow analysis, is the formation of a diazo dye, the strength of which is estimated colorimetrically. This method determines the combined concentration of nitrate and nitrite, present in solution. In order to determine nitrate alone, firstly the sample is tested without the presence of a reducing agent - copper-hydrazine (see APPENDIX B4), thus no reduction of nitrate occurs and it is unable to take part in the formation of the diazo compound, therefore only the concentration of nitrite is determined. The titration is then repeated with the hydrazine-copper reagent present to reduce the nitrate to nitrite enabling it to form a diazo compound and so be estimated. This second determination measures total oxidised nitrogen. The nitrite value from the first determination is then subtracted to give the nitrate concentration in the sample.

Range: Derwent = 0.1 to 5.0mgl^{-1} Range: others = 0.02 to 2.5mgl^{-1}

4.6.5. Specific Conductance.

Specific conductance is defined as "the number and kinds of ions present, their relative charge, and mobility" Hem (1970), and refers to the conductivity of a cube of substance 1 cm long, and 1 cm in cross section, and is measured in microseimens per centimetre (µS cm^{-1}), at a standard temperature of 25°C. In layman's terms conductivity is the ability to conduct an electric current and in the case of water samples, is directly related to the concentration of ions present and to the temperature (Golterman and Clymo, 1969; Edwards et al, 1975) - an increase of 1°C increases conductance by less than 2% (Hem, 1970). Because it is so easy to measure, it is a widely used as a summary of river water quality, and has been shown to be responsive to discharge variation (paragraph 2.3). In this study, conductivity was measured using a LTH hand held conductivity meter, with sealed graphite probe, and maximum error deviation of about ±3%.

Range: Derwent 50-500µScm^{-1} Range: others 30-150µScm^{-1}

4.6.6. pH.

This is defined as the negative logarithm of the dissociated hydrogen ion concentrations. Because the scale is logarithmic small changes in pH actually equate to large changes in the concentration of H+ ions e.g a pH of 7.6 is 2.5×10^{-8} moles of hydrogen ions, pH 7.5 is 3.16 x 10-8 moles of hydrogen ions, a difference of 21%! pH 7.51 to pH 7.50 is a difference of 2.3%! Since the majority of pH meters are accurate to only 1 decimal place (pers com LTH Electronics), then at best, accuracy at about neutrality will be +- 20%. Add to this the fact that glass diffusion electrodes (standard issue for pH meters) are notoriously susceptible to inaccuracies, due to grease and dirt stains on the glass semi permeable membrane and an accuracy of 20% is to be considered very acceptable. In natural waters, pH is usually within the range of 6.0 to about 8.5 (Hem, 1970), and is controlled by the chemical equilibria and reactions of ions in solution, which are largely dependent upon dilute carbonic acid formed when carbon dioxide and its associated salt are dissolved in water (Hem 1970). This carbon dioxide-bicarbonate system is very unstable, and the pH of the sample will change if carbon dioxide escapes from it (Cryer and Trudgill, 1981). Consequently, variations of 0.8 pH units between the laboratory and the field are not unusual (Imeson, 1970). Therefore, if laboratory pH is within about 1 pH unit of the "true" value, results are extremely good.The fact that most natural waters are buffered - pH not greatly changed by the addition of moderate quantities of acid or base - to some extent by reactions which involve dissolved carbon dioxide species, is likely to mean that pH variations during releases will be minor.

Range: Derwent 8.5-3.8 Range: others 7.8-5.9

In an attempt to overcome the problems of chemical change in the samples from the field to the laboratory, with the aid of LTH Electronics a portable automatic conductivity, temperature, dissolved oxygen, and pH meter was designed. Teething troubles, were associated particularly with its two 6 volt dry cell battery power source, but the system was eventually tested during reservoir releases on the River Tryweryn, and River Washburn (see APPENDIX A3 for results). Conductivity values were consistent with laboratory readings from bottle samples, and dissolved oxygen readings were similar to results from a dissolved oxygen only field meter however, pH readings were not comparable to laboratory results, there being as much as 4 units variation! This was primarily because at very low flows the pH glass electrode, which was protected to avoid breakage, established its own glass/water environment leading to eroneously high pH values. During releases, this environment was slowly washed away, lowering pH erratically toward true levels. Because of this unreliability, all pH values quoted in this study were taken from bottle samples - analysed in the laboratory - usually within 24 hours of collection, and although deviations from the in situ water true values may be as high as 1 pH unit, the majority of the analysis was comparative in nature, and therefore assuming relatively constant error, is scientifically valid.

To ensure that instrument and handler error in the measurement of pH was kept to a minimum, a hand held Corning 3D pH meter was used with a glass electrode. To obtain the correct precision and accuracy, the device was calibrated in a standard freshly made buffer solution close to sample pH, immediately prior to testing. Moreover, the electrode bulb was cleared by carefully wiping it with cotton wool soaked in carbon tetrachloride. The probe was placed in the sample bottle, stirred around vigourously but carefully for 10 seconds, and then allowed to stand three quarters immersed for 30 seconds, a reading was then taken. This procedure was followed 3 times and values averaged. In between each sample the probe was washed in deionised water. In this way, readings could be reproduced within 0.05 pH units, approximately 5% operator accuracy.

The measurement ranges of all determinands for the study rivers is summarised in table 4.5.

4. 7. Precision of analysis.

Precision may be defined as the reproducibility of results (Mackereth et al, 1978) and as such is critical to this study. Thus, for 10 different surveys on the River Tryweryn, and the River Derwent, the precision of the Chem Lab results was examined. Effectively, the precision of the results is only as good as the calibration curve, so the peak height of standard values (100 in all) was analysed. Results are given in Table 4.6. Clearly accuracy is greater for the Derwent surveys, which is because analysis was being carried out at a more concentrated level (see table 6.5), however even at the very low concentration levels of solute, to be found in the River Tryweryn, accuracy is still very good - 8% or better. Different chemistries have different % values, and in fact indicate the ease of handling of a particular module. Thus chloride, from a purely practical angle was the easiest to operate (temperature of reagents was unimportant, and mixing of reagents within the timepac module, was fast and efficient), and gave the most consistent results. Whereas phosphate, being the most awkward to run (the temperature of reagents, the surfactant concentration was critical, and the mixing time of reagents was high, leading

	COEFFICIENT OF VARIATION %* TRYWERYN	 DERWENT
Calcium	6	4
Nitrate	7	3
Phosphate	8	7
Chloride	3	2

* Coefficient of variation = SD/mean x 100 n=100

TABLE 4.6. Comparison of coefficients of variation of chemical analysis for the River Tryweryn and River Derwent

	CONCENTRATION mg 1^{-1}	COEFFICIENT OF VARIATION % OF SOLUTE PEAK HEIGHT FROM THE CHEM LAB
Nitrate	0.1 - 0.6	7
	1.0 - 5.0	3
Phosphate	0.05 - 0.5	8
	2.5 - 10	7
Chloride	2.5 - 10	3
	10 - 100	2
Calcium	2 - 10	6
	20 - 100	4

n=100

TABLE 4.7. Coefficient of variation (variance) in chem lab auto-analyser results for nitrate, phosphate, chloride, and calcium.

to a long complicated timepac module, wherein the peristaltic pump pressure was substantially reduced, allowing for the possibility of irregular bubble patterns), gave the least accurate results.

4. 8. Validity of results.

There are three areas when the question of validity arises in a study of this nature. First, is the water sample representative of the body of stream water from which it was taken, both spatially and temporally. Second, is this sample still a true representation after a period of storage. And third, are the chemical analytical techniques giving a "true" representation of river water quality.

The problem of spatial mixing has already been discussed (paragraph 4.1.2). Temporal validity of sampling was examined by taking 6 samples in 2 minutes, at 6 different sites on the River Tryweryn, under established high flow conditions. Results indicate that there is little or no variation temporally between samples at this established flow level (see APPENDIX A2). pH values fluctuate, but this represents the sensitivity of the glass bulb electrode, pH meter, more than a changing acidity of the water. The results confirm, that variation in water quality during the start of a reservoir release, is not simply part of the natural cycle of water quality change, but is really due to physical and chemical effects of the release.

The problem of storage has already been dealt with (paragraph 4.2), and results showed that as long as tests were carried out on the water sample within the week then findings were valid.

To establish the reliability of the auto-analyser, a simple experiment was followed, whereby 100 known value standards were analysed. The results are presented in table 4.7. These values show a maximum % variance of only 7% for nitrate in the range of 0.1-0.6mg 1, and 8% for phosphate in the range 0.05-0.5 mg 1^{-1}. For the remaining determinands, % variance was less than 6%, - an extremely small intra sample variability.

Absolute Chem Lab accuracy i.e inter sample precision, was assessed by comparing results produced on that machine with results from an entirely different system. Values were found to be comparable within a 5% range. In short, the accuracy of the chemical analysis, was similar to that quoted by Foster (1977) and Davies (1971) for auto-analysers, at about 3-5%.

4. 9. Flow Measurement.

For the River Derwent, Severn Trent Water Authority gauged flow data, in the form of mean daily flow records, were used for the monthly comparison of water chemistry data. This level of discharge accuracy was considered to be sufficient for comparative purposes. For the Rivers Tryweryn, Washburn and North Tyne, reservoir release quantity was known (gauged accurately at the dam outfalls) and tributary inflow was measured approximately by standard propellor flow metering techniques (Lewin, 1981). Rate of change of discharge at-a-station, was calculated by the rate of change of stage in the accurately surveyed channel cross-section. As a point of interest it was found that by far the most reliable and accurate method of mapping the river channel cross sections, was by physically wading the rivers, and locating irregularities by a dip stick approach, and measuring the depth of these non-uniformities below the surface of the water. More sophisticated methods of surveying e.g levelling, were found to be insensitive to the level of accuracy necessary.

4.10. Chapter Summary.

For a study of this nature, two critical factors determining the nature of methodology were identified. First, the need for extremely accurate, and yet at the same time sensitive techniques for the measurement of chemical parameters, since water in uplands streams is low in dissolved constituents. Therefore, every practical precaution was taken to avoid sample contamination and deterioration and that the sample taken, truly reflected the chemical nature of the river water, at that point in time. Laboratory work was thus designed to be not only of the highest standards, but also fast and efficient.

Secondly, the need to be able to establish reliable field monitoring sites, in poorly accessible regions of upland Britain, quickly and at times in less than 36 hours notice (depending upon the preceding hydrological conditions). Therefore, the field equipment was designed to be portable, robust and reliable under the most extreme conditions.

CHAPTER 5.

THE RIVER DERWENT: SPATIAL AND SEASONAL PATTERNS OF WATER CHEMISTRY VARIATION.

This chapter examines the influence of impoundments - the Ladybower-Derwent-Howden Reservoir system - on the water chemistry of the River Derwent, Derbyshire. Data have been derived from a point-time survey of the drainage system, and a monthly examination of chemistry changes within the main stream.

The regulation of the River Derwent was authorised in 1899 and the masonry, crest-weir overflow dams of Howden and Derwent, constructed in sequence to impound the runoff from the headwaters, were closed in 1912 and 1914 respectively. However, it was the construction of the Ladybower dam, begun in 1935 and completed in 1945, that had the major impact upon the River Derwent. The earthfill dam with a bellmouth spillway, was constructed downstream of the Ashope confluence so that the runoff supply from a catchment area of 127 km^2 has been impounded. In addition to this water supply, inflow to the reservoir is augmented by input from the diversions constructed on the neighbouring River Ashope, River Alport, River Noe, and Jaggers Clough (Hill, 1949).

5.1 Catchment characteristics.

5.1.1. Catchment area.

The River Derwent rises at an elevation of over 575 m.O.D. on the northeast side of Bleaklow Hill, falls rapidly to below 200 m.O.D. within the first 30km of its length, and subsequently at a decreasing gradient to 44.4 m.O.D. at Longbridge Weir, Derby. The 74km long catchment encompasses an area of 1200 km^2. However, in this study a reach of only 60km, to Ambergate (upstream of the confluence with the River Amber) at 87 m.O.D., was considered, and the catchment area to this point is 870 km^2. This reach was examined because in the near future it may be dominated by flow regulation for the Carsington Reservoir Scheme.

The Carsington reservoir site is located some 8 km from Ashbourne, between the villages of Carsington in the north and Hognaston to the south. It is proposed, that upon the

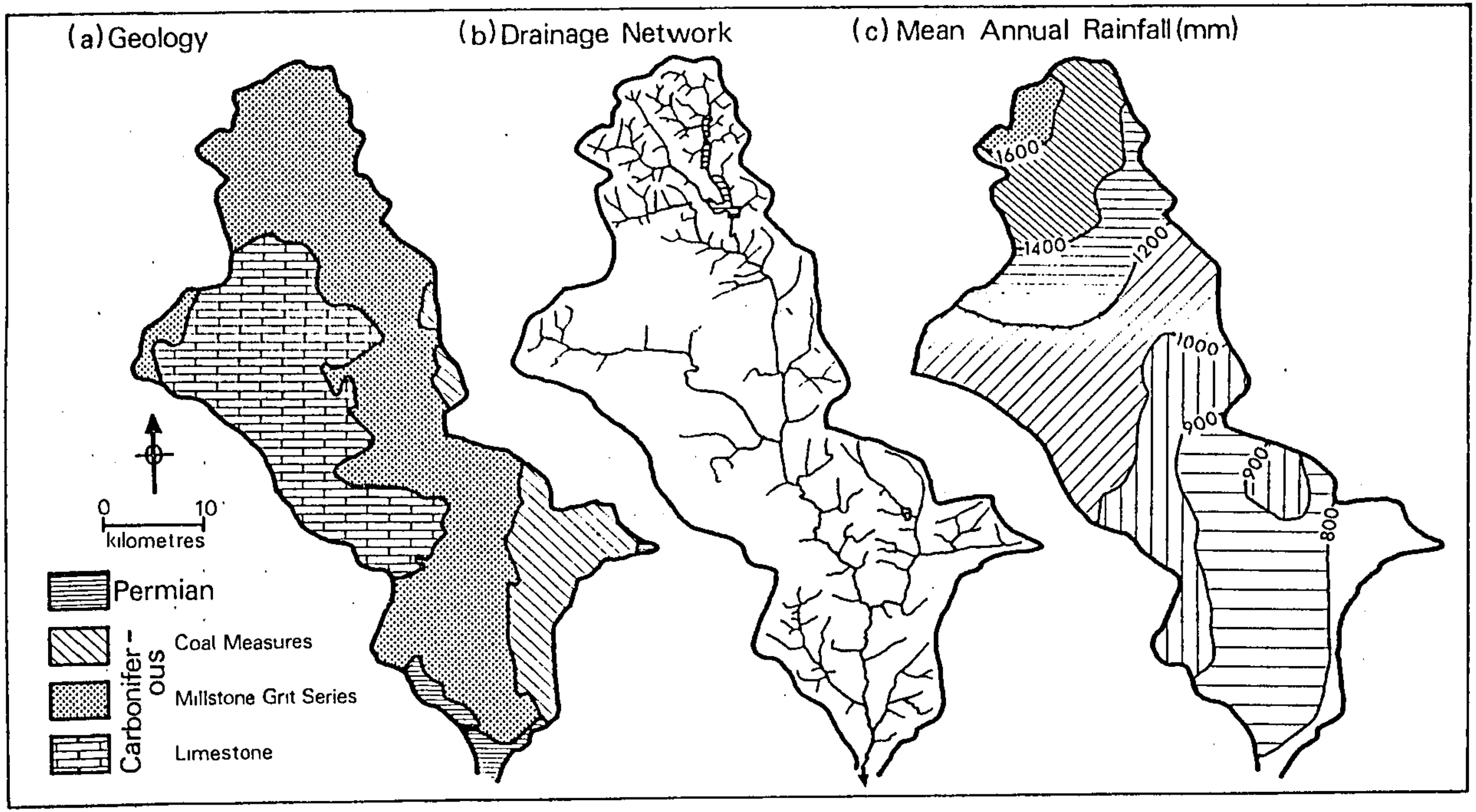


FIGURE 5·1 PHYSICAL CHARACTERISTICS OF THE DERWENT BASIN. (PETTS, 1977) reservoir's completion, which is now anticipated to be in 1986 (see Davey and Eccles, 1983) - although since this announcement much delay has occurred - it will augment the Derwent reservoir's supply potential. Carsington reservoir itself, is to be kept full by water pumped via a series of supply tunnels, from the River Derwent at Ambergate. Sufficient flow to meet the Carsington demand at this location,will be maintained by releases from Ladybower Reservoir. Due to the frequency of such releases the chemical nature of the Derwent down to Ambergate is likely to be seriously affected, and partly this study aims to assess the potential changes that might occur when Carsington Reservoir becomes operable.

5.1.2. Catchment geology.

Geologically, the Derwent study area may be divided into three main units (Fig. 5.1). The most extensive, the Millstone Grit series of alternating sandstones and shales, provides a broad area of outcrop in the north, narrowing southwards to separate the Carboniferous Limestone from the Coal Measures. The frequent beds of shale within the generally permeable grits ensure the impermeability of the Millstone Grit Series as a whole and results in the formation of perched water tables, responsible for frequent springs along the valley sides. In the north, peat often overlies a weathered, fractured gritstone surface, and this provides some regulation of runoff and tends to balance the seasonal irregularities in the rainfall.

The Carboniferous Limestone Series of the Derbyshire Dome dominate the west of the catchment. The series, composed predominantly of pervious limestone with interbedded basaltic lavas and tuffs, typically has little channelised flow in contrast to the remainder of the catchment. Mudstones and sandstones of the Coal Measures in the south and east have an undulating topography with summits up to 180 m.O.D., and restricted outcrops of Permian limestones with mudstones while Bunter sandstones occur in the extreme south of the area. The valley fill is composed of terrace, alluvial fan, and head deposits, while glacial material occurs in rare, scattered patches on the higher slopes. Rock outcrops at several points along the river channel and although the valley is generally wide, at Matlock the river enters a narrow gorge cut in Carboniferous Limestone. The river channel is often tree lined with birch, ash, oak, elm and willow which, together with the outcrops of bedrock and the several weirs and mills, tend to stabilise the slope and planform of the river.

5.1.3. Catchment landuse.

The water quality of the Derwent is undoubtedly affected by landuse. Today, generally there are three types of landuse; high quality grazing and some arable associated with the limestone areas; poorer quality moorland grazing associated with the gritstone areas; and forestry along the river channel itself, and in the headwater catchment zones. Superimposed upon this agricultural pattern, is a degree of industrial working, and an amount of urbanisation. The industrial works, apart from the reservoirs, are mainly associated with limestone quarrying for cement manufacture (e.g The Blue Circle cement plant at Hope), although there are also a few textile mills, and 'modern' warehouse industries (e.g lead reclamation from relict sources, at Darley Dale). The control of effluent from these sources is high, and in comparison with agriculture, their influence on the nature of river water chemistry is limited to short, accidental pollution incidents. Urbanisation, through the input of domestic sewage, and sediment in runoff from much increased paved areas, is probably likely to have a much more consistent effect on the water quality of the Derwent, and may possibly rival the effect of agriculture (paragraph 5.6).

With the industrial revolution, the Derwent Valley, became a very important industrial area. It saw the development of numerous textile mills, (in particular the famous Richard Arkwright Mill) relying on the waters of the Derwent for both power and as a washing agent; and the continuing expansion of underground lead mining, leading to the construction of large scale drainage channels from the limestone located mines to the Derwent. This industrialisation certainly would have introduced amongst other contaminants, trace metal constituents into the river, with damaging ecological implications. However, the long term build up of pollutants would have been unlikely, due to the unregulated flow nature of the Derwent at that time. Thus, high magnitude catchment floods, would have had the overall result of washing contaminants downstream. The mine workings drainage channels, locally referred to as soughs, are particularly important to river water quality, because they are the dominant force in lowering the water tables over the whole mineral field of Derbyshire (Christopher, 1981). The largest soughs affecting the River Derwent are Cromford, Merebrook, Hillscar and Yatestoop. Cromford Sough was the first large scale drain to be driven, and was built between 1670 and 1750, in order to drain the rich Gang vein, and in the process drained much of the land west of the Cromford-Wirksworth road. At minimum flow conditions its input to the Derwent is in the order of 13 Ml d^{-1}. Merebrook Sough is the largest of the Derbyshire soughs, with 45-76 Ml d^{-1} at its outfall. With all its branches it is over 5 miles long, and drains a catchment area of fifteen square miles. It was begun in 1772, and was built primarily to drain lead rakes. Hillscarr Sough was started in 1766, and was operational until 1932, when its use as a lead mine sough finally ceased. Its contribution to low flow in the River Derwent is significant, adding 29 Ml d^{-1} under minimum flow conditions (Pirt, 1983). The sough tail is located in Hillscar wood about 100 m west of the River Derwent (SK258637) and as such is over 1 mile from the nearest road access point. Yatestoop Sough was begun just before the Merebrook project, in 1752, and it drains the Matlock area. Although not as large as Merebrook, it still adds a considerable flow to the Derwent (see Fig. 5.2), estimated to be about 9 Ml d^{-1}(Pirt, 1983). Obviously, this industrialisation would have led to a significant spatial variation in the river water quality, indeed the effect of the lead mine drainage system is still an important factor in the Derwent water quality, not least through the large input of water to the Derwent at low flow (a factor discussed in chapter 6).

After the construction of the Ladybower reservoir system, the effects of which, on water quality, are now being considered, another large scale landuse change in the catchment occurred. This was the afforestation of much of the reservoirs headwaters, a factor that has been shown to be important to water quanity and quality (e.g Newson, 1979), of upland rivers - not least in the raising of sediment load and the reduction of pH of such rivers. These effects are considered in the following sections.

5.2 Flow Regime below Ladybower Dam.

The importance of the basin geology to the rate of runoff within the catchment is shown in table 5.1. Clearly the limestone areas regulate discharge considerably. The significant percentage of reservoired surface area, some 2.7% of the regulated catchment area, indicates that there would be an appreciable reduction in the rate of outflow to reaches below the reservoir (I.C.E., 1933). Nixon (1962) estimated that successive flood peaks in 1960 at Yorkshire Bridge were reduced by over 50 $m^3 s^{-1}$. However, the effective reduction of peak discharges decreased downstream as a progressively small fraction of total catchment is reservoired. The low flow pattern of discharge downstream to Ambergate is summarised by Pirt's

River, gauging station & geology	Drainage area (km^2)	Average rainfall (mm) Year^{-1}	mean	max	min
			gauged flows $m^3 sec^{-1}$		
Derwent, Yorkshire Br., sandstone and shales	127	1220	3.80	150.6	0.47
Wye, Ashford, limestone	154	1150	3.96	37.8	1.05

TABLE 5.1 Comparison of the discharge records of the sandstone-shale and limestone regions of the Derwent. (Petts,1982).

Vertical Scale 10cm = 40km
Horizontal Scale 2cm = 50Mld^{-1}

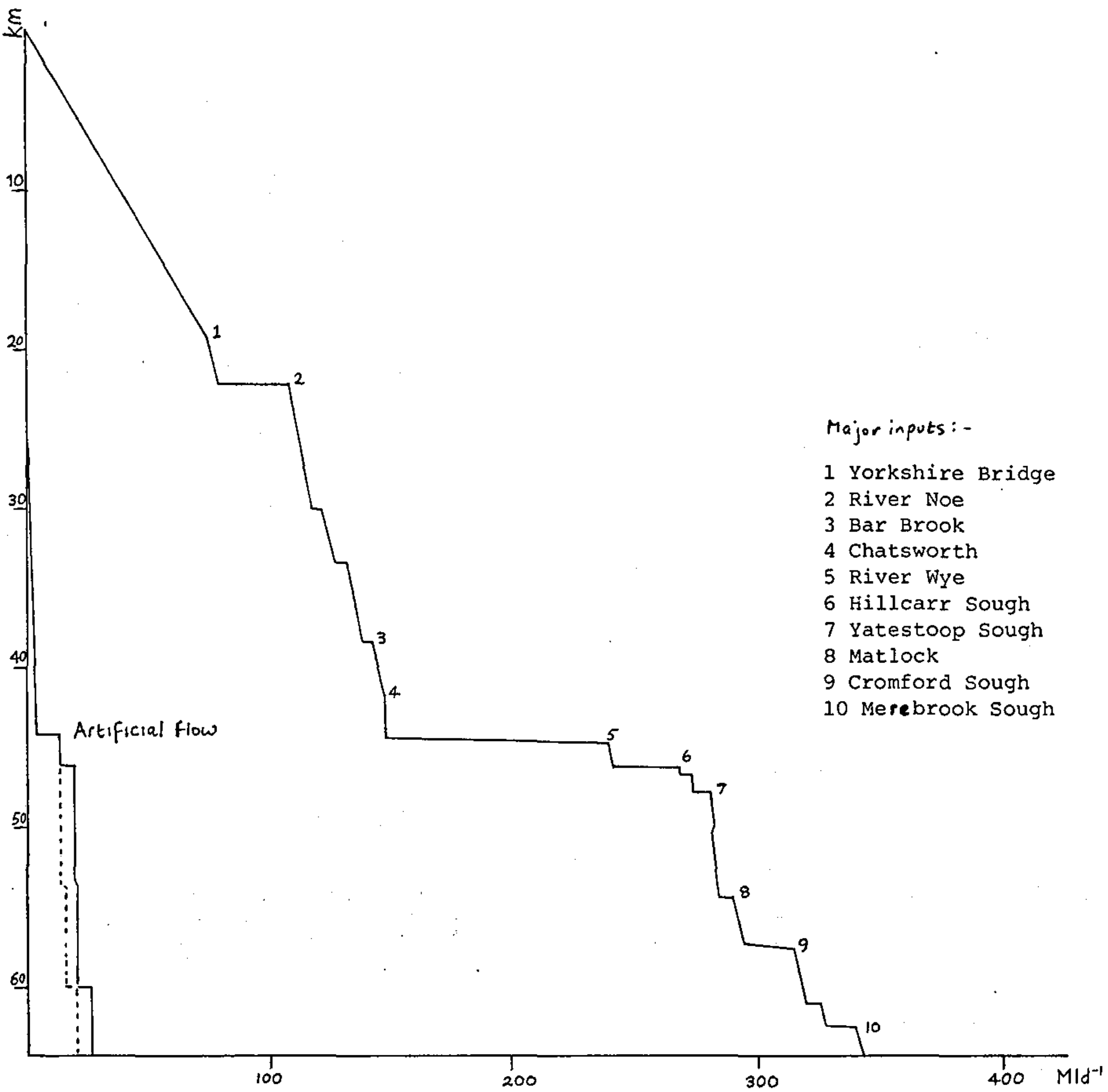


Fig. 5.2. Residual flow diagram showing the contribution to dry weather flow (mean annual seven consecutive days low flow) on the River Derwent - natural and artificial inputs (Pirt, 1983).

(1983) residual flow diagrams (Fig. 5.2), for dry weather flow conditions (mean annual 7 consecutive days lowest flow). This diagram clearly shows the importance of tributary and sough inflow, and the relative insignificance of reservoir input. Thus reservoir discharge increases flow by about 17.3 Ml d^{-1}, in comparison with an input of some 21.6 Ml d^{-1} from the River Noe, 78 Ml d^{-1} from the River Wye, and 8.6 Ml d^{-1} from Merebrook Sough.

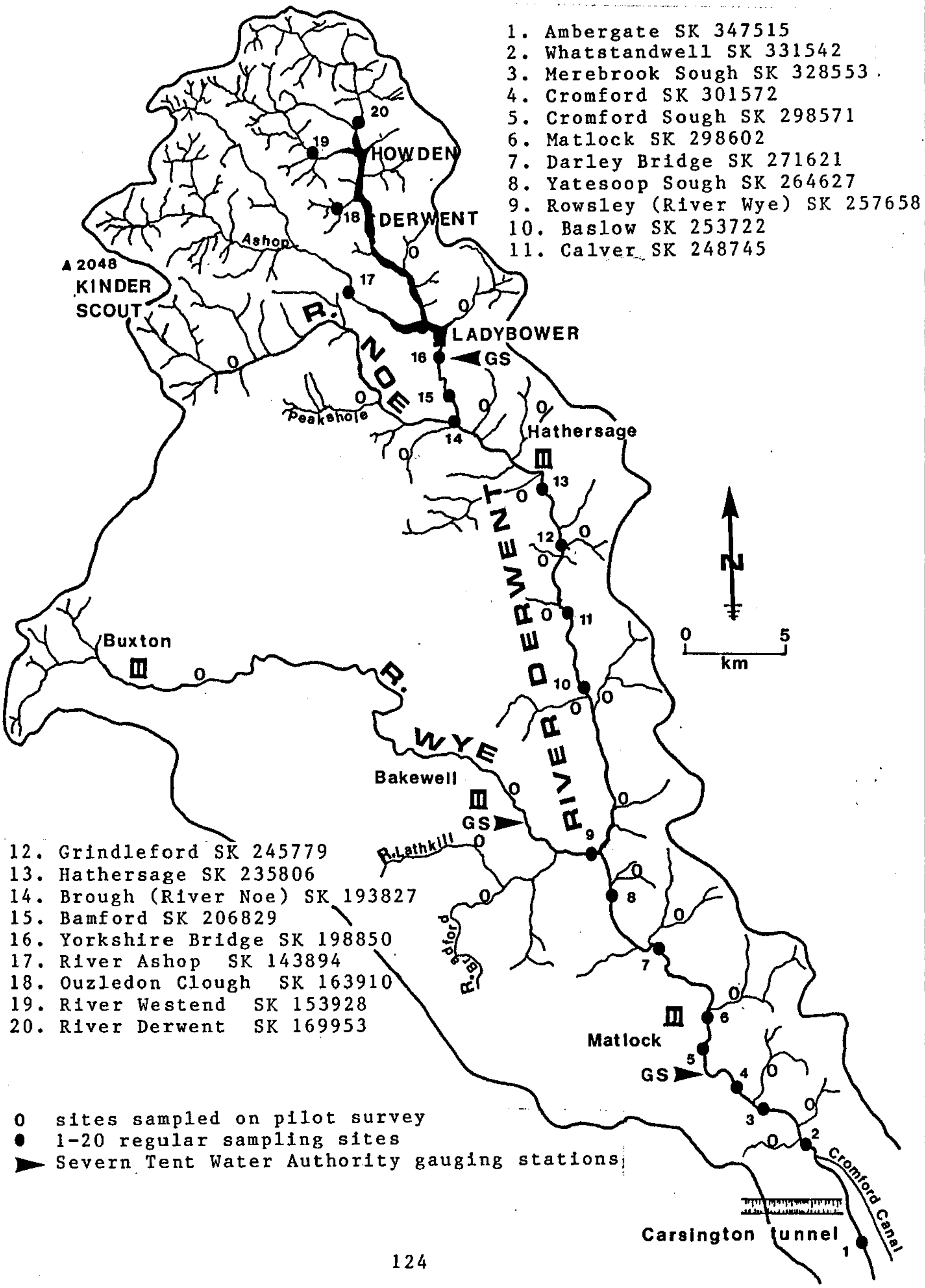
5.3. Selection of Sampling Sites.

5.3.1. Pilot catchment water chemistry survey.

A pilot spatial survey was made of the chemical content of all drainage inputs in the catchment (1.7.82), the location of the sampling points are shown in Fig.5.2a. and results in Table 5.2.Sampling was carried out in the manner outlined in Chapter 4. Essentially, calcium concentrations represent the geological source of the water; whether it is derived from limestone (150mg l) or gritstone sources (less than 20mg l^{-1}). Nitrate, also basically reflects geology, with gritstone nitrate concentrations being below about 1 mg l^{-1}, in comparison with limestone nitrate values being about 3 mg l^{-1}. However, it also shows to an extent, the different agriculture intensities in the catchment, together with the impact of urbanisation. Thus values from the more intensively farmed Lathkill reaches, are slightly greater, than those in the adjacent Wye reaches. To be precise, the differences are about 2.5 to 3.5 mg l^{-1}. Nitrate concentrations within the Derwent below Matlock, are raised by as much as 25%, presumably due to urban influences. Chloride concentrations reflect geological source areas, with lowest values from the gritstone (less than 6mg l^{-1}), highest values from groundwater (more than 18mg l^{-1}), and relatively high values from surface limestone water (about 13-16mg l^{-1}). Values for each of these solutes can be compared with those presented by Edmunds (1971), Table 5.2. Calcium concentrations are comparable, as are limestone and sough chloride levels. However, gritstone chloride and all nitrate concentrations, presented by Edmunds, are much higher than those found during this pilot spatial survey, this must relate to the fact that, Edmunds values represent solute concentrations in all Derbyshire waters, and not just those from river water. This indicates the importance of the reservoir discharge at low flow, showing that it tends to dilute nitrates derived from limestone sources.

The spatial survey, apart from showing the importance of geology on surface waters, also shows the significance of

Fig.5.2a. The spatial location of sampling sites on the River Derwent.



1. Ambergate SK 347515
2. Whatstandwell SK 331542
3. Merebrook Sough SK 328553
4. Cromford SK 301572
5. Cromford Sough SK 298571
6. Matlock SK 298602
7. Darley Bridge SK 271621
8. Yatesoop Sough SK 264627
9. Rowsley (River Wye) SK 257658
10. Baslow SK 253722
11. Calver SK 248745
12. Grindleford SK 245779
13. Hathersage SK 235806
14. Brough (River Noe) SK 193827
15. Bamford SK 206829
16. Yorkshire Bridge SK 198850
17. River Ashop SK 143894
18. Ouzledon Clough SK 163910
19. River Westend SK 153928
20. River Derwent SK 169953

0 sites sampled on pilot survey
● 1-20 regular sampling sites
➤ Severn Tent Water Authority gauging stations

	pH units	Ca^{2+} mg l^{-1}	Cl^- mg l^{-1}	NO_3^- mg l^{-1}
Grit/shale surface waters	7.30	23.5	16.5	0.5-1.5*
General limestone	7.40	102	14	11.5
Soughs	7.69	99.5	25	9.3

* This survey data 1981-84

TABLE 5.2 Median concentrations of river solutes derived from the Major components of the Derbyshire Dome. (Edmunds, 1971.)

localised pollution incidences at low flow. Significantly higher nitrate values, than the surrounding locations, are found at Cromford, Ivy Bar Brook, Hathersage, and the River Noe at Brough. The findings at both Cromford and Hathersage, are undoubtedly related to urban inputs, whilst high concentrations on the River Noe and Ivy Bar Brook, probably relate to a concentrating effect of agriculturally derived nitrates, within the channel. Higher than expected nitrate at Peakshole water, indicates the significance of groundwater supply to this stream (Edmunds, 1971). Unusually high concentrations of chloride, are found in the Ivy Bar Brook, Stoke Brook, Burbage Brook, River Noe at Brough, Peakshole water, and at Yorkshire Bridge. The first three of these locations are very minor tributaries, and high concentrations probably relate to very local sewage inputs, whereas higher levels in the River Noe and Peakshole Water, are probably related to a high contribution of groundwater. High values at Yorkshire Bridge, possibly show the importance of the reservoir acting as an 'umbrella for precipitation' with its relatively high concentration of chloride (see paragraph 5.4).

Conductivity values, throughout the catchment tend to mirror the response of calcium concentrations, indicating that this is the dominant source, contributing to the ability of the water to transmit an electrical current.

5.3.2 Location of routine sampling sites.

From the pilot survey it was clear that, along the course of the River Derwent, the water chemistry is dependent upon major hydrological inputs. The effects of these are then moderated or in some instances exaggerated by changing patterns of landuse, or the degree of urbanisation. Therefore a routine sampling framework was established to monitor the changing chemistry of these major inputs, the chemistry of the River Derwent immediately upstream and downstream of these sources, the effect of the reservoir on inflowing, in comparison with outflowing solutes, and the significance of urbanisation of the catchment on the water quality of the River Derwent. The precise locations of these sampling points is now given:

LOCATION grid reference	Distance upstream from Ambergate (km).
1. Ambergate SK 347515	0.0
2. Whatstandwell SK 331542	3.2
3. Merebrook Sough SK 328553	4.4

4. Cromford SK 301572	7.9
5. Cromford Sough SK 298571	8.2
6. Matlock SK 298602	12.0
7. Darley Bridge SK 271621	16.0
8. Yatesoop Sough SK 264627	17.0
9. Rowsley (River Wye) SK 257658	19.6
10. Baslow SK 253722	26.5
11. Calver SK 248745	29.8
12. Grindleford SK 245779	33.5
13. Hathersage SK 235806	36.9
14. Brough (River Noe) SK 193827	40.7
15. Bamford SK 206829	41.2
16. Yorkshire Bridge SK 198850	44.0
17. River Ashop* SK 143894	48.5
18. Ouzledon Clough* SK 163910	52.5
19. River Westend* SK 153928	56.5
20. River Derwent* SK 169953	59.5

* : above the reservoir.

These sites are selected to describe the solute profile of the River Derwent, which naturally is dominated by geochemical controls, as illustrated by the pilot spatial survey. Edmunds (1971) divided these controls into four types. Grit/shale surface streams, perched water tables, mineralized area waters and thermal waters. The thermal waters themselves are largely governed by the influence of dolomite, leading to high calcium concentrations. These controlling factors within the Derbyshire area lead to three major solute contributing sources to the water chemistry of the Derwent; grit/shale surface waters, general limestone waters and sough inputs. The median concentration of solutes from each source is given in table 5.2 (Edmunds, 1971).

The principal natural controls on the nature of the water sources to the Derwent then are: i) soil and surface rock composition (Bryan,1969), particularly - according to the spatial survey - affecting nitrate values ii) biotic carbon dioxide and limestone (Dearden, 1963), which will determine the pH of river water, and the concentration of calcium ions, downstream of the Wye confluence iii) shale composition (Edmunds, 1971), which will determine the concentration of calcium ions, upstream of the Wye confluence iv) open or closed system evolution (Pitty, 1966), essentially this refers to the contribution of waters from groundwater reservoirs, and has been shown to be particularly important for the Peakshole Water, and for the waters of the Derwent affected by sough inputs v) lava composition and the presence of dolomite (Christopher, 1981), which is important not only to calcium concentration, but also to chloride levels, and is basically of significance to the waters derived from the Noe, Wye and soughs. Although these are the major natural controls on the water of the Derwent, how they interact with man induced variables over time has not been examined. Thus a temporal sampling programme was established, using the sites as indicated.

5.3.3. Temporal sampling strategy.

Surface water was sampled at approximately monthly intervals. The precise sampling interval was allowed to vary in order to obtain samples during periods of stable 'low' flow i.e when possible, insignificant rainfall in the catchment in the previous seven days, thereby minimizing the effects of flow variation upon water quality (this was not always possible, due to the time restraints of the research project). Also the sampling was always made on a weekday, and in the same spatial sequence to ensure that the amount of industrial and domestic sewage input to the river remained relatively constant between surveys. Sampling and analysis were executed as described in chapter 4, with an emphasis on speedy collection and analysis to reduce potential deterioration in storage.

The importance of geology, in particular gritstone and limestone waters to the nature of the Derwent chemistry then, are clear. However, the contribution by the soughs, and other man induced variables, particularly the reservoir, should not be overlooked.

5.4. The effect of the Reservoir on water chemistry.

The difference in chemical nature of reservoir inflow and outflow is presented in tabular form in table 5.5. Almost without exception, even though release water is always from the surface layer of the reservoir, output values are higher than input values. This is unusual because many researchers have found the reservoir to act as a sink for solutes (e.g Martin and Arneson, 1978; Hannan, 1980; and Simons and Voshell, 1978), and surface release water to be more dilute than inflowing water (e.g Hrbacek, 1969). Indeed, higher output values include nitrate, which would not be expected, in view of the pattern of dissolved oxygen depletion likely to occur in large reservoirs (e.g Egborge, 1979; and Odum, 1963), which usually tends to reduce oxidised substances (Hannan and Young, 1974). Similarly,

GRID REFERENCE	Location	cond μScm^{-1}	NO_3^- mg l^{-1}	Cl^- mg l^{-1}	Ca^{2+} mg l^{-1}
SK347515	Ambergate	280	2.01	12.65	78
SK332543	Whatstandwell	290	1.95	14.3	84
SK315560	Peak trail	300	2.07	15.4	92
SK315561	Lea Brook	310	227	17.05	96
SK301573	Cromford	280	4.42	19.25	74
SK297596	Matlock	305	2.4	15.4	94
SK272621	Darley Dale	300	2.27	13.2	102
"	Tributary	280	1.69	13.75	88
"	Tributary	190	2.20	17.05	40
SK259645	Stanton	250	1.76	13.75	76
SK259654	confluence	225	1.76	13.75	72
SK257657	R. Wye	395	2.99	19.25	154
SK244658	R. Wye	390	2.73	19.25	152
SK242659	R. Wye	380	2.60	18.7	152
SK242657	R. Lathkill	430	3.51	13.75	190
SK233648	Ivy Bar Brook	440	4.61	19.8	168
SK2264	R. Lathkill	440	3.57	15.4	196
"	R. Bradford	470	3.57	15.4	196
"	R. Lathkill	400	3.05	13.75	158
SK218687	Bakewell-Wye	400	2.73	18.7	160
SK191695	Ashford-Wye	395	2.79	19.25	166
SK191696	"	410	2.92	18.15	164
SK261684	Chatsworth	250	1.82	11.55	80
SK253722	Baslow	275	1.82	12.65	86
SK246745	Calver	250	1.76	12.65	90
SK244753	Stoke Brook	260	1.69	13.2	90
SK243754	"	440	2.34	27.5	162
SK244761	"	250	1.76	15.17	45
SK244778	Grindleford	250	1.88	12.41	47
SK244779	Trib.	100	0.32	11.03	7
SK243778	Trib.	225	1.82	11.72	46
SK243786	Burbage Brook	110	0.65	17.24	8
SK242787	"	260	1.82	15.17	52
SK237806	Hathersage	275	1.88	15.17	54
SK234803	Trib.	150	2.08	10.34	16
SK228812	Trib.	125	0.91	9.66	12
SK205835	Bamford	100	0.65	12.41	9
SK198849	York Bridge	100	0.84	17.24	8

(CONTD)

SK197827	R.Noe-Shatton	300	1.62	15.17	88
SK189820	Trib.	440	2.73	20.69	79
SK175834	R.Noe-Hope	150	0.91	11.03	50
SK173832	Peakshole Wt.	310	1.43	17.24	74
SK125861	Grinsbrook	75	0.71	8.28	8
SK164877	R. Ashop	100	0.58	8.97	6
SK141905	R. Alport	75	0.58	8.97	4
SK186878	Hurst Clough	110	1.33	6.25	6
SK174896	Derwent Dam	110	0.53	8.12	8
SK169899	Ashton Clough	110	1.33	7.5	4
SK164911	Ouzlendon	78	0.53	6.25	4
SK154928	R. Westend	68	0.47	5.63	3
SK168942	Linch Clough	66	0.33	5.63	3
SK172947	R.Derwent	73	0.33	5.6	3
SK170954	Cranberry Cl.	72	0.07	5.6	3
SK168955	Misden Clough	98	0.4	5.6	2
SK298571	Cromford Sgh	450	2.00	21.0	200
SK328553	Merebrook Sgh	430	1.97	20.0	189
SK264627	Yatesoop Sgh	440	2.1	19.8	195
SK260638	Hillcarr Sgh	395	2.79	19.25	166

TABLE 5.3.Point-time Spatial Survey of the low flow water chemistry of the River Derwent Catchment.1st July, 1982.

the fact that pH, is increased throughout the year, from an average of about 6 in inflowing water to about 7.6 in release water, indicates a lack of the expected reduction processes within an impounded body of water. The Derwent Valley Reservoir system, appears to be an exception to the hypothesis first suggested by Wright (1967) and subsequently confirmed by Martin and Arneson (1978) whereby a reservoir has a dilution effect downstream if withdrawal is from the surface, and a concentrating effect if withdrawal is from basal water. Essentially then the problem is to ascertain why surface water from Ladybower Reservoir is more concentrated than inflowing water.

Basically, there are five factors that may lead to Derwent Valley reservoir water being different in its nature to the River Ashop - its major stream water supply. These are i) stratification of the reservoir ii) the 'umbrella' effect of the reservoir iii) mechanical erosion effects of the reservoir iv) chemically rich water entering the reservoir from sources other than surface streams, and v) the fact that water from the Ashop may be in an unbalanced state prior to entering the reservoir system. Taking each in turn:
i) Stratification:- according to Hannan and Young (1974), stratification is the result of four processes; thermal (see paragraph 3.1.1 and 3.1.2), hypolimnetic dissolved oxygen depletion (3.1.4), overturn (3.1.3), and community metabolism (3.1.4). Of these processes the only one likely to induce a concentrating effect is overturn, if this is the case then a distinct seasonal pattern will be manifest in the data, with higher values in spring and autumn. However, for the Ladybower results there is only a very marginal pattern, with pH and conductivity remaining relatively constant throughout the year, chloride with highest values in summer (16.5mg l^{-1} in comparison with about 13mg l^{-1}), calcium with winter values of 8.5mg l^{-1}, spring 11mg l, summer 10mg l^{-1}, and autumn 12mg l^{-1}, and nitrate with highest values in autumn (0.90mg l^{-1}) and summer (0.70mg l^{-1}), and lowest values in winter (0.35mg l^{-1}) and spring (0.65mg l^{-1}). These results suggest that overturn of stratified layers in Ladybower Reservoir, has little or no effect on the quality of outflowing surface water.
ii) The 'umbrella' effect. This refers to the concentrating of rainwater solutes caught by a large expanse of surface water. The key solute to identifying the significance of this process is chloride (see paragraph 4.6.1). Results in Table 5.5 indicate maximum chloride values in summer at the outflow, and minimum values at the inflow. Therefore, it would seem that the

	Jan	Feb	Mar	Apr	May	Jn	Jl	Aug	Sep	Oct	Nov	Dec
Conductivity μS cm^{-1}												
Ashop	87	94	98	80	80	100	78	100	100	87	94	80
YB*	100	100	85	110	110	100	120	100	100	90	100	90
pH												
Ashop	7.5	7.0	4.4	5.4	5.0	-	5.8	5.3	5.0	5.0	5.5	5.3
YB	7.3	6.8	7.9	7.3	7.8	-	7.4	7.9	7.5	7.9	7.5	7.4
NITRATE mgl^{-1}												
Ashop	-	0.6	0.1	0.6	0.2	0.58	0.66	2.0	t	0.7	0.6	0.7
YB	-	0.6	0.1	0.65	0.5	0.8	0.6	0.8	t	0.96	0.91	0.84
CHLORIDE mgl^{-1}												
Ashop	10	11.5	16	12	12	8.97	7.5	11.5	6	12.8	6.0	6.0
YB	10	12	12	16	15	17	17	19	10	16	9	10
CALCIUM mgl^{-1}												
Ashop	4	8	3	8	8	8	3	8	7	9	10	8
YB	7	9	9	14	10	8	12	10	9	11	13	11

* Yorkshire Bridge; NB Values from the Ashop equate to inflow solute values

TABLE 5. 4 Derwent reservoir system, inflow and outflow monthly solute values, 1983.

major factor influencing the pattern of chloride within the reservoir, is not so much precipitation input (since precipitation is highest in winter), but other effects.
iii) Mechanical erosion effects. Wave action created by strong winds and this effect on stratification has been considered in 3.1.2, although no account has been made of the potential solute input to the reservoir, from the erosion of bank sediments. From observations, the banks of Ladybower reservoir do undergo a degree of erosion, with some undercutting, and the creation of bank cliffs, upto 3 meters high. However, in comparison with the extent of the water body, such erosive processes seem trivial. Furthermore, if such an effect was important, then it would be more significant in winter, when vegetation protection of the banks is at a minimum, and reservoir level potentially at a maximum. Although, it could be argued, that erosive effects will be most important to unconsolidated deposits, i.e in the summer when reservoir level is at its lowest, revealing easily erodable material. Either way, a seasonal pattern in conductivity values would be expected, which however, does not occur. Thus, it would seem from this data at least, the contribution to reservoir surface water solutes, from bank erosion is not important.

iv) Input of chemically rich water, from sources other than surface streams. The fact that Ladybower water volume is increased by water pumped from the limestone Noe catchment (Hill, 1949), is arguably the major factor leading to the enrichment of outflowing surface water, in comparison to inflowing water. The magnitudes of determinands at the outflow, certainly do represent a compromise between, the comparatively rich Noe waters, and the dilute gritstone/moorland streams. Furthermore, the constant high values, do suggest a consistent input of solutes to surface water. However, the Noe waters themselves do have a degree of seasonality, with higher solute concentrations in spring and autumn (Figs.5.7-5.10), a pattern that is not shown in the release water. This suggests that the waters are mixed and modified by reservoir processes already outlined.
v) The nature of the surface input. Without a doubt the chemistry of the inflowing water from the River Ashop, is affected by forestry within its catchment. It is this landuse practice, that leads to the extremely low pH values prevalent in the data. Being unaturally acidic on entering the reservoir, it is possible that rainfall may increase these values, and currents within the reservoir lead to the sinking of this acidic water. However, as already discussed, the lack of seasonal pattern in chemistry at the outflow, tends to discount the

operation of pure limnological processes alone. The regulating effect of the reservoir, by whatever process, is very clearly portrayed in the data in Table 5.4. This is exaggerated by the fact that solute values, were undoubtedly affected by local variations of discharge in the River Ashop, during the course of the sampling programme.

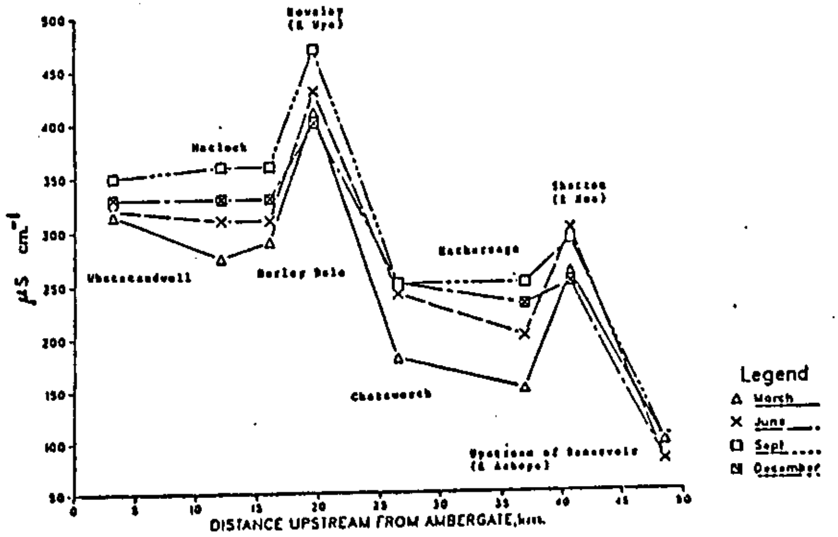
This discussion of the data in Table 5.4, tends to suggest that the Derwent Valley Reservoir, does not fit the hypothesis suggested by Wright (1967). Surface inflow water is actually enriched primarily through the artifical input of solute rich, limestone derived water.

5.5. Spatial Variation of Surface Water Chemistry on the Derwent.

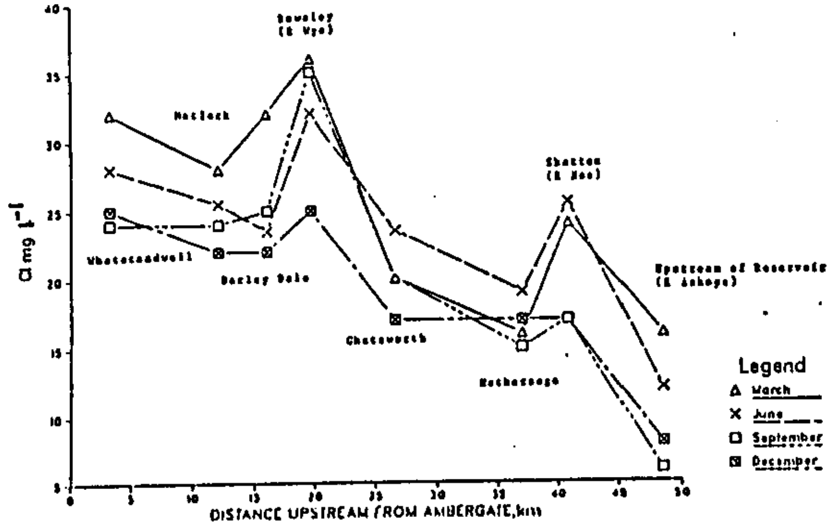
Results from four monthly surveys, with each month representing the average seasonal conditions with which it is associated, are presented for conductivity, pH, calcium, chloride and nitrate (fig.5.3-5.6). These illustrate the quality changes which characterise the River Derwent upstream from Ambergate. Essentially results confirm the conclusions of other surveys (e.g Christopher, 1981; and Edmunds, 1971), which state that the pattern of water chemistry variation is a function of geology, and relates to contributions from tributary inflows. Water quality changes within the reservoir appear to have minimal effect on the spatial patterns identified.

Conductivity, chloride and nitrate all display very similar patterns of change upstream (fig.5.3-5.6), which are directly related to the influx of tributary water. Conductivity, is raised from about 200μS cm^{-1} above the Noe confluence, to a value of about 300μS cm^{-1} immediately below this location. Chloride values are raised by about 8mg l^{-1} to 25mg l^{-1} below the confluence, and nitrate levels are increased from an average of 1.4 mg l^{-1} to about 2.0 mg l^{-1}. Further downstream with the input of water from the predominantly limestone catchment of the River Wye, solute levels are found to increase still further. Conductivity is raised from about 250μS cm^{-1} to nearly 500μS cm^{-1}, an increase of 100%. Chloride values are raised by up to 15 mg l^{-1} to give a maximum of about 35 mg l^{-1}, whilst nitrate concentrations are increased by about 2 mg l^{-1}, nearly 100%. A few kilometres below the immediate impact of these tributaries shows a decline in solute levels, down to a relatively constant value. This decline and consistency is attributable to the influx of gritstone derived water. Below each confluence equilibrium is eventually

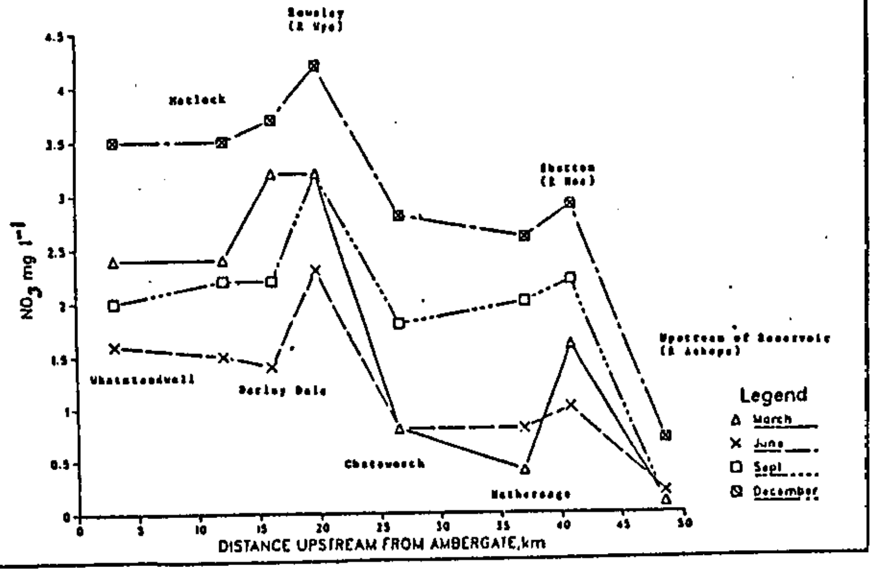
DERWENT CONDUCTIVITY CHANGE UPSTREAM,1983. Fig 5.3



DERWENT CHLORIDE CHANGE UPSTREAM,1983 Fig 5.4



DERWENT NITRATE CHANGE UPSTREAM,1983 Fig 5.5.



DERWENT PH CHANGE UPSTREAM,1983 Fig 5.6

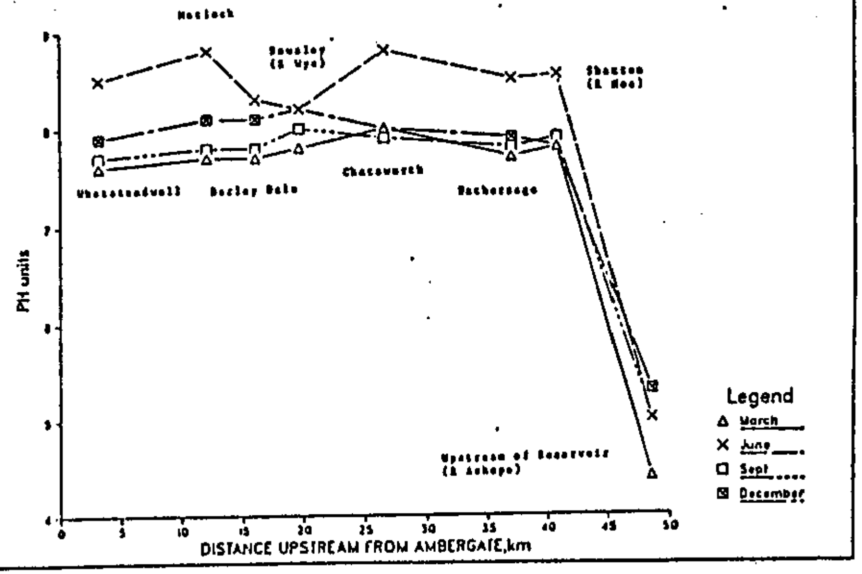


FIG. 5.3.6 The pattern of solute concentration along the River Derwent from Ambergate to above Derwent Reservoir. Data for eight sites were obtained as described in section 5.3.3.

attained between the limestone and the gritstone water, this level is dependent upon the relative solute loads from the two different sources. The distance below the confluence at which the equilibrium is attained is largely governed by mixing processes. Downstream on the Derwent then, the increasing dominance of limestone derived water is reflected in the higher values that are established for conductivity, chloride and nitrate, thus despite the major proportion of the Derwent catchment being comprised of acidic rock, the river water downstream increasingly, reflects basic geology.

In contrast to the stepped pattern of solute variability demonstrated by conductivity, chloride and nitrate, pH patterns are very simple (Fig.5.6). Below the reservoir pH varies between about 8.5 and 9.5 units, however the difference above and below the reservoir is from pH 5 to pH 8. The reservoir, through factors already discussed has clearly had a neutralizing influence. Downstream from the reservoir however, the relatively consistent values, demonstrate not only the buffering capacity of limestone derived water, with acidic water inputs having little or no effect on pH, but also the significance of releasing only neutral surface water from the reservoir.

In general the spatial pattern of water quality in the Derwent, is largely determined by the location of large-scale tributary inputs. However, there is a seasonal effect superimposed over this dominant control. Figs 5.3-5.6 show this to some extent, but it is shown in more detail in Fig 5.7-5.11.

5.6. Seasonal Variation in water Quality.

In order to investigate further the seasonal/spatial patterns of water quality in the Derwent, 3 dimensional and contour catchment graphs were produced using the spatial survey data. Analysis revealed the expected similarities in conductivity and calcium, pH patterns tend to contrast those presented by calcium and conductivity, and nitrate and chloride patterns show a rather confused intermediate pattern between these two extremes (DATA IN APPENDIX C).

5.6.1. Conductivity. (Fig.5.7a&b)

Three outstanding features from the three dimensional and contour representation of water quality in the River Derwent are noticeable. These are the remarkably consistent values throughout the year at 55, 45, and 25 km above Ambergate, which correspond with the River Derwent upstream of the reservoir,

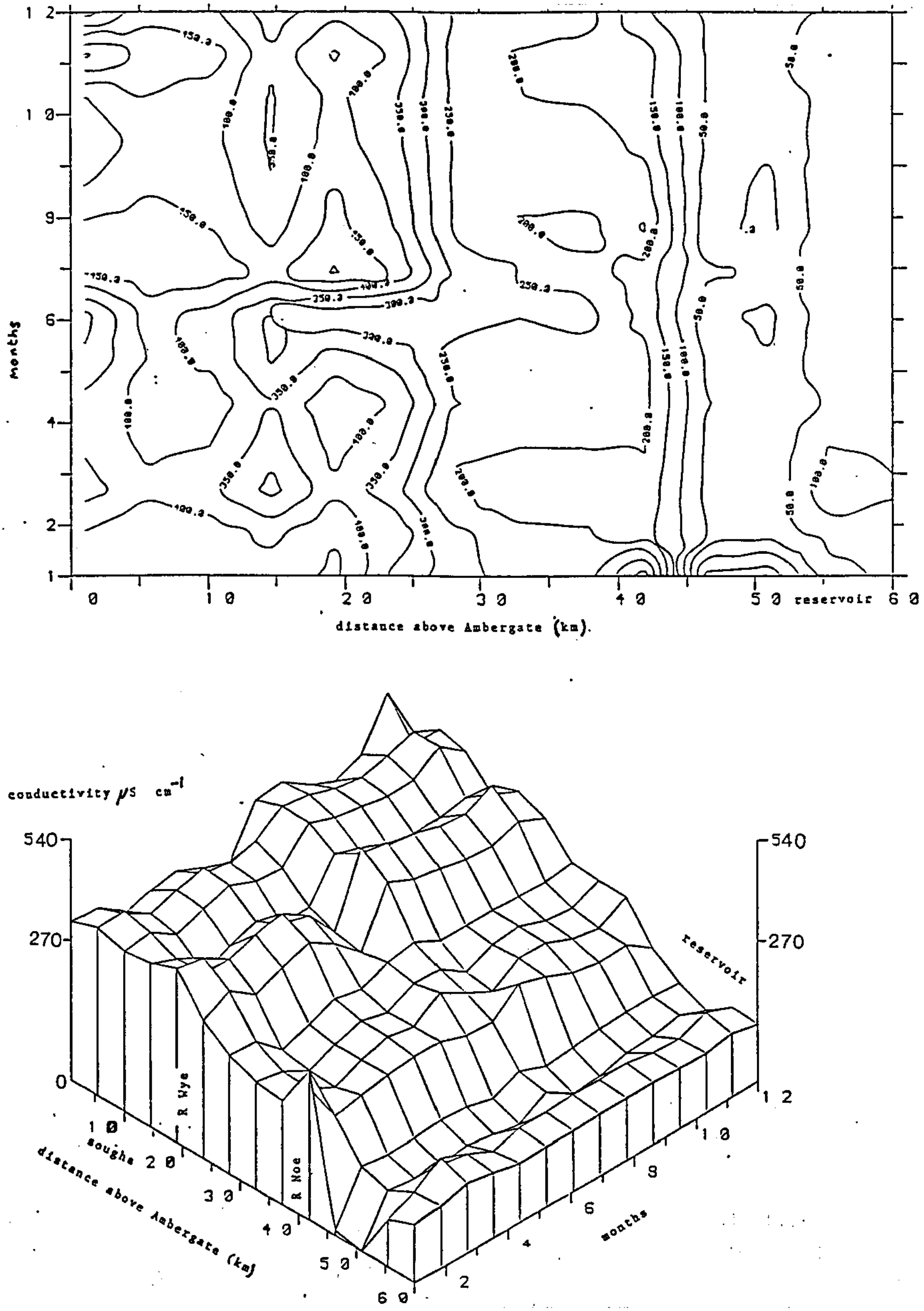


FIG. 5.7 Spatial and temporal patterns of conductivity variation along the River Derwent above Ambergate, based on monthly survey of twenty sites during 1983 (see section 5.3.3): contour interpretation (a) and three dimensional representation (b) - (for data see Appendix C2 - C21).

below the River Noe and below the River Wye confluences, respectively. This consistency is an indication of relatively uniform chemical inputs from these sources throughout the year, regardless of minor fluctuations in low flow discharge. Average values are presented as 50 μS cm^{-1} above the reservoir, 100 μS cm^{-1} below the reservoir, and about 300 μS cm^{-1} between the dominating influences of the Rivers Noe and Wye. At Ambergate/Matlock, two major contour highs during the year are identifiable. The first with a peak during July, and the second with a peak during November. The July peak has a maximum contour value of 450 μS cm^{-1} in comparison with the November high of 550 μS cm^{-1}. Locally these anomalous high values are probably associated with decreased flow, thereby allowing water from the limestone regions of the Wye, and the groundwater drainings of the soughs, to become dominant. Furthermore, since this stretch of the river drains the town of Matlock, at low flow any pollution effects created by sewage input or paved area run-off, will become contracted, but concentrated (Flint, 1971). This explains why the contour highs, although most likely due to rich limestone water, are more pronounced at Matlock and Ambergate, than immediately below the Wye confluence. In fact, the contour pattern between the Wye (25 km) and Matlock (10 km), shows three minor troughs of 300 μS cm^{-1} centred during March, June and September. Such troughs, reflect the changing contribution of groundwater to the River Wye, and through the input of gritstone water, industrial and domestic effluent, these troughs are slowly replaced downstream, by the July and November highs.

Between the River Wye and The River Noe confluences there is little variation in the conductivity value of the water, neither spatially, nor temporally. The only significant change in this contour pattern, is during July, when the concentration is raised from the average 200 μS cm^{-1} to 250 μS cm^{-1}. This high is also apparent immediately below the Wye confluence, and then again at Ambergate/Matlock, indicating that it is associated with reduced discharge, allowing solutes to become concentrated within the river. Above the Noe confluence, the strong regulating nature of the reservoir is marked. Throughout the year conductivity values remain constant at 150 μS cm^{-1} - a 50 μS cm^{-1} increase on reservoir outflow values. This indicates that although solutes are entering the River Derwent, between Ladybower and the Noe, the high percentage of reservoir compensation water in this stretch, is sufficient to dilute these to a constant low, with no seasonal pattern.

The three dimensional representation of conductivity very succinctly divides the study river reach up into four distinctive sections. Reservoir/moorland dominant, River Noe/upland limestone dominant, River Wye/lowland limestone dominant, and Matlock/industrial dominant. These four significant sources, tend to obscure any subtle seasonal patterns, although there is a definite discontinuity from August until the end of the year, with conductivity values tending to rise throughout the catchment below the reservoir. Such a consistent rise is difficult to explain. The summer flushing of solutes stored in the soil, or in plant material, could explain the pattern to an extent. This is unlikely since August is too early in the year for such a solutes to become available for solution. More yearly data is required to determine if the pattern shown in Fig 5.7b is typical.

5.6.2 Calcium variation. (Fig 5.8a&b).

As would be expected calcium variations show an almost exact mirror image to those of conductivity, although the detail is greater. For example, above the reservoir peaks during April and October are manifest. These relate to autumnal and spring flushing processes, as solutes become available for solution. A peak immediately below the Wye confluence in April, almost obscured on the conductivity contour map, is abundantly clear with calcium. As with the peak above the reservoir, the high spring river solute values, relate to the high availability of solute during this season.

5.6.3 Nitrate variation. (Fig.5.9)

The catchment yearly pattern of nitrate, is very similar to that of conductivity and calcium. With low values above the reservoir, an increase associated with the River Noe, and a further rise as the waters from the Wye become important. Temporally, the year can be divided into two; highest values below the reservoir from August to December, and lowest values between January and July. Thus, the catchment may be divided into into three categories. Reservoir-dominant low nitrate concentration (0-1mg l^{-1}) water; upland limestone, agricultural dominant (1-2.5mg l^{-1}); and lowland limestone agricultural/ industrial dominant (2-5mg l^{-1}). The reservoir and upland waters are low in nitrates for two reasons:i) only surface water is released from the reservoir which will be low in nitrate due to the lack of organic material with which it is in contact ii) nitrates are not plentiful in gritstone rocks and their associated acidic soils (Hem, 1970). Further downstream the

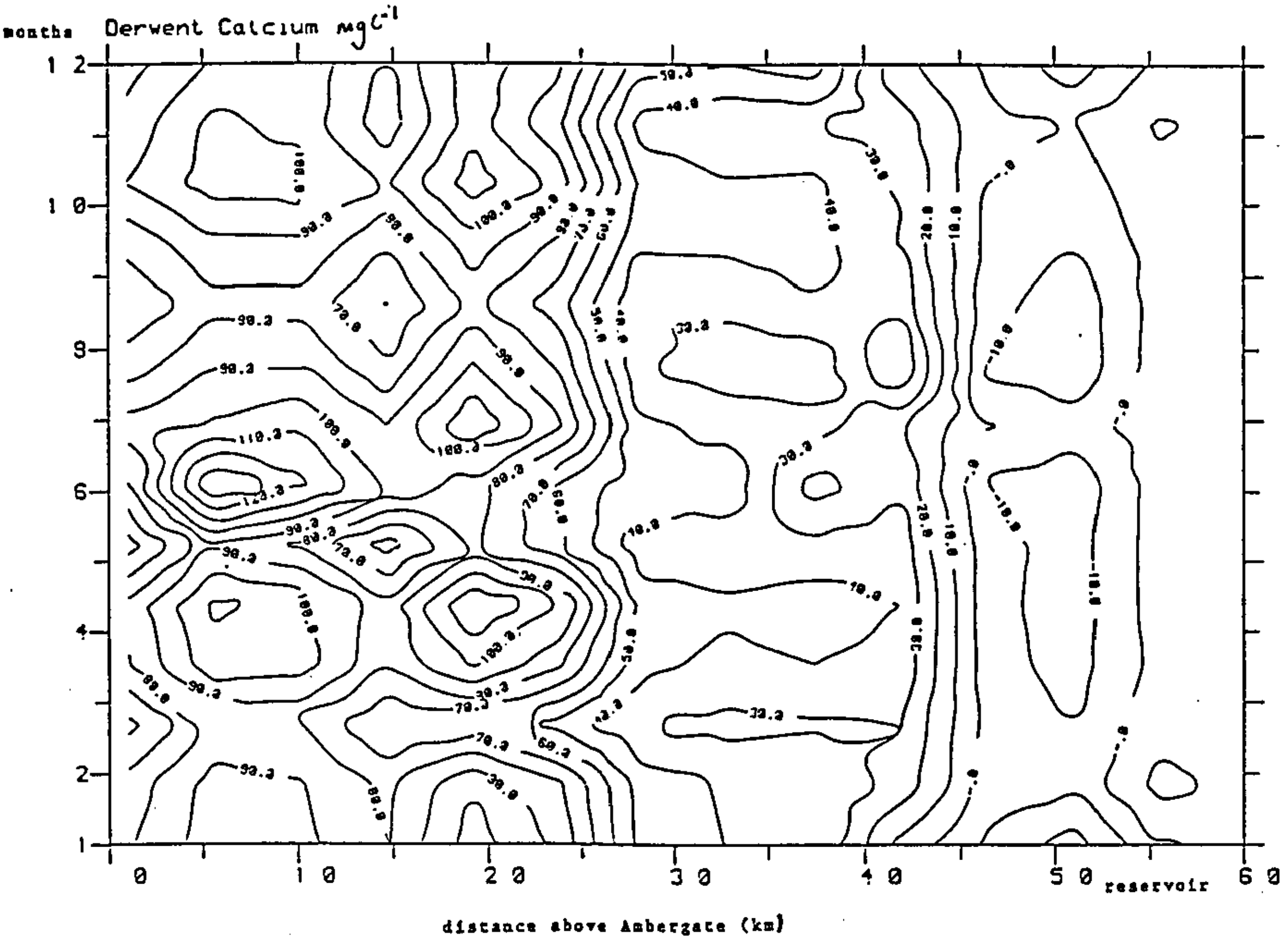


Fig 5.8a. Contour interpretation of Derwent calcium.

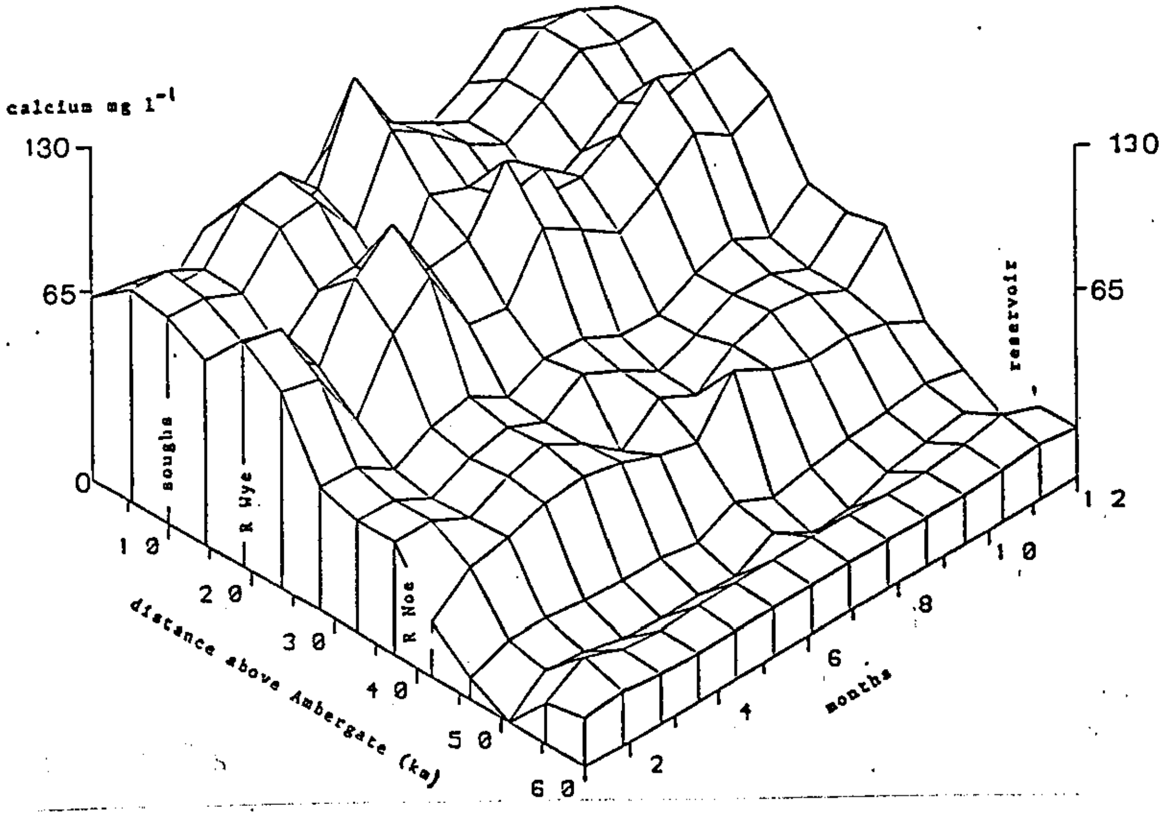


FIG. 5.8 Spatial and temporal patterns of calcium variation along the River Derwent above Ambergate: contour interpretation (a) and three dimensional representation (b) - (for sampling details see Fig. 5.7).

limestone water becomes significant, through the River Noe input. This has a higher nitrate concentration due to the greater contact runoff has with vegetation downstream, the more significant availability of nitrogen compounds from the parent rock (Weyl, 1958), and the input of artificial nitrogenous fertilizers through catchment runoff sources. Below the River Wye confluence, Derwent nitrate levels are increased to an even larger concentration. Fundamentally, this is because River Wye water, which is rich in nitrate, becomes a major contributor at low flow, to the total Derwent discharge. The reasons for River Wye water being rich in nitrates, are similar to those suggested for River Noe water. However, other nitrate sources do become important downstream e.g the Sough input is of note, since average nitrate values in this water source are about 5 mg 1^{-1}, compared with a maximum of 1.0 mg 1 in gritstone derived water. Industrial and domestic sewage is also rich in nitrogen compounds (Paller et al, 1983), which are usually oxidised before being released into the river, thus discharges from Matlock sewage works, will lead to a higher concentration of nitrate throughout the year.

A clear peak in nitrate concentration is discernible during late summer throughout the study area, below the reservoir. Such a demonstration of nitrate boosting - in reality an increase of about 100% - is due to an increase in nitrate concentration primarily, in limestone derived water. Such an increase is associated with i) the increasing availability of soil nitrates, as vegetation cover is reduced both naturally, and by harvesting ii) increased availability of nitrogenous fertilizers, which are applied at this time of year (Tomlinson, 1970) and iii) the beginning of the winter extension of drainage throughout the catchment (Edwards, 1975). Up to December, nitrate values below the reservoir remain high, from January to July however, levels are reduced, as both natural and artificial supplies become depleted. Interestingly, above the reservoir, nitrate values remain constant throughout the year, apart from troughs in late summer and late winter. The trough in late summer actually coincides with a downstream peak, whereby suggesting that the timing to depletion of natural soil and vegetation stores of nitrate, in gritstone, moorland uplands is behind that of limestone, agricultural zones.

For most of the year, the downstream pattern of nitrate remains basically unchanged due to the dominating influences of the Reservoir, River Noe and River Wye producing a step like pattern of downstream nitrate concentration. However, in June

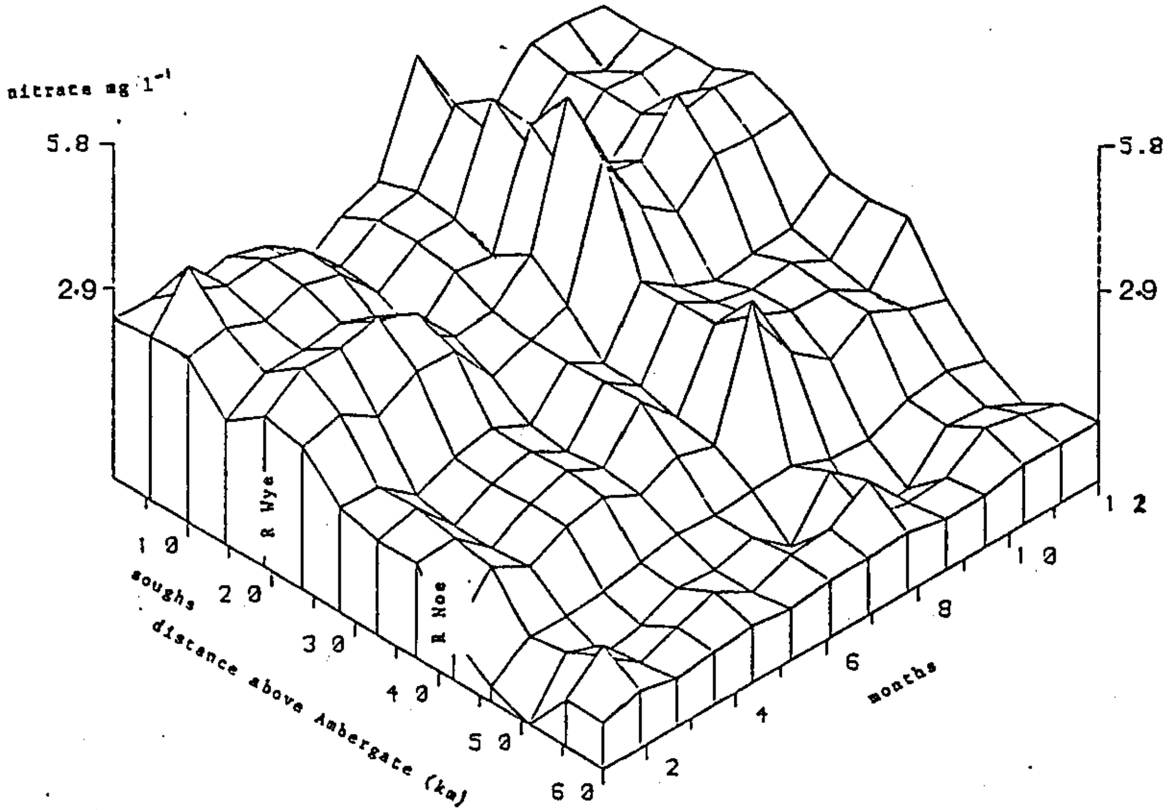


Fig 5.9. 3-d representation of Derwent nitrate.

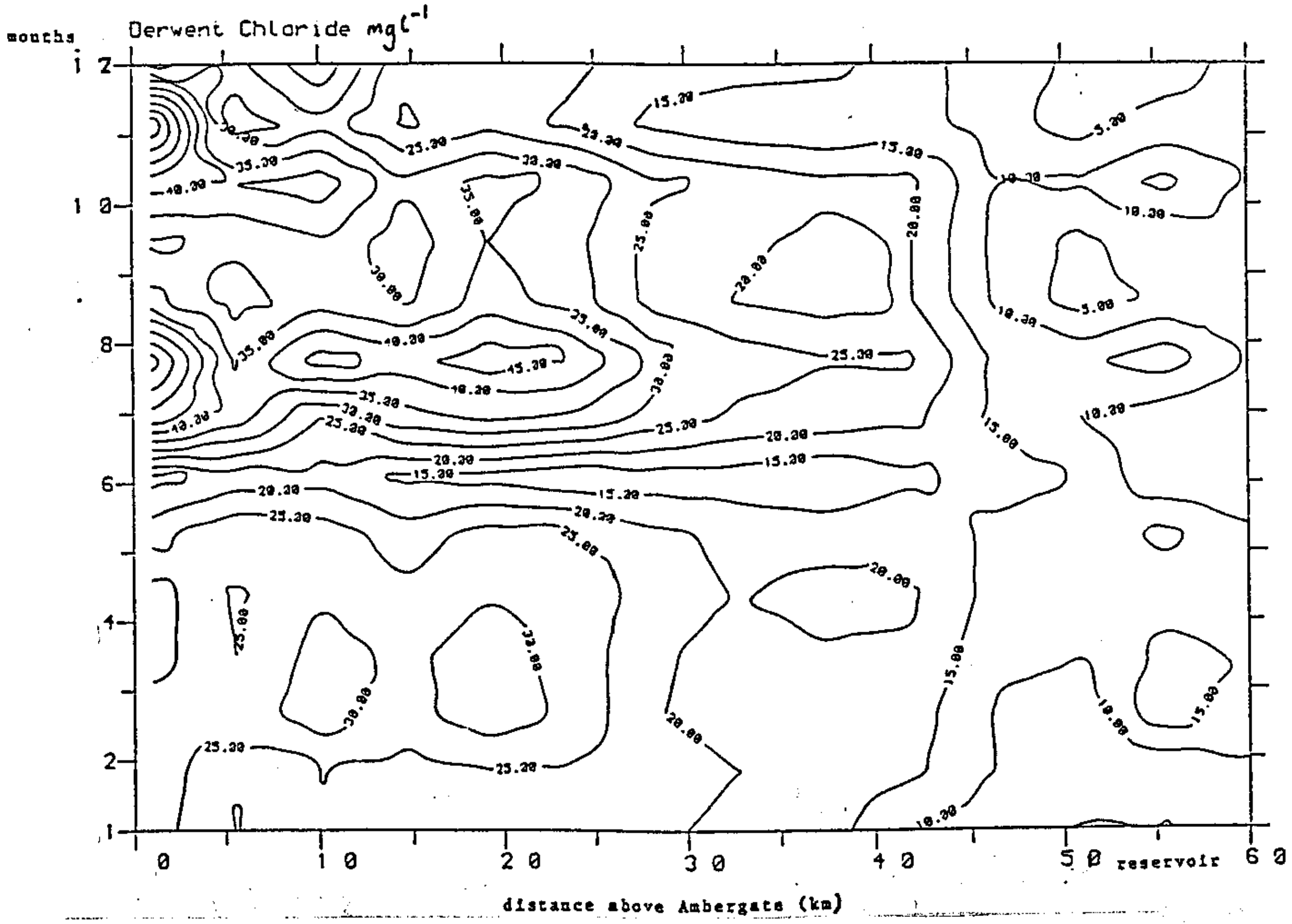


FIG. 5.9 and 5.10 Spatial and temporal solute patterns along the River Derwent above Ambergate based on a monthly survey of twenty sites during 1983 (see section 5.3.3). Three dimensional representation of nitrate Fig. 5.9, and contour interpretation of chloride Fig. 5.10. (For data see Appendix C2 - C21.)

there is little manifestation of these graduations, but rather a steady downstream rise in nitrate levels. This results from the fact that nitrate concentrations in the Noe inputs are less dilute than usual in comparison with Wye inputs. Such a phenomenon could arise due to a number of reasons e.g localised catchment flooding in the River Wye, increased groundwater input to the River Noe, or as is likely to be the case, a combination of both of these factors.

5.6.4 Chloride variation. (Fig.5.10)

The contour pattern for chloride throughout the year is rather confused. However, there are certain similarities with the conductivity data, with clear break in values below the reservoir, and at the Noe and Wye confluences. Below the reservoir, but above the Noe confluence, there is a consistency throughout the year in chloride levels, represented by the 15mgl contour. This uniformity contrasts with the seasonality above the reservoir, with peaks in March, July and November probably relating to lower than average discharges at the time of sampling during these months, allowing solutes to become more concentrated. It is interesting that this pattern is manifest at the other extreme of the catchment (Ambergate) with peaks of 30mg l^{-1}; 55mg l^{-1} and 50mg l^{-1} in March, July, and November respectively. This yearly variation as for conductivity, is most likely to be linked with the increased importance of limestone catchment and sough drainage waters, high in solutes, together with the increased industrial and domestic sewage inputs. Immediately below the Wye confluence, the highs in July and March are identifiable, although the major contour feature is that a deep 'trough' in June, a feature that extends back up to the Noe confluence. This trough must reflect a dilution of limestone water, either by increased precipitation, or an increased proportion of Derwent water during this month to be derived from gritstone sources. Between the Noe and Wye confluence there is the afore mentioned trough in June, bounded on either side by peaks of 20mg l^{-1}. Such a pattern once again illustrates the changing contribution of limestone to gritstone water, exaggerating the seasonal gritstone water response upstream of the reservoir. The variation in seasonal water quality downstream, shows a strong seasonal pattern, with the timing of this response dependent on location. In strong contrast with this is the uniformity of yearly chloride concentrations created by reservoir regulation as far downstream as the Noe confluence.

5.6.5 pH variation

The contour pattern displayed by pH is most interesting and extremely difficult to interpret. It would appear that troughs of pH occur at downstream sites three times per year, but with these troughs becoming earlier further downstream . Unlike conductivity there is no clear indication of the dominance of tributary inflow. Any lake effect of the reservoir is insignificant, and seasonal fluctuations in discharge also appear to have little effect on the pH patterns.To establish the causal effects of these patterns requires an in depth survey of all factors contributing to changes of acidity of the River Derwent. However, it could be assumed that river regulation by raising pH values upstream, has allowed the boundaries between upland acidic water and lowland basic water, to become blurred. Consequently, clear seasonal patterns, that might have been in existence, have become extremely difficult to identify, if of course, they really did occur.

5.7. Chapter summary.

The results from three levels of detailed inquiry i.e a point-time survey of the drainage system, a seasonal survey of the main river, and a monthly survey of the main river reveal the following:

1. The water quality variation on the River Derwent, from its headwaters to Ambergate, is dominated by: gritstone waters above the reservoir; compensation release water (from the reservoir surface) from the dam to the River Noe; a combination of limestone and gritstone water from the Noe to the Wye; virtually all limestone water immediately below the Wye; and a combination of River Wye water, sough drainage water, domestic and industrial sewage/runoff from the Wye to Ambergate.

2. The seasonal pattern of water quality in the study reach, is regulated by the reservoir only as far downstream as the Noe confluence, and variations are then produced by changing solute concentration and dominance of groundwater sources to near surface flow.

3. The mine drainings locally referred to as Soughs, accentuate the pattern of water quality change associated with the Rivers Noe and Wye.

4. Seasonal patterns in water quality from gritstone areas are

essentially discharge independent with relatively constant solute concentrations whatever the discharge.

5. Limnological effects on water chemistry are manifest downstream, in the consistency of water quality released from the reservoir throughout the year. Since it is only a small volume of compensation water that is released, this constraining influence is noticeable chemically, only as far down as the Noe confluence.

CHAPTER 6.

THE INFLUENCE OF REGULATION ON THE CHEMICAL NATURE OF THE RIVER DERWENT.

The previous chapter described the seasonal and spatial water chemistry variations on the Derwent in relation to source area contributions. Biochemical changes associated with reservoir storage apparently have only a minor effect on the river water quality downstream, which is dominated by the character of discharges from the Noe and Wye tributaries, together with sough and urban runoff. However, the impact of a reservoir upon water quality is dependent not only on the direct bio-geo-chemical changes within the impounded water itself, but also on the indirect effects of flow regulation. This chapter seeks to examine the influence of discharge regulation on water chemistry variation along the River Derwent.

Hydrological input, i.e quantity increase along a river may influence existing water quality in one of three ways: i) have no effect ii) create a dilution, or iii) cause solutes to become more concentrated. Which effect occurs, is dependent on the difference in water quality between the receiving and input flow. If input water chemistry concentration is very similar to that of the receiving body then no change will occur, if however input water is more dilute, then generally speaking, dilution will result - assuming negligible inchannel processes e.g that the greater discharge does not lead to a significant increase in channel erosion. Alternatively, if incoming flow is highly concentrated, then an increase in solute load will result. Therefore, at a given time, the water chemistry of a river at-a-station, is dependent upon the combined volumes and chemical natures of those discharges, that contribute to the flow at that station. Thus flow regulation may exert a marked effect upon downstream water quality by changing the relative importance of tributary or other source water quality in the main river.

In order to compare accurately water quality data collected at the same spatial location, but at different times, and with different discharges, the influence of flow volume must be isolated. This has been achieved by using the following procedures:

1. Water samples are collected from the study river over a period of time at standard flow low - SAMPLE BASED.

2. Bivariate relationships are established between discharge and quality parameters so that values of these parameters, at a standard discharge can be determined - STATISTICAL DEFINITION.

3. Computer simulation of discharges and water quality - SIMULATION.

Water chemical concentration was not combined with discharge, since total removal of the flow identity and the subsequent comparison of loads, is not justified as all flood hydraulics will also be erased, leading to the possible comparison of flood induced and low flows at the same time of year, which clearly would not help in identifying seasonal processes. However, each of the above three methods therefore, requires a large data base. On the River Derwent the length of record suitable for reliable statistical interpretation is available only at Matlock Bath, where a Severn Trent Water Authority monitoring site has been automatically recording, at fifteen minute intervals values of discharge, conductivity, pH, temperature and dissolved oxygen, since 1978. The data required for a sample based interpretation of the effect of regulation upon the water quality, ideally should be as comprehensive as that for the statistical interpretation, unfortunately, for the Derwent this is not available. However a mass of Water Authority spatial water quality data is on file, albeit rather irregularly collected. The reliability of these data was established by comparison with the author's own extensive spatial surveys of the water quality of the Derwent, and in this way a reliable volume of sample based data was assimilated for the years 1978-1984.

By taking each method of linking flow and quality in turn, the effect of river regulation on water chemistry may be understood more clearly.

6.1 Comparison of data under standard flow conditions - SAMPLE BASED methodology.

Water-quality data for six sites were analysed for the period 1978-84; the first four years data being supplied by the Severn Trent Water Authority, and the final two years data being a combination of Authority and this survey's data. Daily discharge values at the time of sampling, were obtained from flow records at the Matlock Bath, Chatsworth, Yorkshire Bridge, Shatton (River Noe), and Rowsley (River Wye) gauging stations (Fig.5.3). Flow data for intermediate sites were estimated from these values.

In order to determine the compatability of the two sets of chemical data, those supplied by Severn Trent Water Authority were related to the author's monthly spatial survey results (Table 6.1). Values throughout the study reach of the Derwent compare as follows: minimum pH values of the monthly survey vary at most by 0.7 units with the water authority data, and usually by less than 0.4 units. Nitrate values vary by as much as 75% (upstream of the reservoir), although usually levels are much closer, with variations of about 30%. Minimum values of chloride for the comparative surveys are usually within 10% of each other, although a maximum difference of 50% is noted. For conductivity, however, minimum levels, are always within 20%, probably reflecting the technical ease of monitoring this parameter. At maximum, recorded values of pH vary by 0.5 units, nitrate by 43%, chloride by 33%, and conductivity by 23%. These are the maximum percentage variations, and they usually occur upstream of the reservoir where flow is small and thus chemically sensitive to local variations in geology and land use, making the exact sampling location critical, and any deviation away from this location is likely to be reflected in a change of water quality. Furthermore, variable inputs from these different sources may cause relatively smaller variation in water chemistry at a single site.

One important observation from in Table 6.1 is that the relative variation in downstream water chemistry for both survey data sets is virtually identical. Nitrate, has the most complex analytical methodology of all the parameters under consideration, and therefore potentially the greatest variation in results due to analytical error, particularly when concentrations are low. For minimum nitrate values the downstream variation for both sets of data is 0.4mg l^{-1} as far as Hathersage. From Hathersage to the Derwent/Noe confluence Severn Trent values indicate a change of 0.2mg l^{-1} in comparison with a variation of 0.5mg l^{-1} for the intensive survey. Below the Derwent/Noe confluence to Baslow there is a 0.5mg l^{-1} to a 0.2mg l^{-1} change respectively. From Baslow to the Derwent/Wye confluence change is 2.0mg l^{-1} and 1.0mg l^{-1} respectively, unlike results for Derwent/Wye confluence to Darley Dale where both sets of data record no change. However, from Darley Dale to Matlock levels change 1.0mg l^{-1} and 0.3mg l^{-1} respectively, and finally Matlock to Whatstandwell there is a 0.1mg l^{-1} and 0.6mg l^{-1} change respectively. These results show that although in some instances the actual percentage variation between the two sets of data is as much as 75%, the trends in downstream variations are extremely similar, suggesting that analytical differences

Recording station	ST	T	ST	T	ST	T	ST	T
	pH units		Nitrate mg l^{-1}		Chloride mg l^{-1}		Cond $\mu S\ cm^{-1}$	
Whatstandwell	7.1-8.3	7.7-8.3	1.4-3.0	1.5-4.5	15-40	15-50	250-480	260-480
Matlock	7.4-8.3	7.7-8.7	1.5-2.5	1.5-5.0	15-40	15-43	250-475	260-475
Darley Dale	7.3-8.1	7.7-8.3	2.5-4.0	1.8-5.0	14-36	13-42	240-430	270-440
Derwent/Wye*	7.7-8.3	7.7-8.6	2.5-4.0	1.8-5.0	12-38	12-43	370-560	370-560
Baslow	7.1-8.0	7.4-8.6	0.5-5.0	0.8-5.0	10-35	10-29	160-330	180-300
Hathersage	7.1-8.2	7.4-8.5	0.8-2.7	0.5-2.8	5-35	10-25	130-300	150-280
Derwent/Noe*	7.2-8.2	7.6-8.4	1-5	1-7	15-40	15-37	250-520	200-400
Ashop(upstream)	4-8	4-7.5	0.4-1.4	0.1-0.8	5-35	4-50	50-240	45-320

ST = Severn Trent data; T = this studies data ; n = 288

TABLE 6.1 Comparison of the yearly range of this survey's monthly data (1983-84) and Severn Trent Water Authority monthly data (1978-82).

* Not used in Derweent data set as these values are for tributary inflow water.

are to account for the discrepancies, and not chemical variations within the river itself. Usually however, the percentage variation is below 30% for all substances studied and therefore, it was felt that despite some reservations it was best to include Severn Trent chemistry data in order to give the length of record necessary to have a sample based analysis on the effect of the river regulation upon its water quality.

With such a data base it is possible to compare between samples of similar flow volume. Since this study is particularly interested in the effects of reservoir releases on compensation flow, the individual lowest daily flow (Table 6.2) - from Severn Trent hydrological records (1977-83) - chemical values for each month were used in the analysis i.e real unique data points. By examining this chemical minimum value, the effect of the reservoir is most likely to be observed, because interference factors, such as varying water quality on the rising and falling limb of flood hydrographs, will be removed. Monthly data were then grouped into seasonal values, using the water year, i.e October, November, December termed as autumn; January, February, March - winter; April, May, June - spring; and July, August, September - summer. In this way the true seasonal effects of river regulation were assessed independently of discharge.

6.2 Interpretation of sample-based flow independent seasonal data.

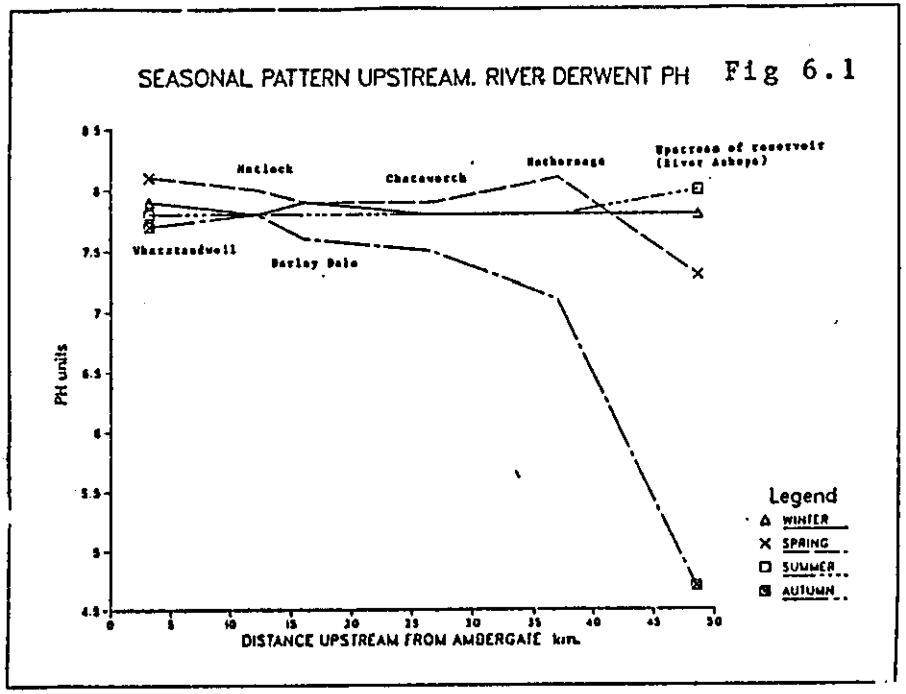
Sample-based flow independent data, real unique data chosen from a field of 216 points, were plotted graphically in order to illustrate the seasonal patterns of change for pH, nitrate, chloride, and conductivity (calcium was not analysed by Severn Trent Water Authority).

6.2.1 pH. (Fig. 6.1)

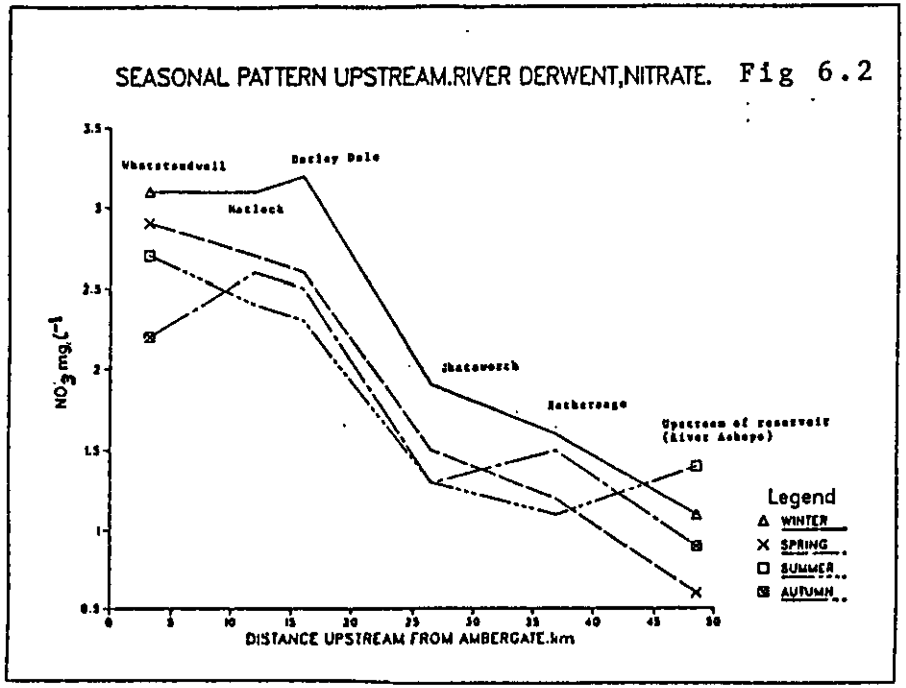
The pH pattern shows virtually no change downstream, and no seasonal variation, with values being constant at about pH 7.9. However, above the reservoir, an extremely large seasonal pH difference occurs, in fact there is a spread between 4.5 and 8.2 pH units. Output from the reservoir has a seasonal span of less than 0.5 pH units. In short, the regulatory effect of the reservoir upon pH is dramatic. The large mass of water tends to smooth out local pH variations (for reasons outlined in paragraph 5.4) and regulates downstream variability. Interestingly, upland local pH variations, from work carried out by the author in 1982 and 1983 were found to be highly significant. Small finger-tip streams draining forested parts of the catchment, had much lower pH values than those draining

MONTH	YB	Chatsworth	R. Wye	Matlock
	Derwent	Catchment Gauging	Stations,	discharge (m^3s^{-1})
Jan	0.863	3.875	1.6	10.078
Feb	0.896	2.925	2.1	9.934
Mar	0.772	5.275	4.1	13.494
April	0.907	4.244	3.9	11.201
May	0.692	2.041	2.0	6.450
June	0.642	1.448	1.5	4.194
July	0.634	1.482	1.9	4.645
Aug	0.651	1.130	1.2	3.377
Sept	0.660	1.577	1.2	3.960
Oct	0.824	1.521	1.2	3.508
Nov	0.856	2.387	1.3	4.551
Dec	1.106	4.883	2.0	11.520

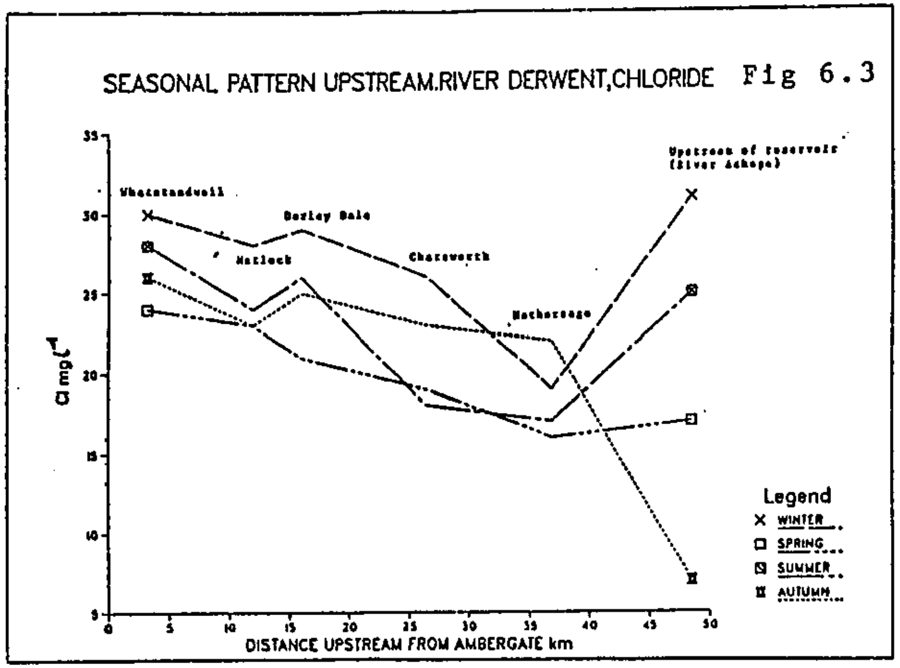
TABLE 6.2. Lowest monthly discharge values at the time of routine water sampling (1978-84). River Derwent Gauging stations.



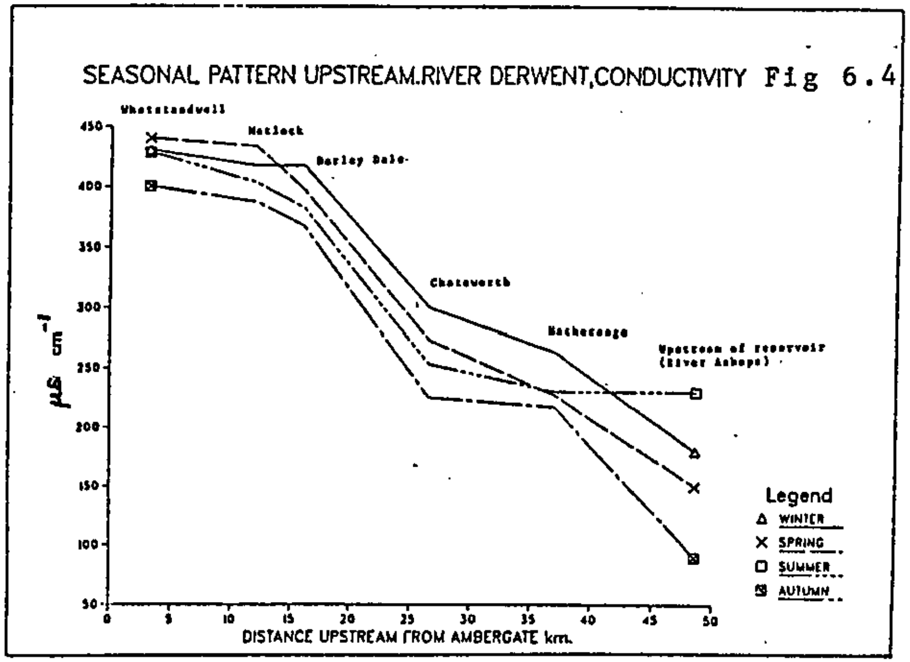
SEASONAL PATTERN UPSTREAM. RIVER DERWENT PH Fig 6.1



SEASONAL PATTERN UPSTREAM.RIVER DERWENT,NITRATE. Fig 6.2



SEASONAL PATTERN UPSTREAM.RIVER DERWENT,CHLORIDE Fig 6.3



SEASONAL PATTERN UPSTREAM.RIVER DERWENT,CONDUCTIVITY Fig 6.4

FIG. 6.1 - 4 Spatial and seasonal water quality patterns along the River Derwent above Ambergate. The graphs show water quality data related to the lowest seasonal minimum flow of a six year monthly survey from 1978-84 (n = 216).

upland pasture in autumn, indeed by as much as 3 pH units. Although the evidence was far from conclusive, it certainly does appear to support work performed in Plynlimon (Newson and Harrison, 1978; Newson, 1979) and in the Hubbard Brook catchment (Pierce et al, 1974), on the acidifying influence of aforestation on drainage water. However, during the remainder of the year pH values above the reservoir, both from pasture and forests were similar, and indeed were similar to the pH of reservoir release water.

6.2.2 Nitrate. (Fig. 6.2)

The downstream nitrate pattern is dominated by steps associated with inputs from the major tributaries. The reservoir itself has a normalising effect, with a seasonal spread upstream of about 1.0mg l^{-1} being reduced to less than 0.4mg l^{-1} at the outfall. In the mid section, between the Noe and the Wye, this normalising effect of the reservoir is combined with the semi-regulating influence of nitrate rich limestone supplies. At the downstream extent of the study reach however, the reservoir's influence is obscured by the effects of industrial, domestic and groundwater inputs, giving a seasonal spread of some 1.2mg l^{-1}.

If the effect of winter was not analysed, then it would be clear that the reservoir, together with limestone groundwater supplies, regulate seasonal patterns of nitrate so considerably, as to make the term seasonality redundant. Unfortunately, winter must be considered! From the pattern, the influence of the River Wye is to cause a marked seasonality effect of about 1.0mg l^{-1} between winter and other seasons. It appears that the expected autumnal flushing of nutrients is delayed in groundwater by a whole season, giving the typically autumnal expected flushing in winter.

Below the Wye confluence, the winter effect of the limestone 'flushes' is reduced, by the input of effluent and sough discharge. Indeed, it is evident that the most significant contribution of nitrate to the River Derwent, is from agricultural and limestone sources and not from domestic and industrial sewage, because the rate of nitrate increase in the purely agricultural part of the catchment - Hathersage to Matlock - is much greater than the semi-industrial part of the catchment - Matlock to Ambergate. Essentially, this greater rate, is due to high nitrate concentrations in River Wye water, in comparison with gritstone derived Derwent water. However, the steepness of the curve is also great from the reservoir to Chatsworth (Fig. 6.2), where the impact of limestone based tributary water, is small. It would appear that there is a marked seasonal pattern in urban (below Matlock) nitrate values, with lowest values in autumn and highest values in winter. The seasonal trend downstream as far as Matlock, including the effects of the River Wye, had been for autumn, spring, and winter nitrate values to be very similar. It can only be either; the variation of nitrate concentrations in runoff derived from urban areas, sewage works, and storm drains; or the influence of the relatively constant discharge of the dolomite dominated Merebrook Sough water, that has given rise to a reversal of'natural' seasonal change. This reversal is simple to describe, in that whilst the rate of change of nitrate values for all seasons other than autumn, is reduced to a negligible positive value, autumn concentrations actually are decreased substantially. This diluting effect of water from sough drainage and the urbanised catchment during autumn, will only be picked up on flow independent data such as that portrayed here. The expected rise in autumnal nitrate values associated with flushing, by standardising the flow data base, is all but removed. In the rural parts of the Derwent catchment nitrate from soil sources will be present in average flow conditions, however in the urban parts of the catchment i.e below Matlock it would appear that in flow independent data, nitrate is not so prevalent during autumn. In short, these patterns demonstrate that the usual rise in nutrient concentration in rivers during the autumn, are associated with spasmodic, large flushes of nitrate rich water (as described in 2.6) and are therefore a hydrological and not strictly a chemical phenomenon.

6.2.3 Chloride. (Fig. 6.3)

The presence of this substance clearly demonstrates the regulating effect of the reservoir upon water quality. Above the reservoir the spread of chloride values is about 25mg l^{-1}, at the reservoir outfall this is reduced to less than 5 mg l^{-1}, primarily as a result of the policy of releasing surface water of the highest quality only downstream. Thus, the seasonal pattern of high winter, low autumn above the reservoir, is inverted to high autumn, low spring at Hathersage.

The downstream pattern for each season shows a steady increase, with no dramatic changes associated with tributary inputs or indeed landuse change. Interestingly, at Whatstandwell and Matlock, of the seasonal concentrations, spring values are lowest and the literature (see paragraph 2.6), has shown chloride values to be highest in the spring time, associated with the in-washing of road salt used as deicer during the winter. As with nitrate, because the data base normalises flow, the flushes, which evidently produce significant chemical change within the river, are removed, and the genuine chemical events revealed. On this point it is interesting that neither industrial nor agricultural chloride effluent have any effect on downstream chloride patterns.

6.2.4 Conductivity. (Fig. 6.4)

The downstream pattern of conductivity change is similar for each season, with the dominance of chemical inputs from the Noe, Wye and limestone soughs producing a step like pattern, similar to Pirt's (1983) Residual flow diagram (Fig 5.2). However, above the reservoir a seasonal pattern is marked, with a range of about 200 μS cm^{-1}. At the outflow from Ladybower, this seasonal spread is negligible, being reduced to about 50 μS cm^{-1}. This may represent the true regulating effect of the reservoir on the seasonal pattern of conductivity.

At Whatstandwell, the other extreme point on the study reach, again there is little seasonal variation, at the most 50 μS cm^{-1}. However, in this instance the regulating influence of the reservoir is at its weakest, because the proportion of reservoir derived flow is at a minimum, and it is probable that the seasonal pattern is a result of water input from limestone sources.

In the mid section of the study reach, that is between the Noe and Wye confluences, it is revealed that conductivity is highest in winter, and lowest during autumn, and that the seasonal 'jump' from autumn to winter is significant, being 100 μS cm^{-1}. The pattern is once again similar to that of other determinands already examined, and as for those, probably relates to the absence of flushing flows used in this data set. During winter vegetation cover is at a minimum, and therefore even low discharge inputs to the river are likely to have a relatively high inorganic chemical concentration, and indeed this characteristic is identifiable on the conductivity graph. In contrast, during autumn although vegetation is decreasing, and revealing stores of minerals built up during the summer, this supply is accessible only to greater than average storm catchment events. For lesser events, the available chemical store is negligible, having been substantially depleted during normal summer runoff events. Thus, autumnal conductivity values are the lowest, and winter values the highest.

If a comparison is made between Fig 5.1 - 4, which represent information collected with no allowance for seasonal variation of discharge, and Fig 6.1 - 4, which do, then the assumption made about the significance of flushing flows is demonstrated. In essence, the downstream patterns of pH, nitrate, chloride, and conductivity demonstrated by both sets of graphs is similar, with the water chemistry significantly influenced by reservoir regulation, tributary, and sough inputs. However, the seasonal relationships are markedly different. Above the reservoir for flow independent data, a large seasonal spread of values is presented, whereas for the point time sample survey the spread is somewhat reduced. However, for both data sets, the influence of the reservoir, acting to unify solute values throughout the year, is important. At the other extreme of the study reach, flow independent values are in most cases greatest for spring and lowest for autumn, whilst for the point time sample survey, the reverse is the case. This latter difference has already been explained in relation to the removal of the important autumnal high flows from the flow independent data, leaving normal autumnal runoff deplete in ions, together with the greater significance that reservoir compensation flows, are able to exert on extreme low flows downstream. Above the reservoir the flushing phenomena is also important. With the flow independent data set, the spread of seasonal values is great, because not only is the flushing phenomenon removed, causing low concentrations in autumn, but also the diluting effect of the occasional summer high flow is removed, tending to exaggerate summer concentration levels. If these two hydrological processes are kept in the data, then as is displayed in the point time sample survey results, the seasonal spread of values is greatly reduced. This flow independent data base has illustrated just how important the hydrological processes of autumnal flushing, summer and winter storms, and flow regulation are in determining the water chemistry of a given river.

6.2.5 At a Station Seasonality.

The previous section examined the changing nature of the water downstream by using flow independent data and indicated that the pattern was dominated by the chemistry of the tributary and sough drainage inputs, although the influence of the reservoir could be clearly seen. However,the absence of flushing flows from the data base it was argued, created a reversal in seasonal river water chemistry to that normally expected. By looking at seasonal patterns at individual sites the significance of these effects is crystallized. These sites are: i) The River Ashop - which reflects the chemistry of water above the reservoir ii) Hathersage - which gives an indication of the changing chemistry from the reservoir and the River Noe tributary input iii). Baslow - shows catchment variation between the reservoir and River Wye iv) Darley Dale - indicates the Wye dominance v) Matlock, and vi) Whatstandwell - give the effect of urban and sough drainage, on the water chemistry of the Derwent.

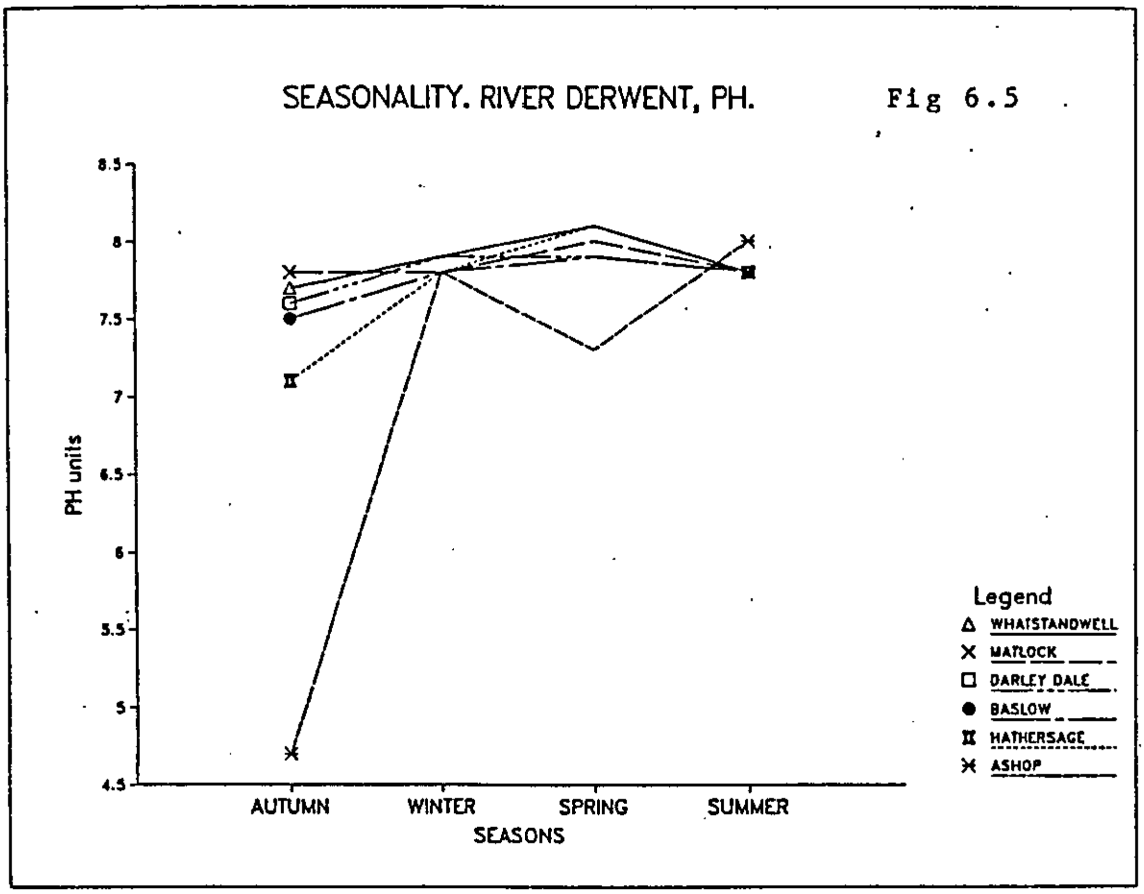
6.2.6 pH seasonal pattern. (Fig 6. 5)

Downstream of the reservoir pH varies little throughout the year, due to the chemical regulating effect of the reservoir, and the buffering capacity of the limestone rich water from the river's Noe and Wye. A marginal peak in pH is noticeable in spring, possibly indicating that a higher percentage of low flow river water is derived from groundwater sources, at least under regulated flow conditions.

Above the reservoir there is a very marked seasonal pattern of pH. Autumnal values are extremely low in comparison with the rest of the year. It is probable that at the small mountain stream catchment scale - as is the case above the reservoir - despite the absence of flushing flows from the data, leaf-fall and acidic water from stem flow, associated with fir plantations, together with peat and vegetation decay are so significant, as to produce pH changes to even the lowflow water. Below the reservoir, because the catchment scale is much greater, and a substantial proportion of low flow water is derived from reservoir and groundwater sources, which are high in bicarbonate ions, the natural buffering capacity of the water is sufficient to mask any potential pH changes associated with catchment seasonality.

6.2.7 Nitrate seasonal pattern. (Fig 6.6)

The pattern of nitrate change is similar at all sites below the reservoir. Maximum values occur in winter, and minimum values occur in autumn and summer. In terms of absolute concentrations, this downstream reach may be divided into two subsections; that above and that below the River Wye confluence. Below the River Wye the pattern of nitrate response, is dominated by limestone groundwater, and sough input, which is shown to have a maximum nitrate value in winter (see paragraph 6.2.2),



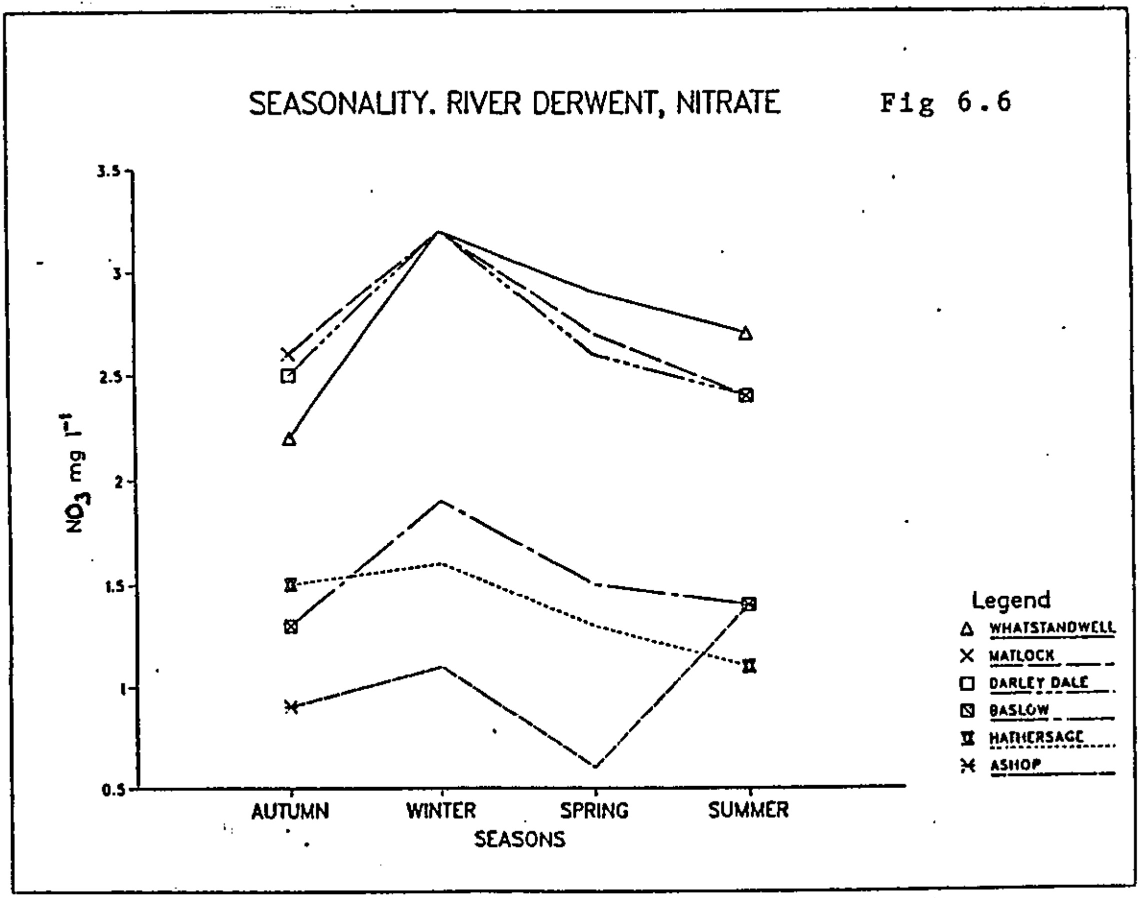


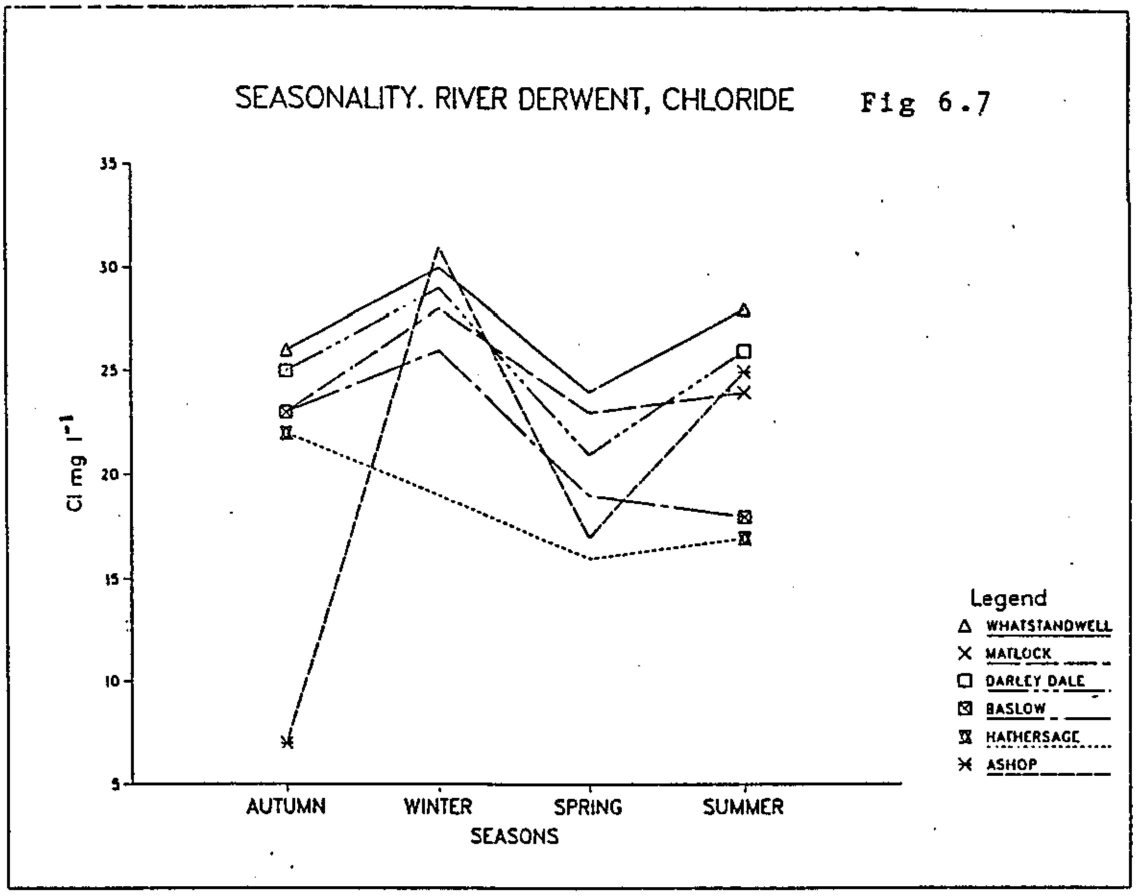
FIG. 6.5 and 6.6 Seasonal patterns of water quality on the Derwent. Quality data related to the lowest seasonal minimum flow of a six year monthly survey from 1978-84 - sample based flow independent data (n = 216).

and secondly due to the moderating influence of reservoir compensation water. Above the Wye confluence, the seasonal pattern is due primarily to the reservoir and its late autumn/winter overturn, and secondly due to the influx of limestone waters from the Noe. Interestingly, at low flow the problem of nitrification of waters in the Derwent, is most likely not during summer, but actually during winter. If water temperature is raised sufficiently around industrial/domestic effluent outfalls (Ross, 1971), then since nitrate concentrations are high in periods of winter low flow, the ideal conditions for algae growth would be prevalent (Battarbee, 1977; and Bachman, 1978). Such growth could be a serious hazard below Matlock, leading to deoxygenation of the waters, hence allowing for the build up of chemically reduced substances from road runoff (Cramer and Hopkins, 1970), stormwater drains (Bryan, 1972), and sewage works (Paller et al, 1983).

Above the reservoir, nitrate levels are low throughout the year, although maximum values are attained in summer and minimum values in spring. Unlike the pattern displayed by pH, there is no semblance of nitrate concentration in autumn, which is strange, because the same leaf fall etc. creating low pH values, would be expected to also raise nitrate values (Slack and Feltz, 1968; and Carlise et al, 1967). However, there is a rise of nitrate concentrations in summer, going from a low of about 0.5 mg l^{-1} in spring, to this high of 1.5 mg l^{-1} This summer high totally contradicts work presented by Tomlinson (1970) who documents low summer nitrate concentrations in stream water. This is due to the prevention of downward movement of water in the soil by plants, and the use of nitrates that are becoming available, as a result of nitrification of organic reserves due to high summer temperatures. The explanation of such a high, probably relates to the fact that runoff at such low flow, used in this data set, would have had a long retention time within the catchment, possibly allowing the leaching of organic reserves. However, more research is needed to expand the low flow data base, in order to explore these upstream seasonal patterns, and particularly to ascertain why pH and nitrate variations are different.

6.2.8 Chloride seasonal pattern. (Fig. 6.7)

The seasonal pattern demonstrated by chloride, shows that apart from the River Ashop, there is virtually identical seasonal variation at-a-station for the complete down reservoir study reach. This pattern shows a maximum chloride concentration



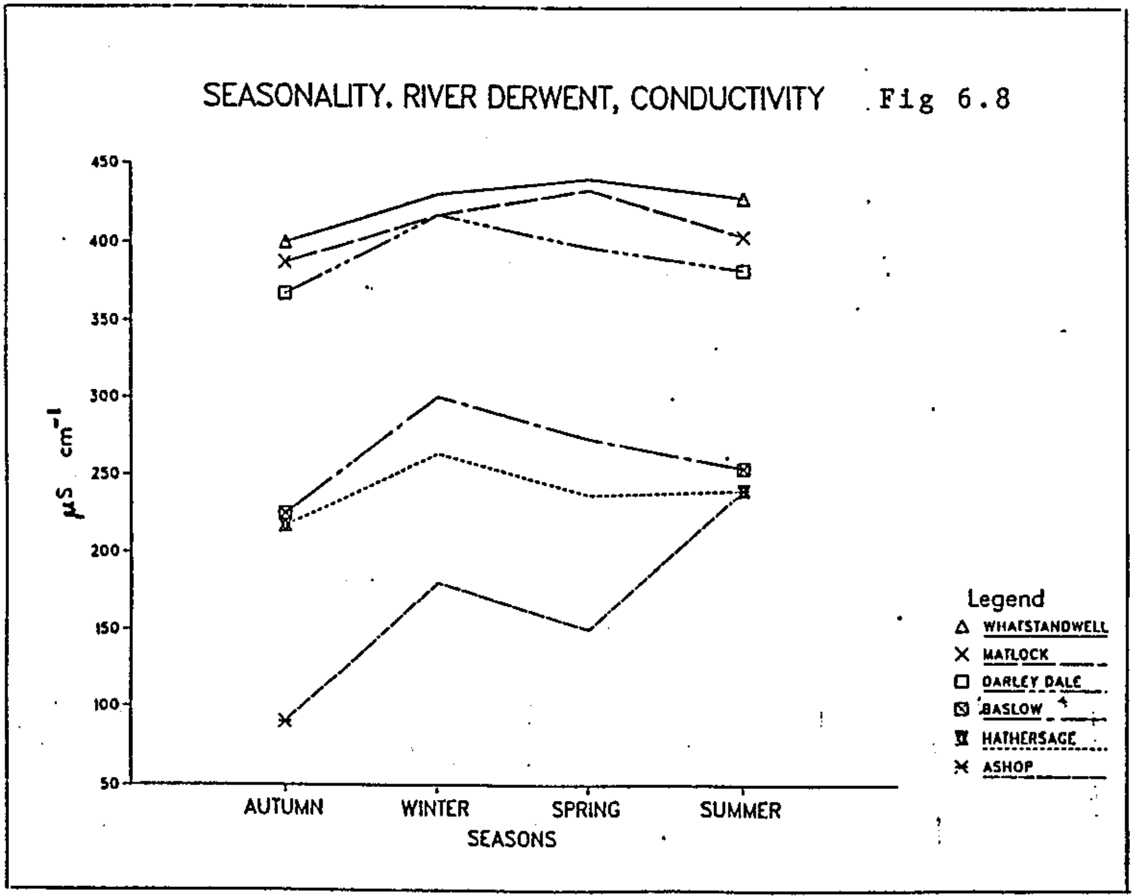


FIG. 6.7 and 6.8 Seasonal patterns of water quality on the Derwent. Quality data related to the lowest seasonal minimum flow of a six year monthly survey from 1978-84 (n = 216).

in winter and a minimum concentration in spring. The regulating influences of the surface reservoir and underground reservoir, combine to produce this pattern at low flow, with sources from the limestone being about 5mg l^{-1} richer in chloride than water from the reservoir.

The wild fluctuations of upstream chloride values, from about 6-33mg l^{-1} compared with 17-23 mg l^{-1} immediately below the reservoir, again serve to illustrate the chemical regulating effect of the reservoir. Relatively high summer chloride values upstream are due to the concentrating effects of evaporation of very low flows (Flint, 1971), together with the longer retention time of runoff water in the catchment. The longer the water is in hydrological pathway storage, the more contact it has with cations adsorped onto the soil exchange complex, and hence the greater possibility of releasing these 'captive' ions. In contrast, high winter values are most probably due to reduced retention time, but increased rock and soil exposure at this time of year when vegetation cover is at a minimum (Dance, 1981). Chlorides are also increased through the leaching of forest litter, and the washing in of dry fallout (Feller, 1977).

6.2.9 Conductivity seasonal pattern. (Fig. 6. 8)

At-a-station seasonal patterns for conductivity divide the study reach into three sections: i) upstream of the reservoir ii) from the reservoir to the River Wye, and iii) below the River Wye.
Taking each in turn:

i) The upstream seasonal pattern of conductivity shows a peak during summer and a low during autumn, (the exact opposite to results usually given in the literature e.g Feller, 1977; and Edwards, 1975 - see paragraph 1.2) with a secondary peak in winter. Such patterns result from a similar set of processes determining the nitrate and chloride response. The summer high is due to the longer retention time of runoff water in the catchment at this time of year, allowing for the concentration of solutes. Autumnal flow, with the absence of flushes, has the chemical nature of rainwater, because catchment stores of minerals, have been depleted during the summer, and are available to only the larger than average flushing flows.
ii) Data for Hathersage and Baslow illustrate the seasonal moderating effect of the reservoir and the River Noe although values throughout the year are higher than those above the

SEASON	n	Correlation	Regression Equation
Winter	2160	-0.741	Cond=421-2.46 discharge
Spring	2160	-0.806	Cond=430-3.38 discharge
Summer	2160	-0.377	Cond=410-4.07 discharge
Autumn	2160	-0.655	Cond=399-2.06 discharge

TABLE 6.3 Relationship between mean daily discharge and mean daily conductivity. Matlock, 1978-82.

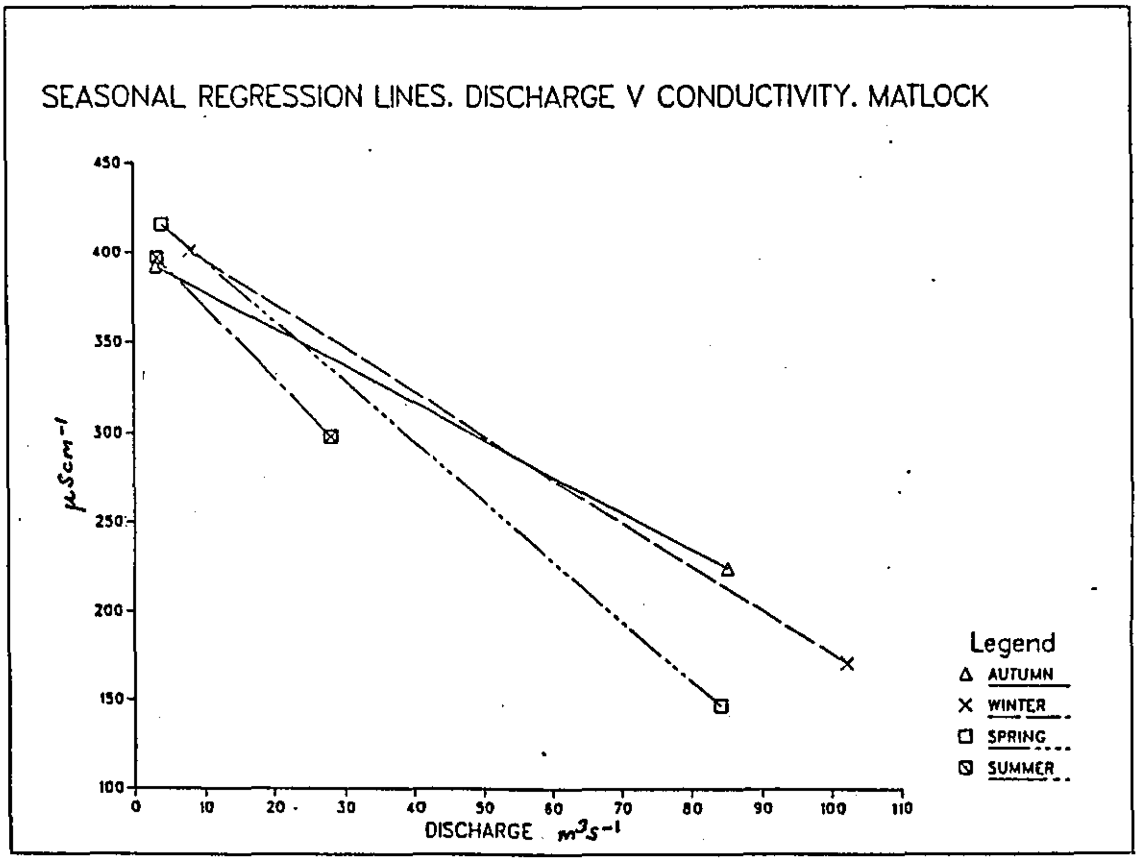


Fig.6.9. Seasonal regression lines for discharge v conductivity for Matlock, River Derwent. Data from a Severn Trent Water Authority automatic recording station.

reservoir. Highest values are found in winter, which are related to the maximum expansion of the drainage system at this time of year (Sutcliffe, 1983; and Edwards, 1975). High values are also possibly linked to limnological overturn of the reservoir itself, once again releasing ions into solution.

iii) Essentially this third section of the study reach, is dominated by the processes occuring in the limestone catchment of the River Wye. Clearly there is little seasonal variation in conductivity, with Matlock, Darley Dale, and Whatstandwell recording sites having low values in autumn (375-400 µS cm^{-1}) and slightly higher values for the rest of the year(385-425 µS cm^{-1}). This lack of variation throughout the year, is to be expected, since the major part of the water, at extreme low flow, will have been derived from groundwater supplies. Such water has little variation in water chemistry.

6.2.10 Summary of sample based flow independent data analysis.

The following points from the analysis of the author's and Severn Trent sample data for the River Derwent at 'low flow' can be made:-

1. The reservoir moderates downstream variability of water chemistry.

2. Limestone derived water has a chemical moderating influence, particularly on pH and conductivity.

3. The study reach may be divided into three sections: upstream of the reservoir, from the reservoir to the River Wye, and below the River Wye confluence.

4. The significance of catchment urbanisation/industrialisation on water quality is only marginal, in comparison with agricultural inputs.

5. The significance of groundwater supply (a high proportion from sough drainage) and its consistent chemical nature during the year is critical for the river section below the Wye confluence.

6. Above the reservoir seasonal effects are marked, and probably relate to changing retention times of water in the catchment.

7. Autumnal flushing flows are absent from the data set, leading to a minimum chemical concentration in autumn, throughout the catchment.

8. Nitrification of the lower reaches of the Derwent could be a problem during low flow in winter.

6.3. Comparison of Discharge and Conductivity at Matlock Automatic Recording Station: STATISTICAL DEFINITION.

Hourly data for flow and conductivity (1978-82) are available from a Severn Trent Water Authority automatic recording station at Matlock (SK 235591). Data were processed to obtain mean daily conductivity and discharge values. Regression relationships were then computed for these variables in order to illustrate the seasonal pattern. (Table 6.3).

The regressional relationships are displayed graphically in Fig. 6.9. Apart from the summer data, correlations between discharge and conductivity are strong, being about -0.7. The summer correlation value is weak, but this is to be expected because the range of flows during this period is small (2-30$m^3 s^{-1}$ in comparison to 2-105$m^3 s^{-1}$for winter), and therefore minor changes in conductivity have a marked effect on the strength of the relationship. Nevertheless, by comparing conductivity values for each season at a given commmon discharge, then the 'true' seasonal influence, devoid of the effects of extreme discharges (e.g storm runoff or extreme lowflow), may be ascertained. In effect by following this technique of returning to first principles, the likely catchment factors influencing river water chemistry can be identified more easily.

6.3.1 Seasonal Regression Lines - an interpretation. (Fig. 6.9)

At the lowest flow for all seasons, 5$m^3 s^{-1}$ the seasonal difference between regression line s is minimal, confirming conclusions from the sample based analysis. In this instance there is a spread of only 24μS cm^{-1}, indicating that the water source at this extreme low flow throughout the year is relatively constant, and from the spatial location of the sampling site, it is likely that river water at these discharges is derived almost entirely from limestone groundwater storage zones, and the mine drainage soughs.

As discharge increases, so the difference between seasonal conductivity values increase, this phenomenon is quantified in Table 6. 4. It is interesting to note that at $15m^3 s^{-1}$conductivity is rising from summer to autumn and to winter, but then falls to spring however, at $80m^3 s^{-1}$ the trend is inverted, with conductivity rising from spring to winter, to autumn (there are no summer discharge values of this magnitude). This pattern fits exactly with the findings from the previous section. At extreme low flow the spread of conductivity as already established and accounted for is minimal (since essentially it is derived entirely from groundwater), as flow increases to about the 15m s level - still in hydrological terms 'low' flow - the seasonal spread is becoming noticeable. At this volume of discharge, it is likely that groundwater flows are accentuated by some catchment throughflow inputs and therefore to a small extent, catchment surface processes and the effects of these on drainage water chemistry are becoming important. Thus summer concentrations become smallest as ions readily available for solution will have been adsorbed by vegetable matter, autumn levels begin to rise as the soil chemical stores begin to be tapped, spring and winter conductivity values begin to decline more rapidly as the evidently more concentrated groundwater during these seasons is diluted by throughflow (Burt, 1979b).

At the $65m^3 s^{-1}$level the seasonal values of conductivity have been inverted as a result of the changing importance of varying hydrological sources to the make up of the total river flow. Thus autumnal concentrations are highest as the associated stormwater flows flush out soil and vegetation stores of ions. Winter levels remain high, as the absence of vegetation cover renders soil and surface geological deposits liable to water erosion (Laronne and Shen, 1982). Spring conductivity values are low (for the exact opposite reasons that autumn and winter seasonal values remain high) because surface ionic sources during the spring time are rapidly being covered and readily soluble ions are rapidly being absorbed during this plant growth period. As discharge increases, the relative contributions different hydrological pathways in producing this volume vary. The chemical nature of water from these sources, in particular that from throughflow, is very much determined by vegetation cover of the catchment, which is governed seasonally. This variation leads to the seasonal pattern of conductivity within the Derwent at Matlock.

The bivariate relationship between seasonal conductivity and the change in seasonal discharge, for the automatic recording

Discharge ($m^3 s^{-1}$)	Spring	CONDUCTIVITY $\mu S\ cm^{-1}$ Summer	Autumn	Winter	Max. difference between regression lines
15	379.3	348.95	368.1	384.1	35.2
30	328.6	287.6	337.2	347.2	59.3
80	159.6	-	234.2	224.2	74.6

TABLE 6.4 Approximate seasonal variation in conductivity at Matlock, for given discharges. Data from regression lines presented in Fig 6.9.

station at Matlock reflects the seasonal catchment processes already discussed, together with the diluting or concentrating effect of hydrological inputs. Indeed, the real hydrological influence creates a clear annual cycle of conductivity (Fig 6.11). From summer to autumn mean discharge increases dramatically (from about 5 to 20 $m^3 s^{-1}$), and conductivity decreases (from about 390 to 360 µS. cm^{-1}). This latter change is due to dilution of the initial flushing throughflow water, containing a high concentration of ions stored within the soil during the summer, by throughflow discharge, and surface water runoff.

From autumn to winter, both discharge and conductivity rise slightly. The absence of a vegetation cover probably allows a certain amount of solute pickup, even by surface water discharges, and thus the purely dilutional effects of increasing discharge, are effectively offset by catchment weathering and erosional processes,introducing ions to solution. As discharge decreases from winter to spring, so conductivity increases (365 to 395 µS cm^{-1}). This increase in conductivity, according to work from chapter 5, is most likely to be associated with the pure hydrological effects of reducing flow and not with an increase in ions from seasonal catchment processes.

From spring to summer, discharge is still falling but at a lesser rate than that from winter to spring, however conductivity is also falling. This is difficult to understand because it would be expected that as discharge decreased, so the level of conductivity would increase. Relatively, however conductivity is still high, and because discharge is now so low, it is likely that the source of this water is almost entirely from limestone aquifers. The fact that the conductivity of such water decreases as summer progresses, probably reflects the time lagged effect of high volumes of dilute autumn and winter water percolating through these groundwater stores, leading to a marginal dilution, which is reflected in the falling conductivity values of summer river low flow.

6.3.2 Summary for STATISTICAL based data.

1. Hydrological pathways do significantly influence the chemical nature of the streamwater at Matlock.

2. It is the changing volume of discharge with different seasons, rather than processes unique to each season that determines the streamwater chemistry.

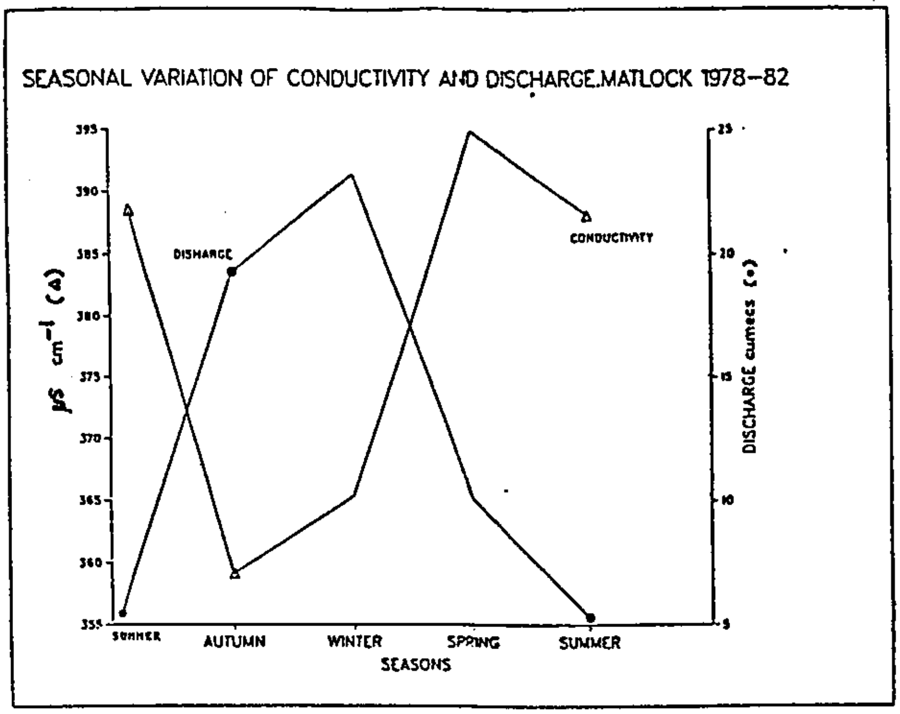


FIG. 6.11 Seasonal variation of conductivity and discharge, Matlock 1978–82, data from Fig. 6.9.

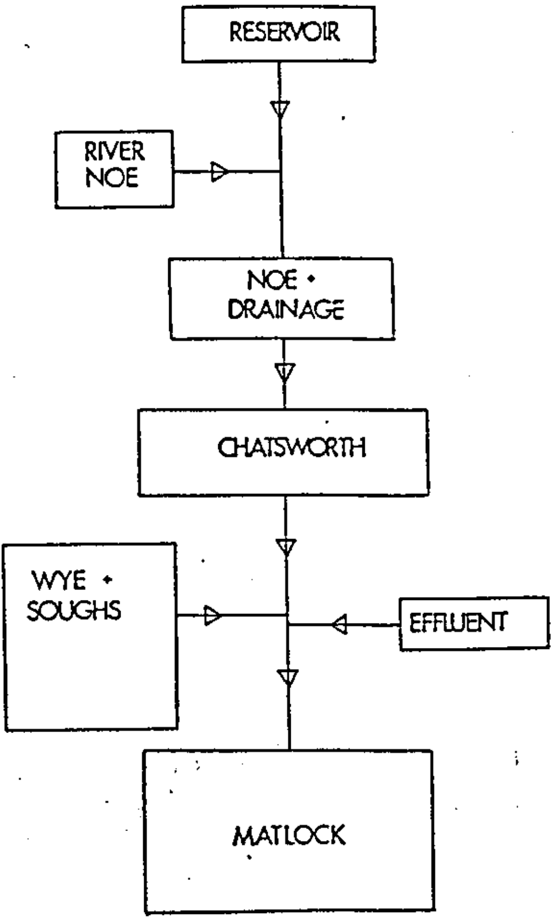


Fig 6.12 Derwent Water Chemistry model – a framework. Based on the dominant chemical inputs to the river down to Matlock.

3. When extreme low flow is considered, seasonal patterns are actually the reverse of that documented by the literature (see chapter 1), with lowest solute concentrations in autumn, and highest concentrations in winter.

Although the above discussion is specifically from a large data base collected at Matlock, because it tends to confirm earlier findings made with regard to the whole study reach from Yorkshire Bridge down to Ambergate, it is likely that if a similar exercise were completed for the other study sites similar conclusions and explanations would be drawn. However, in spite of the effect of river regulation being inherent within the data, its specific role is hidden. The following section through computer simulation seeks to discover the significance of that role to downstream conductivity values.

6.4 SIMULATION - seasonal computer model showing affect of regulation on low flow conductivity.

Using regression equations for downstream sites for the period 1978-83, relating conductivity with discharge and similar equations for a five year period before the reservoir was constructed, it is possible to determine the effect of river regulation upon the downstream seasonal pattern of conductivity. The data used is sample based and as such the record of conductivity was the only record detailed enough to allow this type of exercise.

6.4.1 Principles of the Model.

The fundamental basis of the model is the simple dilution equation:-

$$(Q_1 * C_1) + (Q_2 * C_2) = (Q_3 * C_3) \qquad \text{(eq.6.1)}$$

The above equation is applied at downstream sites to derive from existing data conductivity values under varying discharge values. From the data available the following schematic representation of the Derwent study reach may be made (Fig 6.12). Known values in this diagram, apart from those at Matlock, are from monthly survey data. From this data seasonal regression lines at individual sites were produced. Unknown values, were derived from the dilution equation.

Prior to reservoir construction, flow records are available for the Derwent upstream of the Noe confluence. Water chemistry for these flows can be estimated from present day reservoir inflow chemistry data. Chemistry and discharge data for the Noe input, land drainage input, effluent input, and River Wye and sough input, would have been similar to values post reservoir construction. From these known values, discharge and chemistry levels can be computed (see APPENDIXC23for computer model) for: The River Derwent below the River Noe confluence - summarised by data at Hathersage, the River Derwent from Hathersage to the Wye confluence (Chatsworth), and below the Wye confluence - Matlock.Table 6. 5 shows the simulated seasonal patterns of conductivity downstream on the lowest recorded daily flows, before and after reservoir construction. These patterns are presented graphically in Figs. 6.13 to 6.15. A summary of these data, in terms of percentage variation in conductivity due to reservoir construction is given in Table 6.6. and average mean daily flows before and after river regulation in Fig 6.16. Basically the annual pattern of flows has been undisturbed by reservoir construction, with peak discharges in autumn and winter and low discharges in spring and summer. In fact, according to the flow regime, the year is clearly divided into these two seasons - a combination of autumn and winter, and spring and summer.

6.4.2 Simulated effect of regulation on water conductivity (Fig 6.13-6.15).

Prior to reservoir construction, conductivities immediately below the now reservoir outfall are assumed to have had a seasonal spread of a nearly 100 μS cm^{-1}at low flow (data from paragraph 6.1). Seasonal variations in low flow discharge had significant effect on water quality. After impoundment however, any seasonal pattern was removed (data from the authors monthly survey - see table 5.4). This pattern of reduced variability is related to three factors: i) as part of the impoundment, waters from the limestone part of the Noe catchment were diverted into the reservoir system, leading to a general rise in solute levels ii) any lake effects of thermal stratification and overturn, upon water quality downstream are removed by releasing surface water only, and iii) constant compensation flow throughout the year, has removed any effects of discharge variation.

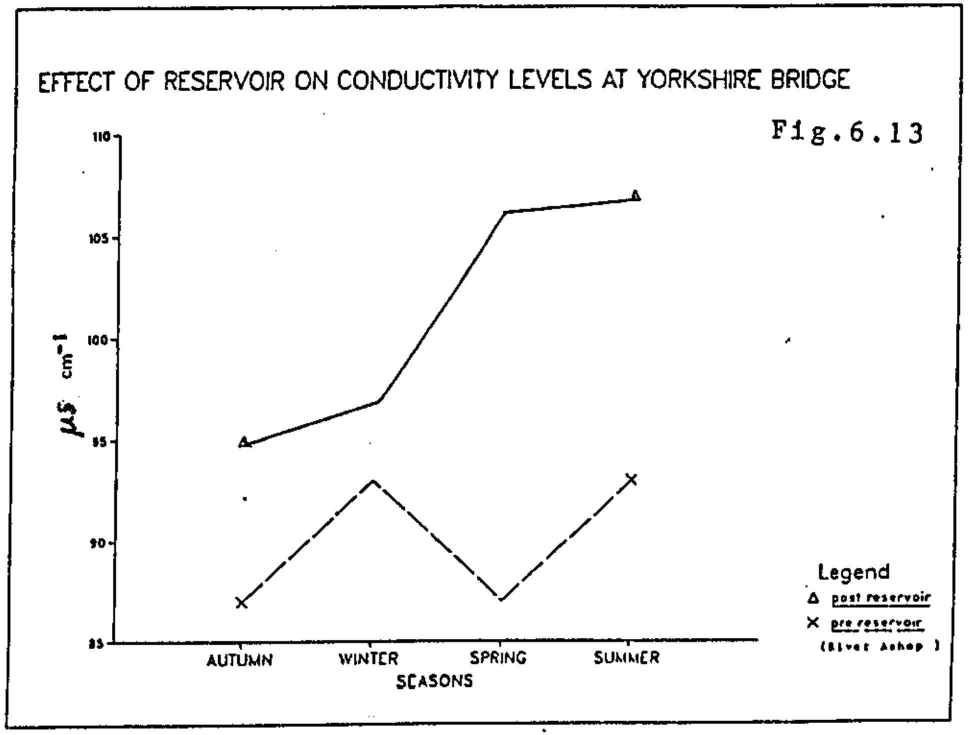
Further downstream at Chatsworth, the difference between pre and post reservoir low flow river water chemistry is even more noticeable, with pre reservoir conductivities falling within the range of 170-190 μS cm^{-1}, and post reservoir values (data from paragraph 6.1) within the range 260-285 μS cm^{-1}. At this site

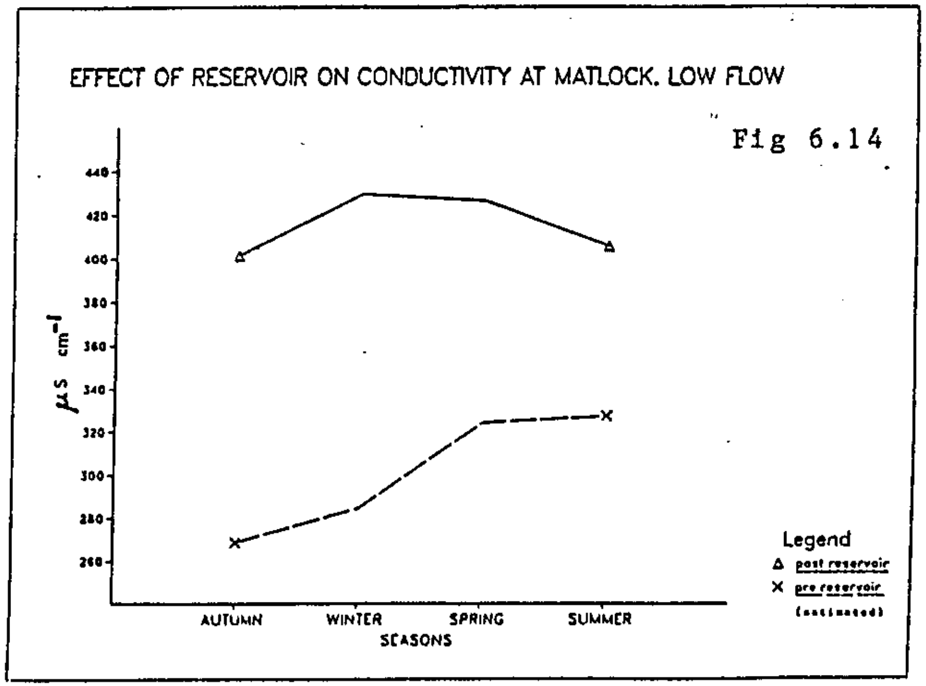
	POST RESERVOIR				PRE RESERVOIR			
	autumn	winter	spring	summer	autumn	winter	spring	summer
YORKSHIRE BRIDGE low Q $m^3 s^{-1}$	1.19	0.89	0.80	0.80	6.2	9.29	3.9	2.1
cond $\mu S\ cm^{-1}$	95	90	105	107	87	93	87	93
CHATSWORTH low Q	4.41	4.89	3.33	2.21	9.42	13.29	6.43	3.51
cond	258.8	283.7	263.3	256.7	166.4	163.4	177.9	193.3
MATLOCK low Q	6.93	11.12	7.24	4.01	11.94	19.5	10.34	5.31
cond	401.4	429.6	426.6	405.7	268.7	284.9	324.5	327.4

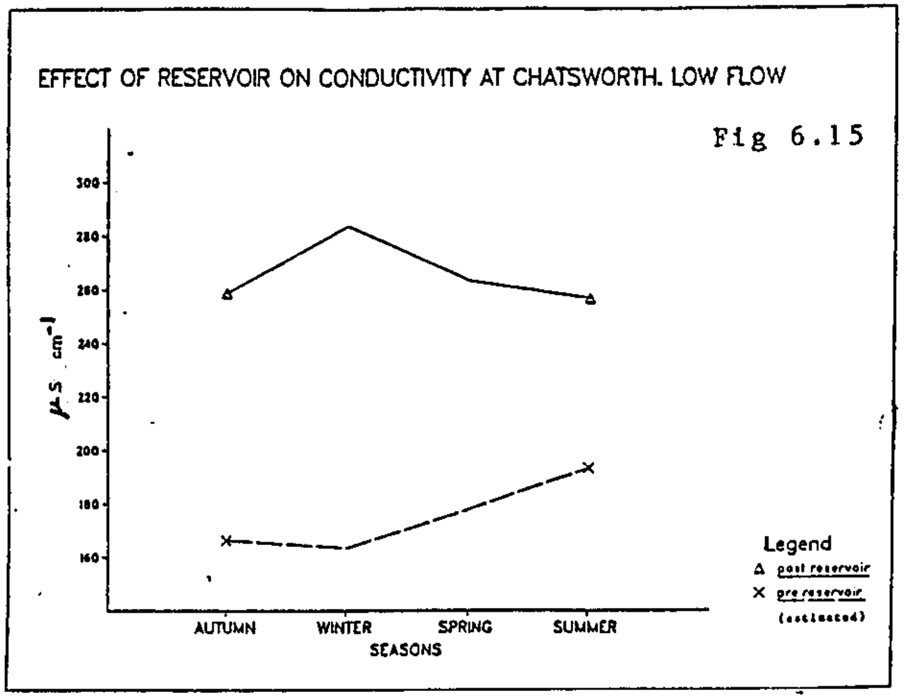
TABLE 6.5. Effect of reservoir construction on downstream seasonal conductivity, at low flow (lowest daily recorded flow for a 5 consecutive yearly period). Simulated by computer model, see Appendix C23.

SEASON	% INCREASE IN CONDUCTIVITY AFTER RESERVOIR CONSTRUCTION		
	Yorkshire Bridge	Chatsworth	Matlock
Autumn	8.4	35.1	33.1
Winter	-3.2	42.4	33.7
Spring	17.1	32.4	23.9
Summer	13	24.7	19.3

TABLE 6.6. Calculated % increase in conductivity after reservoir construction, on the River Derwent at low flow. Simulated from computer model presented in Appendix C23.







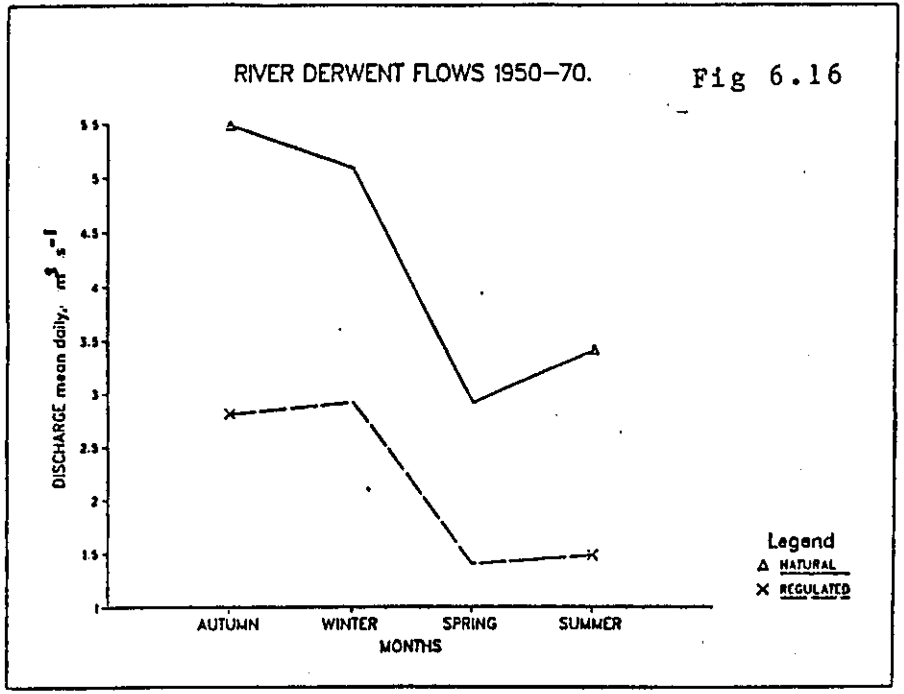


FIG. 6.13 - 15 Simulated effect of impoundment of the River Derwent on conductivity for the lowest daily flow in a 5 year record (see computer model Appendix C23).

FIG. 6.16 Yorkshire Bridge flows, regulated and natural (Severn Trent Water Authority 1950-1970).

there is little seasonal variation in conductivity values, however a pre reservoir summer high is displaced to the winter season after regulation. The difference in pre and post reservoir conductivities, is not so much due to a positive changing in water chemistry by impoundment, but rather by a reduction in the contribution to downstream flow of acidic moorland/gritstone derived water. In effect the water chemistry post reservoir at Chatsworth, reflects the chemistry of the River Noe and not that of the Derwent.

At Matlock, the percentage change induced by impoundment is less than that at Chatsworth, because the sphere of influence of the reservoir is being overshadowed by the input of limestone rich water from the River Wye. Pre reservoir, the seasonal pattern of conductivity essentially followed (as at Chatsworth) the inverse path of natural upstream discharge, after regulation there is little seasonal pattern, except that of relatively constant values. It is important to note that even at a distance of some 40 kilometres and after the input of two major tributaries, the effect of reservoir discharge at low flow is a significant factor influencing the river water chemistry. The importance of river regulation then in terms of water quality, is not merely a factor to be considered immediately below the outfall, but the mere alteration of flow regime, allowing variable water sources to dominate mainstream flow is a factor overlooked in the past. However, as reservoir discharges vary, it would be expected that the effect of this (particularly in the case of the Derwent where reservoir water chemistry is very different to that of the receiving river) on water chemistry would also vary. In order to assess the impact of different reservoir flows another computer model for the catchment was devised.

6.4.3. Catchment Computer Model, for varying Reservoir flow volumes.

Using a similar catchment model to that in the previous section (Fig 6.12), a computer model was designed in order to predict the effects of changing reservoir discharge on given flows downstream (for listing see APPENDIX C 24).

6.4.4. Steps to Model Construction.

The following steps to the construction of the model were under taken:-

	contribution to flow at Matlock m^3s^{-1}				% contribution to flow at Matlock			
	Aut	Win	Spr	Sum	Aut	Win	Spr	Sum
reservoir	1.17	0.89	0.80	0.80	17	8	11	20
Noe	0.82	0.78	0.87	0.49	12	7	12	12
Soughs	2.33	3.24	1.67	0.92	34	29	23	23
Wye	1.72	2.23	2.40	1.32	25	20	33	33
others*	0.82	4.02	1.53	0.48	12	36	21	12

TABLE 6.7. Major contributers to low flow discharge at Matlock.

* land drainage plus domestic and industrial effluent.

1. Percentage contribution of discharge from various sources to low flow discharge at Matlock were derived from the use of mean daily flow data from Matlock, River Wye, River Noe and the Yorkshire Bridge gauging stations 1978-82. (See table 6.7).

2. Conductivity values at the given sites, for differing flows during the year were derived from regression equations, (Table 6.8) using water authority and this survey monthly conductivity data for all sites, except at Matlock where the continuous data record was utilized. Correlation between discharge and conductivity is particularly low during the summer months, due to the very low spread of data collected during this period. However, because standard errors are also small it is justifiable to use this equation in the model building. Correlation in the remaining seasons is high and apart from confirming other authors' findings about the significance of discharge volume on background water quality (see Chapter 1), allows for the model to be calibrated accurately. Using the regression equations from table 6.8 in the general dilution equation (eq.6.1), conductivities on points described on the River were derived.

3. The model sets conditions in the reach according to flow at Matlock. Reservoir outflow may then be altered (reservoir conductivity will remain constant regardless of this alteration in discharge, since the conductivity at the reservoir outflow is a function of chemical input to the reservoir, together with limnological change, and not output discharge). The model also allows for the contribution to flow from the major factor influencing reach water chemistry - namely the River Wye/sough discharge, to be changed.

4. The model can simulate the effects on downstream water chemistry of varying upstream discharge. Table 6.9 shows the predicted effect of an up reservoir flood, pre dam construction, on downstream water quality. In contrast Table 6.10 illustrates the predicted effects of present day reservoir releases on downstream water quality. The results of these simulations are now discussed.

6.4.5. Computed Effect of an upland flood - pre reservoir construction.

Table 6.9 shows the effect that an approximate ten year return period flood pre reservoir construction could have had on

R WYE	Autumn	Winter	Spring	Summer
	relationship between conductivity & discharge			
r*	-0.554	-0.799	-0.584	-0.602
Equation*	513-3.58Q	533-5.56Q	547-13.6Q	530-14.9Q
SE	23.8	14.03	24.52	47.04
n	12	16	14	13
CHATSWORTH				
r	-0.663	-0.796	-0.738	-0.066
Equation	263-1.26Q	298-2.92Q	281-5.31Q	261-1.94Q
SE	35.18	33.47	19.35	29.15
n	16	16	14	16
MATLOCK				
r	-0.655	-0.741	-0.806	-0.377
Equation	399-2.06Q	421-2.46Q	430-3.38Q	410-4.07Q
SE	29.9	33.3	19.87	21.96
n	276	300	303	368

* r = correlation coefficient; equation = regression equation
SE = standard error; n = sample size

TABLE 6.8. Seasonal relationships between discharge and conductivity downstream on the River Derwent. (REGRESSIONS)

	Autumn	Winter	Spring	Summer
YORKSHIRE BRIDGE				
low Q $m^3 s^{-1}$	1.19	0.89	0.80	0.80
flood Q $m^3 s^{-1}$	20	20	20	20
low cond μScm^{-1}	95	90	105	107
flood cond	85	90	85	90
% change	11	0	19	16
CHATSWORTH				
low Q $m^3 s^{-1}$	4.41	4.89	3.33	2.21
flood Q	23.22	24.01	22.53	21.40
low cond μScm^{-1}	258.79	283.71	263.32	256.72
flood cond μScm^{-1}	117.49	129.49	111.18	106.62
% change	55	55	58	58
MATLOCK				
low Q $m^3 s^{-1}$	6.93	11.12	7.24	4.01
flood Q	25.74	30.23	26.44	23.21
low cond μScm^{-1}	401.44	429.65	426.60	405.68
flood cond	169.73	214.94	178.38	144.03
% change	58	49	58	64

TABLE 6.9. The computer simulated effect of a pre reservoir upland flood of 20 $m^3 s^{-1}$ (approx. 10 year return period) on downstream conductivity (from computer model presented in Appendix C24).

RESERVOIR RELEASE (m s^{-1})	Aut	Win	Spr	Sum	Aut	Win	Spr	Sum
	CHATSWORTH				MATLOCK			
	CONDUCTIVITY μS cm^{-1}							
Approx 0.8	259.1	283.7	263.2	256.7	402.2	429.6	426.6	405.7
5	180.3	195.3	174.9	157.3	288.5	337.9	308.5	252.0
% change	30	32	34	39	28	29	28	38
10	147.6	157.7	147.1	134.3	225.9	276.7	246.6	196.3
% change	43	44	44	49	44	36	42	52
20	124.8	129.5	128.4	120.6	174.5	214.9	193.1	156.9
% change	52	55	51	53	57	50	55	61
30	115.8	117.9	121.2	115.7	152.0	183.9	168.9	141.3
% change	55	59	54	53	62	57	60	65
40	110.9	111.5	117.4	-	139.5	165.1	155.3	-
% change	58	60	56	-	66	61	63	-
50	107.8	107.6	115.0	-	131.4	152.7	146.2	-
% change	59	62	56	-	67	64	65	-
60	105.9	104.8	113.4	-	125.9	143.8	140.1	-
% change	60	63	57	-	68	67	67	-
70	104.4	102.8	112.3	-	121.8	137.1	135.5	-
% change	60	64	58	-	69	68	68	-
80	103.3	101.3	111.4	-	118.7	131.9	132.0	-
% change	60	64	58	-	70	69	69	-

TABLE 6.10. The computed effect of different reservoir release volumes, on downstream water conductivity, made at low flow (lowest value in 5 yr consecutive period). For model see Appendix C24.

the downstream water chemistry. The most significant change in downstream low flow conductivity according to the model would occur in summer, with a 58% dilution at Chatsworth and a 64% dilution at Matlock. At the other extreme, the least effect of such a flood on water conductance, would have occured in winter, with a 55% dilution at Chatsworth and a 49% dilution at Matlock. Allowing for the fact that the model is calibrated by discharge and conductivity values from the automatic recording station at Matlock (see Fig 6.9), the change in values is extremely significant because real data has lowest conductivity values at about 320 μS cm^{-1}, whereas these predicted values are as low as 150 μS cm^{-1}. The construction of the reservoir has evidently stopped the possibility of such upland floods affecting Matlock and therefore in terms of the water quality, has removed the potential dramatic changes as predicted by the model.

The model makes no allowance for time scales to reach the predicted low conductivity values, nor the effects of flushing, or varying source effects. It is purely based upon discharge and as such is obviously a simplification of reality. However, it does show the extreme significance of upland floods on the natural variation of downstream water chemistry, prior to river regulation.

6.4.6 Computed Effect of Reservoir Releases.

Table 6.10 shows the effect of different volume releases upon absolute low flow (lowest recorded values associated with water chemistry samples). Regardless of season or location, according to the model, the majority of change in water conductance is achieved by releases up to ten m^3 s^{-1}. Releases from 0.8 to 10 cumecs create a maximum percentage change at Matlock of 52%, from 20 to 80 m^3 s^{-1} there is an additional change of a mere 17%. This is because the simulation is being carried out when the catchment is in an extreme period of low flow. Therefore releases greater than ten m^3 s^{-1} are simply diluting the already dilute earlier release water. At Chatsworth for releases upto 10 cumecs maximum change occurs in summer and minimum change in autumn however, for larger releases, maximum variation occurs in winter, with minimum change in summer or spring. At Matlock result are slightly different. Maximum change for releases is always during summer, and minimum change (except for the smallest release) during winter. The results at Matlock are as might be expected, with winter Derwent low flow water, being slightly closer in its nature to reservoir water, since it is likely that low flow at this time of year, is a combination of precipitation and groundwater. At Chatsworth the results for releases upto 10 cumecs are as would be expected, but then subsequent discharges produce maximum change in winter, and minimum in summer. The explanation to this must be that river flows in summer are lowest, and therefore a maximum dilution will be reached with a lower discharge than during other seasons, which have slightly greater 'low' flows. Consequently, larger discharges in summer will simply be diluting reservoir water.

In terms of operating procedure for reservoir releases, this model is very instructive. It demonstrates that it is not so much the size of release that is important for variation in water chemistry, but rather the percentage above compensation flow that is critical. The model also shows that if this percentage flow difference is high enough, then release water movement downstream should be very easy to trace, simply by monitoring change in conductivty values over time at-a-station.

6.4.7. Summary of Simulation approach.

The final models presented in this chapter are entirely discharge based, although some catchment parameters are included inherently within the seasonal regression equations applied. Therefore as expected, seasonal and downstream changes in water conductivity values simply reflect the changing percentage contribution of reservoir, or in the case of the pre-reservoir model, upland water.

The effect of a given release is dependent not so much upon the size of that release, but upon the change in reservoir contribution to downstream flow. Thus a small release of say 5 $m^3 s^{-1}$ made upon absolute low flow, would have a significant effect on conductivity even as far downstream as Matlock. However, if this same release were made when natural flow was high, then it would be unidentifiable, both in terms of stage and chemistry change. In order to evaluate this simple methodology for linking quantity and quality, a detailed investigation has been undertaken of water quality change associated with reservoir releases to upland rivers. Such a study also introduces an important element missing from the model presented in paragraph 6.4; that of time i.e the rate of change of chemistry at-a-station during a release.

CHAPTER 7.

WATER QUALITY VARIATIONS DURING RESERVOIR RELEASES.

The examination of water quality changes in the regulated River Derwent, demonstrated the hydrological significance of regulation on downstream water chemistry. It is apparent that the influence of reservoirs upon such downstream water quality can be significant at three scales: i.) the long term, through the changing nature of river water as a result of biochemical changes within the reservoir ii.) in the intermediate term, altering seasonal patterns as a result of lacustrine processes and hydrological change and iii.) in the short term associated with controlled flow fluctuation. This section seeks to investigate the water quality changes during pulse releases, that is at the short term time scale.

The research seeks to examine the rate of change of chemistry at-a-station, with the introduction into that system of release water. This relates to two problems: firstly the change in water chemistry at-a-station may be associated not only with the arrival of reservoir water en-masse, but also with the arrival of a hydraulically induced release wave; and secondly, the rate of change of water chemistry at-a-station during the passage of a reservoir release wave, may give an indication of the influence of in-channel processes to the flood chemograph. In order to examine these problems in greater depth than can be achieved on the River Derwent, research was carried out on three upland rivers subject to controlled releases, namely: the Afon Tryweryn, near Bala, North Wales; the River Washburn, near Harrowgate, North Yorkshire; and the River North Tyne, near Hexam, Northumberland. However, before the observed water quality changes are analysed, the hydraulic characteristics of the releases will be examined.

7. 1. Hydraulic characteristics of releases on the rivers Tryweryn, Washburn, and North Tyne.

Twenty three releases were monitored during the two year field work programme. A sequence of eighteen releases on the River Tryweryn formed the core of the study. Comparative data were also obtained for four releases on the River Washburn and one release on the River North Tyne. Research focused on Llyn

Celyn releases made into the River Tryweryn, because these were planned in advance by the Welsh Water Authority. Releases from Thruscross Reservoir into the River Washburn, and from Kielder Water into the River North Tyne were monitored to provide, in the former case, data for a contrasting release strategy, and in the latter data from a larger and gravel-bed (as opposed to boulder-bed) river. The release policies of the Water Authorities involved were as follows.

1.) Llyn Celyn. A stepped release pattern is adopted involving three discharge increments: from 0.368 to $3.94m^3s^{-1}$ during the initial fifteen minutes of the release; from 3.94 to $5.78m^3s^{-1}$ during the next fifteen minutes; and from 5.78 to $12.62m^3s^{-1}$ during a third fifteen minute period. The pattern was adopted in order to avoid a large single wave front travelling down the river. At monitoring stations downstream, this full release produced approximately a two-fold increase in hydraulic area and a maximum stage change of about 60cm.

2.) Thruscross Reservoir. A single release is made from the reservoir, usually stepping compensation flow up from about 0.6 m^3s^{-1} to $6.0m^3s^{-1}$ in less than five minutes. The policy is to achieve the necessary flow for grade 1 white-water canoeing, as quickly as possible. At monitoring stations downstream, this release produced approximately a three fold-increase in hydraulic area, and a maximum stage change of about 70cm.

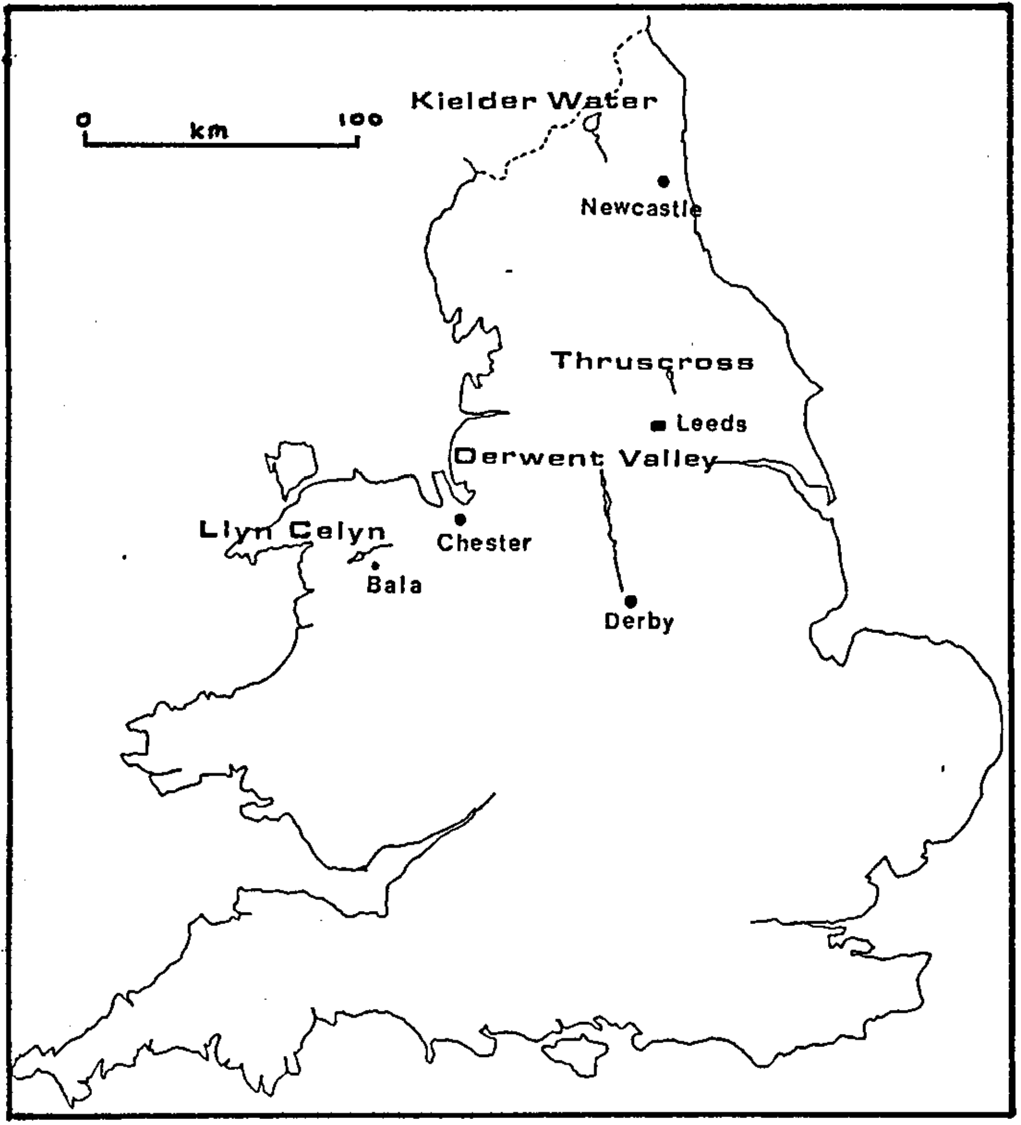
3.) Kielder Water. There was no definitive release policy from Kielder Reservoir (Brady et al, 1983). However, a single experimental release was made for which the following instantaneous release strategy was agreed: 2.5 to $25m^3s^{-1}$, 25 to $50m^3s^{-1}$ and 50 to $40m^3s^{-1}$, remaining steady at 25, 50, and $40m^3s^{-1}$ for a period of forty five minutes. Such discharges were stepped up to maximum in a period of 20 minutes. At monitoring stations downstream, maximum release volume produced approximately a three fold increase in hydraulic area and a maximum stage change of about 100cm.

The time taken for maximum stage change to occur throughout the study reach on each of the three rivers was less than thirty minutes. So in terms of the change in energy level within the rivers during releases the potential for channel disturbance is high.

7. 2. Location of Study Sites.

The location of each river is shown in Fig 7.1 and the

Fig. 7.1. The location of the study Rivers.



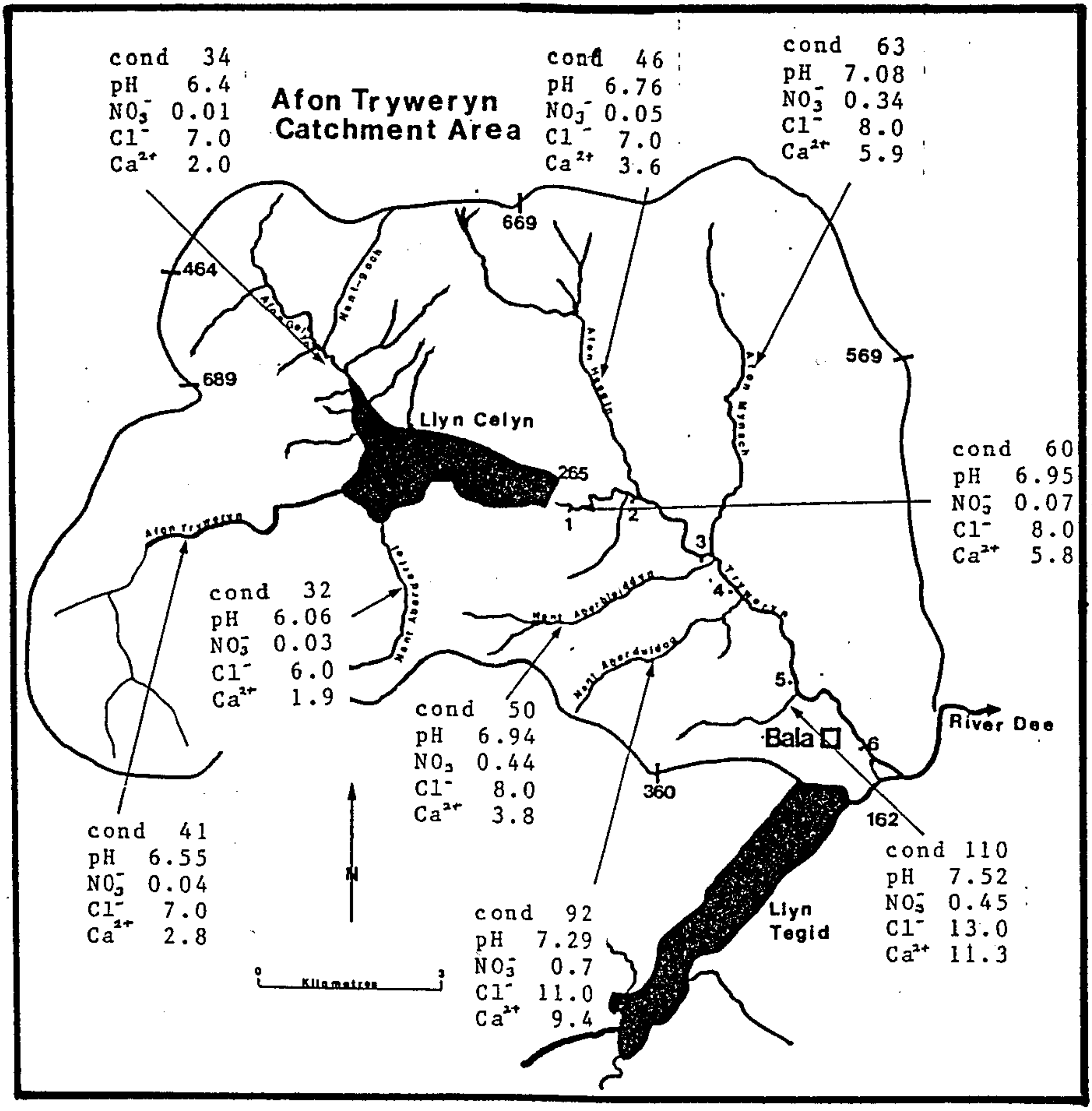
drainage areas and nature of the basins are given in Figs 7.2-7.4. The River Tryweryn and Washburn were chosen because they display similar characteristics, being typical upland streams, with boulder bed channels, steep slopes, extreme turbulence at high flow and extreme roughness at low flow. The River North Tyne was chosen to compare results from this larger, gravel bed channel with the boulder bedded streams. For the Tryweryn and Washburn, study reaches were delineated according to the basin geography. Llyn Celyn to Llyn Tegid for the River Tryweryn, Thruscross Reservoir to Swinstey Reservoir for the River Washburn. However, for the River North Tyne no such simple geographical delineation is applicable, and so for comparative purposes a study length similar to that on the River Tryweryn was considered.

Hydrologically the reaches on the study rivers are dominated by release water from the reservoir, at least as far downstream as the first major tributary input, which tends to create hydrological complications. On the River Tryweryn, such complications are introduced by the Afon Mynach, on the River North tyne by the Tarset and Chirdon Burns but on the River Washburn tributary input was found to be negligible. The significance of tributary input to the River Tryweryn and the River North Tyne, was found to be great when the catchment was in flood - not least because the reach between its confluence and the dam usually only experienced compensation flow - but virtually negligible during periods of dry weather. This finding was valid regardless of the volume of releasing reservoir water. Morover, the theoretical discussion in Chapter 3 demonstrated the significance of baseflow discharge on the character of wave movement. Thus, strategic positioning of sampling sites was needed in order to account for the influence of these tributary inputs on reservoir wave movement. For the location of sampling sites see Figs.7.2-7.4.

7. 3. Background Water Quality of the Rivers Tryweryn, Washburn and North Tyne. (Figs.7.2-7.4)

The fundamental background water quality of the Rivers Tryweryn, Washburn and North Tyne, through catchment spatial surveys, was found to be determined as expected (Walling and Webb, 1975), largely by catchment geology. Essentially, chloride values in all catchments represented precipitation contributions, with nitrate, calcium and conductivity levels, greater in streams draining limestone, glacial clays, and head deposit areas, than those draining gritstone formations.

Fig.7.2. The relative spatial water chemistry of the River Tryweryn catchment, and reservoir release sampling site (1-6) location.

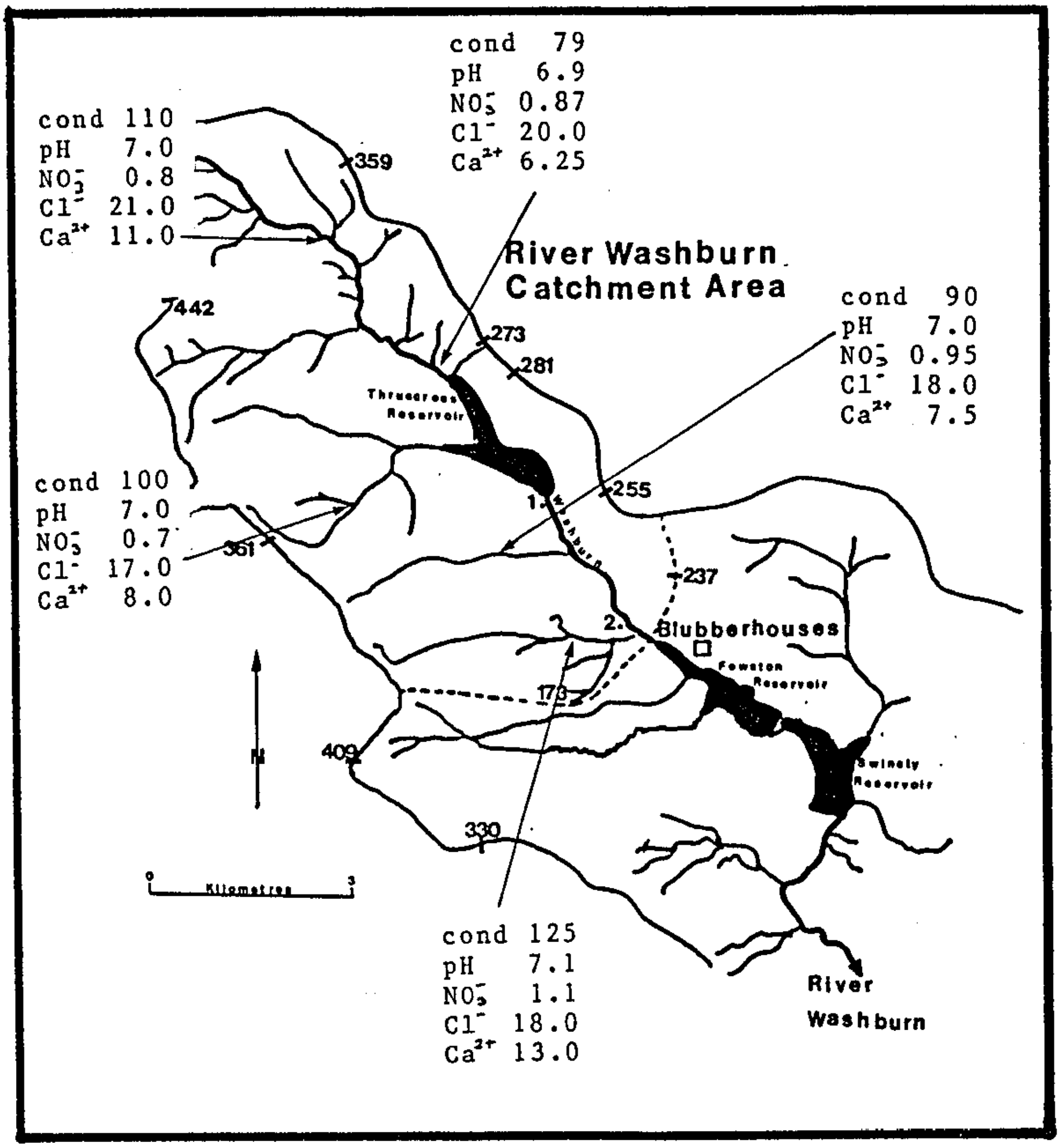


LEGEND FOR FIG. 7.2 - 7.4

1 - 6 sample sites
- 317 spot heights (m)
and conductivity µS cm^{-1}

pH - pH units
NO_3 - nitrate mgl^{-1}
Cl^- - chloride mgl^{-1}
Ca^{2+} - calcium mgl^{-1}

Fig.7.3. The relative spatial water chemistry of the River Washburn catchment, and reservoir release sampling site (1-2) location. (Point time, low flow).



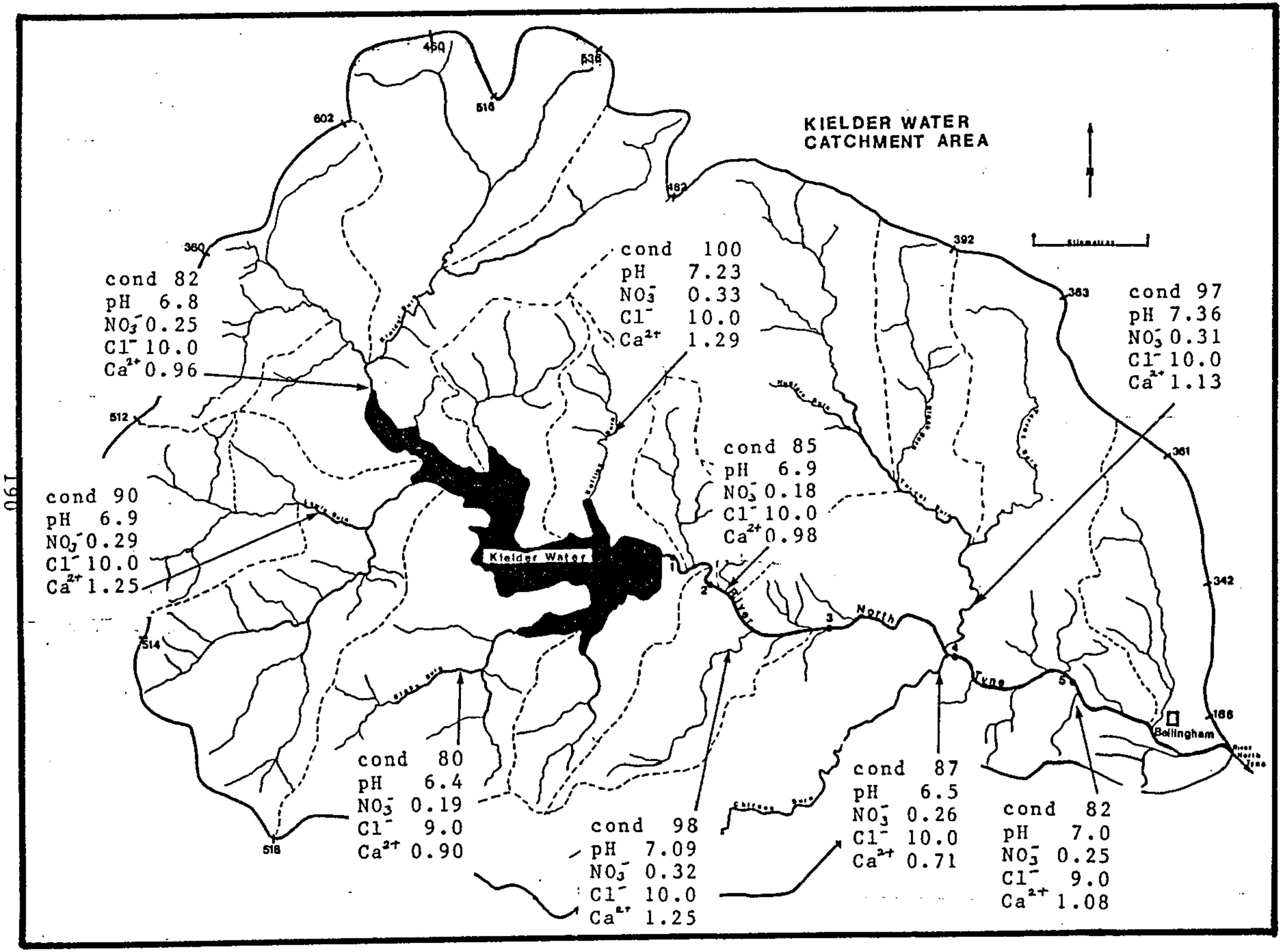


Fig.7.4. The relative spatial water chemistry of the River North Tyne catchment, and reservoir release sampling site (1-5) location. (Point time, low flow).

7.3.1. River Tryweryn Catchment Water Chemistry.

The basin is underlain by Silurian grits, slates and shales and the impermeable slopes produce a flashy river regime, although today this is regulated by reservoir releases. Surface geology is largely dominated by hill peat, with a lesser amount of glacial clay. Solute loads are characteristically low; conductivity ranges from 32µS cm^{-1}in headwater tributaries to 110 uS cm in tributaries draining the lower slopes, but this is dominated by calcium which increases from less than 2mg $l^{-1}$to over 11mg l^{-1}. Nitrate values are also very low ranging from 0.01 mg l^{-1}on the up reservoir tributaries, to a maximum of 0.70mg l^{-1} in the tributaries draining the pasture land to the west of the catchment. pH values, as would be expected in this area of acidic solid geology and surface peat deposits are generally on the acidic side of neutral (pH 7), although streams draining forested parts of the catchment have pH values in the region of pH 5. This circumstantial evidence tends to confirm the findings from Chapter 5, and from studies by Likens et al (1977), Newson (1979), and Fredrickson (1972), relating low pH values in former moorland streams, to aforestation by conferious woodland plantations.

7.3.2. River Washburn Catchment Water Chemistry.

Basically the River Washburn and its catchment are situated in a large expanse of Millstone Grit, although water chemistry in places is influenced by small pockets of Carboniferous Limestone. The surface geology is essentially glacial clay deposits, with a modicum of moorland peat. To a great extent the catchment geology is comparable to that of the up reservoir section of the River Derwent basin, although the solute concentration values are slightly greater, due to the greater influence of glacial clays. Conductivity values range from 70-150µS cm^{-1}, calcium values from 8-20mg l^{-1}; nitrate values from 0.1-2.0mg $l^{-1}$and pH values from 6.8-7.2. The water chemistry of the minor tributaries below the reservoir, is extremely similar to that of the main channel, indicating that the resrvoir does not have a great effect on water chemistry at compensation discharge.

7. 3. 3. River North Tyne Catchment Water Chemistry.

The solid geology of the study area is divided into three major geological groups:

i.) Coal - Scremerston Coal group
ii.) Limestone - Middle and Low group
iii.) Sandstone - Fell Sandstone group

All of these groups are bracketed into the lower carboniferous time period. The coal group extends over virtually the whole of the catchment area, with limestone only significant to the north and south of Bellingham and sandstone high in the catchment area of Kielder Water. Peat overlays much of this moorland catchment whilst glacial clay intrudes onto the lower slopes. This combination of surface and solid geology is not conducive to high solute levels in drainage water and explains the low levels of ionic concentration in the River North Tyne Water, with values of 50-95μS cm^{-1} for conductivity, 0.2-2.0mg l^{-1} for calcium, 0.05-1.5mg $l^{-1}$for nitrate and a pH range of 6.8-7.4.

Despite variations in solid geology between the study catchment sites, the basic pattern of response to process is the same. All areas are underlain with impermeable rocks, mildly acidic, and resistant to mechanical or chemical weathering and erosion, leading to low ionic concentrations in drainage water. Surface lithologies of all three areas are similar, being dominated either by glacial clays or moorland peat, as with solid geology these are poor donators of solutes. However, the relative increase in dominance of glacial clay to surface geology in the River Washburn catchment, is sufficient to raise solute levels to the highest of the three study areas; conversely, the lack of clay deposits in the Kielder catchment has given this region the lowest solute values. Nevertheless for each location the catchment spread of solute values are of similar magnitude and therefore comparison between the study areas of change in solute load during reservoir releases is meaningful. Table 7.1 shows the comparative real and percentage variation of solutes during typical releases on the study rivers. Percentage change of calcium on all rivers is similar, at about 50% however, the change in chloride and conductivity on the River North Tyne is nearly twice and half as much respectively, than on the other two rivers. This is probably due to the greater study reach length on the River North Tyne, reducing the release impact. Nitrate change is greatest on the River Washburn, unlike the other solute variations, this is a increase, and results from a build up of nitrate within the reservoir.

7. 4. Water chemistry variation during reservoir releases.

The previous section described spatial water quality variations in the study catchments and showed how similar chemical conditions are between them. This section aims to describe, in detail, water chemistry changes during releases for each study river and then to compare these changes.

7.4.1. Chemistry variation on the River Tryweryn (further data presented in Appendix D10 and D11).

Change in river water chemistry of the Tryweryn during releases is greatly affected by the fact that, essentially the water course is a natural over spill channel for Celyn reservoir. It is therefore used extensively as the conveyance route of water into the River Dee water supply scheme. Thus, water chemistry is almost continually being subjected to large changes in discharge, implying that solute source build up within the channel can not occur. This would tend to suggest that the passage of individual releases, in terms of influencing water chemistry are likely to be insignificant. However, because this water course is also subjected to periods of extreme low flow, when the water chemistry of tributaries is allowed to dominate, together with the fact that the type of release monitored in this study created extremely large and rapid stage changes, variations in water quality during such releases are likely to induce some change. Detailed investigations made before, during and after of some thirteen releases (for data see Appendix D11) - a further 9 releases were examined purely in terms of the hydraukics of flow - revealed that the rate and degree of change in water chemistry was reliant on; the sampling location, the season, the river chemical conditions immediately prior to the release, and the hydrological conditions immediately prior to the release.

Of the parameters analysed, namely conductivity, calcium, nitrate, chloride and pH, all except chloride responded to change in stage brought about by reservoir releases. During the monitoring of releases conductivity was found to display a total range of 31-77μScm^{-1}throughout the reach; calcium a range of 1.8-8.4mg l^{-1}throughout the reach; nitrate a range of 0.04-1.11mg l^{-1} throughout the reach and pH a range of 5.99-7.31 throughout the reach. Results show (Table 7.2) that the maximum change in conductivity at any site is 38μS cm^{-1}; the maximum change for calcium is 4.64mg l^{-1}; the maximum change for nitrate is 1.02mg l^{-1} and the maximum change for pH is 1.18 units. In comparison with background water quality values these changes are certainly significant. Maximum changes were found to occur at the point furthest away from the reservoir, as Fig 7.6-7.9

RIVER	DATE of RELEASE	DISTANCE DOWNSTREAM (km)	AVERAGE % CHANGE DURING A RELEASE (see 7.1)			
			Nitrate	Chloride	Calcium	Conductivity
TRYWERYN n = 22	23.4.83	7.8	25 (0.16mg l^{-1})	18 (4mg l^{-1})	49 (3.1mg l^{-1})	31 (19μS cm^{-1})
WASHBURN n = 4	10.4.83	2.5	54 (0.6mg l^{-1})	10 (2mg l^{-1})	53 (7mg l^{-1})	36 (45μS cm^{-1})
NORTH TYNE n = 1	4.10.83	12.5	19 (0.05mg l^{-1})	30 (5mg l^{-1})	49 (0.55mg l^{-1})	19 (18μS cm^{-1})

TABLE 7.1. Comparison of the average % change in solute levels during reservoir releases on the study rivers Tryweryn, Washburn and North Tyne.

	Calcium mg l^{-1}	Nitrate mg l^{-1}	pH units	Conductivity μS cm^{-1}
<u>RIVER TRYWERYN</u>				
<u>SITE 1</u>				
24.4.83	1.81	0.38	1.18	10
15.5.82	1.0	0.11	0.4	11
1.6.84	0	0.02	0.4	5
4.9.82	1.1	0.03	0.4	5
25.10.82	2.2	0.05	0.4	12
<u>SITE 2</u>				
24.4.83	2.1	0.14	0.47	8
25.10.82	1.8	0.13	0.7	13
<u>SITE 3</u>				
15.5.82	0	0	0.38	4
<u>SITE 4</u>				
24.4.83	2.9	0.24	0.71	17
1.6.84	1.2	0.02	0.24	10
<u>SITE 5</u>				
24.4.83	4.64	0.24	0.23	22
15.5.82	3.2	0.38	0.57	27
4.9.82	2.4	0.17	0.6	24
25.10.82	3.2	0.42	0.65	21
<u>SITE 6</u>				
24.4.83	4.64	0.26	0.61	24
15.5.82	4.2	1.40	0.33	38
4.9.82	2.6	0.12	0.98	11
4.9.82	3.8	0.32	0.63	26

<u>TABLE 7.2a. Maximum solute variation during reservoir releases (12.252m s^{-1}) on the River Tryweryn</u>. Actual values.

RIVER WASHBURN	Calcium mg l^{-1}	Nitrate mg l^{-1}	pH units	Cond µS cm^{-1}	Chloride mg l^{-1}
SITE 1					
10.4.82	6.75	0.2	0.3	40	5
23.10.82	12	1.1	0.9	70	4
5.11.82	3.3	-	0.5	13	-
SITE 2					
10.4.82	6.75	0.6	0.3	45	-
23.10.82	12	1.3	0.8	64	3
5.11.82	4	-	0.7	14	-
RIVER NORTH TYNE October 1984					
SITE 1	2.3	0.2	0.3	62	-
SITE 2	0.5	0.1	0.3	40	-
SITE 3	0.5	0.8	0.2	22	-
SITE 4	0.5	0.4	0.2	19	-

TABLE 7.2b. Maximum variation of water chemistry on the rivers Washburn and North Tyne during reservoir releases (for release strategy see 7.1) - actual values.

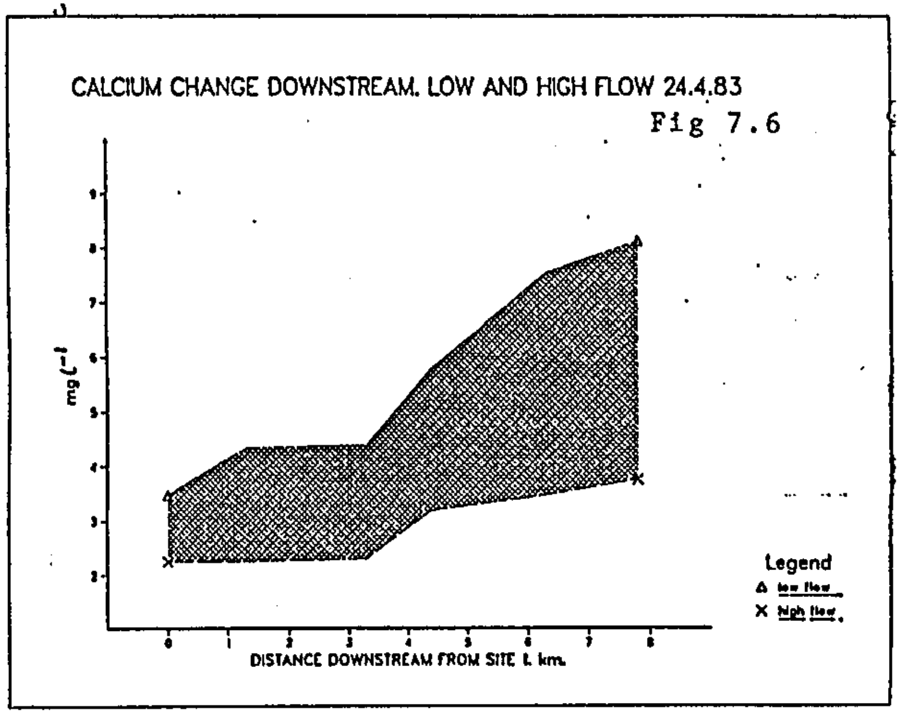

CALCIUM CHANGE DOWNSTREAM. LOW AND HIGH FLOW 24.4.83

Fig 7.6

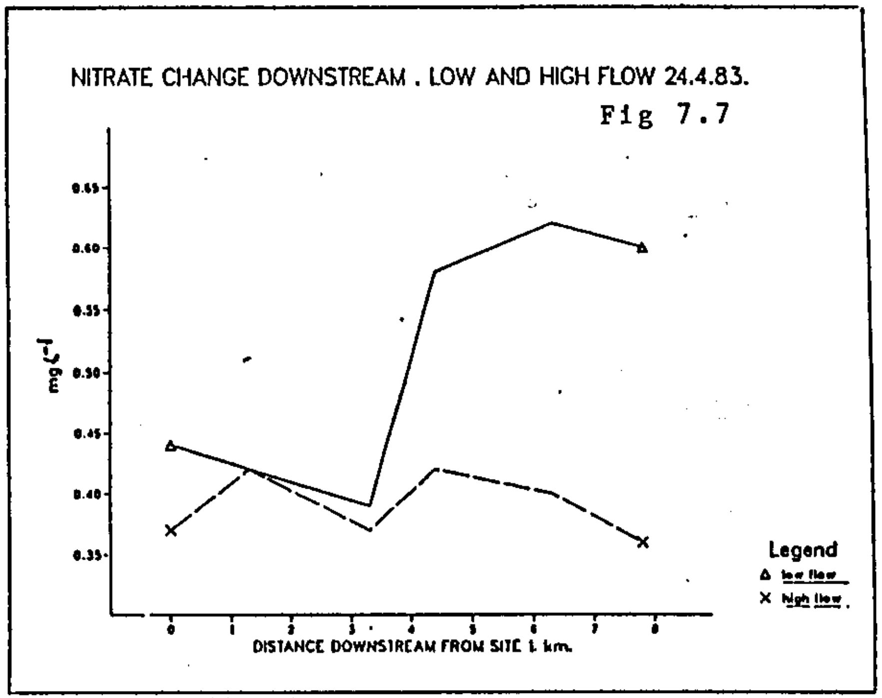

NITRATE CHANGE DOWNSTREAM . LOW AND HIGH FLOW 24.4.83.

Fig 7.7

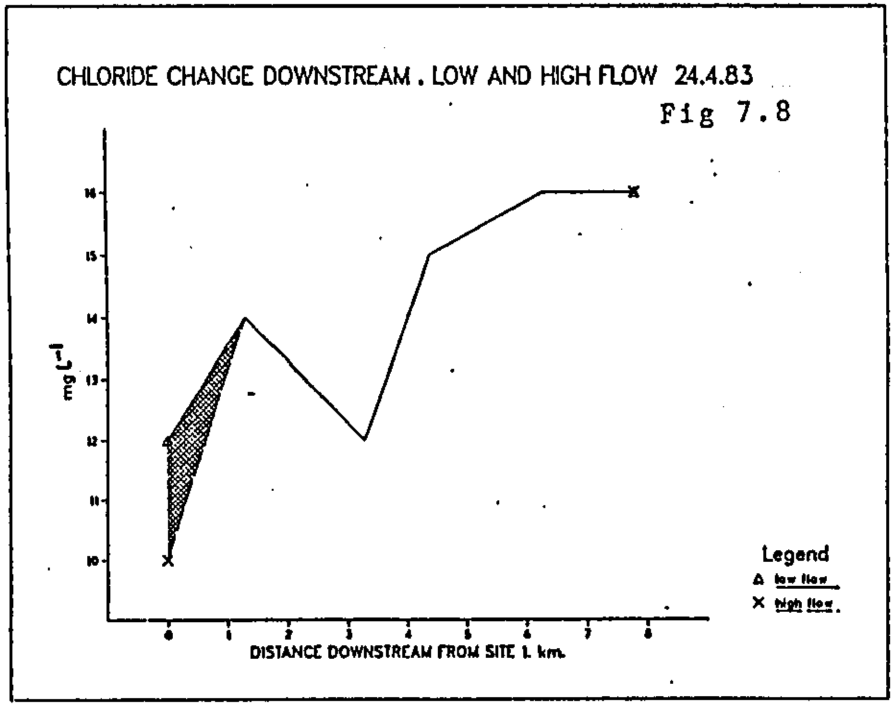

CHLORIDE CHANGE DOWNSTREAM . LOW AND HIGH FLOW 24.4.83

Fig 7.8

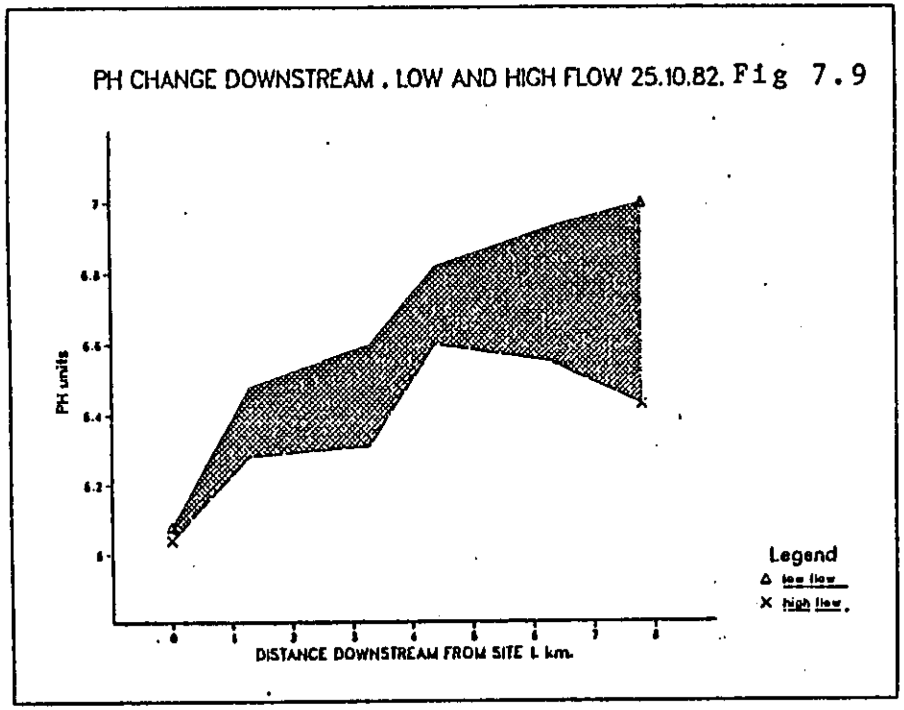

PH CHANGE DOWNSTREAM . LOW AND HIGH FLOW 25.10.82. Fig 7.9

FIG. 7.6 - 9 Examples of high flow (release of 12.252 m^3s^{-1}) and low flow (compensation discharge) solute values on the River Tryweryn (six sampling locations - see Fig. 7.2).

illustrate, and for most releases maximum change was a dilution effect, which became more important downstream. Such a response is similar to results presented by Hall et al (1977) for the River Zambezi, in Africa, where change due to the reservoir increases downstream, as a result of inputs from the Shire River being diluted. For pH this dilution is translated into an increase in the acidity of the water. Generally speaking results in Table 7.2a&b, also show that the change in water chemistry during a release is reduced in the summer months, and that changes are also reduced if the reservoir has been making releases on the previous day. Although there are some exceptions to this general finding, when change is actually greatest on day two of the release - a phenomenon that was found to be attributable to catchment storm events in the intervening period between releases, raising the level of inchannel solutes to abnormally high concentrations. In short, releases on the River Tryweryn lower the ionic concentration to a level that is a compromise between that of reservoir water and that of the channel water at the location of sampling. The releases monitored were not of sufficient magnitude to make any other water source totally negligible in determining the water chemistry of the main flow. However, soon after the release water flow was at a maximum throughout the study reach, channel water reflected more the chemical nature of the reservoir, than that of the river. The way in which this dominance is achieved is now examined.

7. 4. 2 Time scale of change.

Change in water chemistry occurred at all sites during the majority of releases however, significant patterns were only identifiable when the degree of change was somewhat greater than low flow background variations. As such this tended to occur when natural solute river levels were greater than those associated with reservoir water, which was found to be either during late spring and early autumn, or when the release was made following a catchment flood (see data in Appendix D10 and D11)

At site 1 chemistry variations before the release and during the rise are erratic (e.g Fig 7.10). For some releases concentrations were rising before the release (e.g Fig 7.11), for others concentrations were falling (e.g Fig 7.12) and for others there was little change prior to the arrival of the release wave. Explanations of this behaviour relate to Water

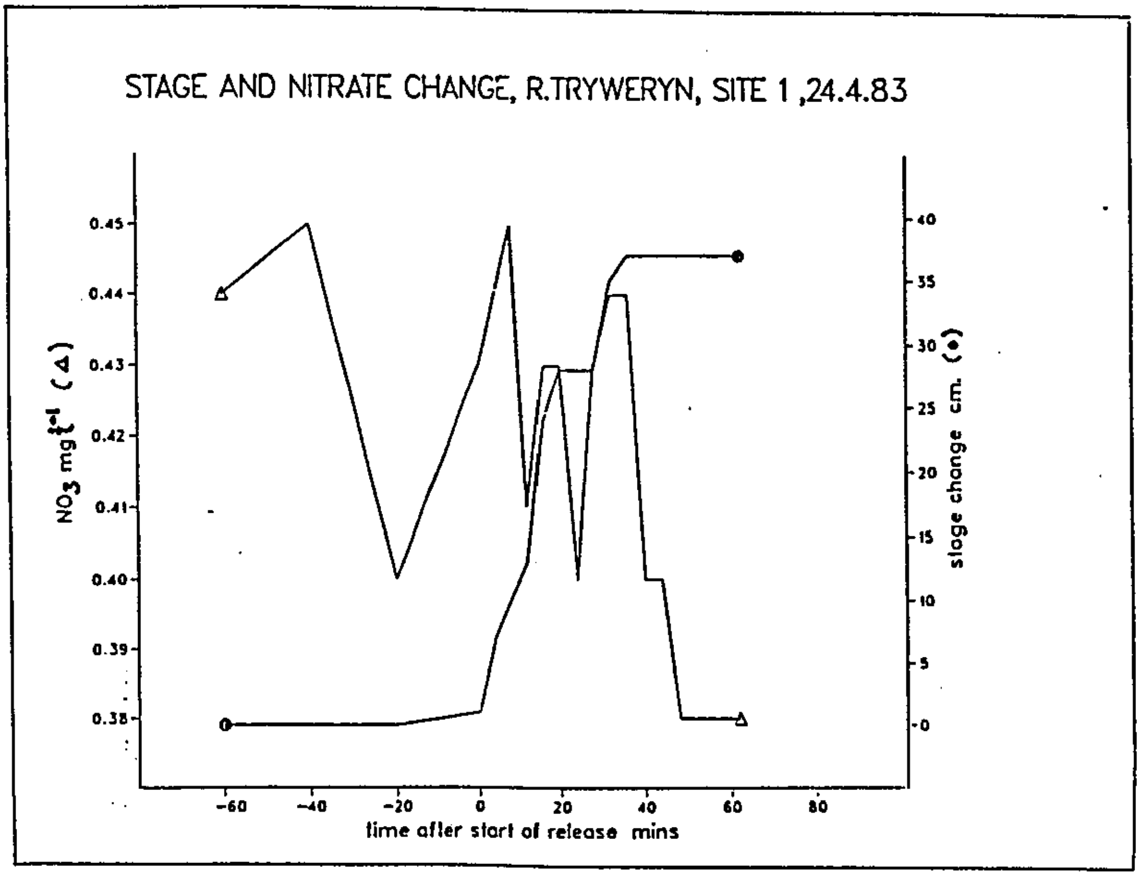


FIG. 7.10 Nitrate response at site 1 on the River Tryweryn prior to and during a full volume ($12.252m^3s^{-1}$) release. Each line is a series of 40-data points (see section 4.2.3).

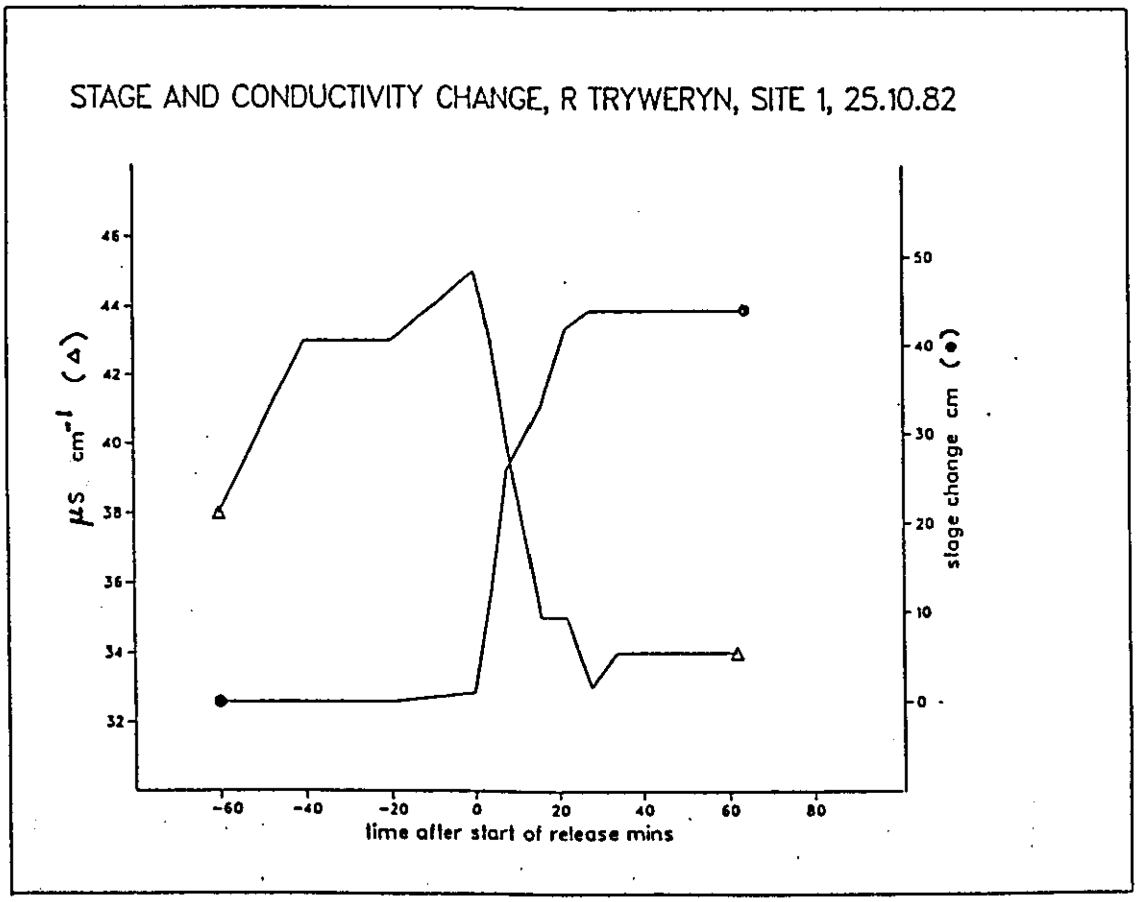


FIG. 7.11 Conductivity response at site 1 on the River Tryweryn, prior to and during a full volume ($12.252m^3s^{-1}$) release. Each line is a series of 40 data points (section 4.2.3).

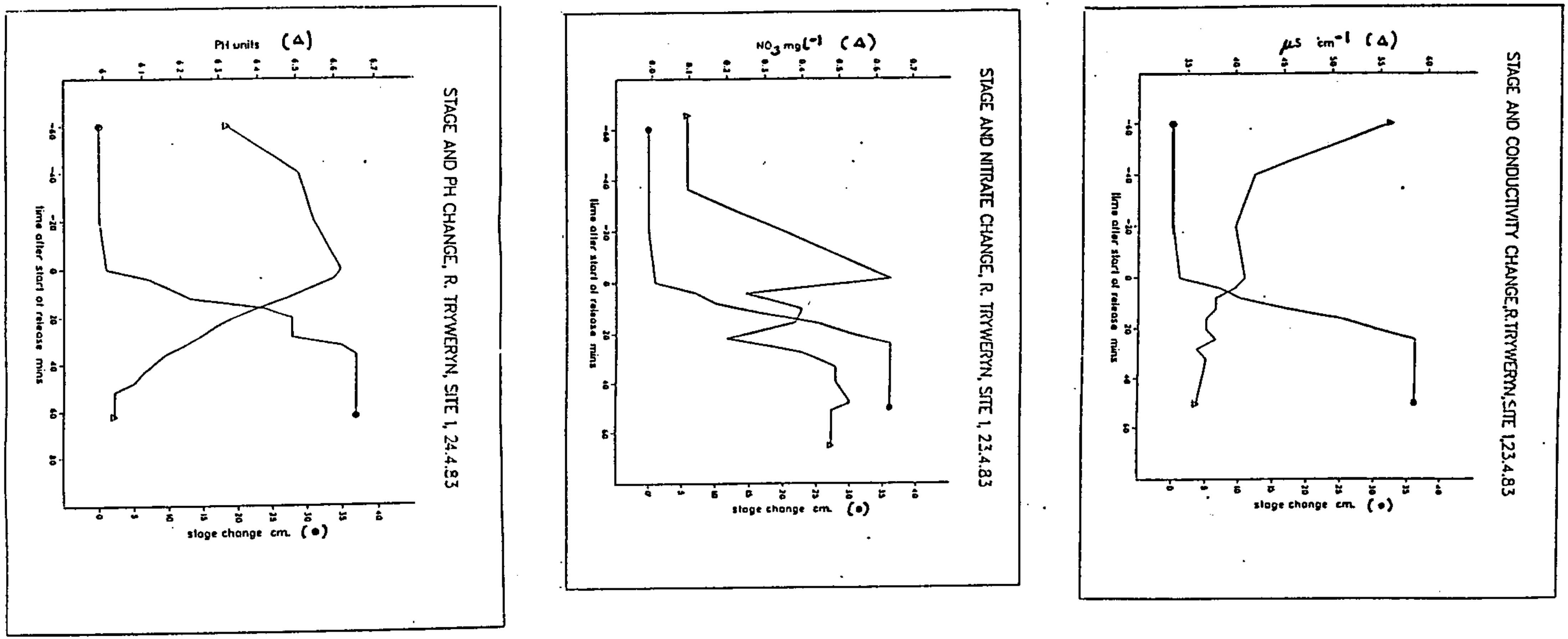


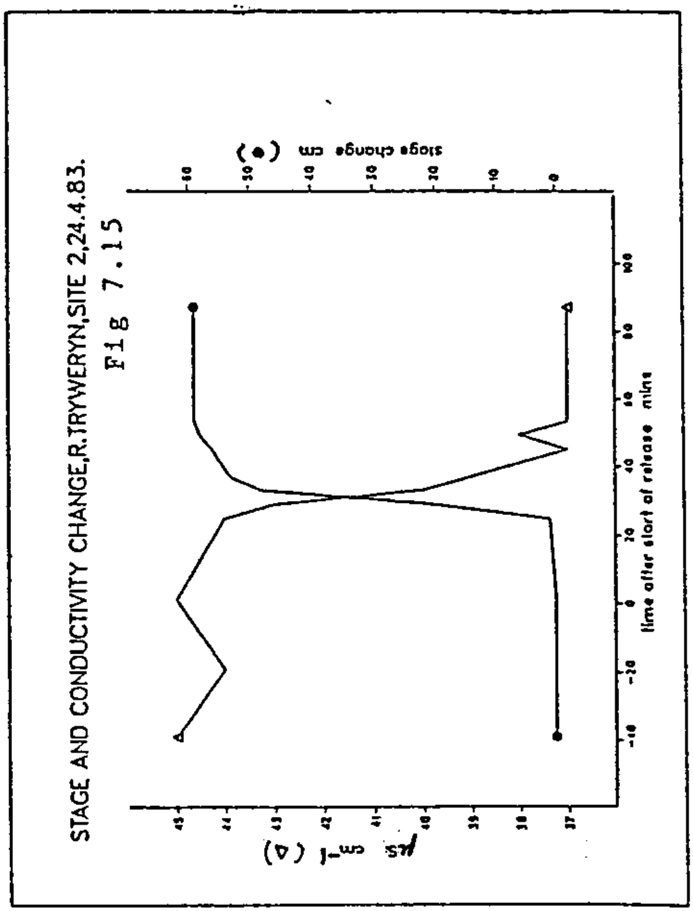
FIG. 7.12 - 14 Water quality response at site 1 on the River Tryweryn prior to and during a full volume (12.252m^{3}s^{-1}) release. Each line is a series of 40 data points (see section 4.2.3).

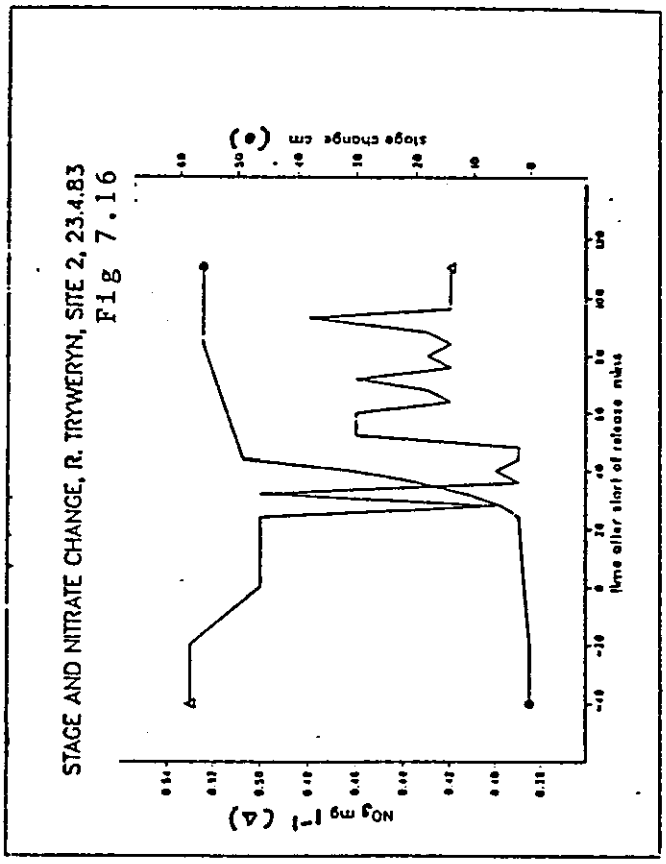
Authority release strategy prior to the main valve openings. However, without fail, as soon as stage began to rise chemical values rise, or in the case of releases where concentrations were rising anyway before the release this process continues (Fig 7.11). At this site, maximum release stage is usually attained within twenty five minutes, and within this period chemistry levels invariably fall to relatively constant values, equating to that of the reservoir water. In some cases, after the initial short lived rise, values actually fall below steady flow concentrations (e.g Fig 7.13) - an over reaction effect (Allen, 1974). Perhaps as would be expected at a site so obviously dominated by the reservoir, pH patterns usually clearly reflect the release strategy (e.g Fig 7.14).

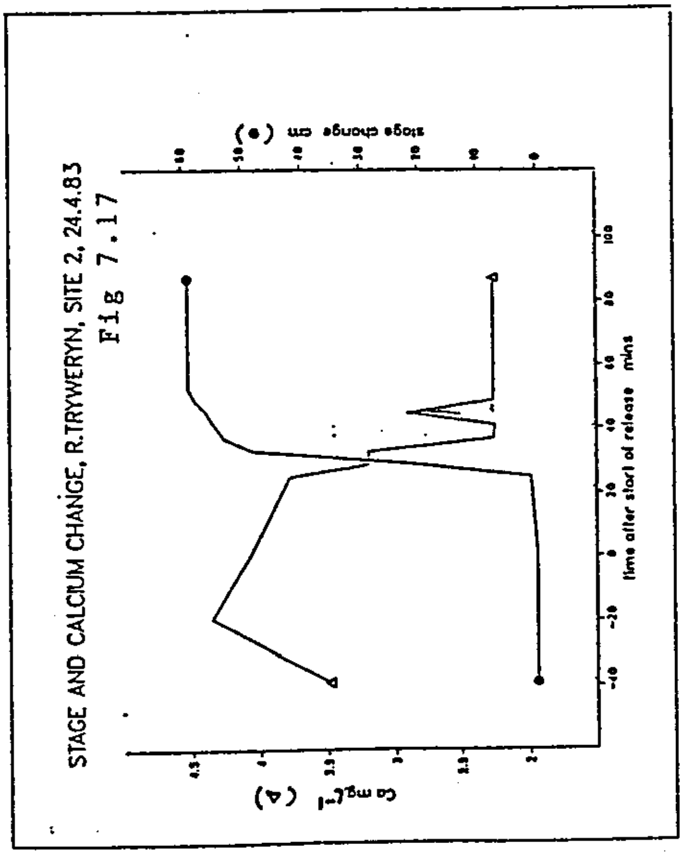
At site 2 some 1.5km below site 1, patterns of change are similar, although chemistries tend to be more consistent prior to stage change (e.g Fig 7.15). Most releases demonstrate the production of some rise in chemical concentration either prior to, coincident with or immediately after initial stage rise (e.g Fig 7.16). Usually a constant low value is attained before maximum stage has been attained, that is within about twenty minutes from the start of stage rise (e.g Fig 7.17), although in some cases, concentrations become more erratic with maximum stage (e.g Fig 7.16). pH patterns reflect release strategy less clearly than at site 1, and tend to follow a pattern similar to that of other chemistries (e.g Fig 7.18).

Only 3 releases were monitored at site 3 and these during the summer months (see Appendix D11). Due to the known hydrological dominance of reservoir water during low flow downstream as far as this site (immediately above the first major tributary input) - hence a lack of solute load - releases had little or no noticeable effect upon the water chemistry. For sites upstream a similar response during these releases was also found, downstream some response was monitored, although patterns were hard to identify because changes were so small.

At site 4, about 4.5km below site 1, significant changes in water chemistry occur in comparison with those upstream, and the patterns of response to the passage of the flood wave already documented, are further demonstrated. However, the initial rise is less marked with chemistries other than nitrate (e.g Fig 7.19), and the time taken to reach maximum dilution is slightly greater than the 8 minutes or so to attain peak stage (e.g Fig 7.20). Some irregularities with the pattern of dilution are also recorded, probably due to the increased solute input via







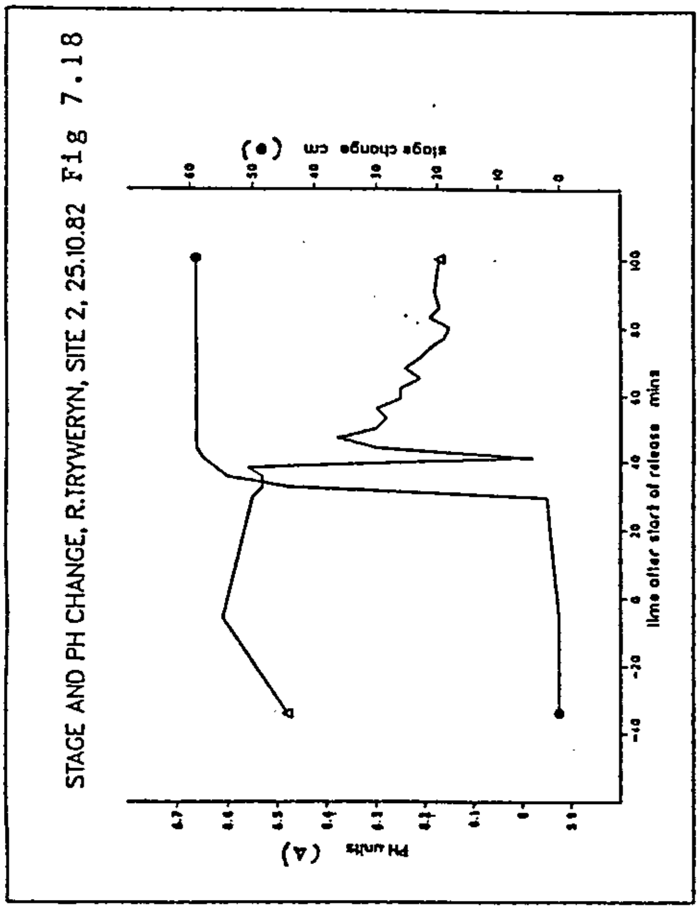


FIG. 7.15 - 7.18 Water quality response at site 2 on the River Tryweryn prior to and during a full volume (12.252m^{3}s^{-1}) release. Each line is a series of 40 data points (see section 4.2.3).

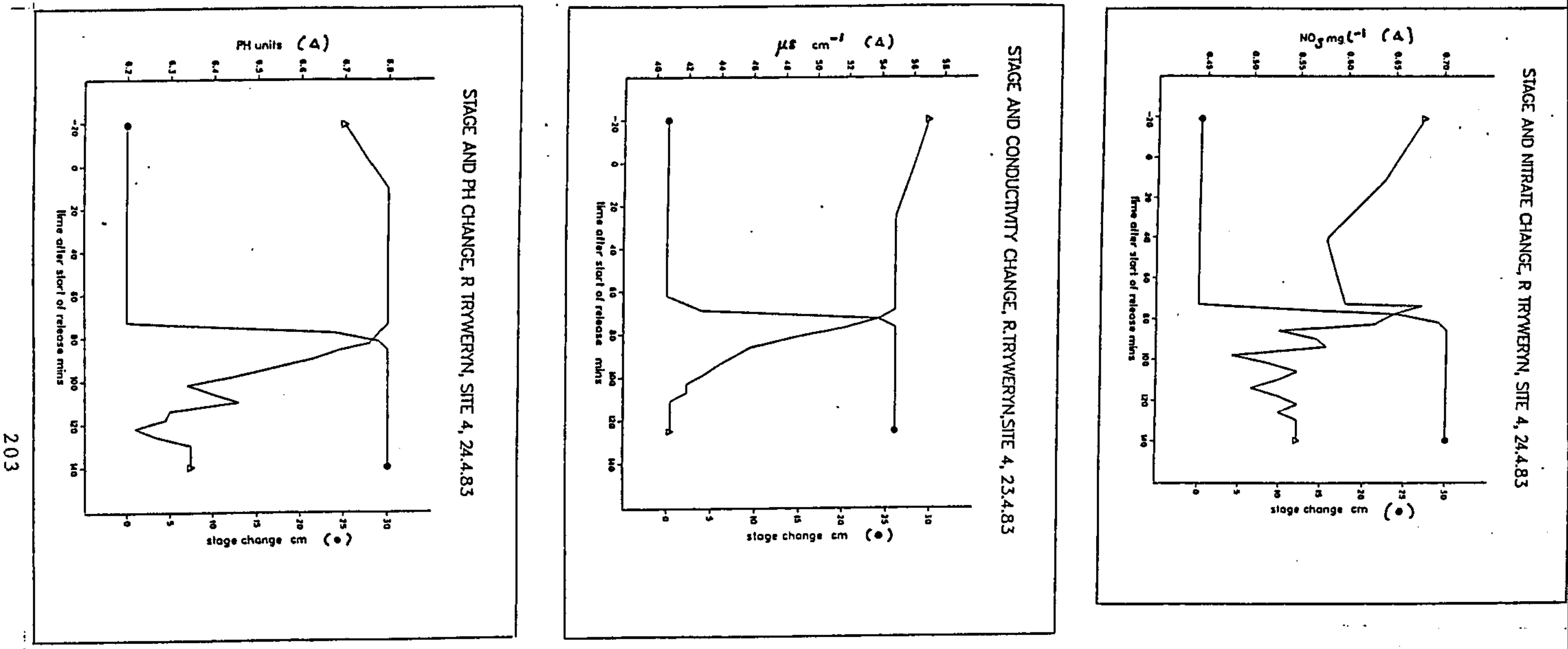


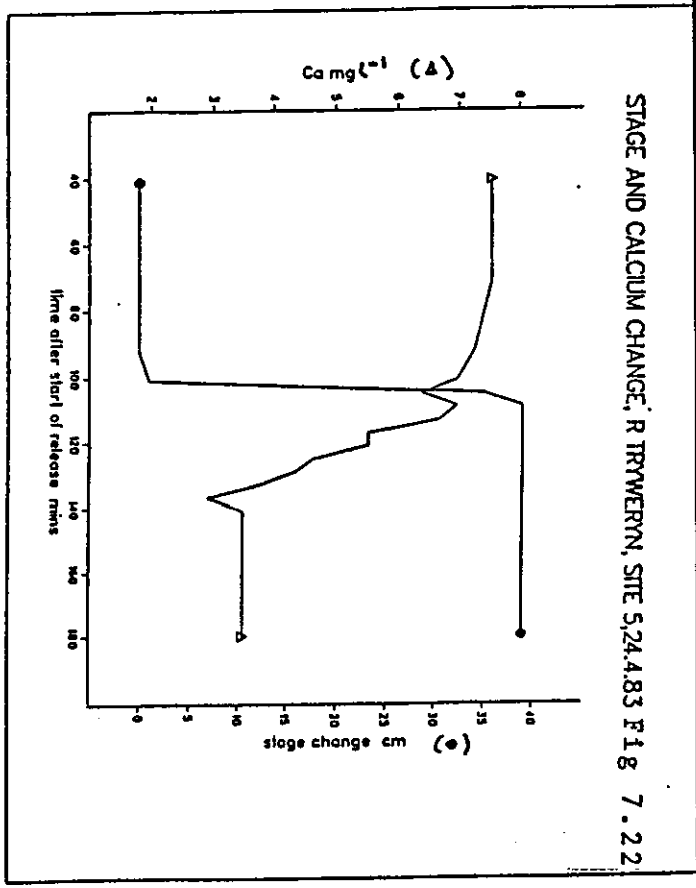
FIG. 7.19 - 7.21 Water quality response at site 4 on the River Tryweryn, prior to and during a full volume ($12.252 m^3 s^{-1}$) release. Each line is a series of 40 data points (see section 4.2.3).

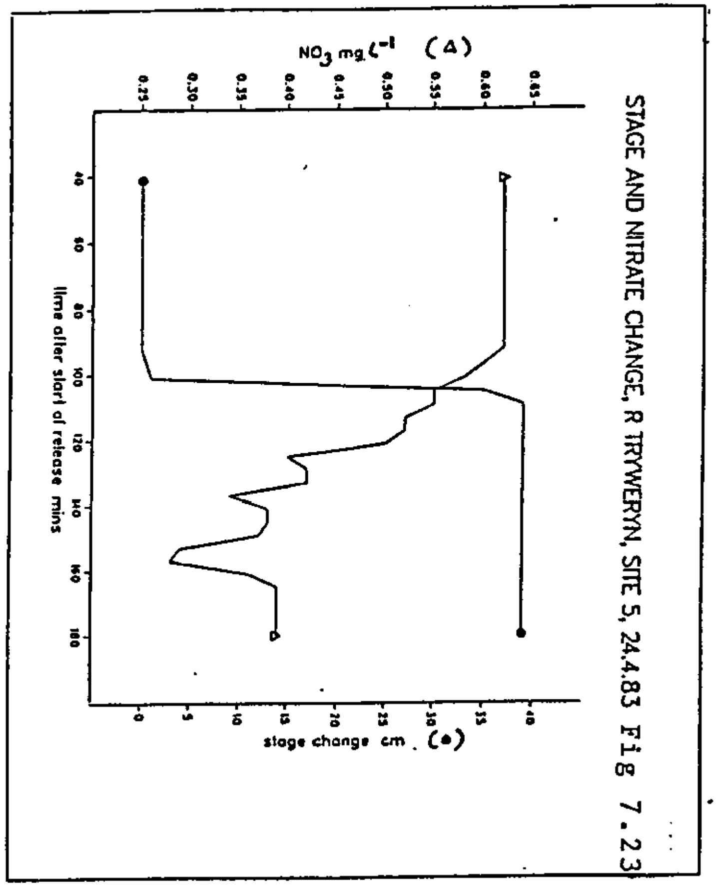
unregulated tributaries. As with site 2, pH usually follows a very similar trend to that of the other chemistries (e.g Fig 7.21).

Site 5 - 7km below site 1 - has conductivity, calcium and nitrate patterns extremely similar to those at site 4, although the pattern of chemical change appears to be even more out of synchronization with stage change. The expected initial rise often occurs a minute or so after initial stage change (e.g calcium in Fig 7.22), and maximum dilution is usually attained for all chemistries well outside the approximate 5 minutes taken to attain maximum discharge (e.g nitrate in Fig 7.23). pH patterns tend to vary considerably between releases, although generally there is a steady increase from the onset of stage change, followed by a reduction in pH any time between 15 and 30 minutes after peak stage (e.g Fig 7.24). The specific pH change is probably dependent on the different tributary contributions to low flow discharge.

At site 6 - the lowest sampling point of the study reach, approximately 8km below site 1 - an established pattern of chemical response to artifical flow regulation has been produced. Relatively stable background water chemistry is subjected to significant change, with the arrival of the release front. Conductivity, calcium and nitrate usually respond to stage change virtually instantaneously with a series of peaks, often lasting until maximum discharge is reached some twenty minutes after the arrival of the wave front. Solute values then fall to a constant low usually about a further twenty five to thirty five minutes later (Fig 7.25-27). pH tends to respond in a very similar manner (e.g Fig 7.28), with a multiple initial response, followed by steady decline to a constant low.

In essence, water chemistry on the River Tryweryn does respond to artifical flow fluctuation. This response is purely due to the increased dicharge effects on water chemistry, and is similar to results presented by Hall et al (1977), but unlike results of stream water quality behaviour during flood flows (e.g Edwards, 1973b; Foster, 1978b; Hendrickson, 1960; and Johnson and East, 1982), where channel water quality varies not only according to discharge, but also to the changing chemical nature of that input. The actual degree of response on the Tryweryn is according to sample site location, and pre-release river water solute load. A pattern of initial rise or series of rises in concentration and pH, corresponding to stage increase usually occurs, followed by a steady decline to a low value


STAGE AND CALCIUM CHANGE, R TRYWERYN, SITE 5,24.4.83 Fig 7.22


STAGE AND NITRATE CHANGE, R TRYWERYN, SITE 5, 24.4.83 Fig 7.23

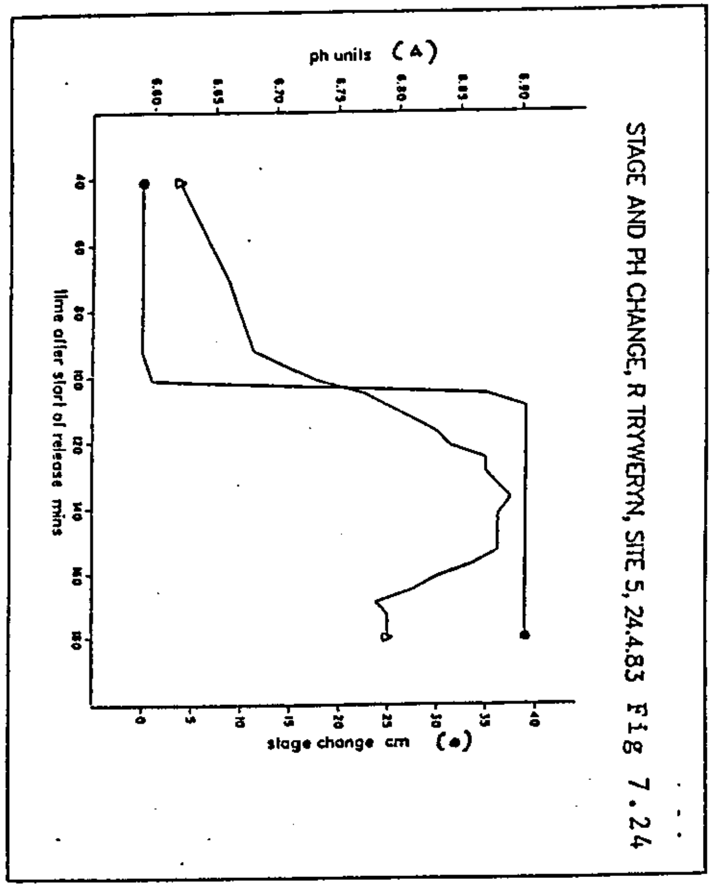
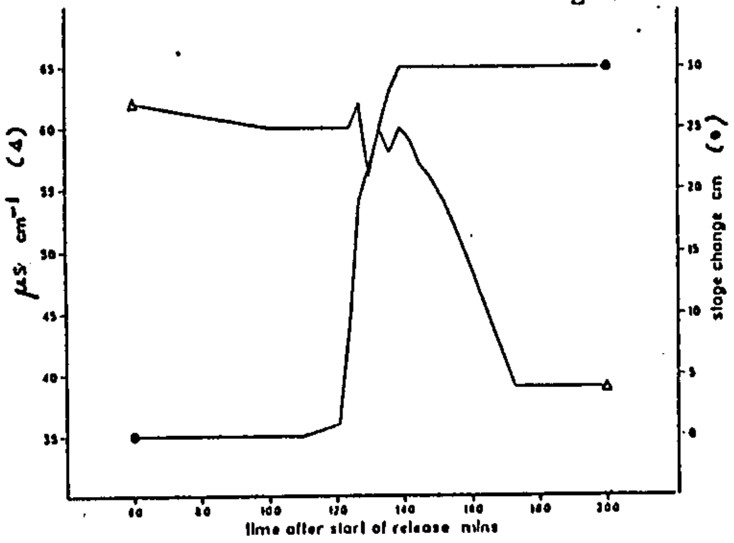

STAGE AND PH CHANGE, R TRYWERYN, SITE 5, 24.4.83 Fig 7.24

FIG. 7.22 – 7.24 Water quality response at site 5 on the River Tryweryn prior to and during a full volume (12.252m^{3}s^{-1}). Each line is a series of 65 data points (see section 4.2.3).

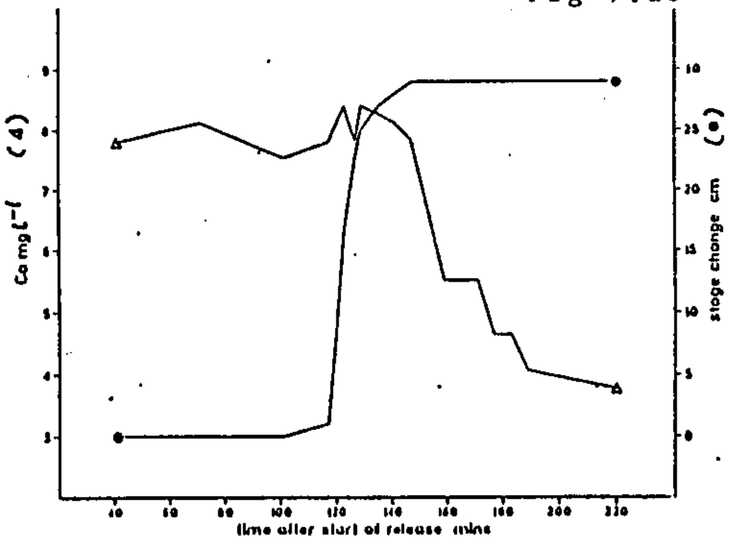
STAGE AND CONDUCTIVITY CHANGE, R.TRYWERYN, SITE 6, 25.10.82

Fig 7.25



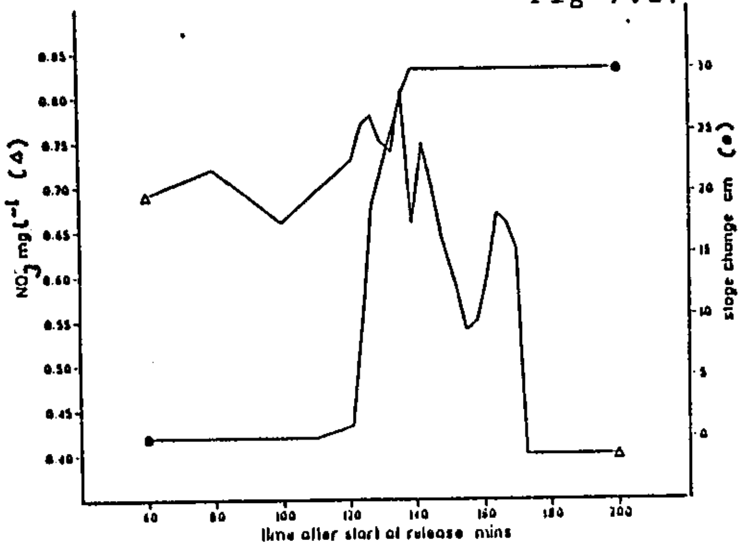
STAGE AND CALCIUM CHANGE, R TRYWERYN, SITE 6, 24.4.83

Fig 7.26



STAGE AND NITRATE CHANGE, R TRYWERYN, SITE 6, 25.10.82

Fig 7.27



STAGE AND PH CHANGE,R TRYWERYN, SITE 6, 24.4.84 Fig 7.28

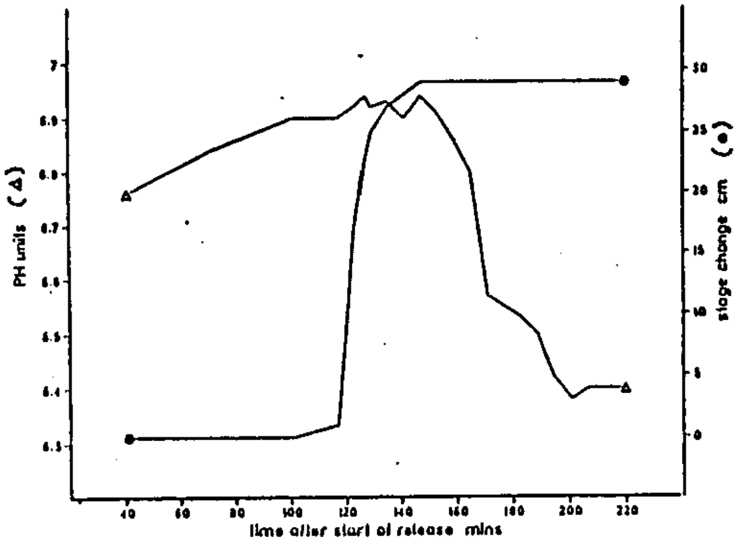


FIG. 7.25 – 7.28 Water quality response at site 6 on the River Tryweryn prior to and during a full volume (12.252m^{3}s^{-1}). Each line is a series of 65 data points (see section 4.2.3).

close to that of the reservoir water. The rate of decline is reduced downstream irrespective of initial solute levels.

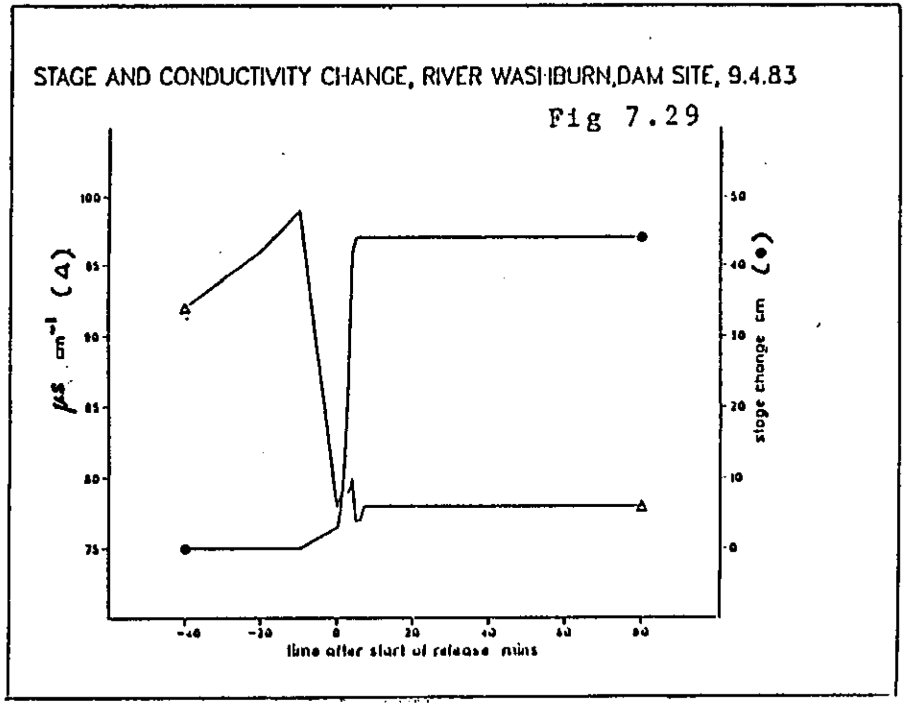
7.4.3. Changes in water chemistry with releases on the River Washburn. (Further data presented in Appendix E2)

The length of the River Washburn between Thruscross and Swinstey Reservoirs is only short, less than 2.8km, and therefore only two monitoring sites were established (Fig 7.3.). One immediately below the dam, and one 2.5km below this consequently, the detail of information collected was much less than that from the River Tryweryn.

As with the Tryweryn the river channel is used primarily as a conveyance method of water from one storage source to another, therefore its hydrology is dominated by the Water Authority's release strategy. However, unlike the Tryweryn the regularity of releases is much reduced, reservoir compensation flow is less, and the significance of tributary input is negligible resulting in low flow water chemistry simply reflecting inchannel processes. Investigation revealed that the degree of change associated with a release was determined primarily by hydrological conditions prior to the release e.g if the reservoir had been releasing only compensation discharge for the previous week, then change in the order of 100% occurred, but if the reservoir had been on overspill, then change if any associated with the release was insignificant.

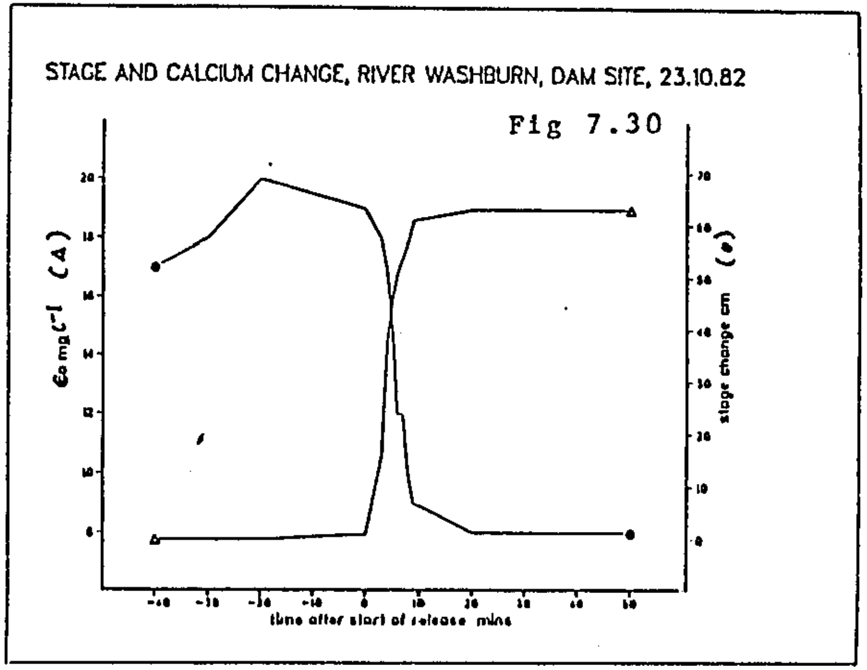
Maximum changes for conductivity, calcium, nitrate, chloride and pH were 64μS cm^{-1}, 12mg l^{-1}, 5mg l^{-1}, 1.3mg l^{-1} and 0.8 units respectively. Although these occurred at site 2, changes at site 1 were of a similar magnitude, therefore represent changes in the chemical nature of the reservoir release water as much as a dilution or concentrating effect of inchannel solutes. Such a response is more consistent with the literature of channel chemical response to discharge (2.3), than to the results from the River Tryweryn. However, the rate of change of solute concentration is rather similar to that on the Tryweryn. At site 1 - less than one hundred metres below the dam - change in ionic concentration almost perfectly mirrors stage change, this is particularly well illustrated by conductivity (e.g Fig 7.29) and calcium (e.g Fig 7.30), where even the stepped nature of the release is identifiable in the changing river water quality. Unlike chloride changes in the River Tryweryn, there is usually

FIG. 7.29 - 7.32 Water quality response at site 1 on the River Washburn prior to and during a 6.0m^{3}s^{-1} release. Each line is a series of 30 data points (section 4.2.3).



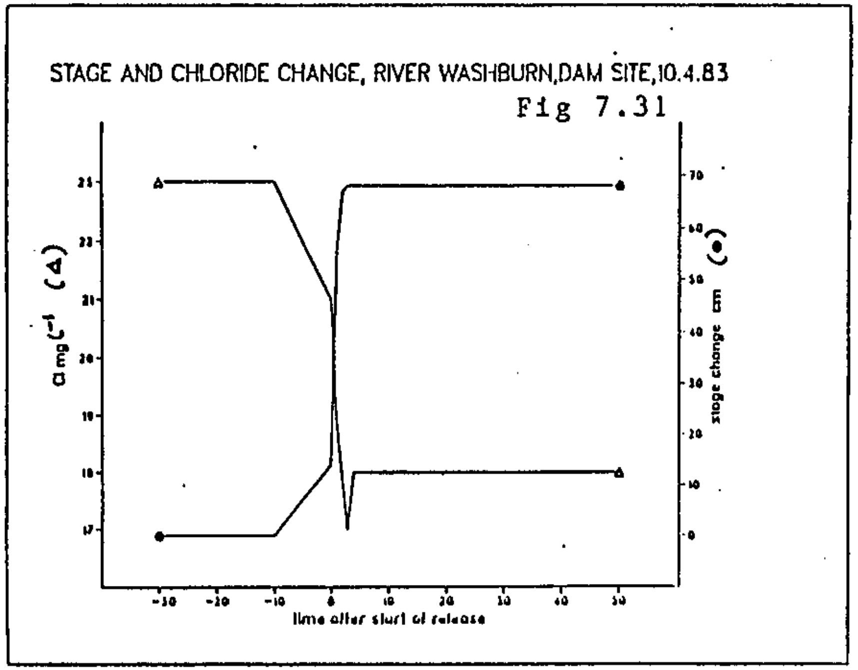
STAGE AND CONDUCTIVITY CHANGE, RIVER WASHBURN,DAM SITE, 9.4.83

Fig 7.29



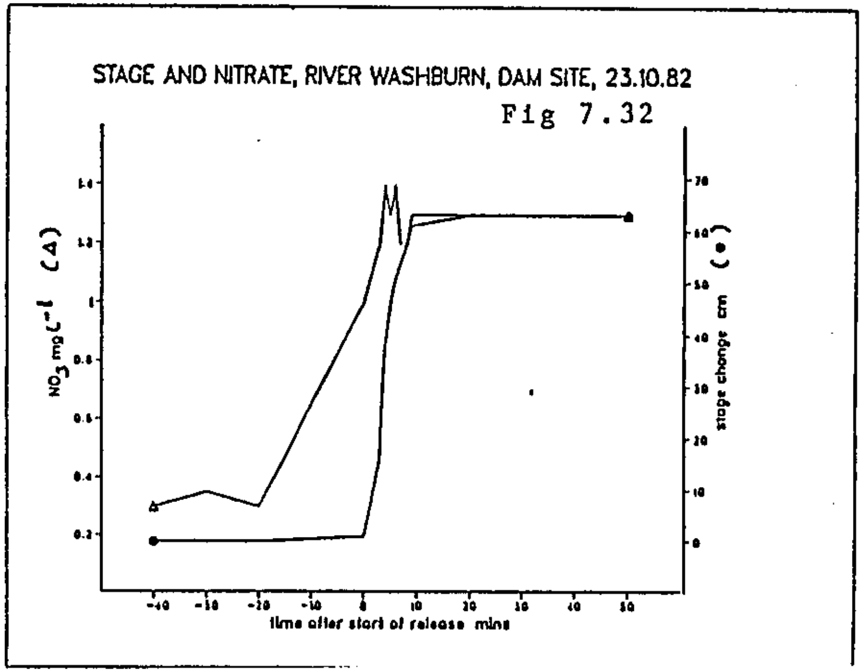
STAGE AND CALCIUM CHANGE, RIVER WASHBURN, DAM SITE, 23.10.82

Fig 7.30



STAGE AND CHLORIDE CHANGE, RIVER WASHBURN,DAM SITE,10.4.83

Fig 7.31



STAGE AND NITRATE, RIVER WASHBURN, DAM SITE, 23.10.82

Fig 7.32

a response on the Washburn (e.g Fig 7.31) and this too mirrors the changing stage. Nitrate levels actually are increased during a release (e.g Fig 7.32), interestingly the concentration begins to rise a few minutes before stage change, but reaches a maximum with peak stage. The fact that nitrate concentrations increase so much at a site so close to the reservoir indicates categorically, that unlike results from the the River Derwent and to a lesser extent the River Tryweryn, that chemical change within the channel is a result of the changing nature of the reservoir water more than a simple hydrological dilution effect.

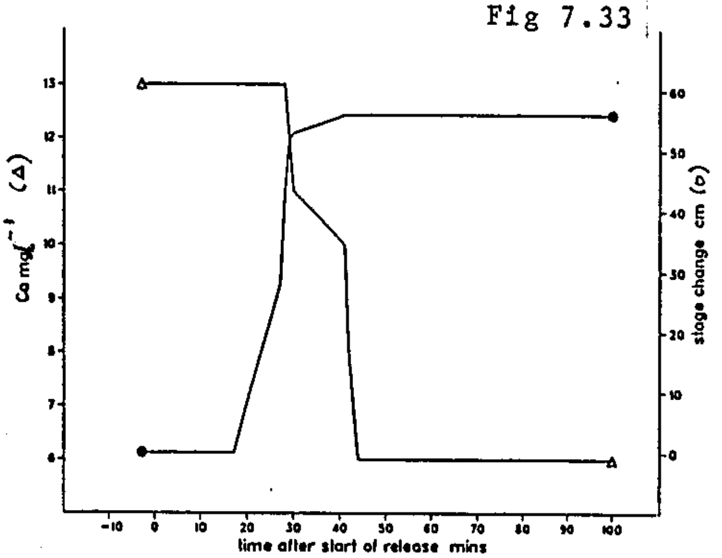
At site 2, solute variation reflects the release pattern, although there is a definite delay in response to initial stage change, often by as much as ten minutes - a similar magnitude of time lag to that presented by Johnson and Glover (1974) from work on releases made to the River Tyne. Calcium and chloride levels for example (Fig 7.33 and 7.34), although following the stepped nature of stage change, lag behind by some eight or nine minutes. Nitrate chemographs also indicate a clear lag, (e.g Fig 7.35), and a steady high value is reached about nine minutes after peak stage. Conductivity usually responds more rapidly to stage change (e.g Fig 7.36), although takes longer than other determinands to attain a steady minimum, a phenomenum that is also exhibited by pH (e.g Fig 7.37). The relatively steady values attained after the arrival of the release water are usually the same as those values reached at site 1, i.e reflect the chemical nature of the reservoir water. Unlike results from the Tryweryn, even at site 2 on the Washburn, there is little or no initial peak associated with the arrival of the release front.

7.4.4. Water Chemistry Changes associated with Releases on the River North Tyne. (Further data presented in Appendix F4)

The study reach length of the River North Tyne is a total distance of about 9km, with four monitoring sites, approximately 2.2km apart. This study reach also includes two substantial tributaries (Fig 7.4), and in these respects is similar in nature to the River Tryweryn. However, unlike the Tryweryn and the Washburn, the channel is not used as a regular routeway for large volume releases, compensation flow in comparison with the other rivers is somewhat higher. The release monitored was in reality a series of three independent releases and the effects of these on the river water chemistry was carefully measured. It

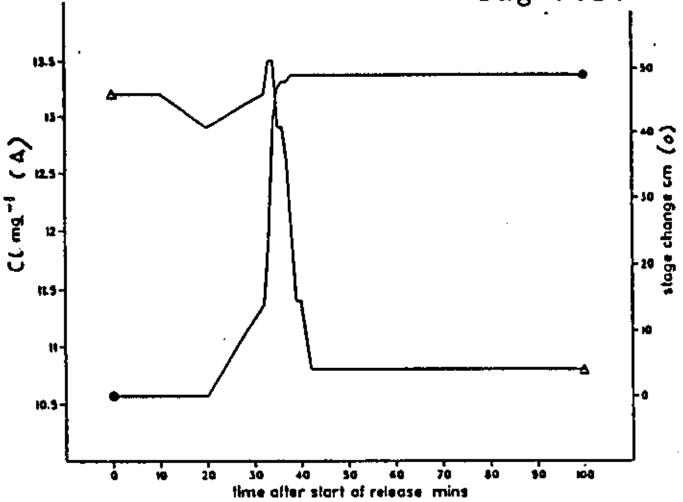
STAGE AND CALCIUM CHANGE,RIVER WASHBURN,SITE 2,10.4.83

Fig 7.33



STAGE AND CHLORIDE CHANGE, RIVER WASHBURN, SITE 2, 23.10.82

Fig 7.34



STAGE AND NITRATE CHANGE, RIVER WASHBURN, 10.4.83

Fig 7.35

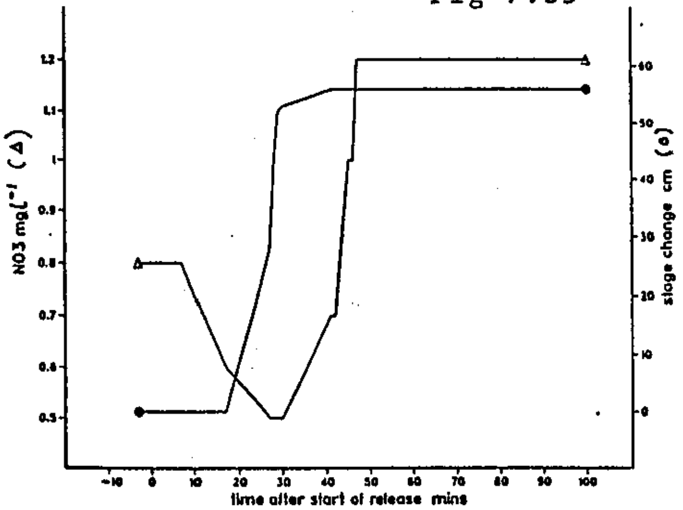
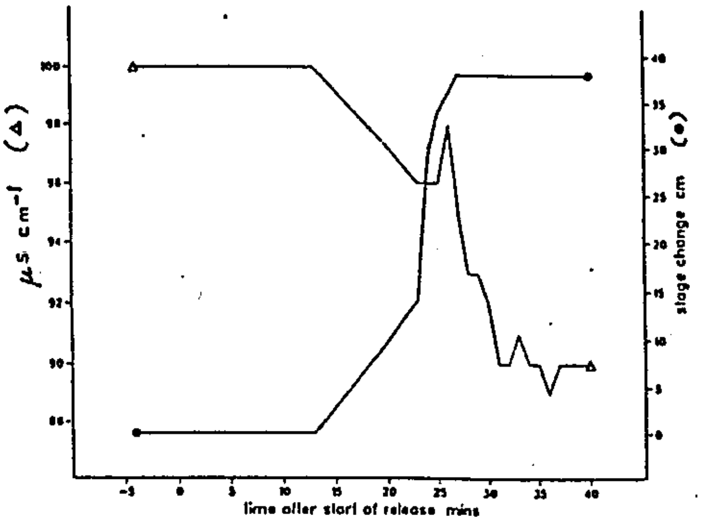
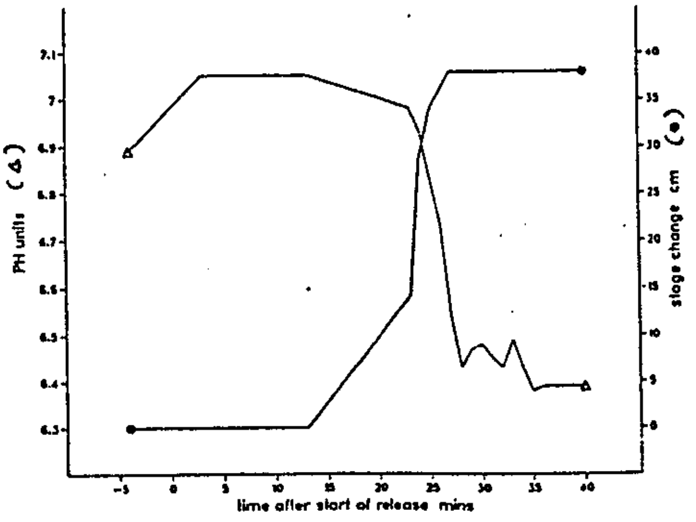


Fig 7.36

STAGE AND CONDUCTIVITY,RIVER WASHBURN SITE 2,5.11.83.



STAGE AND PH,RIVER WASHBURN, SITE 2, 5.11.83. Fig 7.37



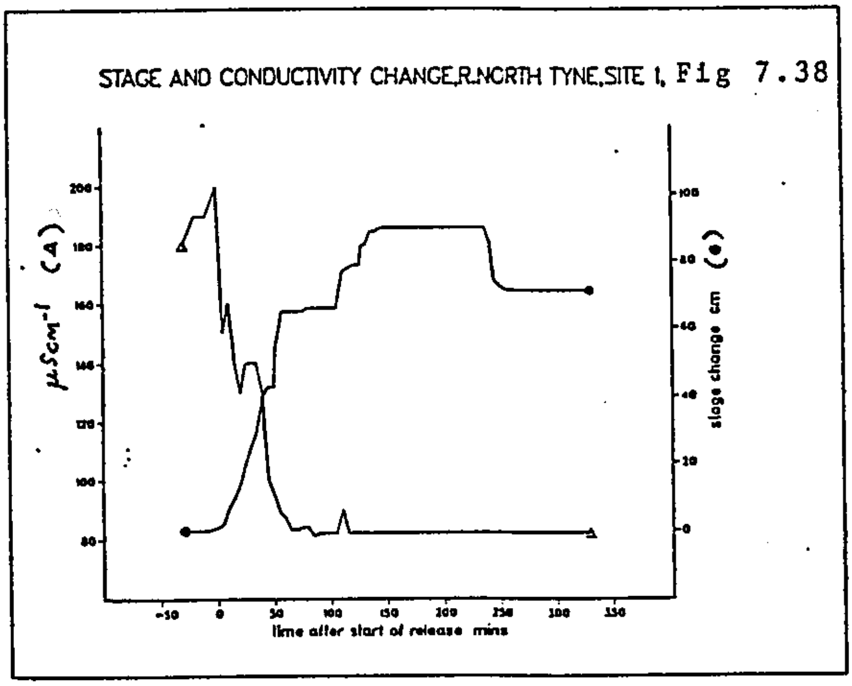
<u>FIG. 7.33 - 7.37</u> Water quality response at site 22 on the River Washburn prior to and during a 6.0m^{3}s^{-1} release. Each line is a series of 35 data points (see section 4.2.3).

is likely that because the release monitored was a unique event, its effects upon the river water chemistry would be perhaps more significant than the routine releases made on the Washburn and Tryweryn however, this did not appear to be the case.

In contrast with results from the River Tryweryn, River Washburn, and those presented by Hall (1977), maximum changes in river water chemistry occurred nearest the dam and declined to virtual insignificance at the downstream end of the study reach. Maximum changes in conductivity, calcium, nitrate and pH were 62 $\mu S\ cm^{-1}$, 2.3 $mg\ l^{-1}$, 0.2 $mg\ l^{-1}$ and 0.3 units respectively, neither chloride nor pH showed any response to the release. As on the Washburn, but not on the Tryweryn, nitrate levels rose with the increased discharge, indicating that chemical change was more as a result of the changing nature of the reservoir water and not in response to a hydrological change within the river.

At site 1, conductivity levels followed closely the stage change associated with the first release, and there was little evidence of any lag effect, although some flushing was apparent with minor peaks as concentration fell (e.g Fig 7.38). The second and third releases had no effect at all on the constant low conductivity. Virtually the same comments can be made for the response of calcium, although this determinand did show a lag to reach steady concentration after the arrival of the initial release front. Nitrate change also mirrored the first release, although unlike conductivity and calcium, values rose to a constant high. This high was attained approximately ten minutes after peak stage for the first release (e.g Fig 7.39), similar in magnitude to results presented by Beschta et al (1981) for the time lag of maximum sediment concentration with a release.

At site 2 as at site 1, marked chemical response was made only to the first release when both conductivity and calcium displayed a response very similar to that documented for the River Tryweryn, with an initial rapid peak in concentration coinciding with the arrival of the release front, followed by a rapid dilution to a constant low approximately fifteen minutes after the attainment of peak discharge (e.g Fig 7.40 and 7.41). Nitrate levels exhibited an interesting response (e.g Fig 7.42), with an initial peak as stage began to rise, followed by a sudden plunge in concentration and then another steady rise to attain a steady value a few minutes after the arrival of peak stage. This sudden fall might be the inverse equivalent of the flushes produced in the calcium and conductivity chemographs.


STAGE AND CONDUCTIVITY CHANGE,R.NORTH TYNE,SITE 1, Fig 7.38

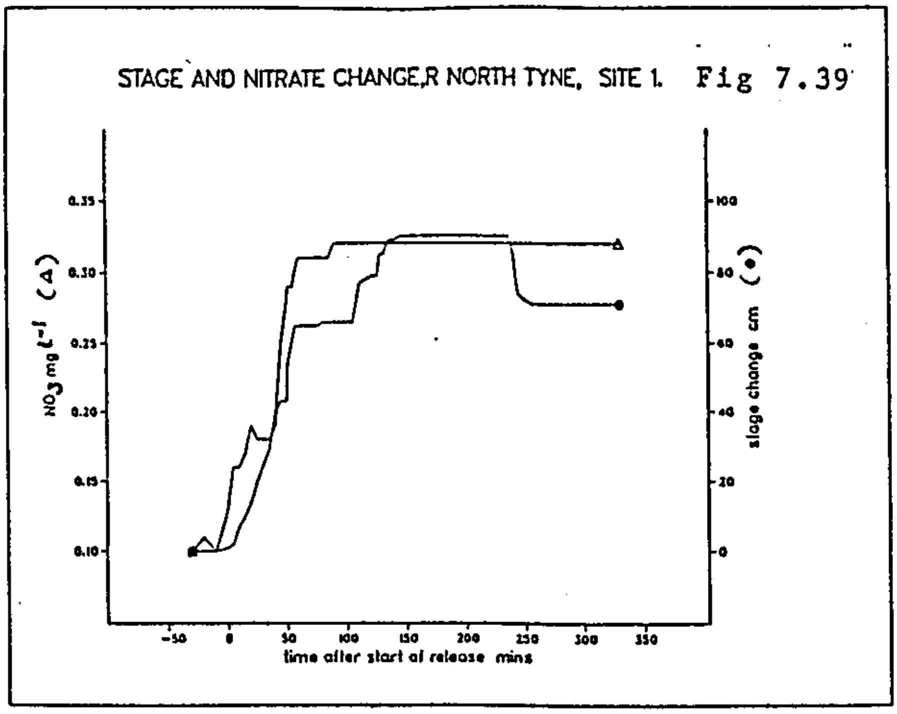
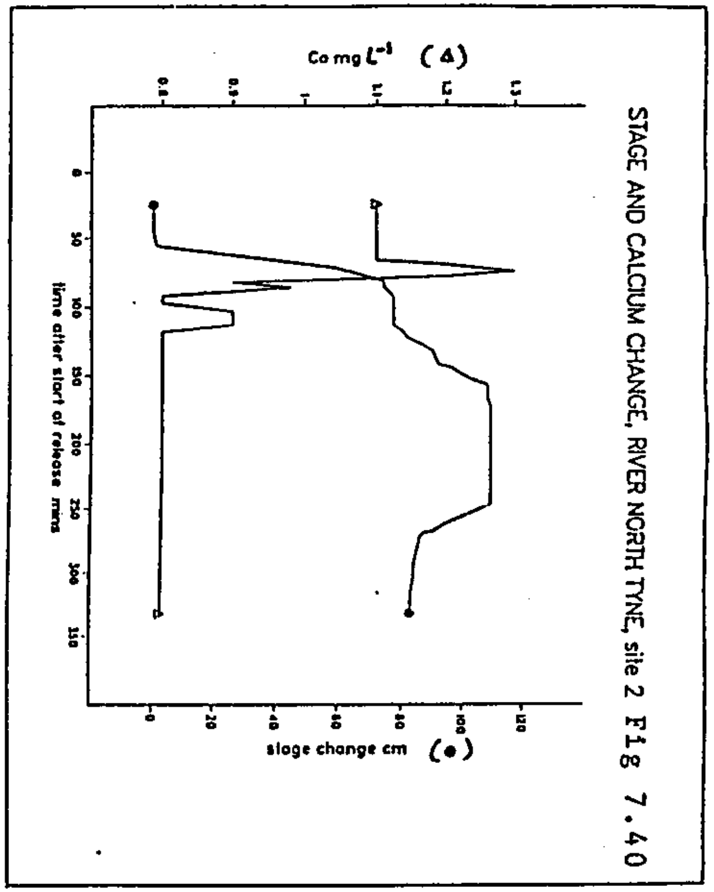
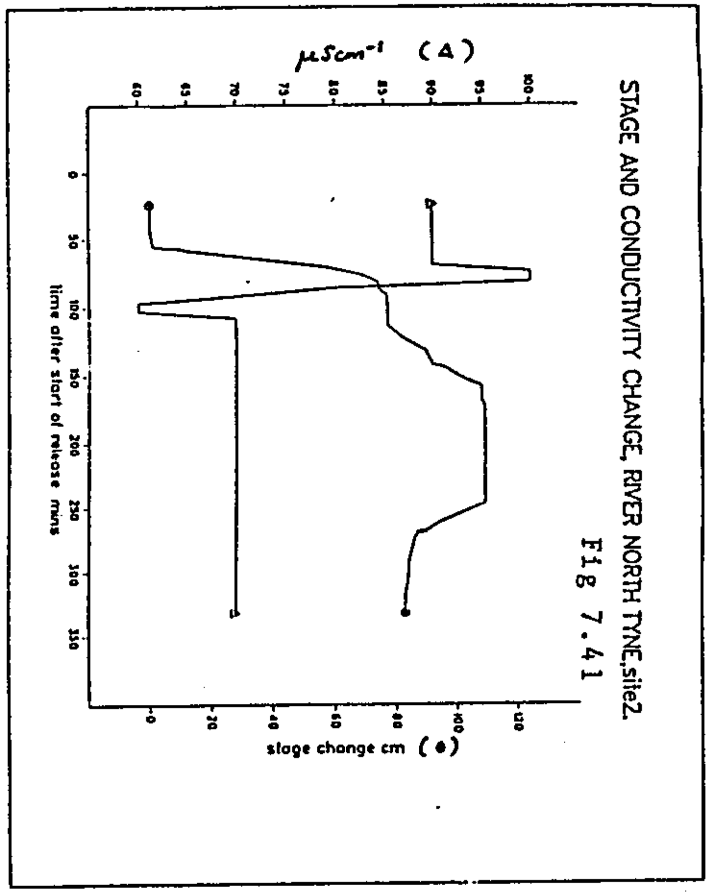

STAGE AND NITRATE CHANGE,R NORTH TYNE, SITE 1. Fig 7.39

FIG. 7.38 - 7.39 Water quality response at site 1 on the River North Tyne prior to and during a $50m^3s^{-1}$ release. Each line is a series of 110 data points (see section 4.2.3).


STAGE AND CALCIUM CHANGE, RIVER NORTH TYNE, site 2 Fig 7.40


STAGE AND CONDUCTIVITY CHANGE, RIVER NORTH TYNE,site2. Fig 7.41

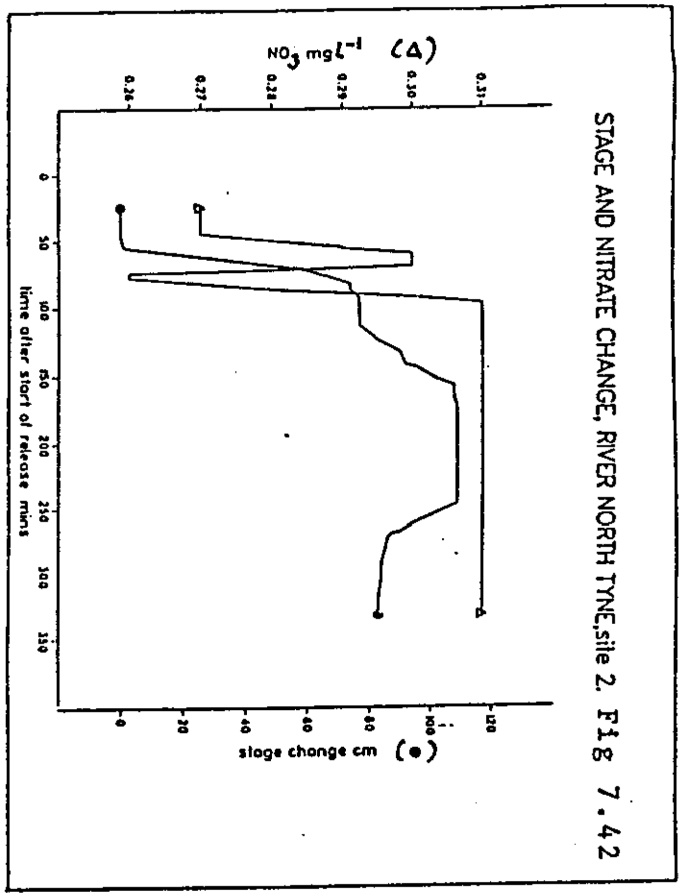

STAGE AND NITRATE CHANGE, RIVER NORTH TYNE,site 2. Fig 7.42

FIG. 7.40 - 7.42 Water quality response at site 2 on the River North Tyne, prior to and during $50m^3s^{-1}$ release. Each line is a series of 100 data points (see section 4.2.3).

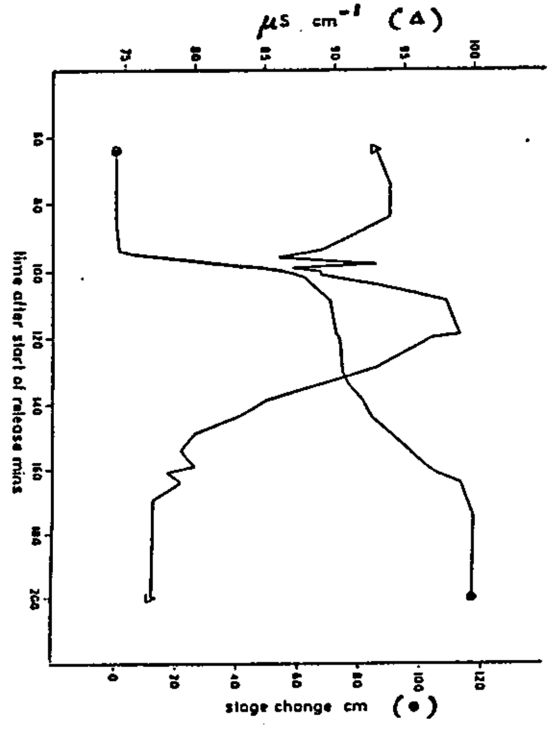
At site 3 the degree of change associated with the release was less than the above two sites, nevertheless similar patterns emerged, with any response associated only with the first release. Both calcium and conductivity displayed initial peaks and then erratic decline to a steady low, with nitrate responding in a similar manner, except by moving from low to higher concentrations (Figs 7.43-7.45).

At site 4, chemical change in response to the release was difficult to identify above natural changes in the water chemistry. However, for conductivity and nitrate at least, it was possible to recognize a response to stage change (e.g Fig 7.46 and 7.47), although the achievement of constant values lagged by some twenty five minutes after the first peak stage.

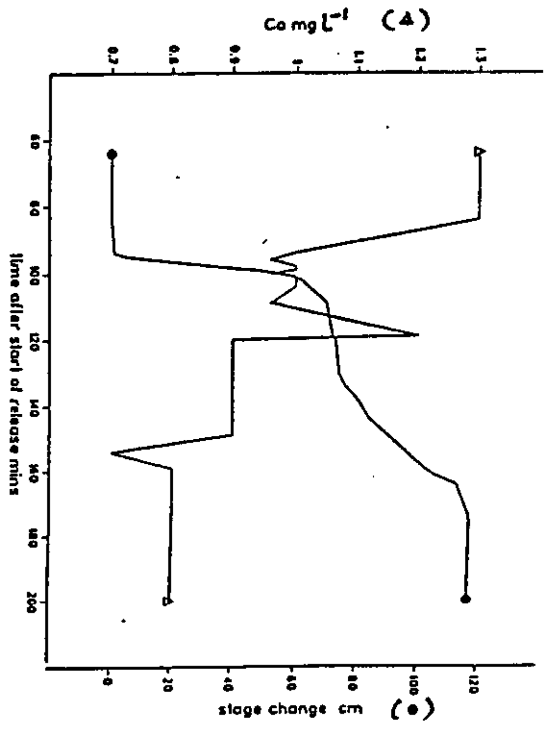
River water chemistry variations during the release monitored on the North Tyne reflect the changing nature of the reservoir water, coupled with a degree of disruption of this pattern, introduced by inchannel solute stores. This change in water chemistry over the background level, unlike the responses found on the River Tryweryn and River Washburn, decreased downstream even after the entry to the main river of two major tributaries. From the spatial survey, it was found that the solute nature of these tributaries was very similar to the nature of the North Tyne itself. Also, their discharge input is significant proportion of low flow. Therefore, it is likely that the increased discharge associated with the reservoir release was not sufficient, in comparison with the tributary input, to disturb solutes stored within the channel.

7.5. Comparison of variation between rivers.

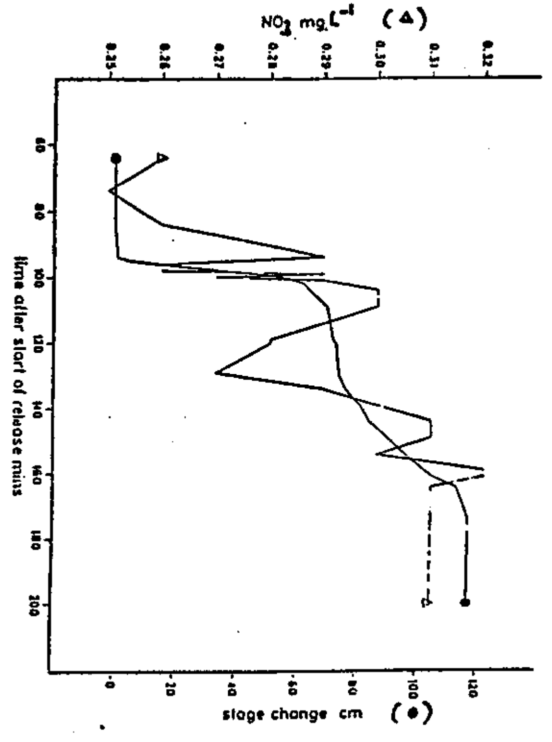
In order to compare chemistry changes during releases from the different rivers, it is useful to keep in mind the different study site dimensions which are given in Table 7.3
From these dimensions, it is clear that the River Washburn total study length for comparative purposes is equivalent to as far downstream as site 2 or 3 on the River Tryweryn and the River North Tyne. With this factor accounted for it is possible to find the following similarities between the effect of releases on background water quality between the three study rivers. (1) The extent of change during a release is largely governed by hydrological conditions prior to that release. Thus, a more significant chemical change occurred when a release was made after a period of low reservoir discharge than after a period of high reservoir discharge. (2) When chemical changes did occur,



STAGE AND CONDUCTIVITY CHANGE,R.NORTH TYNE,SITE 3. Fig 7.43



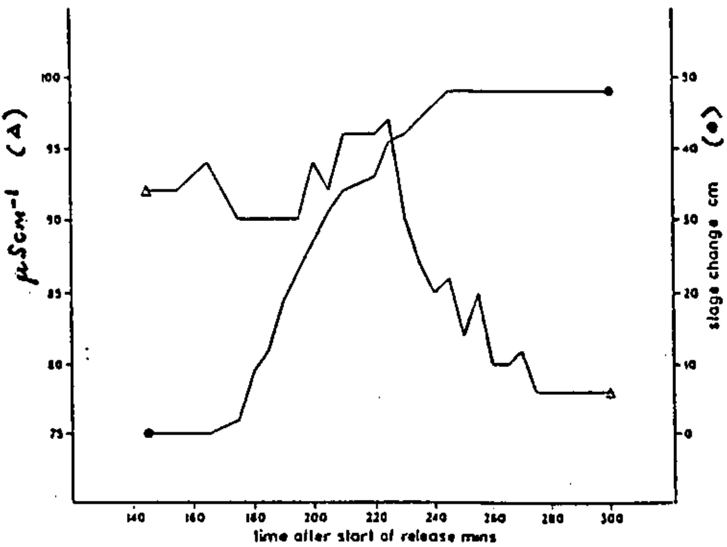
STAGE AND CALCIUM CHANGE,R.NORTH TYNE, SITE 3. Fig 7.44



STAGE AND NITRATE CHANGE,R.NORTH TYNE, SITE 3. Fig 7.45

FIG. 7.43 - 7.45 Water quality response at site 3 on the River North Tyne prior to and during $50m^3s^{-1}$ release. Each line is a series of 50 data points (see section 4.2.3).

STAGE AND CONDUCTIVITY CHANGE, R.NORTH TYNE, SITE 4. Fig 7.46



STAGE AND NITRATE CHANGE,R NORTH TYNE, SITE 4. Fig 7.47

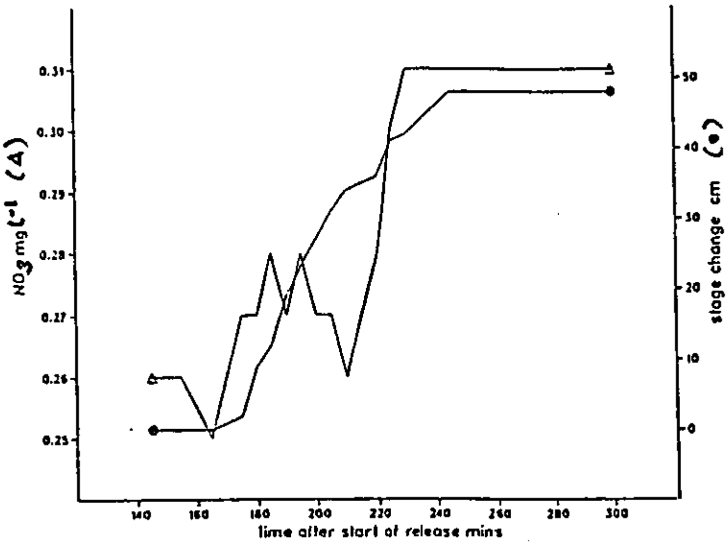


FIG. 7.46 - 7.47 Water quality response at site 4 on the River North Tyne prior to and during a $50m^3s^{-1}$ release. Each line is a series of 50 data points (see section 4.2.3).

	TRYWERYN	WASHBURN	N TYNE
Study length (km)	8	2.5	9
Distance between sites (km)	2	2.5	2.2
No. of sites	5	2	4
Max water travel time (mins)	130	32	110
Max stage change (cm)	80	70	120
Max study width (m)	28	15	45
Average low flow Q (m^3s^{-1})	0.8	0.1	4.5
No of major tribs in the reach	2	0	2

TABLE 7.3. Dimension of Study Rivers.

it was possible to relate these to the arrival of the release front. Moreover, the actual rate of change of water chemistries was similar between rivers, primarily because the releases' wave shapes were similar. (3) The attainment of a relatively steady maximum/minimum concentration was reached in all rivers after the peaking of stage. On the Washburn and the North Tyne this lag value related to the chemistry of the reservoir water, whereas on the Tryweryn the steady rate was a compromise between reservoir and catchment water sources.

Differences in the response to the releases on each river were also noticeable. Fundamentally, it appeared that the chemical nature of Celyn release water remained fairly constant from compensation to release water chemistry, whereas Thruscross and Kielder water release chemistry usually varied considerably from the chemical nature of the compensation flows. This led to the hydrologically dominated response on the River Tryweryn, and the chemically dominated response of the Rivers Washburn and North Tyne, being reflected in the fact that water chemistry change during a release increased with the distance from the reservoir for the Tryweryn, and yet the reverse was the case for the Rivers North Tyne, and Washburn, with change decreasing downstream from the dam.

The River Washburn gave little or no evidence of flushing processes, although this is to be explained by the short travel distance of the release, whereas both the Tryweryn and the North Tyne displayed significant peaks in solute load as stage began to rise. Furthermore, these peaks coincided almost directly with change in stage, unlike the somewhat lagged response on the Washburn. This time-lag was manifested on all rivers by the attainment of steady maximum dilution, and increased with distance from the reservoir. It was most noticeable on the River Tryweryn giving time lags of minimum concentration and maximum stage, of upto more than forty minutes.

In terms of the degree of change associated with different releases, maximum change occurred for all chemistries on the River Washburn - which has the highest background ionic levels of the three rivers. Thus the maximum change of conductivity was found immediately below the dam on the River Washburn, with a change of 70μS cm^{-1}, comparing with maximum changes of 62μS cm^{-1} and 38μS cm^{-1} on the Rivers North Tyne and Tryweryn respectively. Maximum change for calcium was also found immediately below the dam on the River Washburn, with a value of 12 mg l^{-1}, comparing with 4.5 mg l^{-1} on the Tryweryn and a mere 2.3 mg l^{-1} on the North

Tyne. Nitrate change however, was at a maximum on the Tryweryn with a variation of 1.40 mg l^{-1} at the site furthest away from the reservoir, this compared with maximum changes of 0.8 mg l^{-1} on the North Tyne and 1.3 mg l^{-1} on the Washburn. pH changed to any significant extent only on the Tryweryn and chloride on all rivers usually did not respond consistently to a change in discharge.

7.6 Chapter summary.

Water chemistry in each of the study rivers responded to artificial regulation of flow, with patterns of change virtually making a mirror image of the way in which stage changed. On the Rivers Washburn and North Tyne, this change was probably due to a changing chemical nature in release to compensation discharge and thus the effect was reduced with distance from the outlet. However, on the Tryweryn compensation and release water have a similar quality and changes in chemistry are brought about by the dilution of river solutes, thus as the concentration of these increase with increased catchment input, the effect of the release on channel water chemistry therefore, became more marked the further the distance from the dam. The next chapter seeks to explain the factors that lead to a changing response in water chemistry during a release.

CHAPTER 8.

FACTORS AFFECTING WATER QUALITY CHANGES DURING FLOW FLUCTUATIONS.

The significance of reservoirs on downstream water chemistry has been shown to be either of real chemical dominance, or of hydrological importance. Within this general framework several considerations must be discussed. These are the size of release in comparison with baseflow; the rate of rise of the release; the timing of the release in relation to previous large volume reservoir discharges; and the natural chemical state of the receiving river (which is affected by the distance downstream). In short, the significance of a reservoir release on downstream water chemistry is dependent on the difference between the chemistry of the two systems. The greater the difference, the more significant the release in terms of disturbing river water quality.

8.1. Factors influencing chemograph form during releases.

The factors affecting the main channel chemograph on regulated rivers - as outlined above - have not been considered in the literature, and yet clearly they are significant. The degree of importance of each factor, is now examined.

8.1.1. Size of release.

The size of the release is obviously important to the river chemograph, particularly if the receiving water is of markedly different water chemistry to that of the reservoir. The release volume will determine the rate of change of chemistry at-a-station, by a process of longitudinal turbulent mixing at the wave front (Thomann, 1973; Belatos, 1980; and Young and Beer, 1980), as well as determining the downstream significance of a release. A small volume of release water will be rapidly mixed into the existing stream water and any diluting or chemical change effects virtually obscured. However, a large volume of reservoir water will either totally remove existing streamwater by 'pushing' it ahead of the bore (Hem, 1970), or at least become dominant during the release. If the amount of natural streamwater increases substantially downstream, then of course, the reservoir water itself becomes increasingly less significant in determining the nature of the stream water, as was the case for releases on the River North Tyne, where for example, conductivity was reduced by a maximum of 62 μS cm^{-1}at site 1, 20 μS cm^{-1}at site 2, 16 μS cm^{-1}at site 3, and 14 μS cm^{-1}at site 4, whilst low flow discharge rose downstream by about 300%.

8.1.2. Rate of Rise of the Release.

From the monitoring of releases on the Tryweryn, it was found that, except for site 1, the faster the rate of stage rise at-a-station, the shorter was the time taken to reach maximum dilution at that station. Table 8.1 illustrates this for conductivity, although it is true of all the parameters analysed. At site 1, the slowest rate of stage change was 0.67 cm min^{-1}, this gave the longest time to the maximum dilution of conductivity of 42 minutes, in comparison, the fastest rate of stage change, 1.47 cm min^{-1}which gave a shorter (but not the shortest), time to maximum dilution of 30 mins. The shortest time to maximum dilution, was when the rate of stage rise was between 1.2 and 1.3 cm min^{-1}. At all the other sites downstream, maximum rate of stage change, does correspond the the shortest time to maximum dilution. This phenomenom is to be logically expected. The rapid stage change causes inchannel solutes to be quickly mixed into the main body of release water, and the rapid volume change obscures minor mixing processes occurring within the channel. At site 1, a stage change more rapid than 1.2 cm min^{-1}, but less than about 1.3 cm min^{-1}, follows this explanation. However, when the rate of stage change is greater than this, the disturbance of inchannel solutes, is enough to obscure the diluting effect of increased discharge. Thus, in terms of significant chemical change within the river, it is not so much the size of release that is important, but rather the rate of rise at-a-station.

This factor is often demonstrated by the response of calcium to stage change. On the River Washburn at the lowest site, during the release of the 5.11.83, the instantaneous nature of the release is somewhat obscured, and in fact a three-fold stepped appearance of stage change is recorded. If the background fluctuations in the calcium ion are ignored, then the first two steps at least, of the three-fold stage change, are reflected in the response of calcium levels (Fig.8.1). On the River Tryweryn at site 1 (about 0.25km below the outfall) the stepped nature of the release is apparent in the response of the calcium ion (Fig. 8.2). Significantly the major response in

Date of release	stage change (cm)	time to max dilution of conductivity (mins)	rate of stage change (cm min^{-1})
SITE 1			
5. 6.83	34	28	1.21
4.6.83	34	28	1.21
24.4.83	37	35	1.03
23.4.83	36	32	1.64
25.10.82	44	30	1.47
5.9.82	38	29	1.27
4.9.82	39	28	1.30
16.5.82	50	34	1.67
15.5.82	20	42	0.67
30.1.84	38	-	1.23
31.1.84	39	-	1.15
1.2.84	39	-	1.56
5.2.84	33	-	1.38
SITE 2			
24.4.83	69	28	2.76
23.4.83	66	26	4.40
25.10.82	79	21	6.08
SITE 3			
5.6.83	51	30	2.83
4.6.83	53	28	3.31
SITE 4			
5.6.83	36	25	4.50
4.6.83	31	30	3.44
24.4.83	30	52	2.72
23.4.83	23	43	3.29
30.1.84	26	-	2.88
31.1.84	29	-	4.14
1.2.84	30	-	4.29
3.284	30	-	-
5.2.84	28	-	4.00
SITE 5			
24.4.83	39	56	5.57
23.4.83	32	58	4.00
25.10.82	44	42	7.33
5.9.82	45	56	5.00
4.9.82	47	90	2.24
16.5.82	42	52	5.25
15.5.82	19	87	2.34
SITE 6			
24.4.83	29	71	1.04
23.4.83	25	70	1.19
25.10.82	30	65	1.67
5.9.82	38	69	1.46
4.9.82	39	100	0.87
16.5.82	32	54	2.00
15.5.82	18	102	0.75
30.1.84	25	-	1.56
31.1.84	28	-	1.40
1.2.84	29	-	1.61
2.2.84	27	-	1.59
3.2.84	28	-	1.27
5.2.84	28	-	1.56

TABLE 8.1. Stage change and rate of stage change for releases on the River Tryweryn.

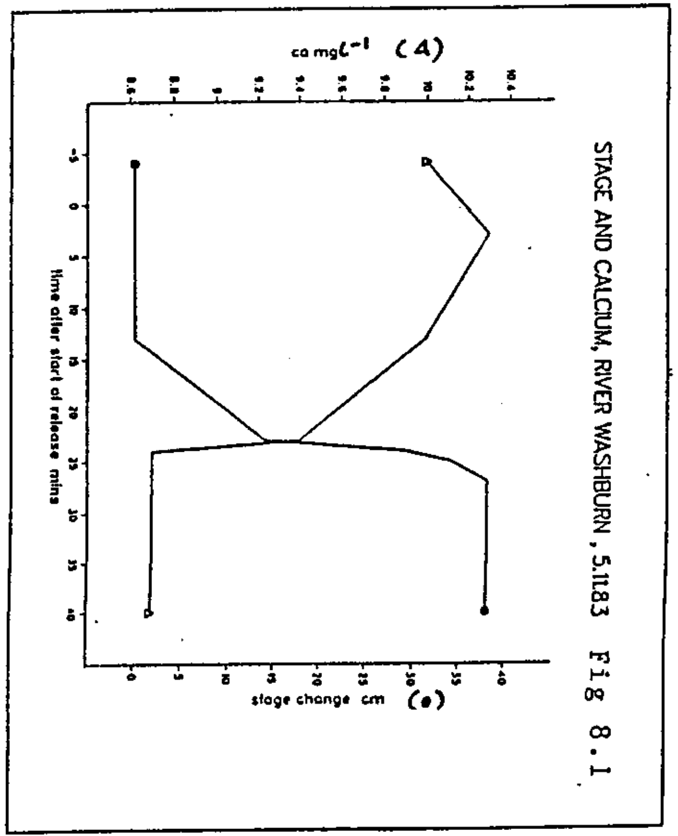


Fig 8.1

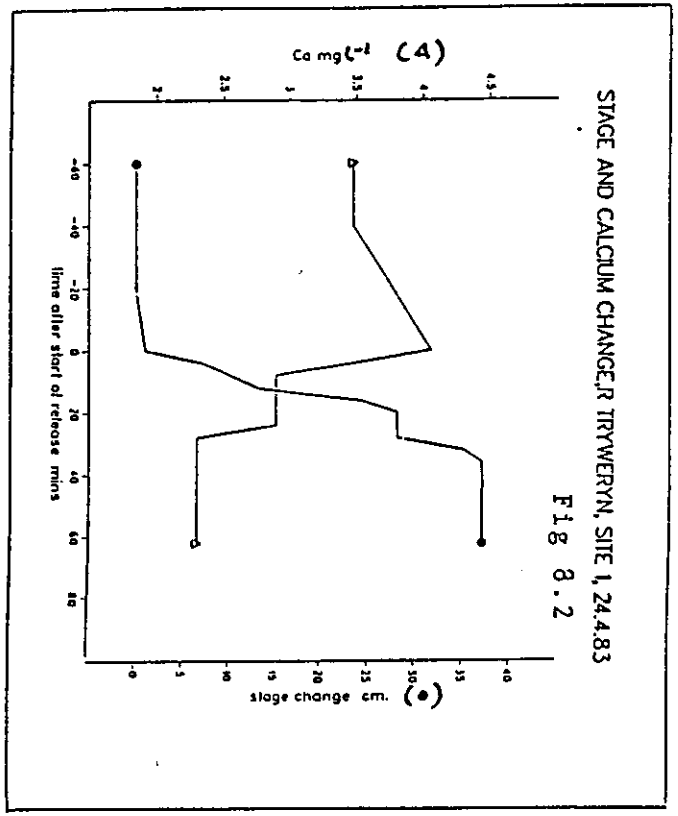


Fig 8.2

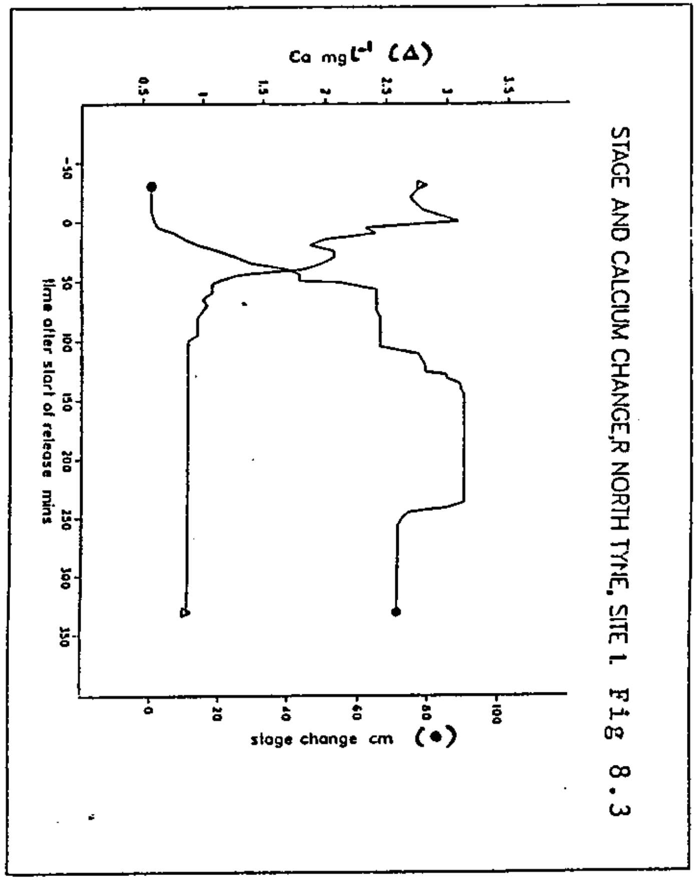


Fig 8.3

FIG. 8.1 - 8.3 Comparison of calcium response prior to and during releases (see section 7.1) on all three study rivers. Each line is a series of between 30-110 data points (see section 4.2.3).

calcium levels is on the initial step in discharge. This is to be expected because the 'pure' river water is being drowned out by reservoir water. However, on step two of the release the channel contains water that is a mixture of river and reservoir water, therefore the domination of the chemical nature of the channel water by the reservoir is less marked. For the River North Tyne at site 1 (about 0.5km below the outfall) again the stepped nature of the release is clear, however in this instance calcium change does not follow stage change (Fig.8.3). This is because the first step of the release, to a stage change of 70 cm, is sufficient to create complete mixing and maximum dilution within the channel (maximum dilution being the uninfluenced concentration of reservoir release water). So in this example, whatever the size of the release above a stage change of 70 cm, there will be little effect upon the calcium concentration within the river, and what has been found to be more important than size of release upon calcium levels is the rate of stage change upto this 'saturation' point.

8.1.3. Chemistry of Receiving Water.

In most instances during this study the chemical nature of the release water was less concentrated in cations than the receiving streamwater on the Tryweryn, this was true also for anions - nitrate in particular - however for the other two study rivers, nitrate values were greater in the reservoir than the river water. The reasons for these differences between release water and river water are basically twofold. Firstly, that the chemical nature of the actual release water is different from the chemical nature of the reservoir compensation flow, presumably due to a difference of reservoir depth from which the release water is being drawn. Such is the case for Kielder Water, where the large volume release was actually made from the basal scour valve. This is also true of Thrusscross reservoir, where large volume releases take water from throughout the water profile, and are therefore subject to the effects of thermal stratification upon water chemistry, as described earlier. However, releases into the River Tryweryn whatever the size are made from the best quality surface water, thus release water and compensation water have a very similar chemical nature.

Secondly, the chemical nature of tributary inflow is different from that of the release water. This is the case on the River Tryweryn, where releases create an increasing dilution effect downstream. On the River North Tyne however, where input from tributaries alters the water chemistry of the main channel marginally (tributary catchment geology is similar to that of the reservoir catchment) the effect of large volume releases diminish very rapidly downstream, due to the increasing percentage dominance of tributary to reservoir water. On the River Washburn major tributary input is insignificant in terms of discharge although minor inputs can alter river water chemistry if compensation flow is low enough to create a series of almost stagnant ponds within the channel.

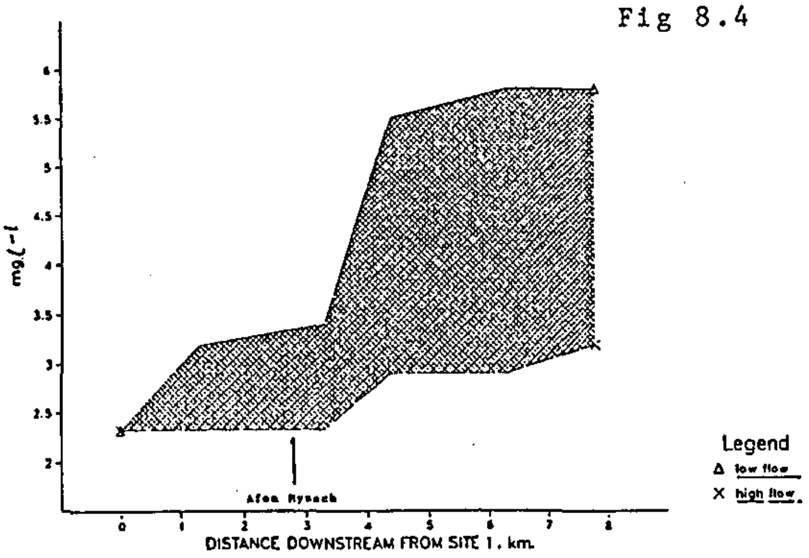
Data from the River Tryweryn illustrate the importance of the chemical nature of the receiving water in comparison with that of the reservoir water. Fig.8.4 shows that at low flow downstream calcium concentration rises, therefore increasingly the chemical nature of the river water is different from the release water, thus the further downstream the release moves the greater its impact. Just below the outfall there is no calcium change during the release, at 4.5km there is a change of about 2.5 mg l^{-1}, and at 8km there is a reduction of about 3.2 mg l^{-1}. A similar pattern is portrayed by nitrate (Fig.8.5), where change at the dam is in the order of 0.05 mg l^{-1} and yet at 8km is about 0.5 mg l^{-1}. It is interesting that the downstream pattern of change at high flow tends to exaggerate the low flow pattern, suggesting that new sources of inchannel nitrate are tapped by the higher discharges.

8.1.4. Distance Downstream.

Results already presented have shown that the effects of a release on water chemistry of the River North Tyne, decrease downstream, whereas on the River Tryweryn the reverse is the case, with the changes actually increasing with the distance from the reservoir (e.g Fig.8.4 and 8.5). This has been accounted for by the fact that the ionic concentration of low flow water downstream is gradually increased by solutes from tributary sources and during a release these solutes are diluted towards the level of the release water. As already mentioned with reference to the nitrate pattern of change downstream, it is interesting that even at high flow, the similar pattern of concentration change, as manifested at low flow, is identifiable: this is also true for other ions, e.g conductivity (Fig.8.6). This underlines the importance of tributary input to the chemical nature of the Tryweryn and that even when the discharge from these sources is negligible in comparison with the discharge in the main channel, their chemical influence is not completely washed out.

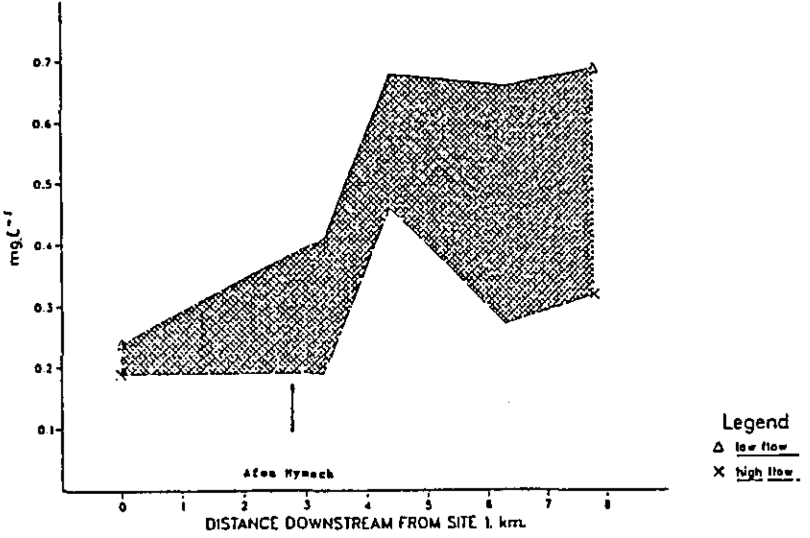
CALCIUM CHANGE DOWNSTREAM . LOW AND HIGH FLOW 23.4.83

Fig 8.4



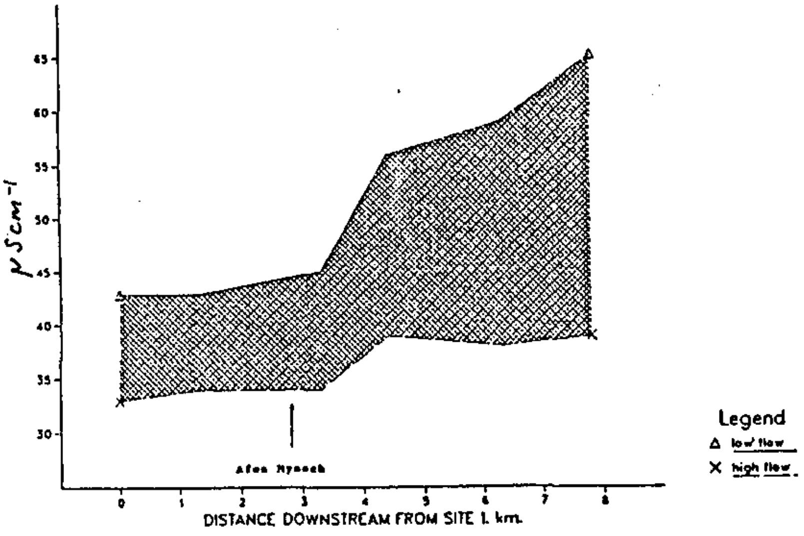
NITRATE CHANGE DOWNSTREAM LOW AND HIGH FLOW 25.10.82

Fig 8.5



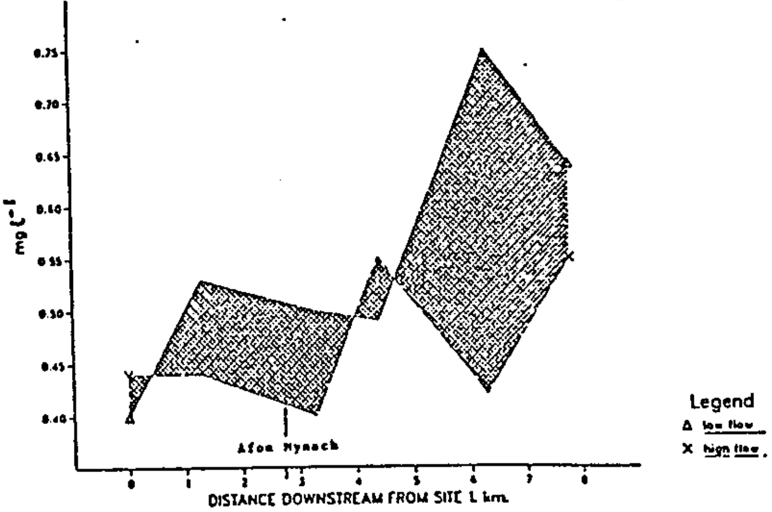
CHANGE IN CONDUCTIVITY DOWNSTREAM. LOW AND HIGH FLOW 25.10.82

Fig 8.6



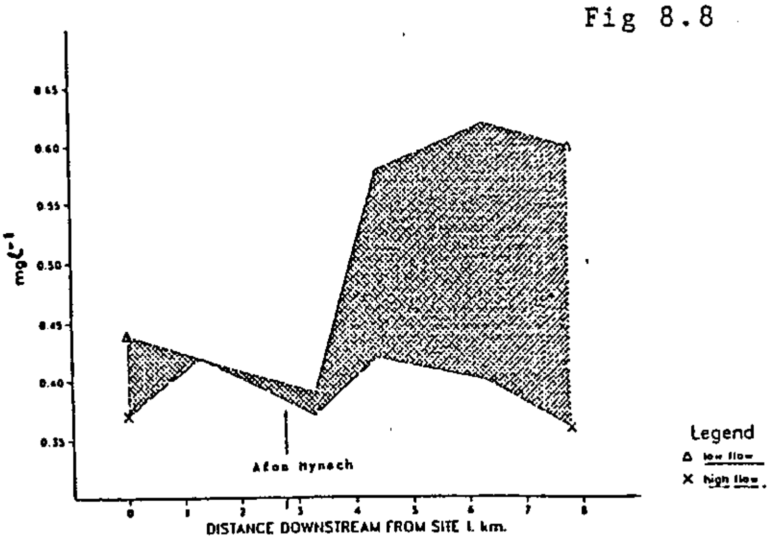
NITRATE CHANGE DOWNSTREAM LOW AND HIGH FLOW 23.4.83

Fig 8.7



NITRATE CHANGE DOWNSTREAM . LOW AND HIGH FLOW 24.4.83.

Fig 8.8



<u>FIG. 8.4 - 8.8</u> Examples of high flow (release of $12.252m^3s^{-1}$) and low flow (compensation flow) solute values on the River Tryweryn (site sampling locations see Fig.7.2)

8.1.5. Timing of Release after Previous Releases.

Unfortunately records of releases are not easily obtainable for the River Tryweryn, or for that matter the Rivers Washburn and North Tyne, so it is difficult to ascertain the exact significance of the time between the releases upon the chemical change within the river that occurs during a release. Fortunately, often releases studied were on consecutive days, and gave some information on the importance of timing. Results from the River Tryweryn on the 23rd and 24th April 1983 serve as illustrations of this important concept.

Nitrate values on the 23.4.83,(Fig.8.7) vary from about 0.4mg l^{-1}at the dam during the height of a release, to about 0.75 mg l^{-1}at site 5 during low flow. The pattern of change downstream both at low and high flow is complex and as already shown demonstrates the importance of tributary inputs to nitrate values within the main flow. On the 24.4.83, after twelve hours of full volume release the previous day and twelve hours of compensation discharge, the range of nitrate values within the study reach is still surprisingly high, with a range of 0.35 to 0.60 mg l^{-1}(Fig.8.8). Above the input of the first tributary on the study reach, namely the Afon Mynach, situated at approximately three kilometres below site 1, on day two of the release there is virtually no change in nitrate values between low and high flow, whereas on day 1, there is a dilution of some 0.15 mg l^{-1} which is about 40% of high flow nitrate values. Suggesting that all inchannel supplies of nitrate above the tributary, have been washed out during the previous days release. However, below this junction the variation between low and high flow nitrate concentrations on day 2, is almost as high as on day 1. This demonstrates the importance of tributary inputs in determining the river channel water chemistry, and it also shows the speed of response of the system back to a pre release equilibrium.

These results show that it is not so much the time between releases that is important when attempting to explain the change in water chemistry with a release, but rather the difference between release water and tributary water chemistry, and then the time between catchment floods, which tend to exaggerate this variation.

8.1.6. The Hysteretic Response of Channel Chemistry to Releases.

The response of water chemistry to varying discharge in natural channels, has attracted much study (see Chapter 1), and usually à delay in the production of change by the discharge fluctuation has been documented. This has resulted in different levels of concentration for equivalent discharges, on the rising and falling limbs of the hydrograph. Therefore, as such there is no direct link between channel discharge and water chemistry. Changes have been associated to the varying chemical nature of the input to main channel flow. For a reservoir release, the water quality of the input is constant, and therefore, if hysteresis is due only to the changing nature of such input, then no such pattern should be found when monitoring water chemistry change at-a-station. To test this theory a record was made of the complete cycle of calcium change during a release on the River Tryweryn at sites 5 and 6 (furthest downstream), and sampling was executed at a the same high intensity (every 20 mins) throughout the release rise and fall: the results of this experiment are presented in Fig.8.9. It is extremely interesting to note the presence of an anti-clockwise hysteretical loop described by the data. Large scale catchment floods have been shown to produce a similar response in the main channel water chemistry (e.g Hendrickson and Krieger, 1964; Toler, 1965; Johnson and East, 1982). Such patterns have usually been ascribed to the different availabilities of chemicals from varying catchment sources, and the exact character (clockwise or anticlockwise) of the cycle due to variations in the quantity of flow from these various geochemically distinct zones (see Chapter 1). In the case of a release made into a single channel there is no distinct change in the dominance of varying hydrological pathways with their own distinctive chemical nature.

There are simply three factors to explain the nature of chemical hysteresis during reservoir releases: i) the chemical nature of the release water ii) the chemical nature of the tributary flow and iii) the inchannel chemical response to the release. From Fig 8.9 a&b it is clear that during the falling limb of the release, the calcium concentration of the river is adjusting back toward a level similar to that recorded prior to the release, illustrating the strong influence of tributary inputs. The fact that calcium is actually increasing in concentration on the rising limb, is attributable to the flushing of inchannel sources - a factor not considered to be of importance in the catchment flood production of a chemical hysteresis within the main channel. Relatively steady calcium values at the peak of the looped response correspond to the nature of the release water itself. Thus on each of the three

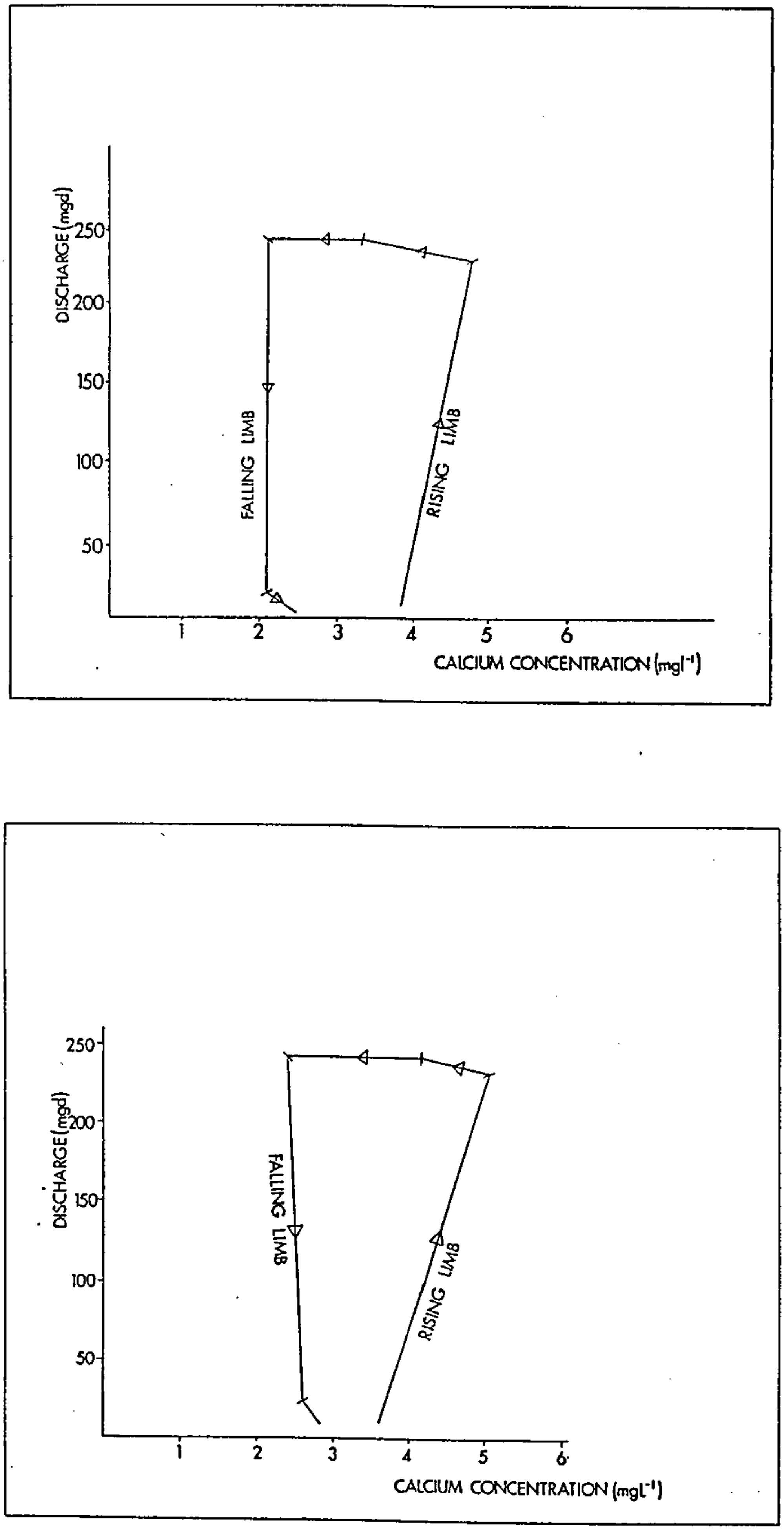


FIG. 8.9 Calcium concentration variation with discharge on the River Tryweryn during the complete cycle (24 hours) of a $12.252 m^3 s^{-1}$ release: site 6 (a) and site 5 (b). Samples collected every 20 mins. (n = 200).

parts of the hydrograph different processes are dominant; inchannel flushing on the rising limb; the chemical nature of the reservoir water during the established release; and the chemical nature of the tributary inflows during the recessional limb. Due to these three factors a hysteretic loop is produced in the response of channel calcium concentrations to releases at sites 5 and 6 on the Tryweryn.

8.2. Water quality variation with the arrival of a release wave.

The response of the natural river chemistry to the arrival of a release wave has been shown to be dependent upon a number of inter-related factors, which basically results in the simple dilution of inchannel water - a function of tributary inputs, and of balance between pre-release discharge and release discharge. However, more often than not although the basic results are predictable, the response timing to a release is of a nature as presented in Fig.8.10.

Initially there is a distinct increase in chemistry concentration, followed by a period of stable high values, despite an increase in discharge. Shortly after maximum stage is attained concentration begins to fall steadily to a minimum value some time after peak stage. Constant chemistry with values similar to that of reservoir water are then observed. This pattern is not the expected response. Theoretically, during a release the rate of change of water chemistry at-a-station is dependent upon the chemical nature of the release water and the rate of its arrival at that station. If the reservoir water is more dilute with respect to the given substance (as is the case with all determinands except nitrate), then dilution will occur. However, the data collected during this study reveals two deviations away from this expected response: firstly a peak in concentration, and secondly a time lag in dilution. The explanations for these phenomena are to be found in i.) the mechanical effects of the water release ii.) inchannel solute storage and iii.) the wave/water dynamics. Each of these factors demonstrates the complexities involved when attempting to link solute and water dynamics, and are now considered in turn.

8.2.1. The mechanical effects of water releases.

It has been suggested, notably by Hem (1970), that as a flood wave moves down a channel, it 'pushes' concentrated river water ahead of it, creating an ever increasingly concentrated initial

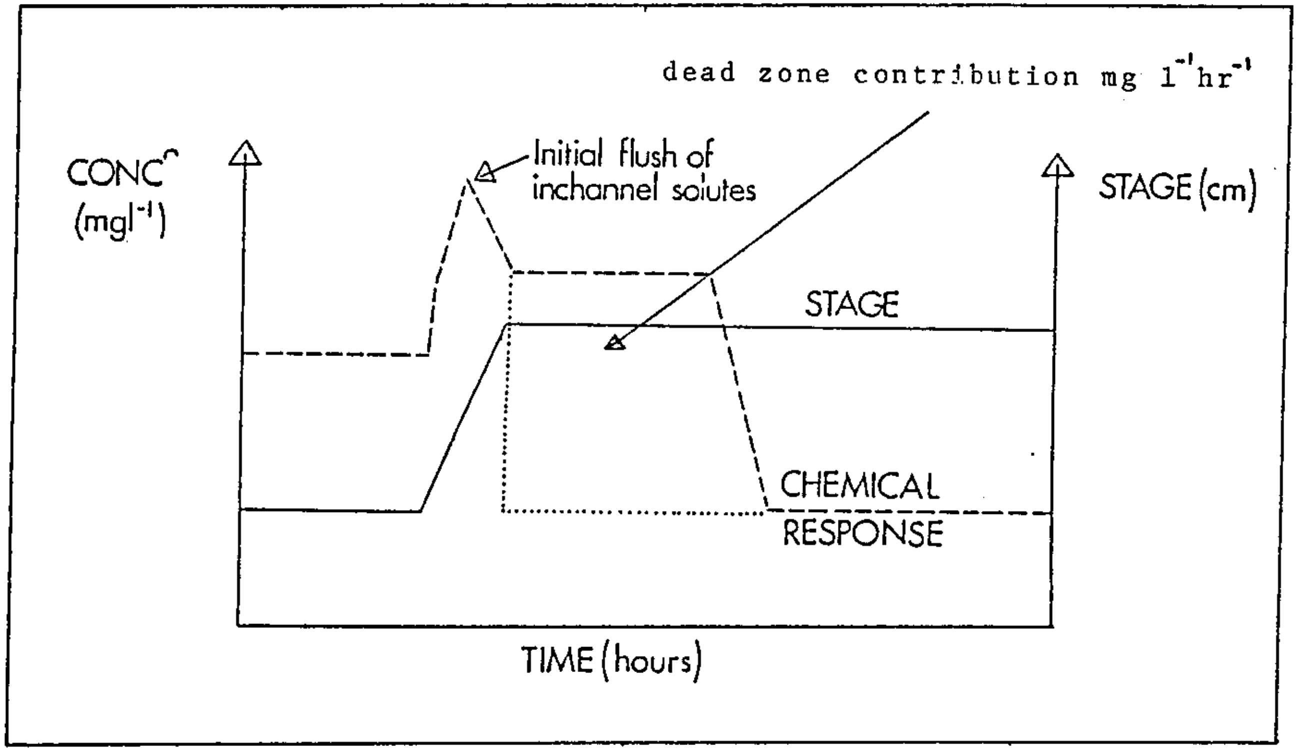


Fig 8.10. Fundamental solute response to release waves on upland boulder bedded channels.

surge downstream. This does at first glance appear to be a very plausible theory, in that it would seem likely that a disturbance of the low flow river state as rapidly as occurs with an artificial release, and of the size that this study monitored, could be sufficient to physically pick-up solutes from areas of concentrated water across the channel profile. Furthermore, the distinctive bore-like wave front character observed whilst measuring the changing nature of the water chemistry did lend itself to this idea of a flood wave sweeping solute rich river water before it. However, by considering the data from releases on the River Tryweryn it can be seen that although at-a-station initially there is a rise, or at least a period of high concentration whilst discharge is increasing, if an entrainment of solutes was occurring into the wave front, then the initial rise of concentration would increase downstream. Data shows that this is not the case (e.g Fig.8.11 and 8.12).

Taking a typical release on the River Tryweryn (Fig.8.11), it is clear that although usually sites do manifest an initial increase in concentration as stage begins to rise, this magnitude varies downstream, indicating very much individual station responses to the rising hydrograph e.g from Fig. 8.12 at site 1 there is no initial calcium rise; at site 2 calcium increases by nearly 1 mg l^{-1}(about 30% of low flow values); at site 5 there is a rise of less than 0.5 mg l^{-1} (less than 8% of low flow values); and at site 6 a rise of less than 0.25 mg l^{-1} above initial values.

In comparison with the significant change in water calcium levels between high and low flow (up to 5 mg l)$^{-1}$; these initial rises in concentration are small, yet conditions within the channel reaches do appear ideally suited to surging; with rapid stage change, steep slopes and large low flow storage areas. If a 'sweep effect' was actually happening then not only would the initial rise in concentrations be expected to increase downstream (in fact the reverse is the case) but the actual magnitude of change would be expected to be at least comparable with the final change in concentration. Therefore, evidence indicates that inchannel solutes disturbed by the passage of water downstream, are quickly diluted by the bulk of reservoir water and not transferred downstream in the wave front as suggested as a possibility by Hem (1970).

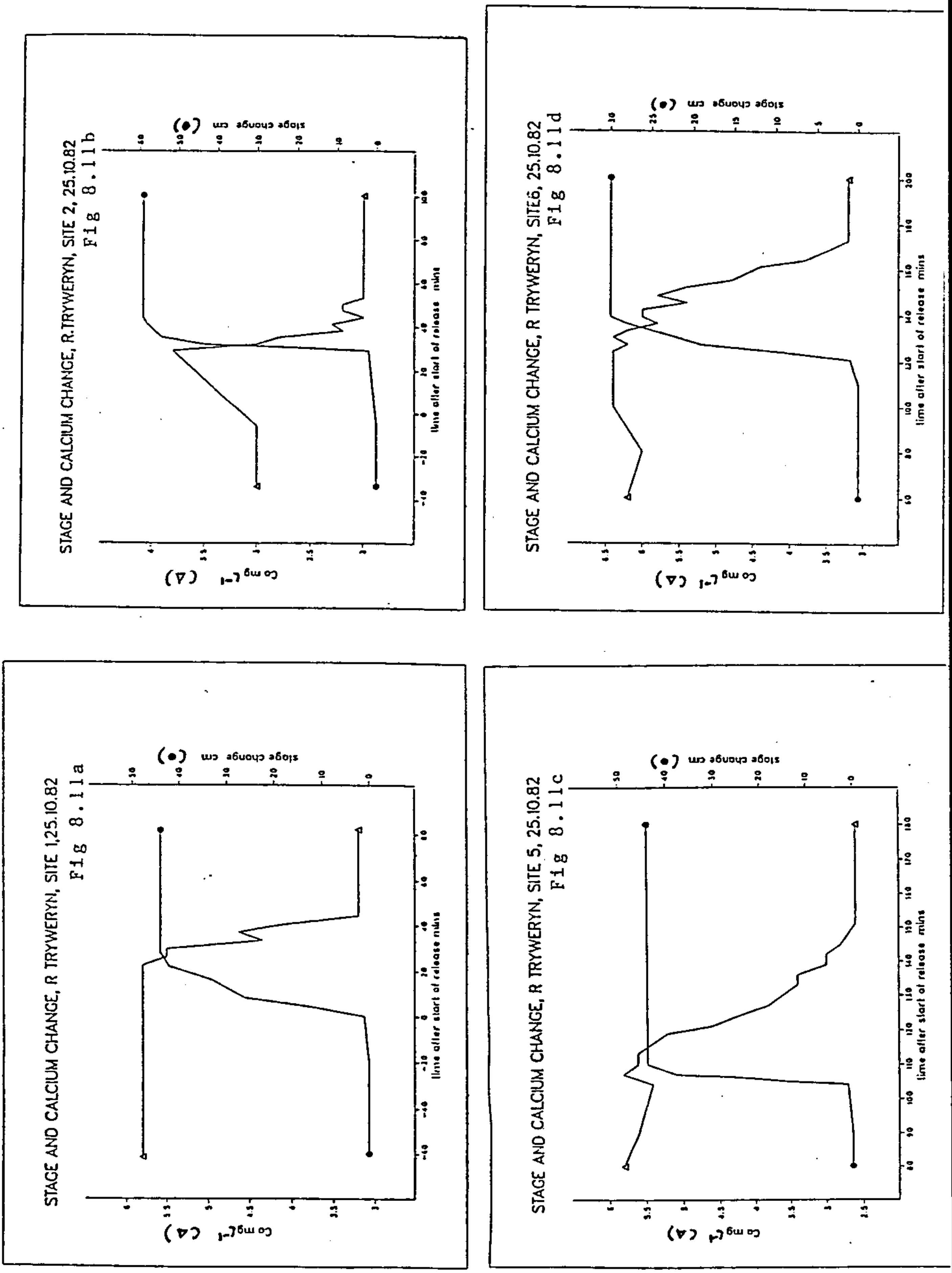


FIG. 8.11 a-d Calcium concentration response prior to and during a full volume release (12.252m^{3}s^{-1}) downstream on the River Tryweryn, 25.10.82. Each line is a series of 40-65 data points (see section 4.2.3).

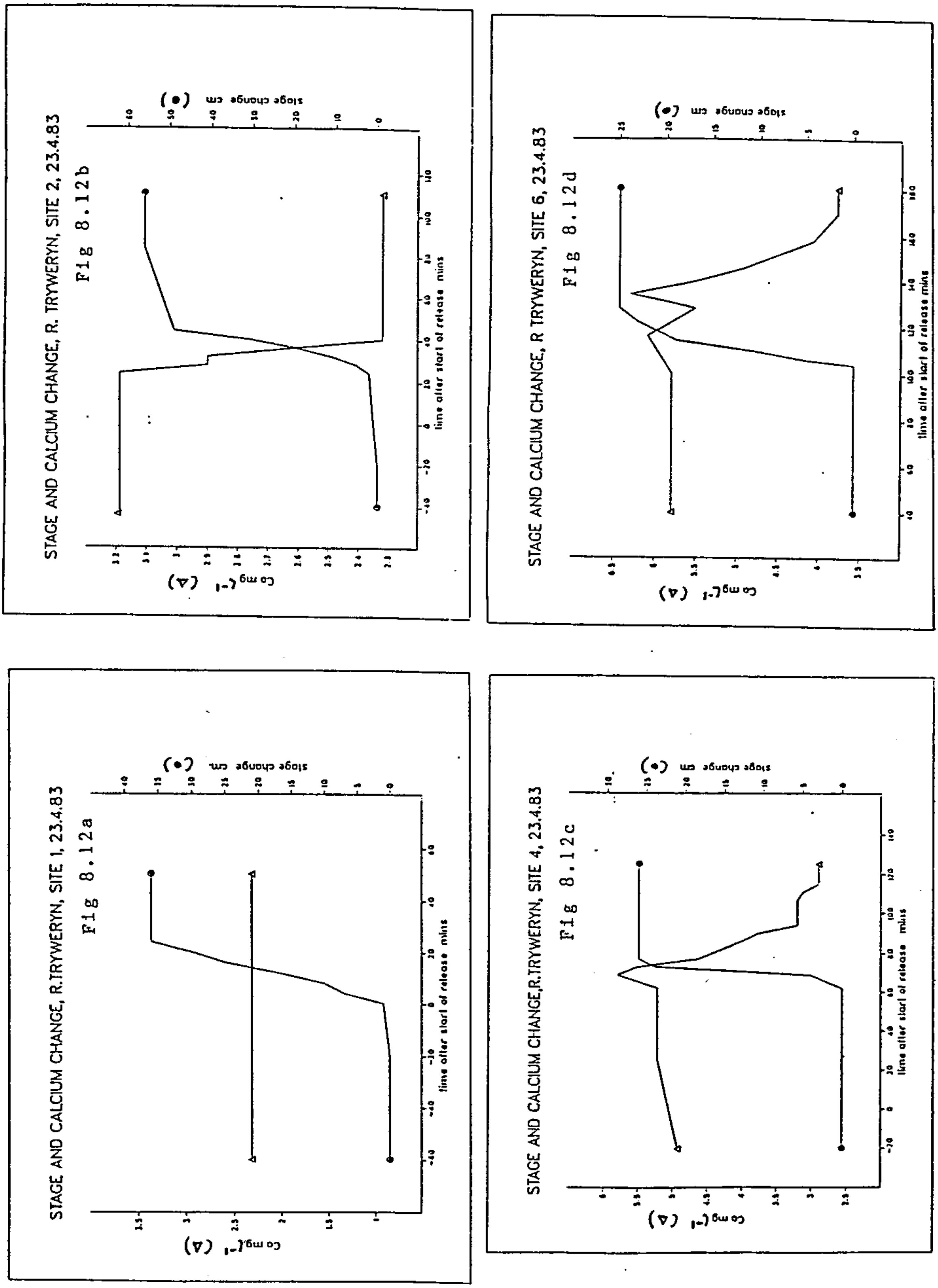


FIG. 8.12 a-d Calcium concentration response prior to and during a full volume release ($12.252 m^3 s^{-1}$) downstream on the River Tryweryn, 23.4.83. Each line is a series of 40 - 65 data points (see section 4.2.3).

8.2.2. Inchannel Solute Storage.

The importance of inchannel solutes in altering the expected response of the chemograph, is illustrated in Fig.8.12. At site 1 as the release appears, there is no change at all in calcium concentration, showing that the concentration of calcium in release water is the same as that of the compensation flow. Therefore, any subsequent increases in calcium values downstream during the release, cannot be due to an addition to low flow concentrations by release water. At site 2, an instantaneous dilution of calcium occurs as discharge begins to rise and maximum dilution coincides identically with maximum stage. The higher calcium values at site 2 during low flow than those at site 1, must be due to inchannel processes, including seepage inputs. At site 4 there is an initial rise in values as stage begins to rise and then a steady dilution to a minimum value occurring about thirty minutes after maximum stage. The initial rise and steady dilution can only be due to the disturbance of inchannel sources of solutes unavailable at low flow. At site 5 a process similar to that taking place at the previous upstream site occurs, except that this happens over a slightly more protracted interval, because clearly the level of solutes and area of inchannel sources are greater than those at site 4. Thus at the lowest downstream site, site 6, the time between the initial rise in calcium concentrations and steady dilution is the longest for all sites where the inchannel potential of calcium stores is greatest, simply because the cross sectional area is greatest.

8.2.3. The Significance of Dead Zone Processes.

The initial rise and lag to maximum dilution as already shown is noticeable on all three study rivers. For sake of clarity, different contributing source areas to the rise in concentration and tail of dilution, may be considered as separate point inputs of tracer. Effectively the monitoring programme is using the changes in natural stream water chemistry as an indication of the arrival of reservoir release water. In fact three major tracer "slugs" can be identified. First, the solutes (if any) brought down in the wave front; secondly tributary inputs; and thirdly solutes released from inchannel storage zones (e.g reservoirs within the banks, or the pool-riffle/boulder, and mud tail bed form systems). If the lag to maximum dilution is to be calculated using this tracer approach then in essence, the problem becomes a case of examining the longitudinal dispersion of these tracer inputs.

Traditionally, longitudinal dispersion of solutes or tracers in a river have been modelled using Fickian diffusion equations (e.g Thormann, 1973; Bansal, 1971; and Belatos, 1980) which show that the rate of diffusion depends on the properties of the medium and the diffusing substance. Pioneer work by Taylor (1953) showed that the concentration c, of a well mixed solute moving down a straight pipe, at time t, and position x, could be described in terms of the Fickian diffusion equation:

$$\frac{\partial c}{\partial t} + \frac{U\partial c}{\partial x} = \frac{D\partial^2 c}{\partial x^2} \qquad \text{(Eq. 8. 1)}$$

where D is a diffusion coefficient.

The solution of the above equation to a slug input of mass M of solute, per unit cross-sectional area, at x=0, and t=0 is;

$$c = \frac{M \exp(-(x - Ut)^2 / 4Dt)}{\sqrt{4\pi Dt}} \qquad \text{(Eq. 8. 2)}$$

which describes a guassian i.e normal distribution curve.

Such a description of the diffusion of tracers as they move downstream, is in fact a gross over simplification. Day (1975) argues that in natural flows, a normal gaussian distribution will never occur, but that due to the presence of meanders, dead zones, side irregularities and pool-riffle sequences that exist in natural rivers, a tail will always result. Such tails are very noticeable on the River Tryweryn (e.g Fig.8.11 and 8.12, sites 4 down). After the initial rise, rate of change to a steady maximum certainly tends to describe a tail as opposed to a normal pattern, which is most probably due to the continuing introduction of solutes from inchannel storage zones, reducing the rate of dilution due to the arrival of low concentration reservoir water.

If inchannel solute zones are contributing to a non-normal dilution curve, then in order to describe this accurately, an attempt must be made to either physically measure or to model the dispersion and diffusion factors from every storage zone on the river, clearly an almost impossible task. However, Young and beer, (1980) and Lau and Krishnappen, (1981) state that in natural streams - defined by the properties of non-uniform velocity and depth - or when the channel is not straight, transverse variations in the downstream velocity are the primary producers of dispersion, and not the simple inherent Fickian solute diffusion. Such transverse variations in downstream velocity are as a result of dead zone processes (Young and Beer, 1980; Bencala, 1983). Dead zones are those areas within the channel, in which water is generally stored, and only slowly re-released into the main flow (Thackston and Schnelle, 1970; and Valentine and Wood, 1977). These areas may be:-

1.) turbulent eddies generated by large-scale basal irregularities.
2.) Large but slowly moving recirculating zones along the sides of pools, particularly located immediately downstream of the entrance to a pool from a riffle section.
3.) Small but very rapidly mixing recirculating zones located behind flow obstructions, particularly located in riffle sections where cobbles, small boulders, and vegetation commonly protrude through the flow.
4.) Side pockets of water effectively acting as dead ends.
5.) Flow into out of and through a coarse gravel and cobble bed.

In the study rivers, solutes trapped in these zones may have been washed out by the rapidly rising water level - a phenomenon similar to that observed by Church (1967). Lateral and vertical mixing in the channel was extremely rapid and uniform, due to the fast moving reservoir release wave. The mixing surveys carried out on the River Tryweryn, particularly at site 5 and 6, show these effects very clearly, with nitrate and calcium at site 5, rising across the channel simultaneously with the arrival of the flood wave, although actual values vary, due to the differing release of solutes from the dead zones. After the initial peak, dilution across the channel is down to a uniform low concentration, with a chemical nature corresponding to an equilibrium between reservoir and river water. Occasional high concentrations are manifested, and result from the release of solutes from a dead zone store. Patterns at site 6 are similar, although the rate of dilution is slower and the magnitude of changes is greater (Fig 8.13 and 8.14), due to the greater areas of dead zone storage, particularly in riffle beds, not prevalent

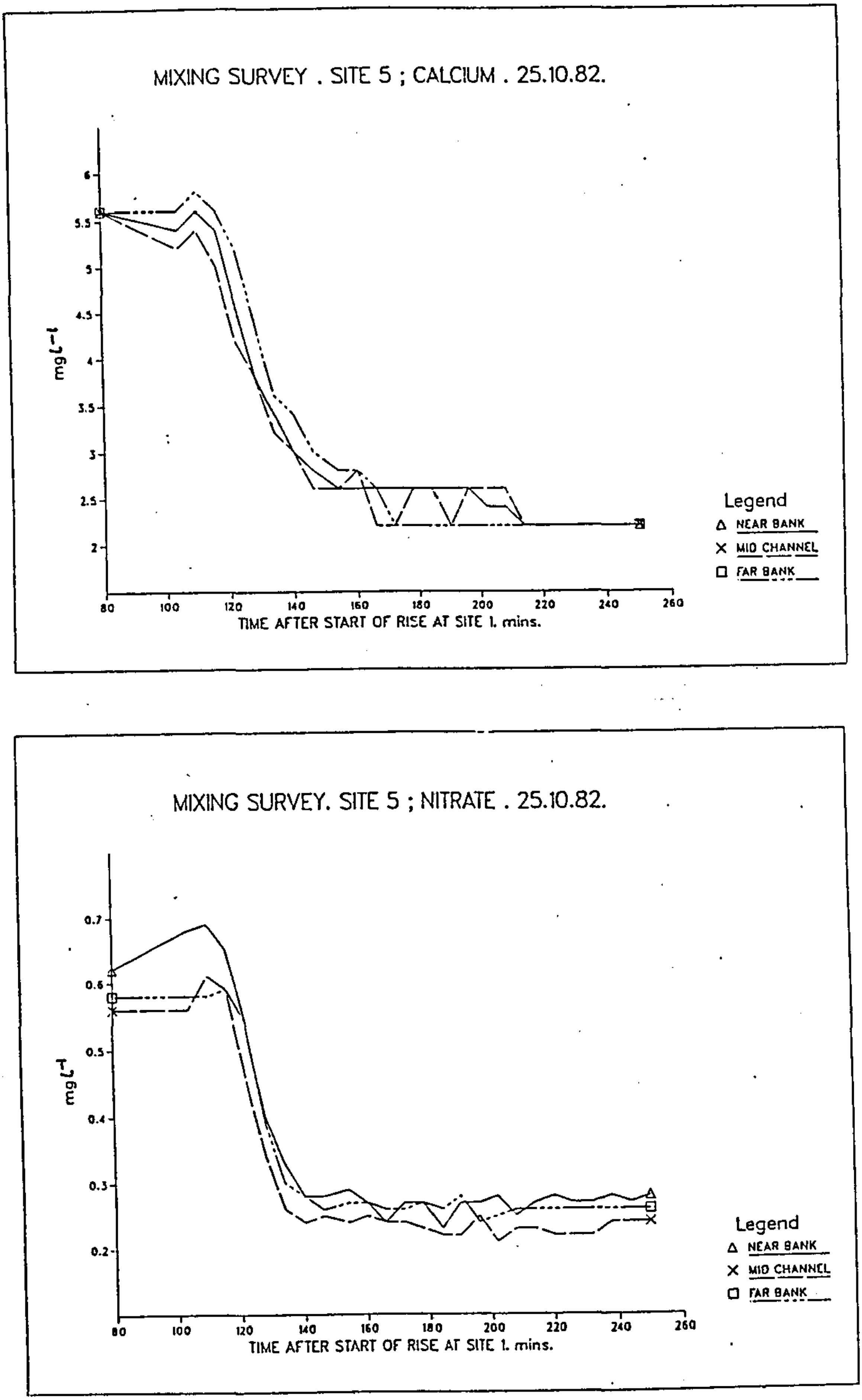


FIG. 8.13 Lateral variation of solute concentration prior to and during a full volume ($12.252 m^3 s^{-1}$) release on the River Tryweryn at site 5: calcium (a) and nitrate (b). Each line is a series of 65 data points (see section 4.2.3).

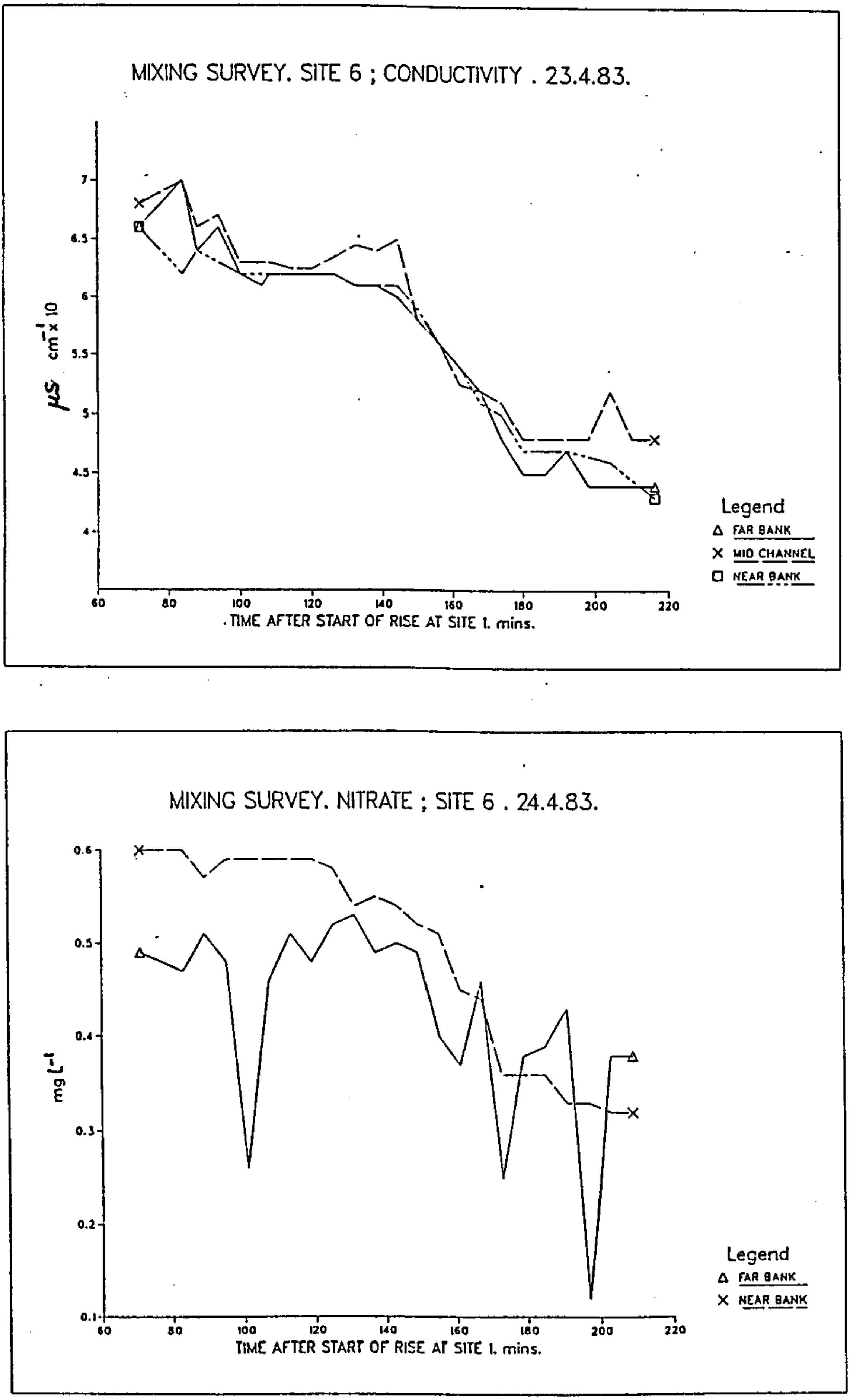


FIG. 8.14 Lateral variation of solute concentration prior to and during a full volume ($12.252 m^3 s^{-1}$) release on the River Tryweryn at site 6: conductivity (a) and nitrate (b). Each line is a series of 65 points (see section 4.2.3).

upstream at site 5.

Since chemical dispersion is the result of irregularities in flow, brought about by dead zone processes, and not complicated by any diffusion functions, Young and Beer (1980) devised a model of inchannel solute behaviour, in which flow is divided into two distinct zones: the mainstream, or thalweg; and a well mixed seperation zone along the bed and banks in which the concentration is taken as uniform i.e the dead storage zone (Fig 8.15). The concentration at a station x, is therefore a function of movement and dispersion of the tracer/solute in the thalweg and in the dead zone, which can be represented by two equations;

$$\frac{\partial c}{\partial t} + \frac{U\partial c}{\partial x} = \frac{D\partial^2 c}{\partial x^2} + j\Gamma_c(s - c) \qquad \text{(Eq 8. 3)}$$

$$\frac{\partial s}{\partial t} = j\Gamma_s(c - s) \qquad \text{(Eq 8. 4)}$$

Where j is the mass exchange coefficient between the dead zone and the main flow (0.02U), Γ_c is the ratio of interfacial area between main flow and the dead zone main flow volume (=1/h) and Γ_s is the ratio of interfacial area to the dead zone volume. U is the mean cross sectional flow velocity.
These equations show how critical the interfacial areas between the dead zone and the main thalweg are in determining the rate of release of solute from these areas. This wetted perimeter, for each reach is difficult to measure physically. However, the problem can be simplified if all the dead zones are aggregated, in which case each reach of the river may be treated as a length, where the solute undergoes pure translational (plug) flow with a concentration s, and then enters a mixing tank, emerging with a concentration c (Fig 8.16). This process can be defined by one equation 8.5:-

$$\frac{c}{t} + U\frac{c}{x} = T\ (s - c) \qquad \text{(Eq 8. 5)}$$

Notice that in this equation, there are no Fickian diffusion terms, and that all effective dispersion is as a function of residence time of the solute in the dead zone. Clearly then the importance of such zones is paramount when considering the rate of change of chemistry at-a-station during a release.

8.2.4. Calculation of solute contribution from dead zones.

The contribution of dead zones to water chemistry change can actually be calculated. Assuming no kinematic effects, then the

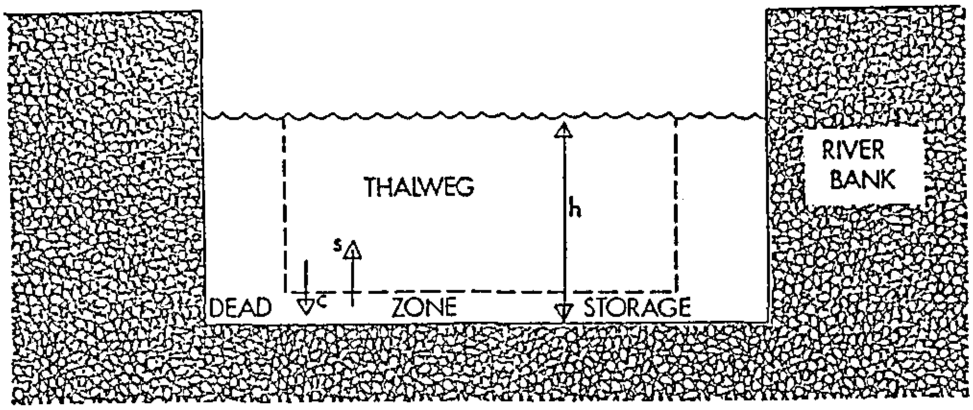


Fig 8.15. Diagrammatic representation of the basis of Young + Beer's (1980) 'Aggregate dead zone model'.

Fig 8.16. Simplistic representation of Young + Beer's aggregate dead zone model. The mixing tank is the aggregated dead zones within the reach.

contribution from dead zones is the area confined underneath the chemograph, between theoretical time of maximum dilution i.e when maximum stage is reached and actual time of maximum dilution (see Fig.8.10). The contribution from reaches on the River Tryweryn have been calculated, and are presented in Table 8.2. Such contribution is measured in mg $l^{-1}min^{-1}$, where the time intervals relates to the time taken to reach maxium dilution - or in other words, complete exhaustion of the storage zone. These results show that dead zones contribute significantly to calcium variation downstream on the Tryweryn. The contribution from such zones depends not only on the amount of solute in storage prior to the release, but also to an extent, the area of dead zone to be disturbed during a release. Therefore in most cases a larger stage change gives a larger contribution of dead zone solutes.

Where storage is already depleted however, even large stage changes cause little solute input from the dead zones. This is illustrated on the Tryweryn at site 4, where on the first day of a release, a stage change of 26cm produces a dead zone contribution of 24 mg l^{-1} calcium, on day 2 of the release, a smaller stage change of 26cm, produces a larger dead zone contibution almost doubling the previous days contributions. Such an anomolous result can only be attributable to the inchannel supplies of solute being replenished between the releases, either by tributary input, or by solute rich return water flow from the banks saturated by the previous days high water levels.

To some extent the term dead zone is misleading, implying a physical zone of storage. Physical zones certainly do occur, as described in the previous section, however they may or may not contain solutes according to prior conditions of flow. Therefore perhaps a better term would be dead solutes - solutes that play little or no role in the general water chemistry at low flow, but which are disturbed and made "alive" during the releases.

8.2.5. Conceptual application of the Dead Zone Model.

Many Water Authority fisheries reports have documented the unsuccessful effect of reservoir releases as freshets to induce the migration of fish upstream (e.g North West Water, 1974; Northumbrian Water, 1977; Severn Trent Water, 1978 and Lancashire River Authority, 1973) however, to date no satisfactory explanation has been given as to why an artifical freshet does not have the equivalent effect as a natural flood

SITE	DATE	STAGE CHANGE (cm)	DEAD ZONE CONTRIBUTION, Ca mg l^{-1} sec*$^{-1}$
6	24.4.83	25	50
5	"	32	56
4	"	26	45
2	"	57	0
1	"	37	0
6	23.4.83	28	123
5	"	39	60
4	"	30	24
2	"	58	3
1	"	40	8
6	25.10.82	30	53
5	"	44	61
2	"	58	7
1	"	42	12

* until exhaustion.

TABLE 8.2. Contribution of calcium from dead zones on the River Tryweryn, during releases.

to the stimulation of fish activity. Using the concepts of Young and Beer's (1980) dead zone model, the reasons for the differences between an artifical and natural freshet may be explained comparatively simply.

As a result of the inter-change of solutes from the thalweg and the dead zone during a release of dilute reservoir water, dead zones are rapidly depleted of their solutes, this is expressed in the form of an equilibrium equation (Eq.8.6). However, during a natural flood, an equilibrium will be reached between the dead zones and flood thalweg, due to a higher concentration of solutes, derived from catchment sources, in the advancing flood wave Eq.8 7:-

DEAD ZONE SOLUTE $\rightleftharpoons$ RESERVOIR THALWEG SOLUTE (Eq 8.6)

DEAD ZONE SOLUTE $\rightleftharpoons$ THALWEG SOLUTE (FLOOD) (Eq 8.7)

Therefore, during a catchment flood a balance of solute rich water is slowly reached within the channel. The effects of natural flushing are offset by flood waters initially raising river solute levels, whereas in the case of a reservoir release, any flushing is highlighted since the expected reaction is for the river to be rapidly diluted.

The recovery of the downstream river system after a natural flood, will be much more steady than occurs after an artifical flood. Solutes transferred into the storage zones will be slowly re-introduced into the main channel chemistry as water levels subside. With artifical regulation however, once the release is over, as solutes in the dead zones have been depleted and not replenished to any great extent, the recovery of water chemistry back to the exact state before the release, is slow. Therefore, during a natural flood, a complete continuum of chemical conditions occur within the channel chemistry, as a result fish can migrate upstream when water quality best suits their physiology (Banks, 1969). During a reservoir release, changes in the nature of the water chemistry are extreme, creating fierce flushing and dilution. These initial changes of the river water quality occur rapidly, giving the migrating fish little chance of a water quality best suited to their physiology.

Using the equilibrium concept a three phase conceptual model may be produced to explain the effects of reservoir releases in upland areas upon water quality downstream. This model is now presented.

8.2.6. Inchannel storage zone model.

Phase 1 - Compensation flow. (Fig.8.17)

Reservoir water chemistry is a function of limnological processes, influenced by basin geology, age of reservoir, and seasonal patterns. Release water quality is thus a result of these combined effects, and its precise nature can be summarised by giving the reservoir depth from which the release water is abstracted.

For rivers in this study, in most cases (except for nitrate) release water is more dilute than the natural river - pre reservoir water. As the compensation flow moves down the channel due to extreme roughness and storage factors prevalent in the upland channels, dead zones proliferate, and solutes diffuse into storage. The nature of the solute store within the dead zone is in itself dependent upon: the time after the last natural flood - if this is short then solute levels will be high; time after the last reservoir release - if this is short the the solute stores will be depleted; local effects of the flow regime - eddies etc; solute inputs from the effects of man - either point inputs such as sewage works, or diffuse inputs such as agricultural runoff; the volume of compensation flow - the higher the flow the lower the dead storage zone capacity; the season - inducing temperature and vegetation complications; and lastly but very importantly catchment geology - determining to a large extent river channel morphology, and solute load.

In general at this compensation flow level, a high proportion of solutes, both from the reservoir compensation water itself and from tributary inputs, tend to be trapped in dead zone storage. These include stagnant pools, circulation zones behind river bed boulders, or into storage in gaps between individual gravel particles in the riffle systems. The water chemistry at a station is a function of the ratio of the dilute reservoir compensation water, to the somewhat more concentrated tributary inflow.

2. The Established Release. Fig.8.18

During an established release i.e a short period after maximum stage, the river water chemistry is almost totally dominated by the nature of the reservoir water. Dead zone stores are depleted, the solute load of reservoir water is low , consequently although an equilibrium is attained between the

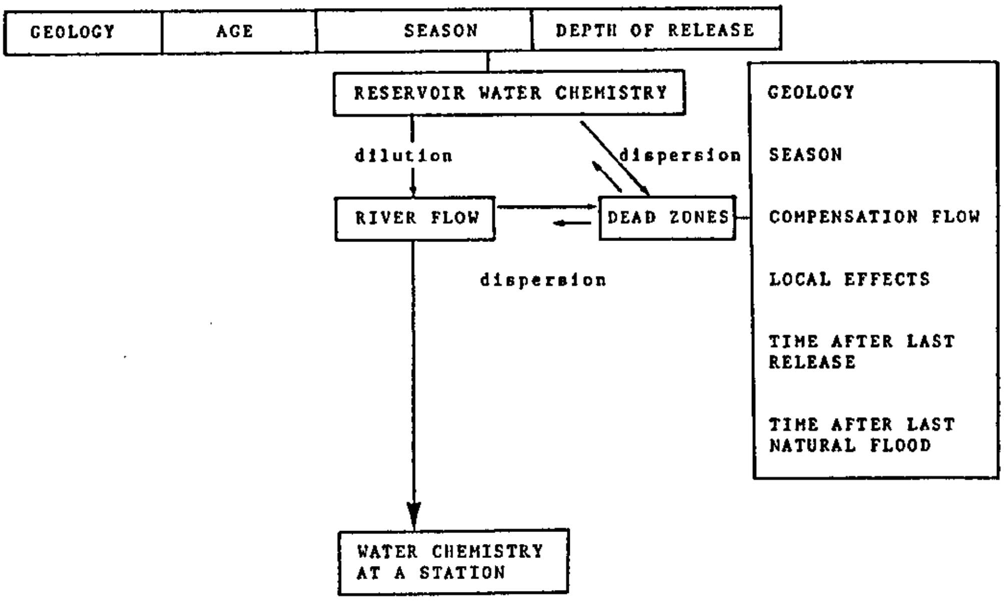


FIG. 8.17 (1) COMPENSATION FLOW: background water chemistry will reflect dominant input source-storage zones or reservoir water.

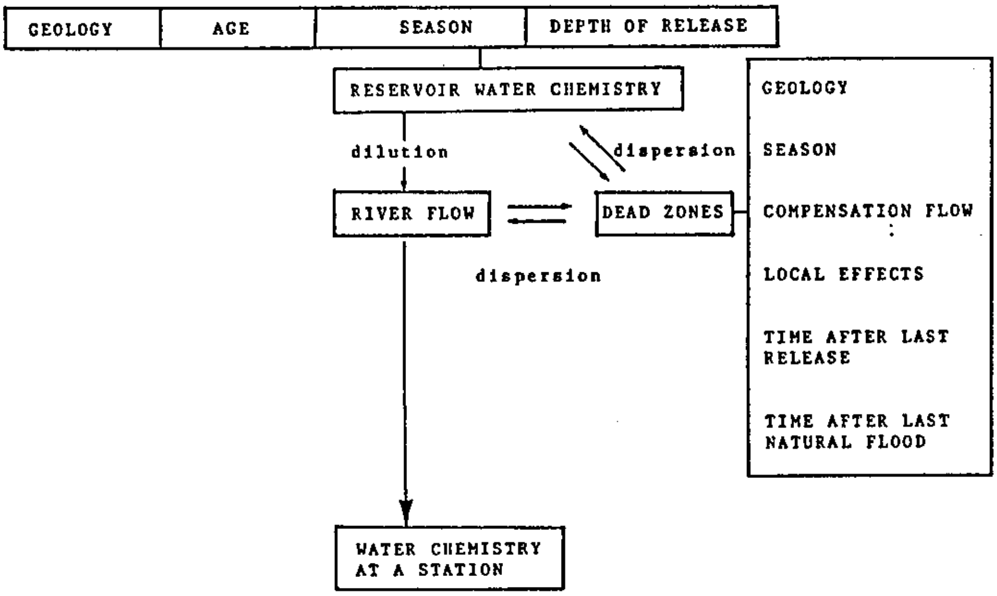


FIG. 8.18 (2) ESTABLISHED RELEASE: background water chemistry dominated by release water.

input to and the output from the dead zones and the input and output to the main thalweg, the real transference of solutes is minimal.

3. The Start of a Release. Fig.8.19

Once again the nature of water at-a-station is essentially dependent upon the same fundamental conditions as during any other phase of the release, although the dead zone storage input can be significant.

As water level rises, so solutes from the storage zones are rapidly flushed out, and since reservoir water is dilute, the dispersion of solutes back into storage is negligible. As a result an imbalance is produced, leading to a rise in solute concentration at-a-station, even with the arrival of dilute reservoir water. This creates a lag between the attainment of maximum dilution and maximum stage, and also ensures that even when the release is well established some rises in chemical concentrations are recorded.

8.2.7. Summary of Inchannel Storage Effects.

The water chemistry of the Rivers Tryweryn, Washburn and to a lesser extent the River North Tyne, are dominated by the reservoir release policy, with standard releases totally determining the nature of downstream water chemistry within a matter of minutes of the arrival of that water. The lag between the arrival of maximum discharge and maximum dilution, is explained by the presence of dead solutes, which are both physically mixed and chemically dispersed throughout the channel as discharge rises. Mixing is such that no chemical surge is formed within the wave front, but the typical rise in chemical concentrations with rising stage is due to the sudden mixing in of at-a-station inchannel solutes.

Up to a critical distance downstream dependent upon - the size of release, rate of rise of release, and dead solutes (a function of tributary input, low flow level, and channel roughness) - the chemical effect of a release actually increases. Beyond this distance (a distance not reached on the Rivers Tryweryn or Washburn), the chemical manifestations of the releases are steadily reduced.

These findings are summarized in a conceptual model and applied to the problem of artifical freshets not inducing fish

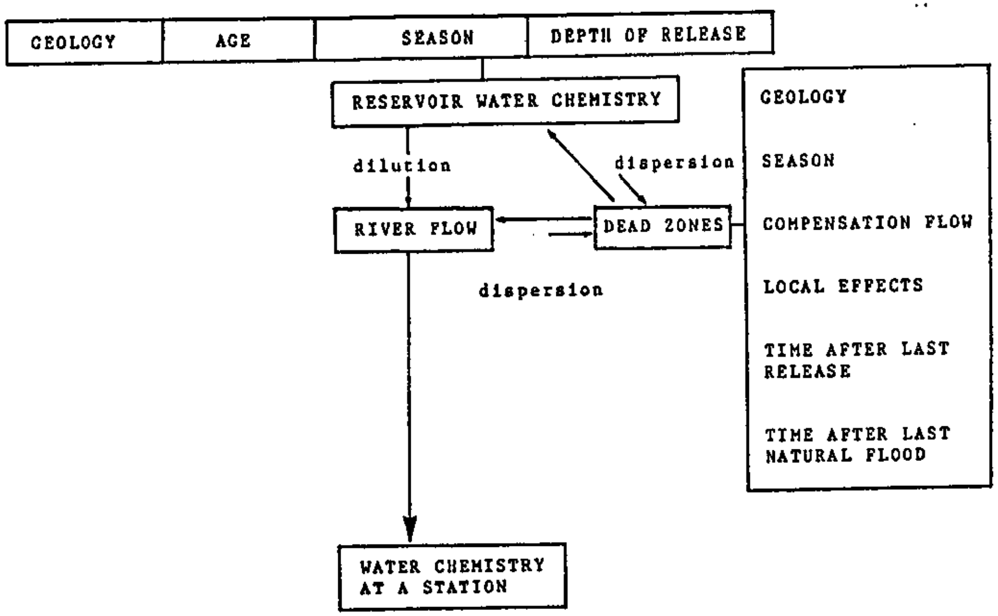


FIG. 8.19 (3) START OF A RELEASE: background water chemistry will show the influence of dead storage zones as they are flushed out.

migration. It is established that due to rapid flushing of dead zones by a release, and the low solute load of the reservoir water - which rapidly comes to dominate the river water chemistry - there is little or no resemblance to the more evenly balanced cyclical response that occurs during a natural flood. Therefore it is suggested that, at no time does the artifical freshet produce water quality conditions suitably similar to a naturals flood, to induce fish migration.

8.3. Wave/water dynamics.

Several workers (e.g Buchanan, 1964; Ponce et al, 1978; Kellerhals, 1970; Brady and Johnson, 1981) have documented results similar to those found in this thesis, with maximum dilution occurring sometime after maximum stage has been attained by the flood wave moving rapidly downstream, and have attributed this solely to a kinematic wave effect with water travelling behind the wave producing a lag in dilution. However, there has never been a satisfactory explanation to an initial rise, or steady high concentration of solutes as stage rapidly increases. The previous section on inchannel dead zones attempted to fill this gap, now this section aims to expand the explanation by considering in detail the significance of wave/water dynamics on the water quality of the Tryweryn, Washburn and North Tyne.

8.3.1. Comparison of hydraulic characteristics of the study rivers.

Table 8.3 shows the hydraulic data for the individual study rivers. In short, the approximate discharge change during releases for the Tryweryn is x30, for the North Tyne x20 and for the Washburn x10. The increase of area from low to high flow is about x2 for the Tryweryn, and x3 for the Washburn and North Tyne. Changes from low to high flow velocities are similar between study rivers, although the problems associated with the collection of accurate hydraulic data from rough, upland, boulder-bedded rivers are legion. In rivers of extreme roughness, at low flow, the main channel is in fact a product of numerous separate braids as the water threads a path through a plethora of boulders. Roughness being so extreme is obviously important on release movement, and in order to compare between rivers should be quantified. Unfortunately this is no easy task, due to the reasons now described.

A typical method for calculating roughness is to use the Manning approach, where:

SITE	DISTANCE (km)	STAGE CHANGE (cm)	LQ $m^3 s^{-1}$	HQ $m^3 s^{-1}$	LA m^2	HA m^2	LV $m \cdot s^{-1}$	OB. VEL. $m\ s^{-1}$	TIME OF TRAVEL (mins)
23.4.83 River Tryweryn									
1	0.08	36	0.4	11.0	6	13	0.07	1.58	5
2	1.3	46	0.4	11.0	3	7	0.13	1.44	15
3	3.3	54	0.4	11.0	6	10	0.14	1.5	12
4	4.4	23	2.6	13.2	6	12	0.43	1.4	51
5	6.3	32	2.6	13.2	10	17	0.26	1.38	76
6	7.8	25	2.6	13.2	7	17	0.37	1.3	103
26.10.83 River North Tyne									
1	0.25	88	2.5	50	15.9	46.4	0.16	0.83	5
2	2.35	110	2.5	50	15.9	46.4	0.16	1.22	29.7
3	4.70	117	2.5	50	14.1	41.8	0.46	1.35	58.7
4	10.40	61	15.5	62.6	26.7	45.0	0.59	1.01	109.7
5	15.20	40	22.0	63	18.7	25.0	0.87	0.98	170.7
9.4.83 River Washburn									
1	0.10	44	0.20	2.99	1.56	5.86	0.13	1.9	2
2	2.45	40	0.21	3.0	1.52	5.75	0.14	1.7	24

TABLE 8.3. Comparison of hydraulic data between study rivers, for typical releases (7.1).

QL = discharge at low flow QH = discharge at high flow
AL = wetted channel area at low flow AH = wetted channel area at high flow
K = Brady-Johnson roughness factor VL = velocity of water at low flow
Vob = observed velocity of wave peak Vk = kinematic water velocity
T1 = observed time of travel of wave peak T2 = calculated time of travel of water.

$$n = \frac{R^{\frac{2}{3}} S^{\frac{1}{2}}}{V} \quad \text{and} \quad V = \frac{Q}{A} \quad >> \quad n = \frac{R^{\frac{2}{3}} S^{\frac{1}{2}} A}{Q}$$

n is the Mannings roughness coefficient
R is the hydraulic radius (wetted cross-sectional area/wetted perimeter)
S is the channel slope
V is the water velocity

Standard practice involves the accurate measurement of the above parameters. In an upland channel this creates problems. The channel is extremely irregular, both in shape and roughness, consequently a subjective decision has to be made in order to select a suitable reach, which is representative of the channel conditions. Within this reach accurate surveys are made of reach low flow velocity and reach slope. However, these values certainly do not account for localised important, variations of slope and low flow velocity. Essentially the problem is that roughness equations in general practice are designed to give a measure of roughness at bankful conditions, and not at extreme low flow. Thus roughness values at high flow, were much more credible than those calculated at low flow. Table 8.4a&b compares high and low flow roughness values on the River Tryweryn. At low flow it was very difficult to determine local slope and local wetted perimeter within a reach because the variations between individual sections were so great, created by the channel braids at this low discharge, leading to unrealistic roughness values. At high flow however, estimates of reach slope, hydraulic radius and velocity were much more reliable - since only one single thread of flow needed to be considered - smoothing out irregularities between sections, resulting in more feasible roughness estimates.

This problem with the reliability of hydraulic data at low flow, makes it extremely difficult to explain quantifiably, the wave/water movement downstream, since most routing models use the differences between low and high flow hydraulics to estimate the rate of wave/water movement. Therefore, in order to determine the effect of differing low flow hydraulic conditions upon the rate of release water/wave movement downstream without having to depend upon a mathematical representation of low flow roughness conditions, time of wave travel was plotted against stage change (Fig.8.20).

8.3.2. Wave movement downstream.

Fig.8.20 shows that the greater the stage change on the

Release date	SITES 1	2	3	4	5	6
Table n	0.05	0.06	0.06	0.05	0.06	0.04
15.5.82	0.12				0.16	0.09
16.5.82	0.6				0.31	0.11
4.9.82	0.56				0.31	0.11
5.9.82	0.56				0.31	0.11
25.10.82	0.6	0.37			0.27	0.11
23.4.83	0.6	0.37		0.10	0.21	
24.4.83	0.6	0.37		0.12	0.27	0.11
4.6.83	0.56		0.42	0.12		
5.6.83	0.56		0.42	0.05		
30.1.84	0.6			0.10		0.09
31.1.84	0.6			0.12		0.11
1.2.84	0.6			0.12		0.11
3.2.84	0.6			0.10		0.09
5.2.84	0.6			0.11		0.10
29.5.84	0.6	0.37	0.37	0.07	0.31	0.11
30.5.84	0.6	0.37	0.37	0.07	0.31	0.11
31.5.84	0.6	0.37	0.37	0.07	0.31	0.11
1.6.84	0.6	0.37	0.37	0.07	0.31	0.11
2.6.84	0.6	0.37	0.37	0.07	0.31	0.11
Slope mm^{-1}	0.01	0.02	0.02	0.01	0.01	0.01

$n = ((R2/3)s^{\frac{1}{2}})/v$ n = Manning's roughness coefficient

TABLE 8.4a. Calculated Manning's roughness on the River Tryweryn, at LOW flow.

Release date			SITES			
	1	2	3	4	5	6
Table n	0.05	0.06	0.06	0.05	0.06	0.04
15.5.82	0.09				0.09	0.07
16.5.82	0.09				0.09	0.08
4.9.82	0.09				0.09	0.08
5.9.82	0.09				0.09	0.08
25.10.82	0.09	0.05			0.09	0.08
23.4.83	0.08	0.05		0.05	0.09	
24.4.83	0.08	0.05		0.06	0.09	0.08
4.6.83	0.09		0.07	0.06		
5.6.83	0.09		0.07	0.05		
30.1.84	0.09			0.05		0.08
31.1.84	0.09			0.06		0.08
1.2.84	0.09			0.05		0.08
3.2.84	0.09			0.06		0.08
5.2.84	0.09			0.06		0.08
29.5.84	0.08	0.05	0.09	0.04	0.09	0.08
30.5.84	0.08	0.05	0.09	0.04	0.09	0.08
31.5.84	0.08	0.05	0.09	0.04	0.09	0.08
1.6.84	0.08	0.05	0.09	0.04	0.09	0.08
2.6.84	0.08	0.05	0.09	0.04	0.09	0.08
Slope mm^{-1}	0.01	0.02	0.02	0.01	0.01	0.01

$n = ((R2/3)s^{\frac{1}{2}})/v$ $\qquad$ n = Manning's roughness coefficient

TABLE 8.4b. Calculated Manning's roughness on the River Tryweryn, at HIGH flow.

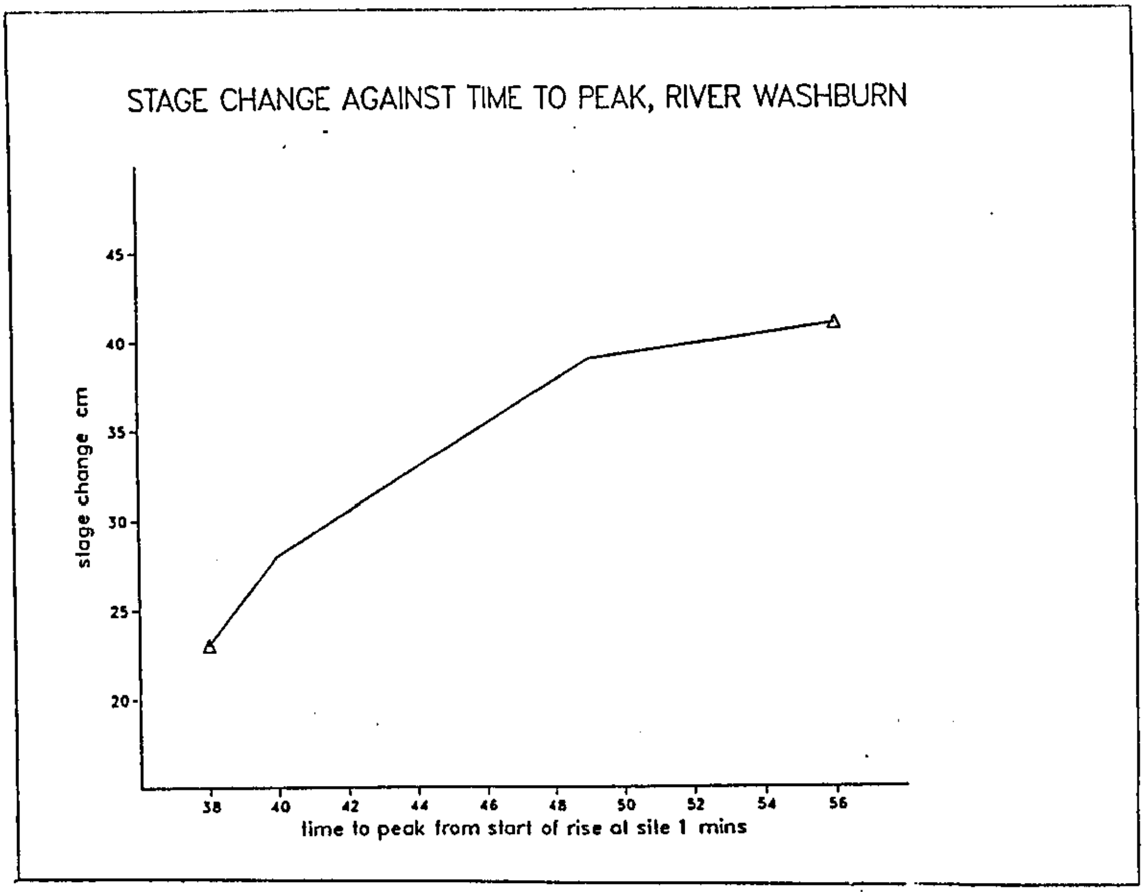


Fig 8.21. Time of wave travel, from site 1 to site 2 on the River Washburn. The smaller the stage change at site 2, the shorter the wave travel time.

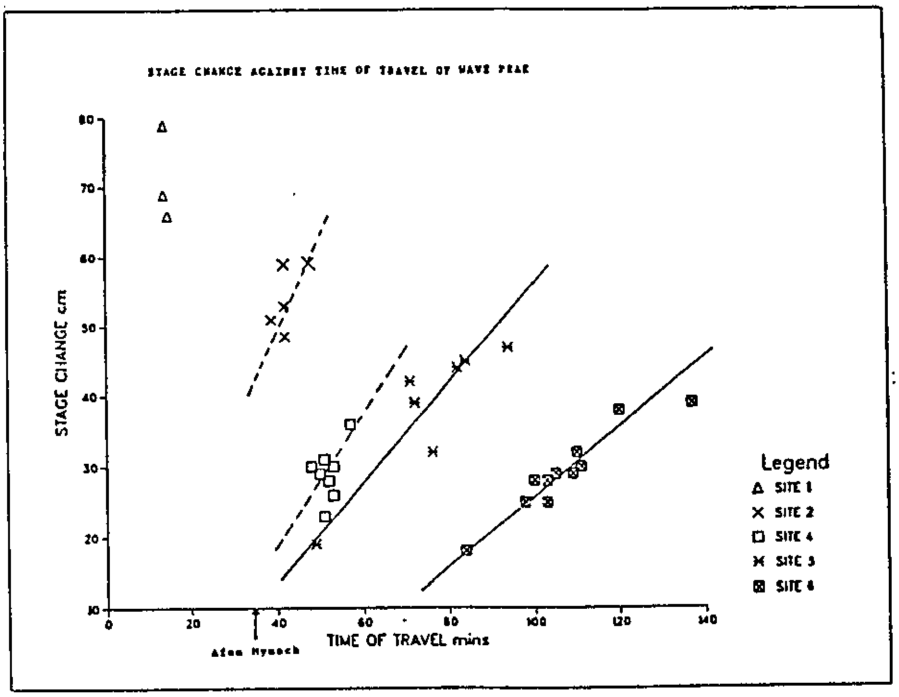


Fig 8.20. Stage change against time of travel for releases on the River Tryweryn. The greater the stage change at a site, the longer the time of wave travel to that station.

Tryweryn associated with a release, the longer the time of travel of the wave front - a fact that becomes more noticeable further downstream. These findings on the Tryweryn are supported by results from the River Washburn, Fig.8.21. It seems at first that results are illogical and go against standard hydraulic equations. In essence the data shows that the larger the discharge into the channel, the slower its rate of movement downstream. Renard and Keppel (1966), from work on ephemeral streams in the southwestern region of the USA, plot graphs of depth against peak wave velocity, which give a totally opposite pattern to those presented in Figs.8.20 and 8.21, with velocity rising (time of travel decreasing) as depth increases. Such findings are confirmed by Wong and Laurenson (1983), who show wave speed increasing as discharge rises, up to a critical level - bankfull - after which the water speed is retarded as it moves across the flood plain. Price (1973), is in agreeement with these authors, except that he found discharge for maximum wave speed to be one half to two thirds that of bank full discharge. This was probably because roughness tended to increase above this level, due to the effects of bank vegetation, and that localized floodplain storage occurs below the general bank level of the reach and before the flood plain flow commences. With this wealth of evidence against the phenomena so clearly exhibited on the Rivers Tryweryn and Washburn, the explanation for it must be very credible, fortunately this is the case.

For each release, maximum discharge is approximately similar, therefore the differences shown in Figs.8.20 and 8.21, are due to changes in the starting discharges, which vary considerably. When stage change is great, that is when starting discharge is low, time of travel is longer than when the starting stage is higher. The reason for the larger discharge moving more slowly than the smaller discharge, is that at extreme low flow the roughness of the channel is considerable. Thus much energy within the water mass is used in overcoming this friction. In effect the frictional force acts as a brake slowing the water movement downstream. When starting discharge is higher, either as a result of a tributary inflows or a larger compensation flow, the extreme roughness at low flow is removed, and this greater starting discharge acts as a cushion over which the release wave can flow. The significance of tributary inputs altering the time of travel of the release is demonstrated by results on the Tryweryn (Fig.8.20). Below the Afon Mynach input, the range of stage variations between releases is high, due to the flashiness of this input, thus the range of wave travel time is also great. Above this junction, stage change varies little between releases since low flow is a function of constant reservoir compensation policy, consequently times of travel of releases also vary little.

The implications of these findings to the routing of artifical releases downstream are critical. It is not the absolute stage or discharge change which affects the time of travel, but rather the stage change above some critical stage determined by channel roughness. In other words a discharge released on a relatively high flow will move faster than the same magnitude of release made on an extremely low flow, because in the latter case the roughness factor will be considerably higher (Bathurst, 1978). This principle is further illustrated in the way the wave front changes shape as it moves downstream.

8.3.3. Wave front shape change downstream.

The characteristics of a release wave front as it moves downstream on all three study rivers does not simply attentuate as described by many authors, in particular Hamill (1983), but can actually steepen, a fact particularly noticeable on the River Tryweryn. Indeed, in some respects the wave front on this river begins to take on the appearance of a bore (Fig 8.22) as described by Jansen (p69, 1979).

On the Tryweryn as far downstream as site 5, the wave front is steeper than the initial wave at a site 1, a fact illustrated in Fig 8.22, where wave steepness although by definition being the stage change against time of rise, is also a function of travel rate. Below site 5, the expected attenuation occurs. This pattern is repeated to a greater extent when compensation and tributary flow are at a minimum, and to a much lesser extent when compensation and tributary flows are higher.

At site 1, the stepped nature of the release is still apparent despite the dampening effect of the Celyn stilling basin, however by site 2, the stepped nature is totally obliterated, and by site 4, maximum wave steepness has been achieved, an effect theorised by King (1954, see paragraph 3.6). In short, the later release water has caught up the earlier release water, due to three reasons:i) the extreme roughness of the channel at low flow slowing down the advance of the initial water pulse ii.) the initial pulse acting as a cushion for the secondary waves to advance over, catching up the initial release front and iii.) the secondary releases on the River Tryweryn are of a greater magnitude than that of the initial release, and

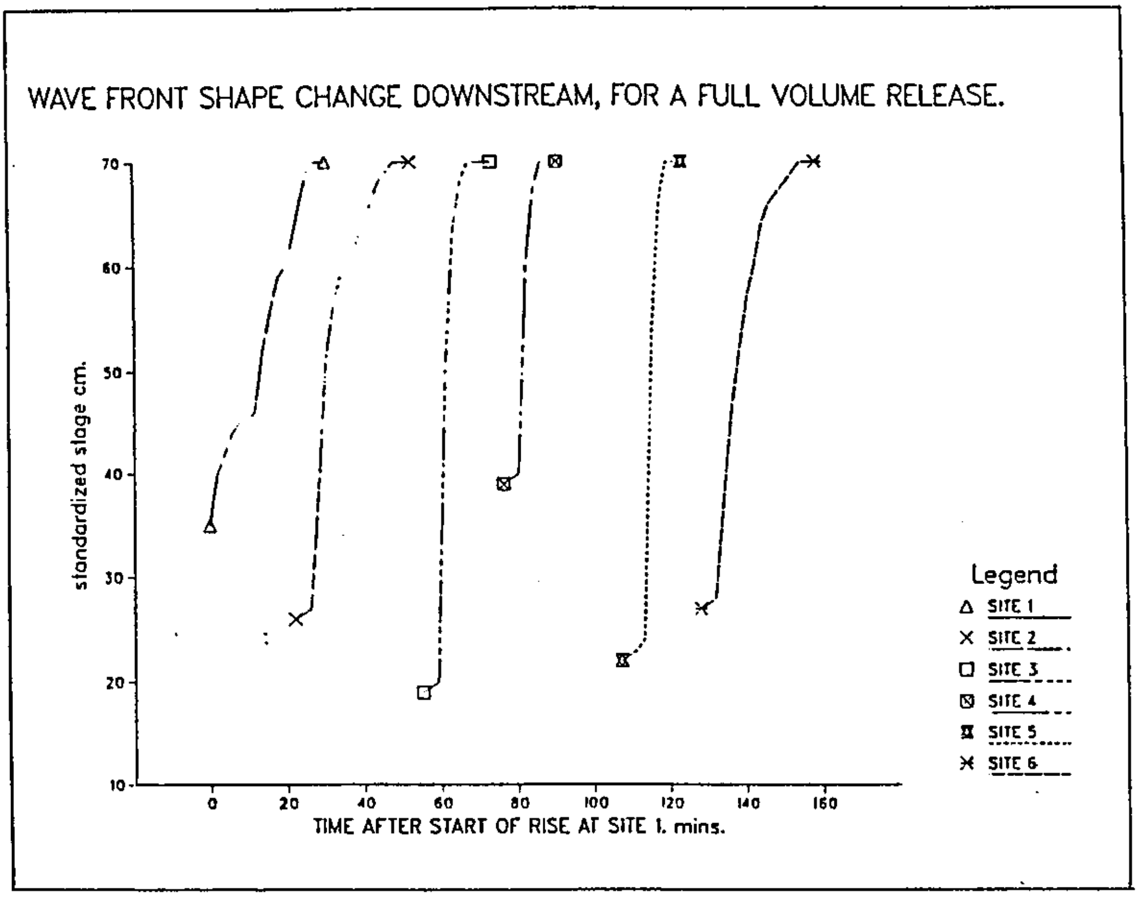


Fig 8.22. Variation in wave front steepness downstream on the River Tryweryn.

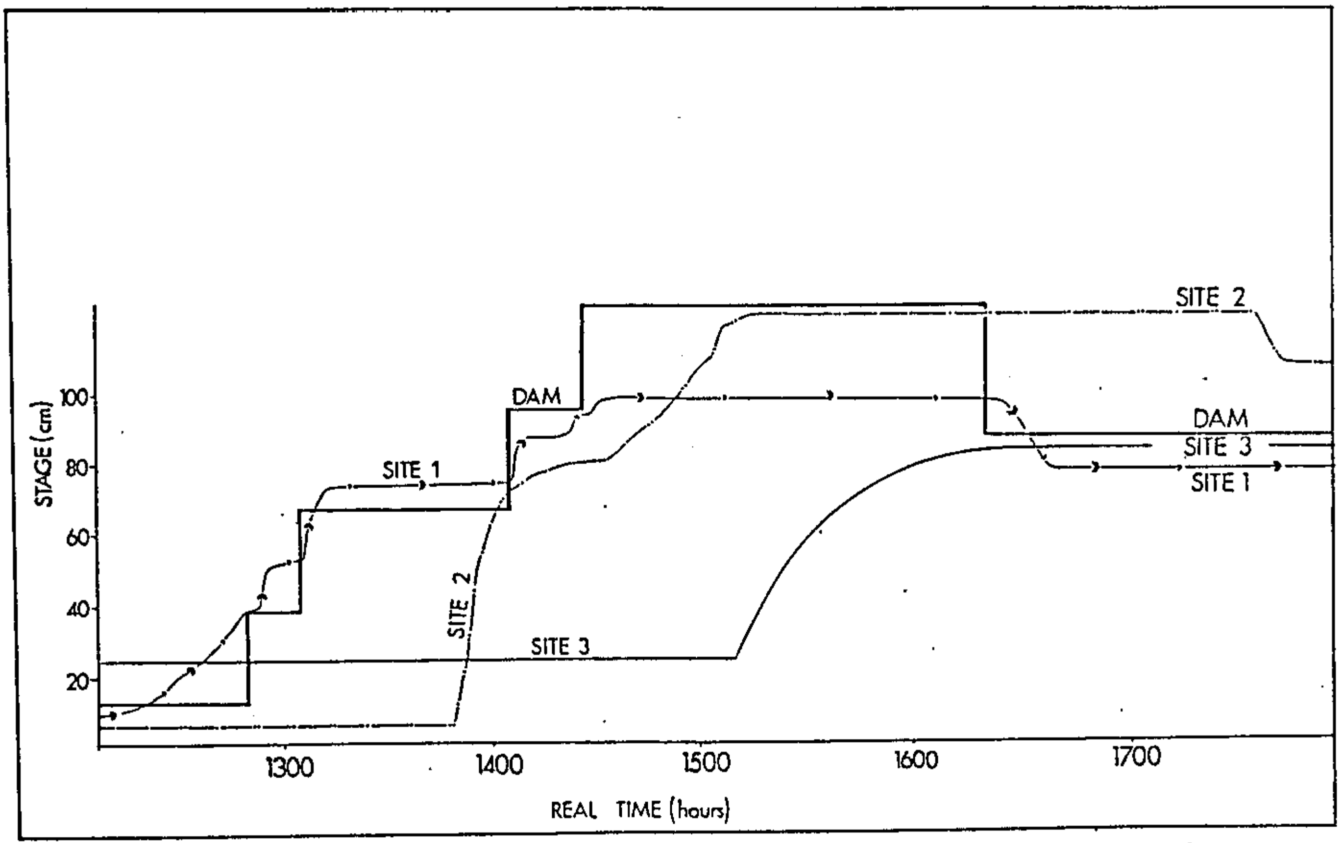


Fig 8.23. Variation in wave front steepness downstream on the River North Tyne.

will therefore theoretically gather more momentum.

Below site 4 the wave front begins to attenuate. This is due to the smaller wave amplitude in comparison with the initial water depth within the river. Such depth increases downstream, as already indicated, due to the influence of tributary flows. The energy contained within the wave front is also reduced as progress is made downstream below site 4, because channel width increases, meaning that a greater frictional force has to be overcome. By the time that site 6 is reached, attentuation has clearly occurred, due to the above two factors, coupled with the extreme storage factor of the channel, in this instance due to the presence of a substantial waterfall, namely Bala Mill Falls situated just below site 5.

On the River North Tyne, a similar steepening and attenuation pattern occurs. However, the catching up of earlier releases by further inputs is even more dramatic than on the River Tryweryn, because channel dimensions, discharge values and time scales are somewhat greater (Fig 8.23). By the time that site 4 is reached there is little distinction between individual releases in the wave front, and by site 5 there is just one single relatively shallow wave. Factors on the River North Tyne, leading to the steepening and attenuation of the wave fronts, are very similar to those on the Tryweryn, with initial releases acting as cushions for the latter inputs to ride over, leading to wave steepening. This occurs until tributary inputs become significant, and the hydraulics of the channel (storage factors and wave to receiving water depth) act to cause wave front attenuation.

On the River Washburn because the reach distance is so short, the dynamics of the wave front are somewhat dissimilar to those on the other two rivers. In brief the wave front does steepen as it travels down the channel, in places approaching the appearance of a tidal bore, and as such is a product of discharge volume and channel slope. In comparison with these two dominant factors, channel roughness although great, is insignificant in affecting the rate of wave travel.

8.3.4. Prediction of release movement downstream.

Routing models of reservoir releases in these rough upland channels must take into account both steepening and attenuation of the wave front, and indeed must allow for the state of the channel onto which the release is being made because results have shown that if receiving discharge is high then the time of travel is low, and vice-versa. A model that encompasses all these factors by necessity will tend to be almost as complicated as the reality that it is attempting to simplify. For predictive purposes. However, it is important to establish if standard models used in the past, can be modified simply, to come close to the real situation.

Given the nature of the streams under study, according to the literature (see chapter 3), the only models in any way applicable are of the kinematic type. The crux of the kinematic model is that it considers changes in hydraulic parameters, and not absolute values. This is an extremely important fact, since the problem of collecting hydraulic data on streams such as those under consideration is great (see paragraph 8.3.2). Furthermore, this type of model has been used with some success on rivers of a similar nature to those in this study e.g River Skerne (Hamill, 1983), River Wear (Glover and Johnson, 1974; Brady and Johnson, 1981) and upland streams in the Coast Mountains of Vancouver, Canada (Kellerhals, 1970).

Unfortunately, it is clear that on the Rivers Tryweryn and North Tyne, the effects of boundary resistance creating inertial forces, are critical in determining wave travel rate downstream. This inertia factor is not implicitly considered by the kinematic routing models (Jansen, 1979). However, Kellerhals (1970) concludes that the propogation of flood waves through upland channels obey a kinematic equation containing a dispersion term. This dispersion term is a surrogate inertial factor, and is the key to using the kinematic model on the study rivers.

Brady and Johnson (1981), applied a derived version of the Kleitz-Seddon law for waves in open channels, to kinematic waves. This law assumes that waves behave as monoclinal rising flood waves travelling at constant velocity therefore, wave speed may be shown to be a function of cross-sectional area and discharge:

$$V_w = dQ / dA \qquad \text{(the Kleitz Seddon Law) (Eq. 8.8)}$$

where Vw is the wave speed; and dQ / dA is the rate of change of quasi-steady discharge Q, with respect to cross sectional area of flow A.

During a flood, Brady and Johnson assumed changes in cross-sectional area within the reach, to be equal to the average of the product of change in stage height during the rising stage of the hydrograph and the top width of the channel at the up and downstream end of the reach. Discharge was also averaged between up and downstream ends of the reach. To allow for channel irregularities, an inertial or dispersion term k was introduced:

$$V_{wo} = k(dQ / dA) \qquad \text{(Eq. 8.9)}$$

where Vwo is the observed wave speed; k is a factor to adjust theoretical wave speeds - based on average conditions at both ends of the reach - to actual wave speeds in the reach. This formula assumes that the wave travels at a constant velocity in the reach. Unfortunately, when it is applied to releases made in the River Tryweryn, the results are not very convincing, as shown in Table 8.5. This table indicates that for exactly the same reach, k values vary between 1.3 and 0.9, which is due to the differing roughness conditions within the reach, created by differing low flow discharges, upon which the release is being made. Generally speaking, when starting discharge is high, k values are high, which is because the theoretical part of equation 8.9 (dQ / dA) in rough upland channels, underestimates the rapidly increasing velocity of the release wave once the initial low flow boundary roughness is overcome. The factor k therefore, is not a true representation of channel storage and irregularities at all, because if it were then when starting stage is higher, the k coefficient should be lower, even given the fact that storage potential may increase slightly with increased stage - a fact far outweighed in the majority of reaches on the study reaches, by the extreme boulder bed created storage at low flow. Therefore, for reservoir releases in upland channels with extreme roughness, a more realistic inertial term would be to multiply Vwo by k:

$$k\,V_{wo} = dQ / dA \quad \text{or} \quad k = (dQ / dA) / V_{wo} \qquad \text{(Eq. 8.10)}$$

In this way, if the wave speed is great as occurs when irregularities within the channel are small, then k will be low; conversely, if the irregularities are great leading to slower wave speeds, then k will be large, thus k really does reflect roughness conditions within the channel and is not merely a correction factor. However, this adaptation of the k coefficient is only applicable to the situation where a larger change in stage, results in a lower wave velocity. This is the case in the reservoir releases studied, when a large change in stage occurred when starting compensation discharge was small and

Reach	Date of rel.	LQ (m^3s^{-1})	HQ (m^3s^{-1})	Wave travel time(mins)*	Brady k factor
1 - 6	5.9.82	1.0	12.8	120	0.9
1 - 6	15.5.82	4.5	12.6	84	1.2
1 - 6	25.10.82	0.8	13.2	111	1.0
1 - 6	31.1.84	1.15	13.4	103	1.3

* travel time of the peak

TABLE 8.5. <u>Comparison of k values for the same reach at different starting discharges. River Tryweryn.</u>

hence a high roughness factor, resulting in reduced wave speeds.

In order to test the applicability of the kinematic theory and the modified kinematic theory, to reservoir pulses in upland channels, an attempt was made to link water travel to the changing chemical nature within the channel for study releases.

8.3.5. Relationship between release movement and chemical change.

The effect of wave and water movement downstream on chemistry change at-a-station, has been argued to create a mechanical dispersion of solutes from dead zone storage, followed by dilution to a water chemistry that is in equilibrium between the chemistry of tributary flows and reservoir water. However, if the wave is behaving kinematically (as suggested by routing models) with the water lagging behind the wave front, then the chemical response within the channel - in relation to the release movement - is likely to be considerably complicated. A dilution in stream water will be created sometime after peak stage. Indeed, the pattern of water chemistry change at-a-station, could be explained purely by this kinematic effect, with the initial rise in solute load exhibited on all of the study rivers, due to the mechanical stirring of inchannel solutes by the wave arrival, and dilution lagging behind the maximum stage attainment resulting from the lag of the water, which will lead in turn to maximum dilution occurring sometime after maximum stage. If such is the case, then argument so far, presenting the importance of dead zones on the effect of water chemistry could be unfounded. The kinematic effect must therefore be considered in depth.

Buchanan (1964) examined the problem of the relationship between the velocity of a flood wave and the mean velocity of water particles in the same reach of the stream. In particular, the time of travel of high quality reservoir release water down a channel was considered. The application of the Manning and Chezy formulas for different types of stream channels, allows the determination of the expected velocity of the flood wave (Vw) and the mean velocity of the stream (v); Table 8.6. This shows that regardless of Manning or Chezy formulas, wide rectangular channels lead to the largest theoretical lag times. Buchanan (1964) using a fluorescent dye tracer for a release of water from Spruce Run reservoir in New Jersey, USA found that the dye lagged behind the leading edge of the wave front by the ratios shown in Table 8.7. Clearly beyond

Channel Type	Ratio vw/v Manning	Chezy
Triangular	1.33	1.25
Wide rectangular	1.67	1.50
Wide parabolic	1.44	1.33

TABLE 8.6. Ratios of velocity of flood wave to mean velocity of stream for three types of channel. (Buchanan, 1964).

Distance below reservoir (miles)	Ratio of leading edge of flood wave to leading edge of dye	Ratio of full effect of flood wave to peak of dye
3.9	1.4	1.1
7.8	1.6	1.3
21.4	2.2	1.6
31.3	2.4	2.2
33.7	2.7	2.0

TABLE 8.7. Relationship between dye and wave movement during a reservoir release (adapted from Buchanan, 1964).

the distance of 21.4 miles from the reservoir ratios are much larger than the highest values predicted for wide rectangular channels from the Chezy or Manning formulae . Buchanan accounts for this by assuming that higher ratios are as a result of inchannel storage of dye in large pools prevalent in the river 25 miles or so below the reservoir. The values found in Buchanan's study demonstrate once again the difficulty of applying theoretical formulae of the Manning or Chezy type to the prediction of wave/water velocities in natural channels. In this instance the problem was created by massive inchannel ponding. For the study rivers of the Tryweryn, Washburn, and North Tyne, the problem was not so much storage, but the estimate of channel roughness at low flow. It can be concluded that this particular theoretical approach to the analysis of kinematic waves is not suitable in this context.

Hamill (1983) used a derived version of the Kleitz-Seddon law to channels of extreme roughness with some success. An adaptation of the formula given by Brady and Johnson (1981) was used:

since $Vwo = k\ (dQ/dA)$ >>

$$Vwo = k\ ((Q_2 - Q_1)/(A_2 - A_1))$$

replacing A_1 with Q_1/v_1 and A_2 with Q_2/v_2 gives:

$$Vwo = k((Q_2 - Q_1)/(Q_2/v_2 - Q_1/v_1))$$

which may be simplified down to:

$$v_2 = (Vwo/k)/(1-(Q_1/Q_2)*((1-vwo)/(k*v_1))) \qquad (Eq.8.11)$$

where suffixes 1 and 2 denote baseflow and wave flow conditions respectively in the reach of the river; v_2 is the velocity of the water to be determined.

For the River Tryweryn, it has already been argued that calculated values of k in the above equation are impractical, because k is assumed to be a constant for channel irregularities. When k is greater than 1 channel storage and irregularities are high, when k is less than 1, channel storage is at a minimum, and the wave is moving at a greater rate than theoretically predicted by the continuity equation (Q=A*V). However, for the study rivers when calculated k is highest, channel irregularities are observed to be lowest. Conversely, when k is low, observed roughness is high. Clearly an important contradiction between theory and practice. In order to assess this contradiction, the derived Kleitz-Seddon law was applied to all releases made on the study rivers (for calculation of travel times, see APPENDIX D1, D2, E1, F1, F2, F3). Results are presented in Table 8.8a-c.

Table 8.8a-c shows an inverse relationship between calculated k and observed wave travel time, and a direct relationship between calculated k and theoretical water travel time. In short, as k increases so the observed wave travel time decreases, and the calculated water travel time increases - a phenomenom that occurs on all three rivers. This pair of relationships is physically improbable, since many of the factors influencing water and wave travel are similar. An extremely rough channel will slow a wave down as well as the associated water moving behind it, although it could be argued that the degree of retardation is likely to be more significant in this instance to the wave, than to the following water because the releases are made on such low flow that the wave energy will be greatly dissipated downstream in overcoming reach irregularities, which are rapidly smoothed out by advancing water particles.

Calculated kinematic values of water movement are generally as would be expected, slower than observed time of travel of the wave however, in some cases predicted water movement is actually faster than observed wave travel, particularly on the upper reaches of the River North Tyne and the 1984 releases on the River Tryweryn. On rough upland channels such an idea is implausable, since water movement downstream is a function of the transverse dispersion of particles through the dead zones and main thalweg. The larger the area of dead zone, the higher the roughness and the greater the residence time of water particles within these areas, hence the less rapidly the water will move downstream. Although wave movement itself will certainly be retarded by such roughness - because its translational is one of energy down a gradient - it is impossible for the actual release of water creating this surge of energy to out run itself. Predictions of water moving ahead of the wave in this study can only be due to errors in the prediction equation.

In defence of the kinematic model, the majority of results in Table 8.8a-c show kinematically calculated water travel times lagging behind observed wave times. Indeed there are lags of anything up to ninety minutes, with the interval increasing

DATE of release	1-2 T_1*	T_2*	1-3 T_1	T_2	1-4 T_1	T	1-5 T	T	1-6 T	T_2
15.5.82							49	110	84	133
k							1.30		1.18	
16.5.82							71	97	110	121
k							1.10		1.03	
4.9.82							94	77	137	105
k							0.75		0.81	
5.9.82							84	84	120	110
k							0.85		0.89	
25.10.82	14	15					82	87	111	120
k	0.89						0.89		1.03	
23.4.83	15	14			51	55	76	91	103	123
k	0.80				0.86		0.91		1.04	
24.4.83	14	14			48	56	72	92	109	120
k	0.80				0.92		0.96		1.01	
30.1.84					53	57			98	132
k					0.90				1.17	
31.1.84					50	61			103	140
k					1.04				1.28	
1.2.84					53	56			105	131
k					0.92				1.20	
5.2.84					52	58			100	134
k					0.91				0.97	
29.5.84	22	14	36	38	57	50			121	116
k	0.80		0.85		0.80				1.12	
30.5.84	22	14	37	38	55	50			121	116
k	0.80		0.85		0.80				1.12	
31.5.84	21	14	37	38	51	50			120	116
k	0.80		0.85		0.80				1.12	
1.6.84	22	14	41	35	60	49			128	110
k	0.80		0.96		0.70				1.18	
2.6.84	15	14	32	39	51	51			116	116
k	0.80		0.96		0.80				1.12	

* T_1 = observed time of travel of the wave (peak to peak) in mins

* T_2 = calculated time of travel of the water (Brady formula, mins)

TABLE 8.8a. Observed wave travel and calculated water travel times. River Tryweryn.

DATE of release	T_1 (mins)	T_2 (mins)	k (Brady)
23.10.82	32	65	2.0
9.4.83	24	71	2.6
10.4.83	27	65	2.3
5.11.83	23	68	2.7

TABLE 8.8b. River Washburn Site 1 to Site 2, comparison between observed wave movement and calculated water movement.

RELEASE volume	0-1		0-2		0-3		0-4		0-5	
	T_1	T_2	T_1	T_2	T_1	T_2	T_1	T_2	T_1	T_2
2.5 - 25	7	5.4	45	43	75	89	155	180	-	-
k	0.44		0.51		0.65		0.78		-	-
2.5 - 50	5	3.8	29.7	30.7	58.7	69.1	109.7	142	107.7	194
k	0.53		0.65		0.84		1.07		0.89	
25 - 50	5	4.6	29	31.6	58	62	109	128	-	-
k	0.46		0.55		0.84		0.95		-	

TABLE 8.8c. River North Tyne. Time of travel of water and wave.

further downstream. Thus, as wave front attenuates, so the rate of water movement slows, presumably due to an increase in area of storage downstream and a reduced energy level. However, in an attempt to produce results more consistent with those expected from the channel conditions the seemingly more realistic inertial k factor (Eq 8.10) was applied to data from the River Tryweryn.

In this way the change in wetted area within the channel during an increase in discharge is given a greater degree of significance, which for reservoir releases at least, the computed k will lead in the calculation to longer time lags for the water behind the wave, and will not produce the unrealistic situation of water actually moving ahead of the wave that its release has instigated. Results are presented for releases made on the River Tryweryn and River North Tyne, in Table 8.9a-d. As the observed time of travel decreases, so theoretical travel time of water increases. This implies that there is an observed wave travel time equivalent to water travel time e.g for reach 1-6 on thr River Tryweryn, this value would approximate to 150 minutes. In order for the wave to travel so slowly, the friction within the channel would have to be great, hence an extreme low flow. In this case, water particles travelling behind the wave would have the opportunity to 'catch' up.

Conversely, when wave travel time is small, hence velocity great - which occurs when releases are made on a high baseflow, with reduced friction - water particle movement will be retarded anyway by friction with virtually stationary old water particles, leading to a storage or ponding effect. So considering the new k results from this angle, would tend to suggest that values are reasonable, although because the rate of water to wave movement has only been estimated purely hypothetically, it is difficult to say if the estimates are accurate. Knowledge of the channel conditions together with detailed observations, have tended to suggest that the theoretically derived new k values, although plausible do predict rather long lag times. Moreover, as discussed earlier Brady and Johnson k values in some cases actually predict water movement to be ahead of wave travel, and thus results seem to be unreliable. In order to assess if these models are really predicting water movement accurately, some objective analysis is required. One way of achieving this is to examine the rate of dilution of inchannel solutes, which will give an indication of water arrival time inspite of the facts that dead solute storage zones could lead to lags between water arrival and maximum

DATE of release	NEW k *	V_2 (m s^{-1})	T_2 (mins)	T_1 (mins)	T_2-T_1
15.5.82	2.16	0.63	212.15	84	138
16.5.82	1.39	0.81	159.64	110	49.64
4.9.82	1.24	0.80	161.47	137	24.47
5.9.82	1.37	0.78	166.90	120	46.90
25.10.82	1.39	0.82	159.46	111	48.46
23.4.83	1.62	0.72	181.18	103	78.18
24.4.83	1.41	0.80	162.68	109	53.68
30.1.84	1.45	0.81	160.35	98	62.35
31.1.84	1.32	0.91	143.65	103	40.65
1.2.84	1.27	0.89	146.29	105	41.29
5.2.84	1.44	0.81	160.49	100	60.49
29.5.84	1.30	0.82	158.46	121	37.46
30.5.84	1.30	0.82	158.46	121	37.46
31.5.84	1.30	0.82	158.46	120	36.46
1.5.84	1.31	0.82	158.46	128	30.46
2.5.84	1.30	0.82	158.46	116	42.46

NEW k = V_1 x (A/Q)
V_2 = calculated velocity (using new k)
T_2 = calculated time of travel of water (using new k)
T_1 = observed time of travel of wave(" ")
T_2-T_1 = time lag between wave and water arrival(" ")

TABLE 8.9a. Time lag between observed wave and calculated water travel, using a new k value. River Tryweryn site 1-6.

DATE of release	NEW k	V_2 (m s^{-1})	T'_2 (mins)	T_1 (mins)	T_2-T_1
SITE 1 - 4					
4.6.83	2.34	0.56	132	51	81
5.6.83	1.91	0.65	112	57	55
30.1.84	2.18	0.59	124	53	71
31.1.84	2.15	0.64	115	50	65
1.2.84	2.14	0.61	120	53	67
5.2.84	2.01	0.63	116	52	64
29.5.84	2.12	0.59	125	57	68
30.5.84	2.12	0.59	125	55	70
31.5.84	2.12	0.59	125	57	68
1.6.84	1.96	0.60	123	60	65
2.6.84	2.27	0.58	126	51	68
23.4.84	2.28	0.56	130	51	79
24.4.84	2.45	0.56	130	48	82
SITE 1 - 3					
4.6.83	2.6	0.48	114	42	72
5.6.83	2.8	0.47	116	39	67
29.5.84	2.7	0.53	104	36	68
30.5.84	2.7	0.53	104	37	67
31.5.84	2.7	0.53	104	37	67
1.6.84	2.3	0.54	102	41	61
2.6.84	3.0	0.52	105	32	73
SITE 1 - 2					
25.10.82	2.7	0.54	40.2	14	26.2
23.4.83	2.8	0.49	44	15	29
24.4.83	2.7	0.54	40.2	14	26.2
29.5.84	1.9	0.52	42	22	20
30.5.84	1.9	0.52	42	22	20
31.5.84	2.0	0.52	42	21	21
1.6.84	1.9	0.52	42	22	20
2.6.84	2.7	0.54	40.2	15	35.2

TABLE 8.9b. Time lag between observed wave and calculated water travel , using a new k value. River Tryweryn sites; 1-4, 1-3, 1-2.

SITE	NEW k	V_2 (m s^{-1})	T_2 (mins)	T_1 (mins)	T_2-T_1
0-1	1.3	0.67	6.2	5	1.2
1-2	1.8	0.62	47	25	22
2-3	1.9	0.68	58	29	29
0-3	1.9	0.65	112	59	53
3-4	3.1	0.55	174	51	123
4-5	2.8	0.45	177	61	116

TABLE 8.9c. River North Tyne, release of 50 $m^3 s^{-1}$ on baseflow of 2.5 $m^3 s^{-1}$, comparison of wave and water movement.

RELEASE OF 25 m^3s^{-1} ON BASEFLOW OF 2.5 m^3s^{-1}

SITE	NEW k	V_2 (m s^{-1})	T_2 (mins)	T_1 (mins)	T_2-T_1
0-1	0.81	1.06	3.9	7	-3.1
1-2	1.04	0.86	34	38	-4
2-3	1.95	0.61	64	30	34
0-3	1.5	0.67	108	75	33
3-4	1.35	0.82	115	80	35

RELEASE OF 50 m^3s^{-1} ON BASEFLOW OF 25 m^3s^{-1}

0-1	1.5	0.61	7	5	2
1-2	2.2	0.52	56	25	31
2-3	1.8	0.71	55	29	26
0-3	1.8	0.63	114	58	56
3-4	6.0	0.30	321	51	270

TABLE 8.9d. River North Tyne, comparison of wave and water movement.

dilution, and that maximum dilution of inchannel solutes could be attained before maximum discharge.

8.3.6. Natural chemical tracers.

The relationship between maximum dilution for calcium and conductivity, and the theoretical maximum water discharge - as calculated by the kinematic wave equation using the Brady-Johnson k, and the inverse of this k - has been considered for the Tryweryn and the North Tyne, Table 8.10. Actual time for maximum dilution is the time taken to reach a stable low after the arrival of the wave (peak stage) whereas, the theoretical time to maximum dilution is the difference between observed wave travel time and calculated water travel time.

For the Tryweryn the mean times to maximum dilution for reaches 1-6, 1-5, 1-4, 1-3 and 1-2 are 41, 38, 26, 15, and 6 minutes respectively. The predicted times according to the Brady-Johnson k factor, of maximum dilution for the same reaches are 7, 14, 3, -2, and 0 minutes; and using the inverse k factor are 63, 89, 75, 70, and 27 minutes respectively.

For the River North Tyne the mean times to maximum dilution for reaches 0-1, 0-2, 0-3, and 0-4 are 27, 30, 46, and 25 minutes respectively, after the attainment of peak stage. The predicted times of maximum dilution are -1, 1, 10, and 32 minutes using the Brady-Johnson k; and 1.2, 23, 53, and 176 minutes using inverse k.

When the Brady-Johnson k is used, in every case apart from site 0-4 on the River North Tyne, theoretical rates of dilution are faster than the observed. In contrast, the inverse k formula, predicts maximum time of dilution substantially after observed dilution. Furthermore, in comparison with observed dilution values, new k theoretical water travel times, except for reach 0-4 on the River North Tyne, follow a similar trend to wave travel times, with steadily decreasing lag times upstream on both rivers. From the Brady and Johnson k viewpoint, it is possible that maximum dilution does occur before maximum discharge. This is illustrated by the stepped releases on the River North Tyne, where the initial release diluted inchannel water to a level equivalent to that of subsequent reservoir release water, leading to maximum dilution before maximum discharge. However, on the North Tyne, the results in table 8.10 refer only to the first release, and if dilution is reached a long time before the theoretical arrival of the water, it is

DATE of release	Time to steady Ca dilution (T3)* (mins)	MODE OF T_3	NEW k T_2-T_1 (theoretical time to max dilution)	BRADY k T_2-T_1 (theoretical time to max dilution)
SITE 1 TO SITE 6				
15.5.82	35to 45	40	138	49
16.5.82	40	40	50	11
4.9.82	60 to 70	65	24	-32
5.9.82	35 to 38	37	47	-10
25.10.82	38 to 40	39	48	9
23.4.83	42 to 80	61	78	10
24.4.83	42 to 44	43	54	10
mean		41	63	7
SITE 1 to SITE 5				
15.5.82	30 to 35	33	49	50
16.5.82	30	30	71	26
4.9.82	54 to 56	55	94	-17
5.9.82	30 to 35	33	84	0
25.10.82	30 to 30	35	82	5
23.4.83	36 to 48	42	76	15
24.4.83	28 to 35	37	172	20
mean		38	89	14
SITE 1 to SITE 4				
23.4.83	13 to 45	29	82	4
24.4.83	12 to 30	21	82	8
4.6.83	15 to 42	29	81	2
5.6.83	20 to 30	25	55	-3
mean		26	75	3
SITE 1 to SITE 3				
23.4.83	10 to 30	20	-	2
24.4.83	8 to 20	15	-	1
4.6.83	0 to 28	14	72	-8
5.6.83	0 to 20	10	67	-3
mean		15	70	-2
SITE 1 to SITE 2				
25.10.82	6 to 11	9	26	1
23.4.83	0 to 7	3.5	29	-1
24.4.83	0 to 12	6	26	0
mean		6	27	0

TABLE 8.10. Comparison of actual time of maximum dilution of calcium and conductivity, with theoretical times, on the Tryweryn.

difficult to understand exactly why the inchannel water is being diluted shortly after the wave has arrived. Similarly for the River Tryweryn, if the water lags so much behind the wave front,then observed dilution must be the result of factors other than the arrival of reservoir water, an idea that is rather improbable. Therefore, it must be concluded, that although the inverse k in the kinematic wave formula gives a more realistic evaluation of the inertial forces within the channel, on its own it does not help with the estimation of water travel time from wave travel time.

The Brady-Johnson k, predicts the arrival of the water to actually be ahead of observed maximum dilution, a fact that is consistent with the findings already presented. The effects of inchannel solute stores becoming operative during the release are likely to lead to maximum dilution occurring sometime after maximum discharge. This makes the use of end point dilution as a tool for tracing 'clean' water movement down a channel impractical. However, the study does show that the kinematic theory alone does not explain chemical response within a channel to releases. Furthermore it indicates why different solutes behave differently during a sudden rise in discharge. The response of individual solutes is dependent upon the volume and position of storage of that solute in the channel dead zones. Thus on the River North Tyne, calcium reaches a minimum value at site 2, approximately 20 minutes before nitrate; at site 3 calcium and nitrate reach minimums simultaneously, however, at site 4, nitrate is diluted almost instantaneously whereas, calcium takes 20 minutes to reach a low (see Table 8.11). This demonstrates the very local response of solutes to a reservoir release, and shows that at site 2 calcium ions are either more accessible to the rising water level, or are less abundant, than nitrate ions. Whereas, at site 3 accessibility and concentrations of the two ions are similar, in contrast to site 4, where admittedly the effect of the release is reduced, but the accessibilty and abundance of calcium is significantly greater than that of nitrate.

8.4. Chapter summary.

The kinematic wave theory alone, modified or otherwise, is not sufficient to explain the rates of chemical change with reservoir releases on the rivers Tryweryn, Washburn or North Tyne, indeed these conclusions may be generalised to most boulder-bed channels receiving reservoir releases. The problem is too complex for a simple routing model to provide the

	Time to max dilution after wave arrival (mins)			
Site	Cond	pH	Nitrate	calcium
1	25	-	20	30
2	20	65	60	41
3	50	-	42	41
4	30	20	2	20

TABLE 8.11. Time to maximum dilution after arrival of the major first peak of the release, River North Tyne.

solution. Areas of dead zone storage release solutes into the main thalweg at a rate equivalent to the volume of solute in storage and the dispersion of water through that zone. Consequently, if solute supply is high the time to maximum dilution is likely to be great, although of course this is dependent upon the rate of water movement into the zone i.e the rate of stage rise at-a-station. Conversely, if solute supply is limited, then maximum dilution will be reached well before the arrival of maximum discharge.

Fig. 8.24, attempts to summarise the effect of a release on channel water chemistry, by linking dead zone processes with flow routing. From the diagram it is clear that there are three vital factors joining together the hydraulic and quality response, namely; channel roughness (which determines to a large extent potential solute storage zones, and is in itself governed by the level of compensation discharge); rate of rise of the release front at-a-station (which determines the degree of disturbance of dead zones, and is itself limited by release strategy); and the relationship between wave and water movement (which governs the amount and degree of solute disturbance, and is basically a function of the release strategy and the rate of rise). The data collected show at-a-station inchannel water chemistry response, to the combined effects of kinematic routing and the dispersion of solutes in and out of dead storage zones. The study cannot definitely confirm or otherwise, the validity of the kinematic routing model, nor can it satisfactorily produce an elaborate model predicting quantifiably the input from aggregated dead zones. What however it does do, is to show that in upland channels the effect of dead storage zones are significant to the rate of change of individual chemistries at-a-station during a rise of water level, and that such naturally occurring solutes cannot be used as surrogate tracers, for water particles.

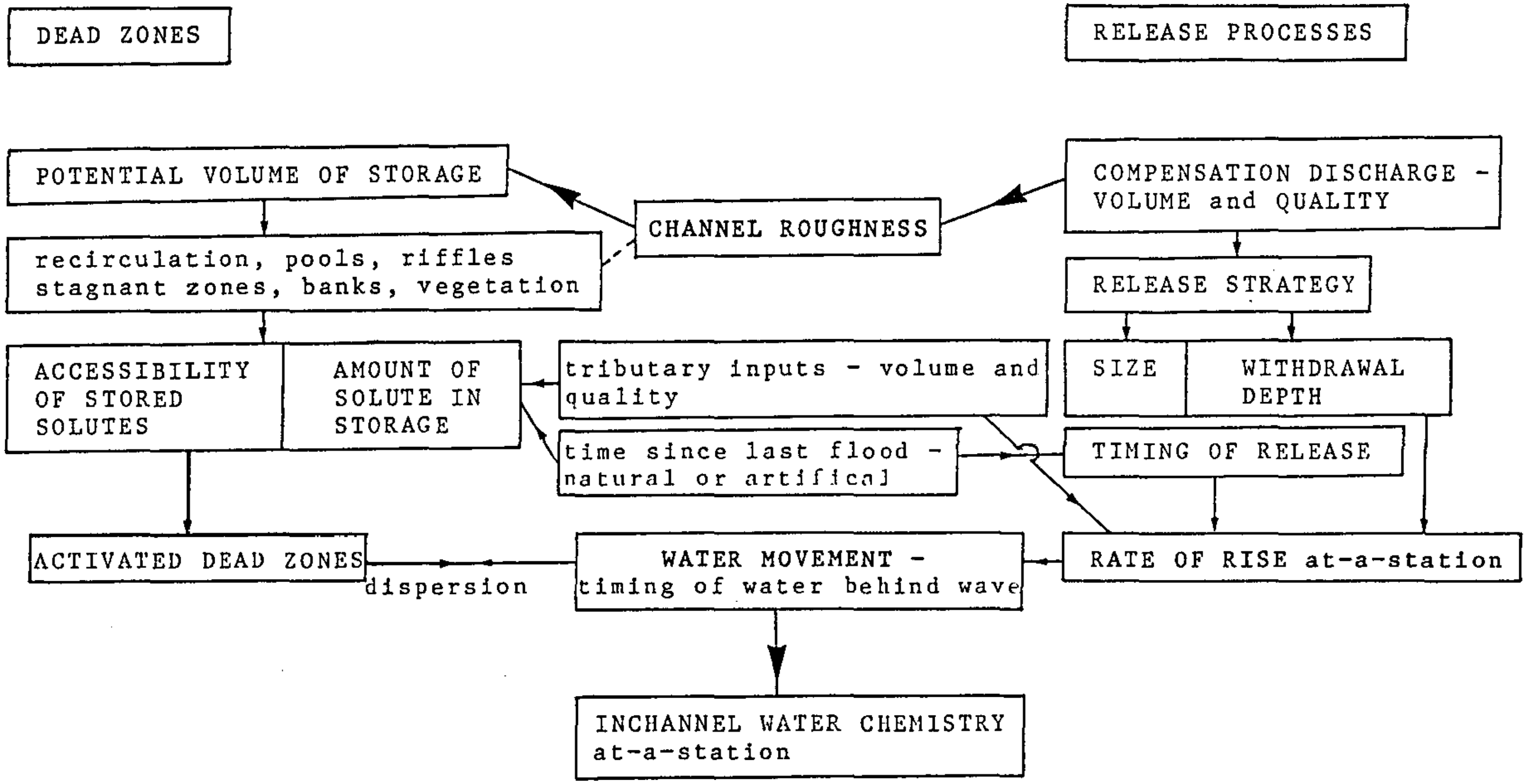


Fig. 8.24. The linkage between release water routing, dead zone storage and at-a-station water chemistry.

CHAPTER 9.

CONCLUSION.

"...what sort of universe do we demand?
If it were small enough to be cosy, it
would not be big enough to be sublime. If
it is large enough for us to stretch our
spiritual wings in, it must be large
enough to baffle us." C. S. Lewis, 1971.

9.1. Objectives restated.

This thesis has attempted to identify water quantity - quality relationships within the context of regulated rivers. Different responses at different timescales have been considered, together with the spatial implications of such impacts. This chapter seeks to draw conclusions from the research and to suggest some implications of these findings.

9.1.1. Chemical modification of stream water in reservoirs.

Most work on reservoirs cited in the literature tends to suggest that impoundment of stream water generally improves water quality by reducing the solute load through various bio-geo-chemical processes. For example Harding et al (1981) report the depositing of harmful heavy metals in an upstream reservoir; Garnett (1975) and Soltero et al (1973) suggest that nitrates and other nutrients are reduced in concentration; and calcification has been recorded (Hannan, 1980; Garnett, 1975; Crisp, 1977). However, when considering the effect of impoundment on outflowing water, it is important to distinguish at which level releases are being made from (Martin and Arneson, 1978), if water is released from basal layers there is a possibility of severe deoxygenation problems (Gordon and Nicholas, 1977; Egborge, 1979).

For releases made on all the rivers in this study, with the exception of the River North Tyne, only surface layer sources were used. Findings to some extent were not those expected according to the literature, which points to a general reduction of solute concentrations in release water from such strata. Compensation flow from the Derwent Valley system of reservoirs was actually more concentrated in nitrate, conductivity, and calcium levels, than the inflowing water. Furthermore, any seasonal effects of thermal stratification, overturn, or eutrophication reflected in the chemical nature of release water were negligible. For the River Washburn, release water was also more concentrated in calcium and nitrate than the inflowing river water, indicating a concentrating influence of the reservoir even in the surface strata. Similar results were found for the River North Tyne, which is to be expected since basal water (after overturn) was the source of release discharge. Thus, during major releases when reservoir flow became the major water source, a concentrating of some solutes within the river channel was recorded. In contrast, releases from the Tryweryn were either of very similar quality to water immediately below the outfall, or indeed in some instances, lower in solutes than the recieving river water. This contrast, on the Tryweryn was exaggerated with distance from the dam.

9.1.2. Comparison of reservoir impact with other man induced catchment events.

In order to put the effects of reservoir releases on downstream water chemistry into context, a comparison was made with other man induced changes within the catchment. From the literature a summary table of the extent of such changes was produced (Table 1.9). Urbanisation is shown to increase conductivity by upto four times the original value, calcium 1.5x, nitrate 6-13x, chloride by anything from 4.5-500x, and pH by upto 3.9 units. Various agricultural practices are shown to alter conductivity by 0.9x, and nitrate by 1.5 and 4.7x. Comparatively, vegetation removal is documented to increase solute concentrations by 1.8 for conductivity, 0.9-2.6 for calcium, anything from 1.6-50x for nitrate, 2x for chloride, and 0.8 pH units. Irrigation effects are also significant with changes in conductivity levels of 5x, calcium 4x, nitrate 10x, chloride 12x, and pH by 0.4 units. Results collected in this study for the potential increase in conductivity after the construction of the Derwent Valley reservoir system, gives a change in values at low flow of upto 0.42x, and the estimated difference between low flow and high flow conductivities for releases made at extreme low flow, could be in the order of 3x - similar to the effects of other man induced catchment changes. During releases on the rivers Tryweryn, Washburn and North Tyne (Table 7.1), typical solute variation during a release was about 1.4-2.2x, and a change in pH by upto 1.8 units, which although much below the documented upper values of other man induced change, is certainly comparable with the lower levels, and represents a significant impact on natural water chemistry.

9.2. The timescale of response in relation to hydrologic factors.

Three timescales of response were considered (although only two of these in detail), and it was found that it was not so much the chemical effects of impoundment that were important, but rather changes associated with the new flow regime. From the long term perspective, the significance of construction of the Derwent Valley reservoir system was examined hypothetically, and results indicated that upland floods (which have now been removed), could have had significant impacts on downstream water chemistry, changing conductivity values by as much as a third of original values, for distances beyond 40 kilometres below the now dam outfall. At the seasonal and instantaneous time-scales more data were able to be collected than for the long term perspective, and therefore most discussion focused on these two levels of response.

At the seasonal time-scale (Fig 9.1), work from the River Derwent showed that the reduced flow variability, enabled tributary water from limestone areas of the catchment to dominate the chemical nature of river throughout the year, and that minor seasonal patterns reflected the changing dominance of different hydrological pathways supplying water to these tributaries. The constant reduced (when comparing naturalised and regulated flow data - Fig. 6.16) low flow from the reservoir, reduced flood flows from gritstone sources, the aquifer regulated inputs from the rivers' Noe and Wye and the chemically consistent water from the mine drainings, governs the seasonal variation in water chemistry. Reduced low flow has allowed the potential intensification of polluted areas below the River Wye, due to increased residence time of pollutants, thus leading to the possibility of winter nitrification. In short as a result of the flow regime created by river regulation, the River Derwent from the River Noe down at least as far as Ambergate, has been changed from being essentially a limestone stream, with periods of extreme dilution due to the influx of large volumes of gritstone derived water, to one almost entirely of limestone character water, modified minimally by reservoir water inputs.

At the instantaneous timescale (Fig 9.1), that is during pulse releases on the Rivers Tryweryn, Washburn and North Tyne, the hydrological impacts were found to relate to physical

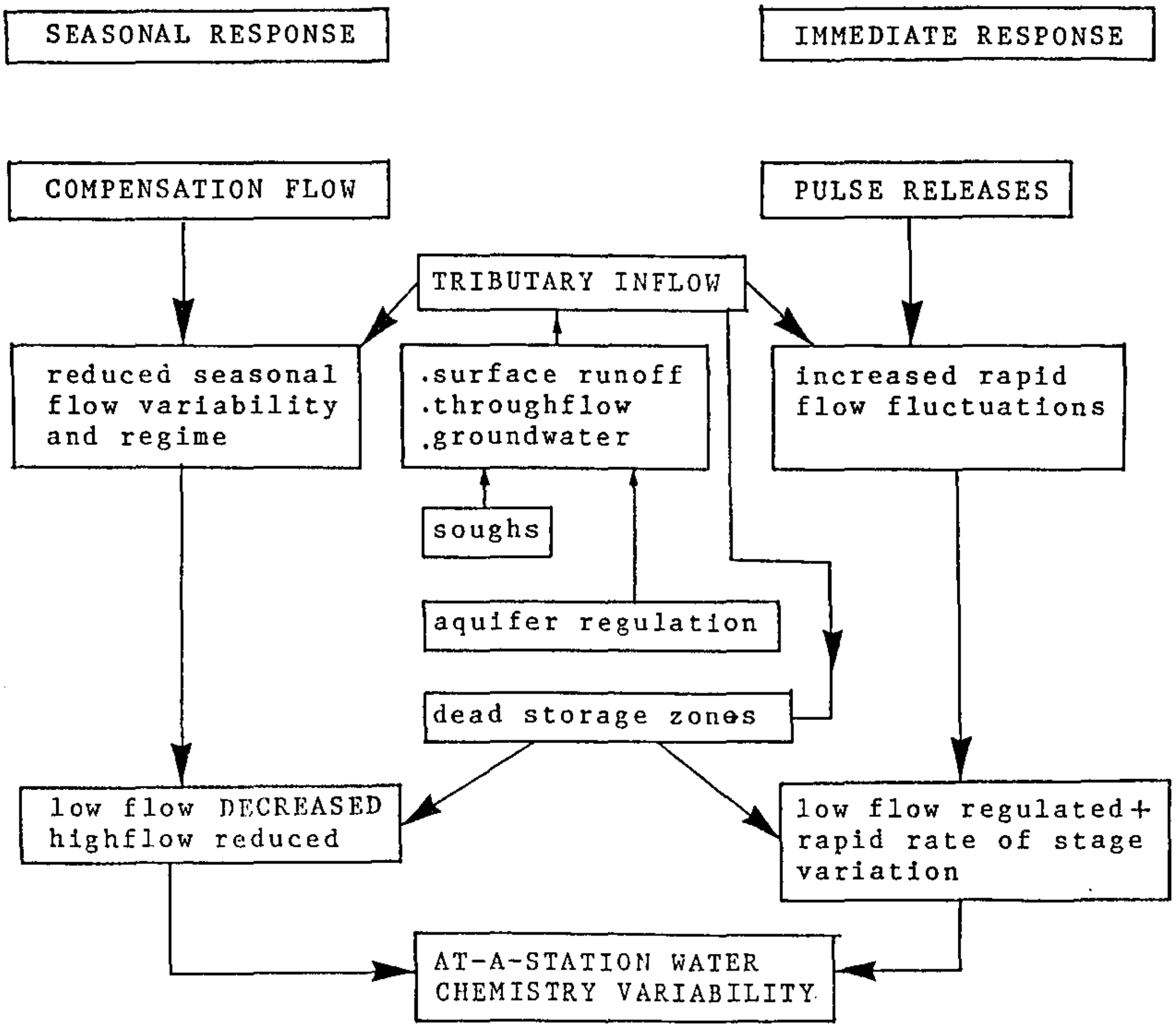


Fig.9.1. A summary of the timescale of water quality response in regulated rivers, in relation to hydrological factors.

disturbance of inchannel storage zones, followed by the dilution of these to a level of compromise between low flow channel and reservoir water chemistry. The concentration of individual solutes in the dead storage zones, was found to be dependent upon the physical characteristics of the channel, the level of low flow, the time since the last reservoir release or catchment flood, and the significance of tributary input to low flow discharge. The degree of response to the releases due to the significance of dead zone storage, was found to be not so much dependent on the volume of release, but rather on the steepness of the wave front i.e the rate of stage change at-a-station, and on the low flow depth upon which the release was made.

9.3. Seasonal water quality changes.

Changes in water quality at a seasonal timescale were considered on the River Derwent. The effects of the reservoir upon such patterns could either be from the physical, and subsequent changes associated with the impoundment of the river, or as a result of regulation policy.

9.3.1. Impoundment.

The effect of impoundment on river water quality is summarised by comparing inflow and outflow values for the River Derwent and Derwent Valley reservoir (Table 5.4). Different determinands behave in different ways. Conductivity has a yearly spread of some 25 $\mu S\ cm^{-1}$ in inflowing water, which is increased by a further 15 $\mu S\ cm^{-1}$ in outflowing water. pH becomes considerably more uniform as a result of impoundment, with a variation of about 2 pH units in inflowing water, as compared with a span of 1.1 units in outflowing water. Furthermore, average yearly pH is raised markedly in reservoir water, from about pH 5.6 to pH 7.4. In balance the effect of the reservoir on nitrate levels is to actually increase them. The reverse is the expected response (e.g Garnett, 1975). However, high summer nitrate values upstream are removed by impoundment, although this is replaced by a reservoir peak in autumn. On average chloride values are increased in outflowing water by approximately 5 $mg\ l^{-1}$. The rough seasonal pattern of high chloride in spring/summer, and low in winter upstream, is also apparent in down reservoir water. Calcium concentrations are raised considerably by the impoundment, on average an increase of 30% is found. Such results correspond not so much to lacustrine processes of thermal stratification, and density currents, but rather to the hydrological changes in the catchment of diverting limestone derived water into the Derwent Valley reservoir system.

In comparison with results presented from another upland reservoir in the UK, namely, Cow Green Reservoir (Crisp, 1977), data from the Derwent Reservoir have certain similarities (Table 9.1). Maximum nitrate concentration, for example, is increased in outflowing water for both water bodies, although Cow Green Reservoir unlike Derwent Reservoir, considerably reduces the seasonal range. It also causes a reduction in range of chloride and calcium, whereas these determinands are altered little by impoundment in the Derwent Reservoir. Calcium concentrations in particular from Cow Green, are reduced both in range and magnitude as a result of storage, from 3.5-37.5 to 6.4-8.9mg l^{-1}, in comparison the effect of the Derwent is insignificant, varying the range and values of calcium from 3-10 to 7-14mg l^{-1}. This increase was found to relate to inflows from the River Noe. Interestingly, calcium seasonal values at the outflow of both reservoirs compare, with maxima in autumn and a minimum in winter. However, chloride seasonal peaks do not coincide, with a high for Cow Green in spring, as opposed to a maximum for the Derwent during summer, and minimum values for the former in autumn, and for the latter in winter. Nitrate maximums at the outfalls of the two reservoirs is found during autumn, although lows are out of synchronisation, with a minimum at Cow Green during summer, and a minimum for the Derwent during winter. In short, it seems that whereas Cow Green Reservoir reduces the amplitude of chemical fluctuations, primarily through reducing maximum values of solutes in inflowing water, the Derwent Valley Reservoir raises the levels of solutes in inflowing water relatively uniformly throughout the year. Both reservoirs however, do have the effect of reducing seasonal variabilty of solute concentrations.

9.3.2. Flow regulation.

In itself the change in chemical concentration of the inflowing River Derwent water, by storage within the reservoir, coupled with the addition of limestone derived inputs to the Derwent Valley Reservoir, has only a marginal effect on downstream water chemistry. Primarily, this is due to the rapid insignificance of reservoir compensation flow in comparison to other inputs, in particular contributions from the rivers' Noe and Wye, and mine working drainage. However, the fact that the reservoir has reduced flow variability from the gritstone part of the catchment, means that the chemical nature of the Derwent

Determinand	INFLOW RANGE mg l^{-1}		OUTFLOW RANGE mg, l^{-1}	
	Cow Green	Derwent	Cow Green	Derwent
Calcium	3.5-37.2	3.0-10.0	6.4-8.9	7.0-14.0
Chloride	3.0-5.0	7.5-16.0	4.2-4.9	9.0-19.0
Nitrate	0-0.151	t-0.66	0.085-0.16	t-0.96
	SEASONAL MAXIMUM (OUTFLOW)		SEASONAL MINIMUM (OUTFLOW)	
Calcium	Aut 8.2-9.2	Aut 11-13	Win 7.2-8.2	Win 7-9
Chloride	Spr 4.6-4.9	Sum 17-19	Aut 4.3-4.6	Win 10-12
Nitrate	Aut 0.12-0.16	Aut 0.84-0.96	Sum 0.09-0.12	Win .1-.6

t: trace

Table 9.1. Comparison of inflow and outflow solute concentrations, and seasonal maximum and minimum outflow solute concentrations, between Cow Green Reservoir and Derwent Valley Reservoir.

below the River Noe, reflects the processes occurring within the tributary catchments, modified to an extent by sough water input. The seasonal pattern of the downstream River Derwent chemistry therefore, is the result of the altered hydrological regime by regulation. The seasonal pattern of conductivity serves to illustrate this. Above the reservoir the seasonal march of conductivity is (highest values first) from; summer-autumn-winter-spring, at Matlock this pattern is dependent upon the discharge level at which seasons are compared. At 15 $m^3 s^{-1}$ for example, the seasonal march is totally opposite to that above the reservoir i.e. spring-winter-autumn-summer. However, if a discharge of 5 $m^3 s^{-1}$ is taken, then the pattern is; winter-spring-summer-autumn (Fig.9.2).

Effectively, the downstream water quality of the Derwent is determined by the changing contribution of discharge from separate hydrological pathways, as portrayed in Fig. 9.2. This pattern is allowed to establish because, and not inspite of the reservoir. By keeping the contribution of low solute load gritstone derived water constant, the effect of other hydrological sources at different discharge volume, are allowed to dominate the water chemistry. Furthermore, the spread of conductivity values between seasons is greater at higher discharges, a phenomenom that would be unlikely to occur but for regulation. Since high volume, low concentration upstream catchment water would tend to reduce downstream conductivities to a uniform low, regardless of the season. Indeed, for the Derwent Reservoir system at least, where eutrophication is unimportant, hydrological changes have had far greater significance on downstream water chemistry, than chemical (bio or geo) changes in the reservoir itself.

9.4. Short term water quality changes during pulse releases.

Most work on the effect of reservoirs on the riverine system has tended to suggest that the impact on water quality is restricted to a short distance below the dam (less than one kilometre) e.g Lavis and Smith (1972), Crisp (1977), Hannan (1980). However, results from this study show that due to tributary inflow, the hydrological effect of compensation discharge or pulsed releases, on the River Derwent can be monitored at leat fifty kilometres below the dam. In that respect findings confirm work by Roux (1984). It was found that on the River Tryweryn the chemical change induced by releases actually increased downstream, due to the higher concentration of solutes in low flow downstream resulting from tributary

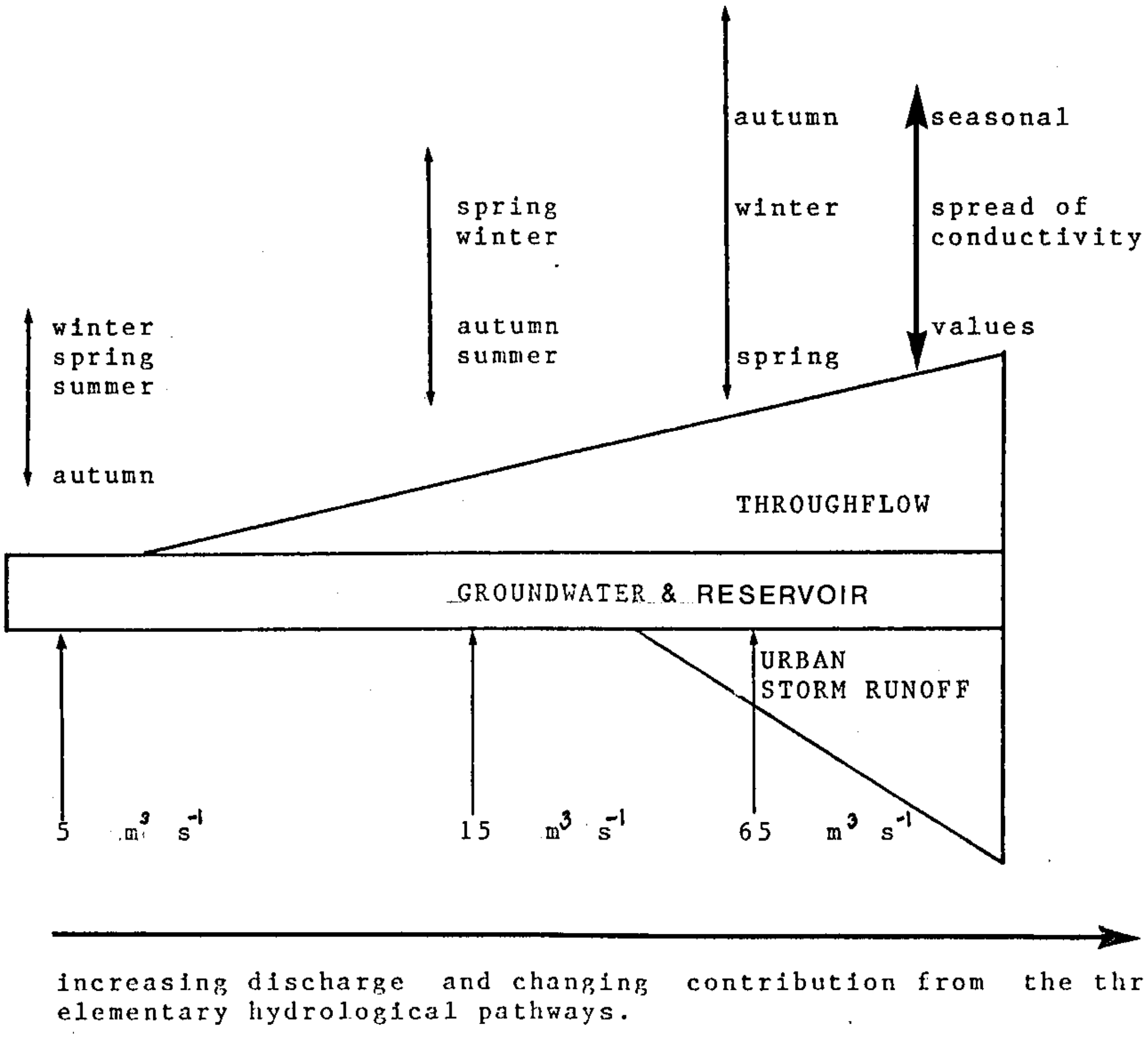


Fig. 9.2. The true seasonal variation of background water conductivity, at Matlock.

inputs whilst the reservoir is releasing only compensation discharge.

In contrast to this, on both the River Washburn and the River North Tyne, chemical change due to releases decreased with distance below the outfall. For the case of the River Washburn, this was because, more highly concentrated release water was gradually being diluted downstream by existing low concentration inchannel water. Due to the absence of significant tributary inputs to the main channel below the dam, these findings suggest that either major releases are made from a reservoir strata more highly concentrated in solutes than that released as compensation flow, or that there is rapid ecological utilisation of compensation flow solutes. From the data collected, the former explanation is the more likely. On the River North Tyne the reason for a reduction of chemical change downstream, was that large tributary flows masked any influence of the reservoir water. This may be explained by reference back to the simple dilution equation (Eq. 6.1). The combined chemical nature of the two water sources was extremely similar to that of the tributary input.

Findings from the River Derwent and the River Tryweryn for nitrate and calcium are similar to results presented by Wright (1984) for pH, where the regulation of main channel flow by release policy, and the unregulated nature of tributary inflow, tended to allow the chemistry of the tributaries to become dominant, leading to considerable lowering of main channel pH.

From work on the River Tryweryn, and supported by findings from the River Washburn and River North Tyne, the effects of pulse releases on water quality downstream were found to be very short lived , and that channel water chemistry begins to move rapidly back to a level equivalent to that of compensation water plus tributary inflow, as soon as the release is finished. Thus one minor subcatchment tributary flood on the Tryweryn, was found to totally obscure the scouring and diluting effect of a large scale pulsed release. The consequences of releases made into channels that have not adjusted to regular artificial flow fluctuations however, are likely to be somewhat more permanent.

The short term impacts of pulse releases are remarkably consistent for each release, on each of the three study rivers. The basic response is for solute values (either nitrate, conductivity or calcium) to increase, as stage rises, then to rapidly return to a level below pre-release solute concentration and to stay relatively constant at this value throughout the remainder of the release. Such a pattern of change becomes more marked downstream on the River Tryweryn, in contrast with the reduced response downstream on the Rivers Washburn and North Tyne. This is explained by the initial physical disturbance of so called 'dead zone' solutes, which are washed into solution rapidly as stage rises. These solutes and existing channel solutes are then diluted to a constant low equivalent to a compromise between that of reservoir and channel water. On the River Tryweryn, the changes are greatest downstream, due to the larger difference in solute concentration of channel and reservoir water, plus the increasing area of potential dead zone stores downstream.

For the River Washburn change is less marked the further away from the reservoir the release water moves, and is explained by:- i) the fact that reservoir release water is often higher in some solutes, in particular nitrate, than receiving river water, and so will tend to be diluted downstream, and ii) that there is little tributary inflow to the Washburn to replenish dead storage between releases, and therefore since stage change is reduced downstream, the access to storage zones is reduced. On the River North Tyne, the reverse reasons can be given to explain decreasing change downstream. Tributary inflow becomes so significant as to considerably reduce the impact of the reservoir release, thus even at the peak of the release, tributary discharge is actually in the majority in terms of water quantity downstream.

Different solutes give roughly similar patterns of response to release strategy, however rates of change vary considerably. This is directly due to to the contribution to channel solute levels by dead zone storage, and the release of these into solution with rising water levels. Different solutes will be stored in different spatial locations, and at different amounts, hence the variation.

9.5. Combined hydraulic-water quality models.

The lag between wave and water documented by for example Heidel (1956), Beschta et al (1981), Johnson and Glover (1974), may be in excess of seventy hours, over a sixty kilometre stretch. For the releases monitored however it was difficult accurately to quantify the lag time, due to the disturbance of inchannel solutes. Nevertheless even with these stores accounted for, the lag between wave and water movement, proportionally, was found to be much smaller than results presented by the above authors. Furthermore, unlike these studies, it was found that it was not so much the size of release that was important in determining the lag time between wave and water movement, and the impact on water chemistry, but rather the depth of low flow of the receiving river, together with the rate of rise of the release front at-a-station. The depth of low flow determined the magnitude of frictional forces acting on the release water and wave, and the rate of rise of the release front was also in part dependent on low flow frictional forces, but also upon the release strategy.

The study showed the importance of both channel form and resistance elements in determining the character of wave movement and hydrochemical lags. Such lags were found to be exaggerated by the importance of dead zones, actively contributing to solute concentration as stage rose. Thus, identification of the precise time of water arrival by dilution of inchannel solutes, the maximum of which might be thought to coincide with the first arrival of maximum water volume, could not be relied on. Therefore it was found that the value of naturally occurring solutes either as tracers, or as agents of dilution gauging is minimal for accurate analysis. However, the time between initial disturbance and maximum dilution of inchannel solutes, does give a good indication of the lag time between the start of wave arrival and the start of water arrival, since maximum dilution will occur sometime between the start of water increase, and maximum discharge, whereas solute stores will be initially disturbed by physical changes within the channel associated with wave arrival.

Thus flow and water quality changes along the channel, are more closely related to the travel rate of the wave front, rather than the speed or magnitude of the wave peak. In particular, the lag effect is not simply related to the magnitude of discharge change, but to the pre-release flow conditions. These are important in determining the degree of channel resistance, incorporating skin and form roughness, and also the potential storage area for inchannel solutes. Although hydraulic routing models, in particular applications of the kinematic wave theory (Brady and Johnson, 1981) did not accurately fit results from releases on the three study rivers, primarily due to the ineffectiveness of the formulation of inchannel resistance, this study's work on adapting these, could not be substantiated without the use of artificial tracers, the application of which are simply not practical on rivers used as portable water supplies.

9.6. A perspective.

A study of this nature inevitably raises questions as to the ecological implications of river regulation by large reservoirs, as well as possible management ramifications. It also highlights other areas that require research.

9.6.1. Ecological implications.

The degree of impact of regulation on downstream ecology is closely dependent upon the time-scale of consideration. Thus different problems are created by the release policy of the River Derwent, to those of the Rivers Tryweryn, Washburn, and North Tyne.

On the River Derwent, regulation has changed the chemical character of the water quality, from being gritstone/limestone dominant, to solely limestone dominant. Flow regulation has removed the 'cleansing' effect of low solute, gritstone water floods. Thus, a potential has arisen for the build up of eutrophic zones. Indeed, it has been suggested (Chapter 6), that the problem of algal blooms could be significant in winter at Matlock. High nitrate concentrations (resulting from agricultural practices) in the streams of the Wye catchment, draining into the Derwent, could create the ideal nutrient environment for algal growth and the subsequent deoxygenation problems (Gordon and Nicholas, 1977). Indeed raised summer low flow could lead to reduced aeration of the river water, as result of increased depth, leading to ecological stress of the form presented in a simulation model for the River Moselle, France by Gras and Albignat (1985).

In contrast, on the River Tryweryn where reservoir releases are so frequent, and the change of water depth so erratic, that it is unlikely that a raised low flow will be maintained for a sufficient length of time to enable a deoxygenation problem to occur, although further research could prove otherwise. Further more, the lack of suspended sediment transportation during releases, coupled with labeled pebble experiments, have implied that the substrate has stabilised to accomodate such rapid flow changes, thus there is a potential for the all-year-round growth of periphyton and macrophytes (Petts, 1984). Changes in water quality below dams can directly affect fauna in three ways: by tolerance limits; by inhibiting normal sequence of reproduction, development and survival; and by altering the competitive balance of predator-prey relationships. In particular this study has shown the significant rate of change of water quality at-a-station, and the extremely rapid changes of water velocity that can be achieved by releases. Such instantaneous changes in velocity and water quality may initially cause considerable stress to fauna within the regulated channel. Indeed the initial flushing effect of inchannel solutes, may be sufficient in some instances to raise solute concentrations or pH to near lethal levels, not least if toxic metals are involved. The rapid change give biota little chance to adapt to the new environment. It could be argued that it is this sudden change in chemical conditions, which render reservoir releases unsuitable as artificial freshet to stimulate salmonid migration (Chapter 8).

9.6.2 Management implications.

The management implications of this study are significant, and are basically four fold. First, river impoundment in Great Britain at least, is more likely to have a hydrological impact on the downstream water chemistry, than a limnological impact. Control policy within regulated rivers must focus attention from this angle therefore, on both quality and quantity of releases, not only of the instantaneous pulses, but also of the compensation flow. Second, the release strategy from regulatory reservoirs, must be very carefully considered if permanent damage to the stream substrate, quality, and biota is not to be done. Releases on the River Tryweryn showed three important factors:- i) that release waves made upto one hour apart, can 'catch' each other up within minimal distances (less than one kilometre), so that a stepped pattern of releases at the dam outfall, may represent a large single fronted shock wave downstream ii) that single release waves, can actually steepen - as opposed to attenuate - downstream, even in channels of extreme skin and form resistance iii) that it is not so much the volume of discharge which is important to its travel rate downstream, but rather the depth of compensation flow (determining the extent of channel downstream resistance) upon which the release is made.

Third, water chemistry changes associated with reservoir releases, may actually increase with distance downstream. Therefore it is important to consider the nature of release water in comparison with that of receiving channel water a considerable distance downstream (at least 10 kilometres), if stress is not to placed on river ecology, or indeed a water of particular quality is required. Fourth, if the waterway is to be used as an aqueduct for the transport of water, the changed chemical nature of the regulated river, primarily due to the relatively increased hydrological dominance of tributary inputs, is likely to be seriously changed by releases of different quality reservoir water. Furthermore, the initial concentrating effect of such releases, due to the flushing of dead zone solute stores, is liable to produce considerable stress on the ecological system, and indeed make the water unsuitable for either industrial or domestic users. Thus, considerable expensive reservoir water will be wasted at the abstraction point whilst the initial flush is being diluted.

9.6.3. Needs.

The study identifies four areas of need. First, there is a need to compare over a longer timescale the difference between inflowing and outflowing water quality in Britain's regulating reservoirs in order to assess the impact of regulation on river water chemistry. Secondly, the need exists to examine the downstream patterns of chemical change created by regulation, over longer channel reaches, within the order of 10-100 kilometres. Thirdly, there is a need to continue the development of relationships between water routing models and water quality models. In this context the calculation and representation of channel resistance at lowflow must be improved, as must models of longitudinal dispersion of solutes in upland channels. Fourthly, the use of reservoir release strategies for maintaining downstream water-quality need examination. The maintenance of compensation flows is assumed to be a major benefit of river impoundment because they can provide dilution for various pollutants. However, in practice, the elevation of 'low flows' reduces both the reaeration of the water, because the oxygen exchange at the surface is distributed over a greater depth, and the residence time between two points of injection, thereby reducing the natural biodegradation potential (Gras and Albignat, 1985). Therefore if a release is not aerated by the time it reaches, for example, the first sewage outfall, severe oxygen depletion could occur in the river.

This study has demonstrated the pattern of chemical response in upland channels with pulse releases, showing the importance of the pre-release compensation flow, rate of stage rise at-a-station, and the effects of dead storage zones. It has also shown the importance of tributary input in determining not only the chemical response within the main channel, but also the hydraulic response. Although the study did advance significantly the knowledge of connection between hydraulic and chemical processes in upland regulated channels, improved simulations are required in order to predict the magnitude and timing of the response of inchannel water chemistry to reservoir releases.

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APPENDIX A.

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University of Technology

LOUGHBOROUGH LEICESTERSHIRE LE11 3TU Tel: 0509 63171 Telex 34319 Telegrams Technology Loughborough

DEPARTMENT OF GEOGRAPHY
Head of Department: Professor R. A. Butlin

TRF/JJ

Dear Sir

I am working on a research project at Loughborough University, supervised by Dr G.E. PETTS (Loughborough University) and Dr R. WOOD (Severn-Trent Water Authority), with regard to the effects of reservoir construction on low flows and water quality, aiming to produce a generally applicable model directed particularly to predicting the effects of flow augmentation releases.

A very important part of the research is to gain an appreciation of the country-wide impact of reservoirs on low river flow, and hence how applicable the model could be. It is with this aim that I have enclosed a simple questionnaire and would be grateful if you would complete it, adding any information that might be of importance when considering rivers receiving releases from man-made reservoirs.

Yours faithfully

T. R. FOULGER

Appendix A.1

FOR WHAT YOU CONSIDER TO BE YOUR FIVE MAJOR RESERVOIRS:

1)What is the maximum depth and capacity of each reservoir?

RESERVOIR NAME & 4fig. GR of outflow.	MAX.DEPTH (m)	MAX CAPACITY (m^3)

2)What is the mean daily compensation flow from each reservoir during the year?

RESERVOIR NAME	DAILY COMPENSATION FLOW (m^3 per day)			
	SPRING	SUMMER	AUTUMN	WINTER

3)Are these general seasonal flows ever augmented by further reservoir release?
F for frequently(3 or more per season) O for occasionally(less than 3/season)

RESERVOIR NAME	FREQUENCY OF RESERVOIR RELEASES			
	SPRING	SUMMER	AUTUMN	WINTER

4)What purposes are these extra augmentation flows made for? Please tick:

PURPOSE	RESERVOIR NAME				
Domestic use					
Industrial use					
Recreational					
Aesthetic					
Safety(Pollution) or legal					
Reduce chance of overspill					
Other					

5) In what manner are these augmentations made?Please tick:

TYPE OF RELEASE	RESERVOIR NAME				
SINGLE					
STEPPED					

6)From what level of the reservoir are the releases usually made?please tick:

WATER LEVEL	RESERVOIR NAME				
UPPER					
MIDDLE					
LOWER					
THROUGHOUT STRATA					

7)Any comments or additional information on reservoir releases......

(P.T.O FOR EXTRA SPACE)

SITE	conductivity	pH	Nitrate	Chloride	Calcium
	$\mu S cm^{-1}$	units	$mg l^{-1}$	$mg l^{-1}$	$mg l^{-1}$
1	41	6.70	0.05	10	2.31
1	40	6.54	"	"	"
1	40	6.52	"	"	"
1	43	6.50	"	"	"
1	40	6.52	"	"	"
1	40	6.43	"	"	"
2	40	6.17	0.05	10	2.31
2	"	6.38	"	10	2.31
2	"	6.36	"	11	2.32
2	"	6.29	"	10	2.31
2	"	6.24	"	11	2.33
2	"	6.26	"	10	2.31
3	40	6.62	0.05	10	2.31
3	40	6.49	"	10	2.31
3	42	6.49	"	10	2.31
3	40	6.49	"	11	2.34
3	40	6.56	"	10	2.31
3	41	6.43	"	10	2.32
4	40	6.13	0.05	10	2.31
4	40	6.13	"	11	2.31
4	40	6.14	"	10	2.31
4	41	6.11	"	11	2.33
4	42	6.15	"	10	2.33
4	40	6.14	"	10	2.33
5	41	6.34	0.05	10	2.23
5	40	6.27	"	10	2.31
5	40	6.21	"	11	2.30
5	39	6.22	"	12	2.29
5	40	6.19	"	11	2.31
6	40	6.18	0.05	10	2.31
6	40	6.18	"	10	2.31
6	40	6.20	"	11	2.34
6	41	6.16	"	10	2.41
6	50	6.36	"	11	3.00
6	40	6.30	"	10	2.31

<u>Temporal variation of water quality at high flow.</u> River Tryweryn - 6 samples in two minutes.

UNITS

Appendix A.2

TIME	Lab pH	MP4 pH	Lab cond	MP4 cond	Stage cm
	units	units	μScm⁻¹	μScm⁻¹	
0822	6.8	9.0	55.0	70.0	16
0832	6.78	8.6	55.0	69.0	20
0840	6.76	8.4	53.0	68.0	45
0850	6.63	8.0	47.0	67.0	46
0858	6.45	7.4	42.0	66.0	46
0900	6.34	7.4	42.0	52.0	"
0902	6.45	7.4	42.0	52.0	"
0904	6.40	7.3	42.0	51.0	"
0906	6.42	7.3	42.0	50.0	"
0908	6.46	7.2	42.0	49.0	"
0910	6.40	7.1	41.0	48.0	"
0914	6.31	7.1	41.0	46.0	"
0918	6.24	7.0	41.0	45.0	"
0922	6.26	6.9	41.0	45.0	"
0926	6.31	6.9	41.0	44.0	"
0930	6.34	6.8	41.0	44.0	"
0934	6.24	6.8	40.0	44.0	"
0938	6.20	6.8	41.0	44.0	"
0942	6.70	6.7	41.0	44.0	"
0946	6.70	6.7	41.0	44.0	"
0950	6.21	6.7	41.0	44.0	"
0954	6.18	6.7	41.0	44.0	"
0958	6.15	6.7	41.0	44.0	"
1002	6.18	6.7	41.0	44.0	"
1006	6.20	6.7	41.0	44.0	"
1010	6.20	6.7	41.0	44.0	"

Laboratory and MP4 (field moniter) values for pH and Conductivity compared. 24.4.84. Site 4 River Tryweryn.

Sp

UNITS

Appendix A.3

TIME	Lab pH	MP4 pH	Lab cond	MP4 cond	Stage cm
	units	units	μScm⁻¹	μScm⁻¹	
0800	6.78	12.1	54.0	54.0	22
0828	6.79	11.0	55.0	55.0	25
0830	6.80	11.2	55.0	55.0	32
0840	6.81	10.1	49.0	49.0	47
0850	6.80	9.0	45.0	46.0	47
0900	6.76	8.8	43.0	45.0	"
0910	6.69	7.9	41.0	44.0	"
0920	6.67	7.8	41.0	42.0	"
0930	6.65	8.0	40.0	41.0	"
0932	6.65	7.8	43.0	43.0	"
0934	6.62	7.6	44.0	44.0	"
0936	6.72	7.7	54.0	44.0	"
0938	6.72	7.8	41.0	44.0	"
0940	6.72	7.8	44.0	44.0	"
0942	6.72	7.8	44.0	44.0	"
0944	6.72	7.7	41.0	44.0	"
0946	6.71	7.6	44.0	44.0	"
0948	6.71	7.4	44.0	44.0	"
0950	6.70	7.40	41.0	44.0	"
0952	6.64	7.40	47.0	44.0	"
0954	6.62	7.3	44.0	44.0	"
0956	6.66	7.3	46.0	44.0	"
1000	6.69	7.3	41.0	44.0	"
1002	6.70	6.70	42.0	44.0	"
1004	6.70	6.70	43.0	44.0	"
1006	6.70	6.70	41.0	45.0	"

Laboratory and MP4 (field monitor) values of pH and Conductivity compared. 23.4.84. Site 4 River Tryweryn.

SC, UNITS

River Tryweryn	Distance from near bank (m)							
SITE 1	1.0	2.5	5.0	7.5	9.0	mean	SD	%VAR
Phosphate mg l^{-1}	0.009	0.009	0.009	0.007	0.007	0.008	0.0001	12
Nitrate mg l^{-1}	0.14	0.14	0.13	0.14	0.14	0.138	0.005	4
Calcium mg l^{-1}	2.27	2.27	2.27	2.27	2.27	2.27	0	0
Chloride mg l^{-1}	7.14	7.14	7.14	7.14	7.14	7.14	0	0
Cond μS cm^{-1}	40	37.5	37	37	37	37.7	1.3	3
PH units	6.52	6.42	6.34	6.30	6.30	6.38	0.09	5

Solute values across the channel for the River Tryweryn at low flow (0.735 $m^3 s^{-1}$), at site 1.

17.7.82.

Appendix A.4

River Tryweryn SITE 5 Determinand	Distance from near bank (m) 0.5	5.0	10.5	15.0	21.0	mean	SD	%VAR
Phosphate mg l^{-1}	0.019	0.019	0.013	0.019	0.022	0.0184	0.003	16
Nitrate mg l^{-1}	0.30	0.30	0.29	0.30	0.28	0.29	0.09	3
Calcium mg l^{-1}	5.23	5.91	5.23	5.23	5.00	5.32	0.35	6
Chloride mg l^{-1}	7.86	7.86	7.14	7.14	7.14	7.43	0.39	5

Solute values across the channel on the River Tryweryn at site 5, during low flow (0.735 $m^3 s^{-1}$)

17.7.82.

Appendix A.5

APPENDIX B.

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B.2 Chem lab method sheet :- Phosphate 332
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B.4 " " Nitrate 334
B.5 " " Calcium 335

Appendix B.1

CONTINUOUS FLOW TROUBLE SHOOTING GUIDE.

1. Initial appraisal.

. what is the general state of cleanliness of the laboratory?
. what is the condition of the reagents - age, precipitation?
. is the sampler moving freely?
. is there surfactant in the wash reagent?
. is there a at least a centimetre separation bubble between the sample and the wash?
. is there any sign of dirt trapped at the joints?
. what is the state of the pump tubes - age, elasticity- grease on them at the pump end?
. are the transmission lines longer than necessary?
. is the correct size bubble forming at the injector?
. is there any sign of leakage from any joints?
. are the sleeved joints butted closely?
. is the dialyser membrane in good condition?
. is the heating bath at the correct temperature?
. is there any bubble break up?
. are the waste lines connected properly?
. is ther any obvious surging? - check peristaltic pump operation.
. what are the colorimeter gain setting, position of shutter (it should be in the middle) and recorder input voltage?

2. Stopped flow.

The most useful immediate action that can be taken is to stop the flow through the flow cell by clamping off the return line (never the inlet line).
a) A marked change in baseline indicates a trapped bubble or possibly some dirt. Releasing the return line usually clears this.

b) Continuing noise indicates an instrument fault. Relatively simple faults causing noise are dying lamp, defective power pack, spillage on detector, worn gain potentiometer, bad connections, worn slidewire potentiometer. Check by connecting to another colorimeter.

c) A smooth line proves conclusively that there is nothing wrong with the colorimeter or recorder. The problem is probably in fluid dynamics rather than chemistry.

d) A smooth rising curve is evidence for an incomplete reaction.

If the rise is slow it should not result in noise under normal circumstance. If it is marked in a standard method, it could suggest that a reagent has deteriorated or was made up incorrectly. Possibly the heating bath is not working. For a nonstandard method a further coil may need to be added.

e) A smooth falling curve usually indicates solids or a small bubble in the flowcell

f) Small spikes on an otherwise smooth trace indicates either dirty reagents or chemical precipitation in line. Check the reagents, and check that stainless steel connectors are not being used with acid samples or reagents.

g) Small spikes which persist when the flow is stopped indicate mains electrical noise. this should be checked as damage to the machine may be caused.

3. Systematic examination.

a) Increase chart speed to 1-2 cm/min so that changes are clear.

b) Run a water baseline (with surfactant). This should be smooth and steady within 30 min. of switching on of the colorimeter. The shutter should be fairly central - if not then look for instrument faults.

c) Change to reagent baseline and note the change in absorbance. Generally it will be less than 10% (except for chloride). excessively raised baselines indicate some form of contamination.

d) Small abrupt steps in the baseline indicate mechanical movement or, a dirty flowcell. Check that the flow cell and reference block are secure. Clean the flow cell with the acid or base being used in the analysis.

4. Surging.

When a top standard is run the noise is frequently seen to be rhythmic in character. Measure the frequency (F)/ wavelength ( ) of the oscillation.

a) Very high frequencies are invariably electrical in origin, with worn colorimeter parts.

b) Pulsing. = 2.5, F = 24/min. This frequency corresponds to the frequency of the rollers coming down on the pump tubes or lifting them off, and creates a hesitation in flow. To a certain extent this is normal however, if this becomes a sharp kick back the most likely reason is that the pump tubes need replacing or stretching. Another reason for this kind of surging may be a blockage, acting as a natural valve.

Pulses of this frequency but of large amplitude indicate dirt trapped in the flow cell, simply pinch the return line to clear.

c) Rolling. = 3-6, F = 10-20/min. If the length of a liquid plus air segment is close to the length of one turn of the coil an asymmetrical weight distribution will result. In order to drive all of the liqiud segments together over the top of the coil loops there has to be cyclical pressure change and a velocity change through the tubing. This can give rise to noise at the above frequency and often leads to more widespread problems. It is therefore necessary to shorten the segment length, to do this the following may be used. i) alter the surfactant concentration. ii) alter the orientation of the injector iii) Increase the size of the air pump tube.

d) Surging = 10sec-5min, F = 0.2-6/min. The air liquid interface generates a considerable resistance to flow. The value of this resistance is a function of a number of inter-related factors. These include:-
length of system
nature of tubing
bubble size and frequency
viscosity of reagents
surfactant content
presence of solids or microorganisms
vertical effects i.e back pressure or siphoning
temperature

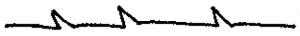
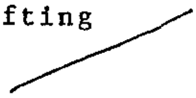
Often a small change in any one of these factors is sufficient to cure the surging problem:-
Length of system. The longer the system the greater the risk of surging.
Nature of tubing. P.V.C tubing has greater resistance to flow than glass. Also the plasticisers in the plastic tubing increase this tendency. Usually it is cured by pumping the system full of concentrated detergent. Transmission lines should not be changed unless absolutely necessary. In some instances it may be

advisable to take glass tubing right through to the flow cell.
Bubble size and frequency - clearly the more air-liquid interfaces in the system the greater the resistance to flow. Generally however, the advantages outweigh the disadvantages, and surging is more likely to be found when there are too few segments. Thus a useful step in trouble shooting is to disconnect the debubble waste line and run it into a beaker close to the colorimeter
Viscocity. This problem can be removed by increasing surfactant level and/or increasing the flow rate.
Surfactant concentrations are crucial to the operation of a continuous flow system. Lack of surfactant almost invariably leads to surging, whilst too much results in poor resolution and bubble break up.
Solids, dirt and microorganisms can cause noise directly by getting into the flow cell, and also by coating the walls of the coils, particularly the heating bath coils. The solution is to change the reagents and to clean the system with concentrated surfactant and the appropriate acid or base, according to the chemistry involved.
Effect of height. If a debubble line or other unpumped waste line is higher than the manifold it will exert a back pressure, which can lead to surging.
Temperature. Heating causes the air pressure to increase so that the flow rate increases, this should not be a problem if the air content is constant, which assuming the sampler is working satisfactorily it should be. Another related problem is created if the separation bubble is too big, this can be cured by changing the debubble rate line.

5. Drift.

a) To some extent drift is a normal feature of continuous flow. Instruments may continue to warm up and pump tubes are slowly stretched altering their flow rates.

b) More serious drift usually indicates either that a reagent has not been allowed to reach room temperature after removal from a refrigerator or that the reagent is decomposing.

Symptom	Cause	Remedy
Irregular bubble pattern	1) Ruptured dialyser membrane	1) Replace
	2) Dirt in air injector ports	2) Clean or replace
	3) Defective sleeve connector	3) Replace
	4) Lack of surfactant	4) Add as directed
Unsatisfactory baseline		
1) Large regular deviation	1) Air in flow cell	1) Pinch debubble line
2) Noisy i.e 	2) lack of surfactant bad connector sediments in flow dirty membrane	2) Add as directed Replace Replace reagents Replace
3) Wandering i.e 	3) Worn pump tubes	3) Tension/replace
4) 	4) Bubble dipping into light path	4) Reduce bubble size, reduce surfactant
5) 	5) Air pulled through cell or blockage in cell	5) Clean or replace cell & debubble line
6) Drifting 	6) Reagents not at room temperature Decomposing Lack of surfactant	6) Warm up Replace Add as directed
Unsatisfactory peak shape		
1) Sample carry over 	1) lack of wash time	1) Increase wash
2) Irregular shaped peaks 	2) Misalignment of pump tubes	2) Re-align tubes
3) Poor wash characteristics 	3) Wrong size sample sample line	3) Replace
Control standard out of control	1) sample cup empty	1) repeat
	2) Wrong concentration	2) remake
	3) stock changed	3) remake

CHEM LAB TROUBLE SHOOTING QUICK GUIDE.

Appendix B.2

METHOD SHEET:- PHOSPHATE.

1. Ammonium Molybdate.

Ammonium molybdate	10g
Potassium antimony tartrate	0.2g
Sulphuric acid conc	62ml

Add acid to 900ml of deionised water (carefully), dissolve remaining substances, and make up to 1 litre with deionised water.

2. Sulphuric Acid.

Deionsed water	1 litre
sulphuric acid conc	10ml
Aerosol 22	1ml

3. Ascorbic Acid.

Ascorbic acid	0.3g
Acetone	5ml
Deionised water	1 litre

Make this solution fresh daily.

4. Standards. Phoshate 1000mg l^{-1}

Potassium dihydrogen orthophosphate	4.8959g l^{-1}

Dissolve potassium phosphate previously dried and dessicated in deionised water. Add 1ml of sulphuric acid and dilute to 1 litre with deionised water.

Aerosol 22 is available from Cyanamid Ltd (0329-236131).

Appendix B.3

METHOD SHEET:- Chloride.

1. Stock Ferric Nitrate.

Ferric nitrate	202g
Nitric acid conc.	32ml
Deionised water	1 litre

Filter and store in a brown bottle.

2. Stock Mercuric Thiocyanate.

Mercuric thiocyanate	4.20g

dissolve in metanol and dilute to 1 litre with methanol

3. Chloride colour.

Mix 30mls stock ferric nitrate with 30mls stock mecuric thiocyanate and dilute to 200mls with deionised water.

4. Nitric Acid.0.75M

Nitric acid conc.	48ml
Deionised water	1 litre
Brij 35 (25%w/v)	2ml

5. Standards: Stock Chloride 1000mg l^{-1}

Sodium chloride AR	1.65g l^{-1}

Make up to 1 litre with deionised water.

Appendix B.4

METHOD SHEET:- NITRATE

1. Sodium hydroxide 0.4M.

Sodium hydroxide	16g l^{-1} water
Add 4 drops of Aerosol 22	
Store in a plastic bottle	

2. Sodium Hydroxide 0.2M

Sodium hydroxide	8g l^{-1}
Add 4 drops of Aerosol 22	
Store in a plastic bottle	

3. Stock Copper Sulphate.

Copper sulphate	4g l^{-1}

disolve in 1 litre of deionised water

4. Hydrazine-Copper Reagent.

Hydrazine sulphate	1.8g
Stock copper sulphate	4.0ml
deionised water	1 litre

Store in a brown bottle in the fridge.

5. Sulphanilamide Reagent.

Sulphanilamide	10g
Phosphoric acid conc.	100ml
N-1-Naphthylethylene-diamine dihydrochloride	0.5g
deionised water	1litre

Store in a brown bottle in the fridge.

6. Nitrate Standard. 1000mg l^{-1}

Potassium nitrate AR	7.2221g

Dissolve in deionised water, make up to 1 litre, store in a brown bottle in the fridge with 2ml of chloroform.

Appendix B.5

METHOD SHEET:- CALCIUM.

Reagents.

1. Hydroxyquinoline solution.

8- Hydroxyquinoline	2.5g
Hydrochloric acid, conc.	25.0ml
Brij-33 (25%w/v)	1.0ml
water (distilled)	to make 1 litre

Add the acid to about half of the water. Add the hydroxyquinoline and mix until dissolved. Make up to volume and then add Brij.

2. Cresolphthalein Complexone.

8-Hydroxyquinoline	2.5g
Cresolphthalein complexone	70mg
Hydrochloric acid, conc.	16.5ml
Brij-33	1ml
Water	to make 1 litre

Add the acid to about half of the water. add the hydroxyquinoline and dissolve completely. Completely dissolve the cresolphthalein, make up to volume and add the Brij.

3. A.M.P. Base (1M).

2-Amino-2-metyl-propan-1-ol	90g
Potassium cyanide	1.0g
Brij-33	1.0ml
Water	to make 1 litre

Without the correct facilities due to the presence of potassium cyanide, it is suggested that this is obtained reagent is obtained ready manufactored from BDH.

4. Stock Calcium Solution.

Calcuim carbonate	5.0g
Hydrochloric acid, conc.	5.0ml

Ensure complete solution of calcium carbonate in the acid, and then make up to 1 litre with distilled water.

5. Disposal of cyanide waste.

Cyanide at the concentrations used must not be poured into the drains. Collect the waste in a plastic bottle containing one tenth of its volume of domestic bleach (sodium hypochlorite solution). When full , cap bottle and mix , leave for 24 hours. Waste may then be washed down drain with an excess of tap water.

APPENDIX C.

RIVER DERWENT SUMMARY DATA

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Computer model for the prediction of changing reservoir discharge or River Wye contribution on the seasonal pattern of conductivity on the River Derwent:-

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Sampling site	Natural flow (Ml d^{-1})-cumulative
Yorkshire Bridge	29.1
Hope	34.0
River Noe	50.1
Stoke Brook	65.6
Bar Brook	72.0
Chatsworth	76.0
River Wye	148.0
Hillcarr Sough	177.0
Yatestoop Sough	185.0
Bentley Brook	197.0
Matlock	198.3
Cromford Sough	211.0
Matlock Bath	213.0
Merebrook Sough	264.0
Ambergate	265.0

Minimum flow condition - River Derwent (Severn Trent Water Authority).

Over what time period?

Appendix C.1

month	cond µS cm^{-1}	pH	nitrate mg l^{-1}	chloride mg l^{-1}	calcium mg l^{-1}
Merebrook Sough					
Jan	440	7.7	3.0	20	95
Feb	440	7.7	3.0	20	95
Mar	400	7.8	3.2	25	90
Apr	460	8.0	3.4	18	130
May	400	8.0	2.1	32	95
Jun	420	-	2.5	17	140
Jul	490	7.5	2.8	20	100
Aug	440	7.8	4.2	28	90
Sep	440	7.5	2.5	25	87
Oct	470	7.5	3.4	43	107
Nov	490	7.8	2.9	22	107
Dec	430	7.9	3.5	28	90
mean	443.3	7.7	3.0	24.8	102
SD	29.9	0.19	0.56	7.3	16.7
% var	6.7	2.5	18.5	29.5	16.4
Cromford Sough					
Jan	450	7.8	3.6	26	100
Feb	450	7.8	3.6	26	100
Mar	410	7.8	3.2	36	100
Apr	470	8.5	3.9	30	142
May	430	8.2	2.3	32	94
Jun	450	-	2.6	18	152
Jul	520	7.6	2.9	39	122
Aug	520	8.0	5.4	50	100
Sep	510	7.8	2.6	29	91
Oct	460	8.0	3.5	55	120
Nov	570	7.91	3.8	33	115
Dec	470	8.07	3.6	49	106
Mean	475.8	7.95	3.4	35.3	111.8
SD	45.4	0.24	0.8	11.0	19.2
% var*	9.5	6.0	23	31	17

* (SD/mean) x 100

Chemical data from the River Derwent.

Appendix C.2 & C.3

months	cond $\mu S\ cm^{-1}$	pH	nitrate mg l^{-1}	chloride mg l^{-1}	calcium mg l^{-1}
River Derwent upstream of the Reservoir					
Jan	64	7.1	0.1	7.	3
Feb	80	7.2	0.4	9.5	6.4
Mar	110	3.8	0.1	16	3.0
Apr	70	4.8	0.4	12	3.0
May	70	5.0	0.2	12	3.0
Jun	73	-	0.33	5.6	3.0
Jul	73	5.9	0.33	5.6	3.0
Aug	72	5.0	0.4	9.8	3.0
Sep	70	5.0	0.1	6.	3
Oct	64	5.0	0.4	10.2	4
Nov	84	5.1	0.4	6	7
Dec	60	5.9	0.4	6	3
mean	74.5	5.6	0.28	8.67	3.65
SD	12.3	1.1	0.14	3.2	1.4
% var	16.5	19	49	37	38
Yatestoop Sough					
Jan	420	7.4	4.5	52	57
Feb	400	7.4	4.8	50	60
Mar	590	7.1	2.0	71	76
Apr	460	8.2	3.9	25	75
May	400	8.0	4.0	40	75
Jun	410	-	3.6	28	90
Jul	590	7.1	2.0	71	76
Aug	580	7.8	2.4	78	72
Sep	650	7.1	2.6	71	104
Oct	580	7.2	2.3	90	116
Nov	620	7.4	1.8	48	110
Dec	460	7.8	6.6	48	65
mean	513	7.5	3.2	56	81.3
SD	96	0.4	1.6	20	19.4
% var	19	5	47	36	24

Appendix C.4 & C.5

months	cond $\mu S\ cm^{-1}$	pH	nitrate mg l^{-1}	chloride mg l^{-1}	calcium mg l^{-1}
Ouzledon Clough					
Jan	86	7.1	0.1	8	4
Feb	100	7.1	0.7	11.5	7.3
Mar	92	4.2	0.1	16	3
Apr	75	5.2	0.7	12	4
May	75	5.0	0.2	10	4
Jun	78	-	0.53	6.25	4
Jul	78	5.7	0.53	6.24	4.4
Aug	78	5.3	0.5	11.5	4.0
Sep	78	5.0	0.1	6	3.0
Oct	86	5.1	0.8	11.5	5.0
Nov	100	5.1	0.7	6	8
Dec	82	5.9	0.5	6	4
mean	84.7	5.65	0.43	9.2	4.5
SD	8.7	0.97	0.27	3.2	1.5
% var	10	17	63	35	33

River Westend

Jan	70	7.0	0.1	7.0	3
Feb	85	7.7	0.4	10.2	6.9
Mar	110	3.9	0.1	16	3
Apr	65	4.9	0.4	12	4
May	65	5.0	0.3	10	4
Jun	68	-	0.47	5.6	4
Jul	68	5.5	0.47	5.6	4
Aug	70	5.2	0.4	10.2	4
Sep	68	5.0	0.1	6	3
Oct	70	5.0	0.6	11.5	3
Nov	85	5.0	0.4	6	9
Dec	68	5.8	0.4	6	3
mean	73.8	5.58	0.33	8.7	4.1
SD	12.7	1.1	0.17	3.22	1.8
% var	17	20	52	37	44

Appendix C.6 & C.7

month	cond $\mu S\ cm^{-1}$	pH	nitrate mg l^{-1}	chloride mg l^{-1}	calcium mg l^{-1}
YORKSHIRE BRIDGE					
Jan	100	7.3	0.1	10	7
Feb	100	6.8	0.6	12.8	9.3
Mar	85	7.9	0.1	12.0	9
Apr	110	7.33	0.65	16.0	14
May	110	7.82	0.5	15.01	10
Jun	100	-	0.8	17.2	8
Jul	120	7.4	0.6	17	12
Aug	100	7.86	2.0	18.75	10.4
Sep	100	7.49	0.1	10	9.1
Oct	90	7.97	0.96	16.2	10.8
Nov	100	7.51	0.91	9	12.6
Dec	90	7.36	0.84	9.8	10.64
mean	100	7.53	0.68	13.6	9.9
SD	9.4	0.33	0.50	3.3	2.2
% var	9.4	4	73	24	22
River Ashop					
Jan	87	7.5	0.1	10	4
Feb	94	7.0	.6	11.5	7.8
Mar	98	4.4	0.1	16	3
Apr	80	5.4	0.6	12	8
May	80	5.0	0.2	12	8
Jun	100	-	0.58	8.97	8
Jul	78	5.8	0.66	7.5	3
Aug	100	5.3	0.8	11.5	8
Sep	100	5.0	0.1	6	7
Oct	87	5.0	0.7	12.8	9
Nov	94	5.5	0.6	6	10
Dec	80	5.3	0.7	6	8
mean	89.6	5.4	0.45	10	6.75
SD	8.5	1.5	0.28	3.1	2.4
% var	9	34	62	30	35

Appendix C.8 & C.9

month	cond µS cm^{-1}	pH	nitrate mg. l^{-1}	chloride mg. l^{-1}	calcium mg l^{-1}
RIVER NOE - BROUGH					
Jan	400	7.5	2.9	21	79
Feb	260	7.7	1.8	19.9	50.9
Mar	260	7.8	0.7	24	57
Apr	420	8.45	2.99	23	120
May	300	8.54	1.0	25.46	63
Jun	410	-	2.34	20.0	79
Jul	280	7.5	2.1	28	44
Aug	410	8.02	7.0	37.5	100.1
Sep	290	7.85	2.2	17	49.4
Oct	240	7.81	2.72	27	55.2
Nov	260	7.8	2.21	16.5	42
Dec	250	7.82	2.88	16.8	63.8
mean	320.8	7.9	2.6	22.8	65.6
SD	72.2	0.32	1.5	5.8	23.2
% var	22.4	4.1	58	26	35

BAMFORD

month	cond µS cm^{-1}	pH	nitrate mg. l^{-1}	chloride mg. l^{-1}	calcium mg l^{-1}
Jan	100	7.4	0.8	14.0	9.5
Feb	110	8.0	0.4	12.0	9.0
Mar	140	7.38	0.91	15	16
Apr	140	8.01	0.5	16.08	14
May	125	-	0.9	11.7	14
Jun	150	7.7	0.7	20	16
Jul	140	7.86	2.0	21.25	13
Aug	120	7.66	0.4	11	10.4
Sep	100	7.88	1.44	19.8	10.8
Oct	120	7.74	1.04	10.5	13.8
Nov	110	7.94	1.2	12.6	14.0
Dec	100	7.80	0.98	15	10
mean	119.6	7.76	0.94	14.9	12.5
SD	18.08	0.22	0.46	3.7	2.5
% var	15	2	48.7	24.9	20

Appendix C.10 & C.11

month	cond $\mu S\ cm^{-1}$	pH	nitrate $mg\ l^{-1}$	chloride $mg\ l^{-1}$	calcium $mg\ l^{-1}$
GRINDLEFORD					
Jan	220	7.4	1.3	17	38
Feb	200	7.5	1.5	18.7	36.2
Mar	160	7.7	0.4	16	25.8
Apr	230	7.93	1.56	19	44
May	200	8.36	0.6	18.76	32
Jun	250	-	1.9	12.4	47
Jul	240	7.5	1.4	23	34
Aug	170	7.91	3.0	25	22.1
Sep	250	7.76	2.0	16	39
Oct	200	7.79	2.24	25.2	40.8
Nov	180	7.63	1.56	10.5	29.4
Dec	230	7.76	2.52	16.8	49.23
mean	211.5	7.77	1.69	18.3	35.97
SD	29.4	0.26	0.71	4.4	8.14
% var	14	3.4	42.1	24	23

HATHERSAGE

Jan	220	7.4	1.3	17	40
Feb	200	7.6	1.3	17.8	38.7
Mar	150	7.7	0.4	16	27
Apr	190	7.55	0.91	19	23
May	200	8.47	0.75	19.43	34
Jun	275	-	2.0	10.3	16
Jul	220	7.45	1.1	23	34
Aug	170	7.85	3.0	25	22.1
Sep	250	7.83	2.0	15	42.9
Oct	200	7.8	2.08	23.4	44.4
Nov	170	7.6	1.3	10.5	29.4
Dec	230	7.85	2.64	16.8	54.88
mean	207.3	7.76	1.6	17.94	33.95
SD	34	29	0.76	4.48	10.56
% var	16.4	3.7	47	25	31

Appendix C.12 & C.13

month BASLOW	cond $\mu S.\ cm^{-1}$	pH	nitrate mg l^{-1}	chloride mg l^{-1}	calcium mg l^{-1}
Jan	275	75	1.7	21	49
Feb	275	7.6	1.5	22.9	46.5
Mar	180	8.0	0.8	20	31.5
Apr	270	8.05	1.69	25	56
May	240	8.76	0.8	23.45	36
Jun	275	-	1.8	12.7	43
Jul	300	7.6	1.4	29	44
Aug	250	8.04	3.0	33.75	33.8
Sep	250	7.91	1.8	20	35.1
Oct	250	7.93	1.76	28.8	54
Nov	240	7.99	1.95	15	39
Dec	250	7.97	2.76	16.8	57.12
mean	255	7.95	1.78	22.3	43.4
SD	28.4	0.32	0.64	5.85	8.6
% var	11	4	36	26	20

CALVER

Jan	260	7.5	1.3	21	45
Feb	225	7.6	1.5	22.5	41.1
Mar	160	7.8	0.4	20	28.5
Apr	250	7.97	1.5	20	50
May	210	8.54	0.65	22.11	32
Jun	250	-	1.8	12.7	45
Jul	260	7.5	1.2	27	40
Aug	220	8.0	3.0	32.5	28.6
Sep	250	7.78	1.6	19	36.4
Oct	230	7.86	2.24	28.8	50.4
Nov	220	7.85	1.56	15	33.6
Dec	240	7.88	2.64	18.2	53.2
mean	217.3	7.86	1.64	21.8	40
SD	54	0.28	0.72	5.4	8.3
% var	25	3.6	44	25	21

Appendix C.14 & C.15

Month	cond μS cm^{-1}	pH	Nitrate mg l^{-1}	chloride mg l^{-1}	calcium mg l^{-1}
DARLEY DALE					
Jan	420	7.7	2.1	22	82
Feb	380	7.8	2.8	24.1	77.3
Mar	290	7.7	3.2	32	60
Apr	380	8.29	2.6	28	99
May	310	8.25	1.35	23.5	58
Jun	300	-	2.3	13.2	102
Jul	440	7.7	2.4	34	92
Aug	370	8.1	5.0	42.5	70.2
Sep	360	7.83	2.2	25	62.4
Oct	350	7.97	3.68	34.2	90
Nov	370	7.97	2.99	21	76.8
Dec	330	8.06	3.72	22.4	83.44
mean	365.4	7.97	3.00	27.0	80.5
SD	50.6	0.23	1.05	7.5	14.7
% var	13.9	2.9	35	28	18.2
ROWSLEY					
Jan	460	7.9	2.9	24	112
Feb	450	7.9	3.6	26.2	101.3
Mar	410	7.8	3.2	36	60
Apr	470	8.49	3.9	30	142
May	430	8.17	2.25	32.16	94
Jun	250	-	1.8	13.75	76
Jul	540	8.00	2.9	39	130
Aug	490	8.21	7.0	50	105.5
Sep	470	8.02	3.2	35	87.1
Oct	420	8.1	4.96	41.4	123.6
Nov	490	8.02	4.81	25.5	116.4
Dec	400	8.21	4.2	25.2	113.7
mean	440.8	8.09	3.81	31.3	104.2
SD	68.6	0.19	1.37	9.19	22.5
% var	15.6	2.4	36	29	22

Appendix C.16 & C.17

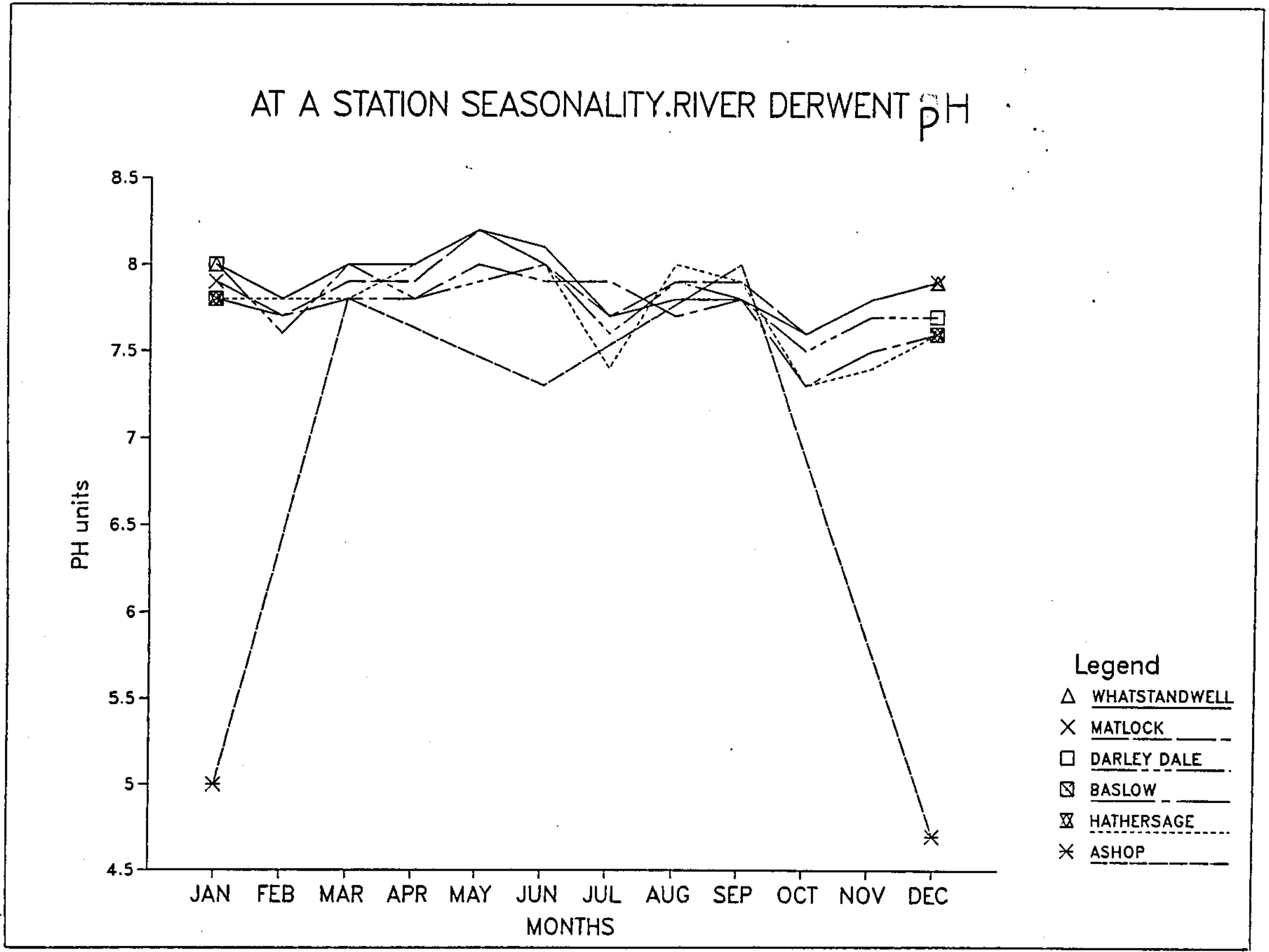
Month	cond $\mu S\ cm^{-1}$	pH	nitrate $mg\ l^{-1}$	chloride $mg\ l^{-1}$	calcium $mg\ l^{-1}$
CROMFORD					
Jan	410	7.7	2.4	22	82
Feb	390	7.8	3.0	25.8	79.3
Mar	320	7.6	2.4	34.4	63.6
Apr	420	8.27	2.86	28	101
May	330	8.59	1.4	27.47	60
Jun	280	-	4.42	19.25	74
Jly	450	7.7	2.4	35	86
Aug	390	8.09	4.9	47.5	71.5
Sep	360	7.78	2.0	24	61.1
Oct	360	7.97	3.52	36	90
Nov	400	7.94	3.25	25.5	77.4
Dec	330	8.01	3.6	23.8	80.46
mean	372.3	8.0	3.06	29.13	76.8
SD	44.6	0.28	0.97	7.52	11.7
% var	12	3.5	32	25.8	15
MATLOCK					
Jan	410	7.7	2.1	22	82
Feb	380	7.8	2.7	24.1	76.8
Mar	275	7.7	2.4	28	64.5
Apr	380	8.27	2.99	28	98
May	310	8.75	1.5	25.5	55
Jun	430	7.7	2.4	34	88
Jul	380	8.05	5.2	42.5	70.2
Aug	360	7.82	2.2	24	62.4
Sep	350	7.97	3.68	34.2	92.4
Oct	370	7.95	3.12	21	76.8
Nov	330	8.07	3.6	22.4	81.76
Dec	370	8.15	3.64	30	67
mean	357.7	8.00	2.92	27.0	77.6
SD	43.3	0.3	0.95	7	13.3
% var	12	3.7	33	26	17.2

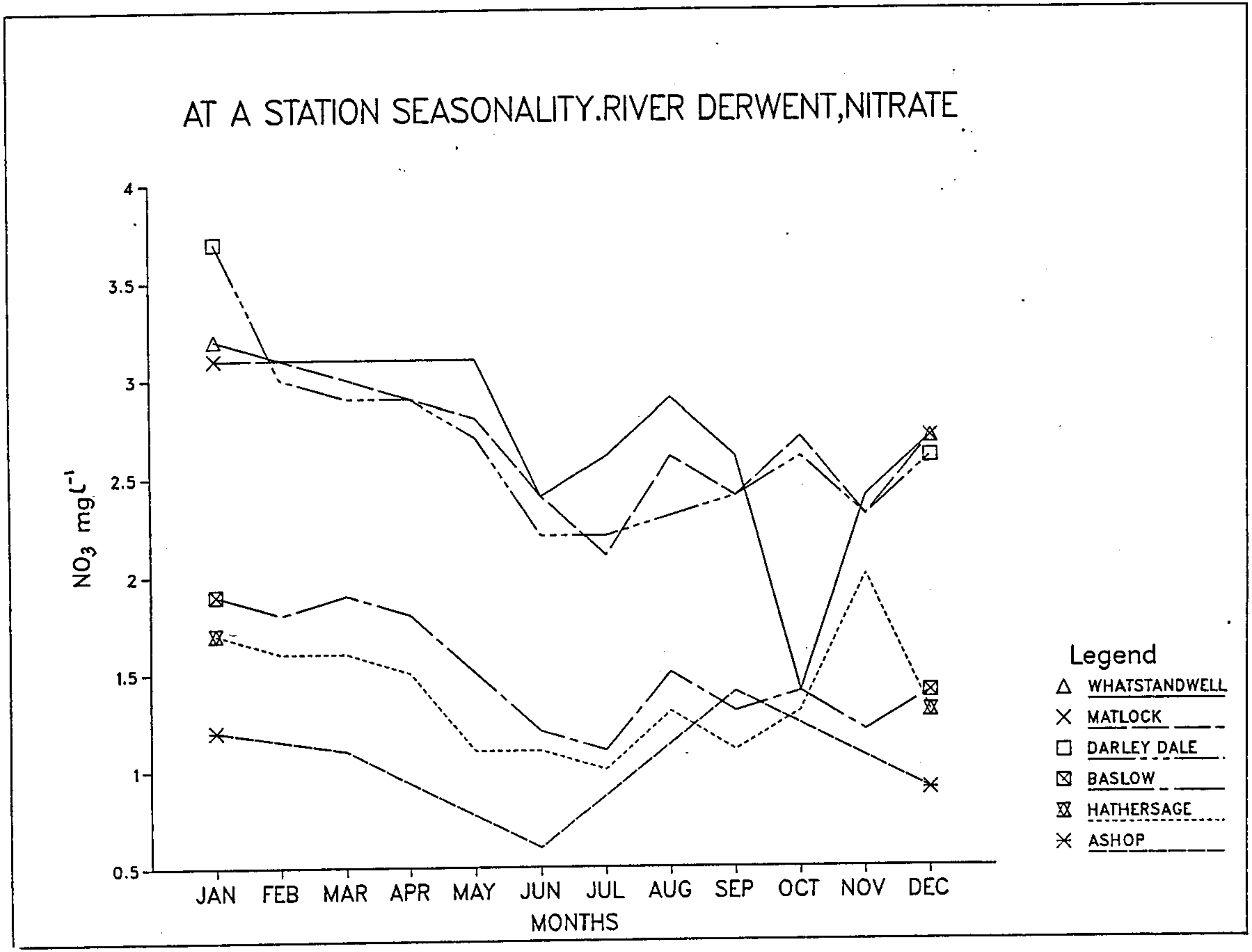
Appendix C.18 & C.19

Month	cond $\mu S\ cm^{-1}$	pH	nitrate $mg\ l^{-1}$	chloride $mg\ l^{-1}$	calcium $mg\ l^{-1}$
AMBERGATE					
Jan	410	7.7	2.9	27	79
Feb	400	7.6	2.8	28.4	73.4
Mar	320	7.5	2.4	28	57
Apr	390	8.16	2.9	35	95
May	320	7.91	1.4	25.5	55
Jun	280	-	2.01	12.7	78
Jul	460	7.40	2.5	49	94
Aug	460	7.38	5.2	62.5	71.5
Sep	380	7.65	2.0	27	62.4
Oct	360	7.79	3.52	30.6	90.0
Nov	570	7.58	3.64	67.5	85.2
Dec	330	7.82	3.48	23.8	76.16
mean	390.8	7.7	2.94	34.5	75.7
SD	76	0.23	0.97	15.7	13.1
% var	19.5	2.0	32.8	45.6	17.4

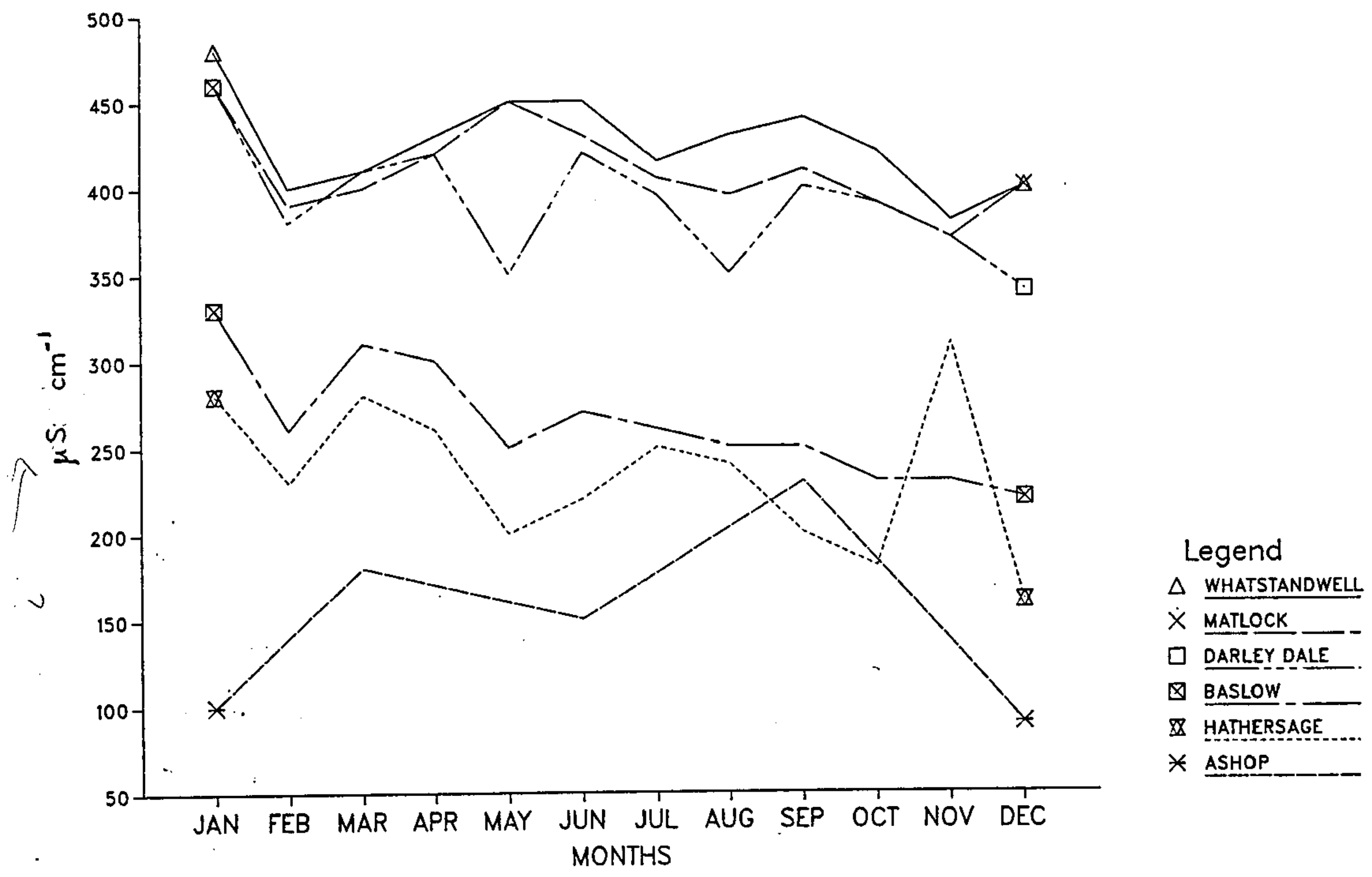
WHATSTANDWELL					
Jan	410	7.7	2.9	23	82
Feb	390	7.6	2.9	25.4	75.9
Mar	315	7.6	2.4	32	64.5
Apr	390	8.24	3.12	29	98
May	320	8.49	1.55	28.14	56
Jun	290	-	2.0	14.3	84
Jul	460	7.6	2.7	37	94
Aug	420	7.77	5.0	52.5	68.9
Sep	350	7.73	2.8	24	55.9
Oct	360	7.91	3.52	36	90
Nov	420	7.86	3.38	28.5	78
Dec	330	7.92	3.6	25.2	77.28
mean	372.1	7.86	3.05	29.8	76.34
SD	49.9	0.27	0.86	8.9	13.4
%var	13.4	3.4	28.4	30	17.6

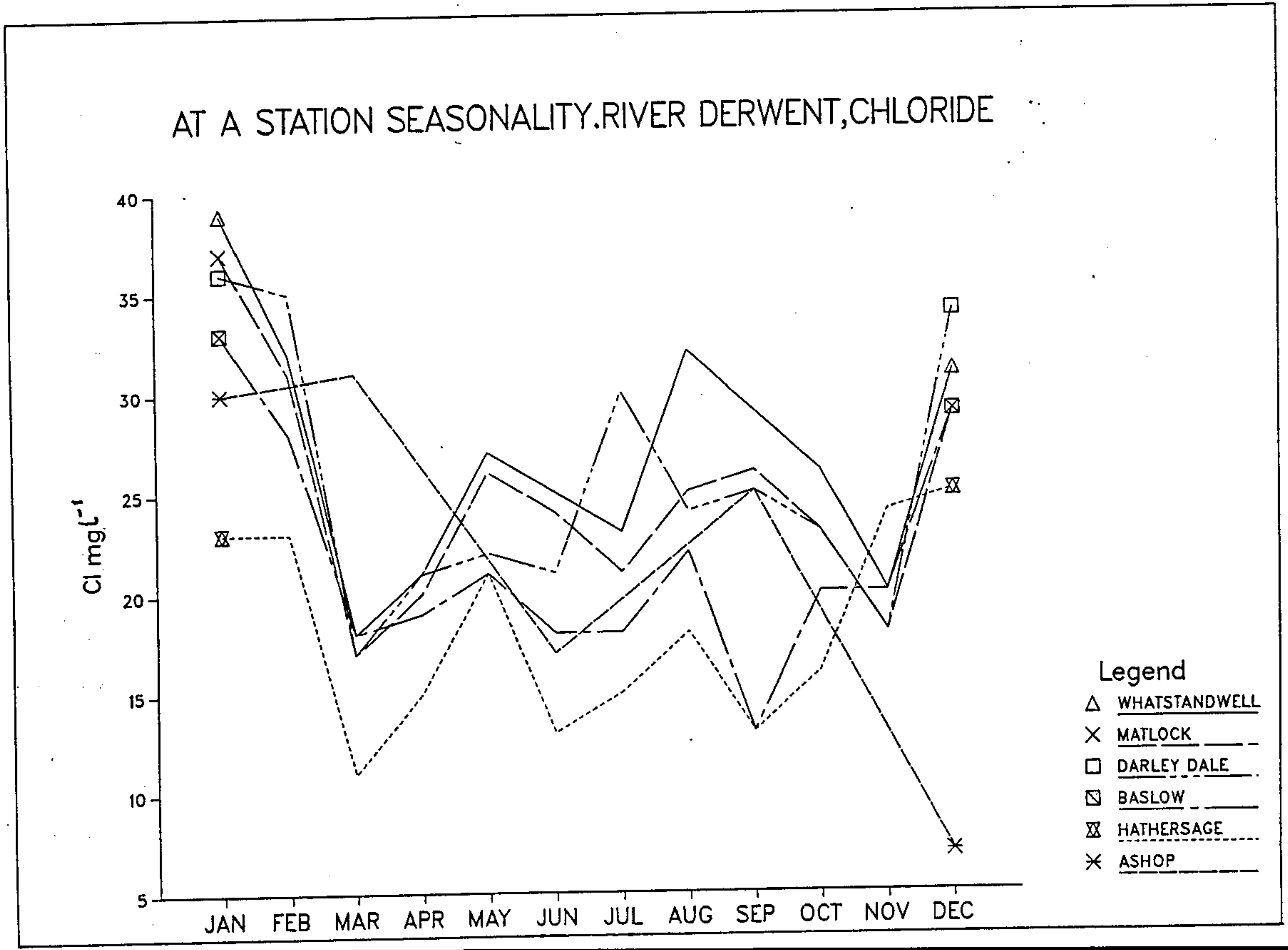
Appendix C.20 & C.21


AT A STATION SEASONALITY.RIVER DERWENT pH
PH units
8.5
8
7.5
7
6.5
6
5.5
5
4.5
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
MONTHS
Legend
△ WHATSTANDWELL
✕ MATLOCK
☐ DARLEY DALE
⊠ BASLOW
⧗ HATHERSAGE
✳ ASHOP


AT A STATION SEASONALITY.RIVER DERWENT,NITRATE
NO_3 mgl^{-1}
4
3.5
3
2.5
2
1.5
1
0.5
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
MONTHS
Legend
△ WHATSTANDWELL
× MATLOCK
□ DARLEY DALE
⊠ BASLOW
⧖ HATHERSAGE
✳ ASHOP

AT A STATION SEASONALITY.RIVER DERWENT,CONDUCTIVITY




AT A STATION SEASONALITY.RIVER DERWENT,CHLORIDE
Cl mg l⁻¹
40
35
30
25
20
15
10
5
JAN
FEB
MAR
APR
MAY
JUN
JUL
AUG
SEP
OCT
NOV
DEC
Legend
△ WHATSTANDWELL
× MATLOCK
□ DARLEY DALE
⊠ BASLOW
⧖ HATHERSAGE
✳ ASHOP

Appendix C.23. Computer Model predicting the effects of reservoir construction on the water chemistry of the River Derwent.

```
10  HOME
14  FLASH
15  PRINT  TAB( 16);"BEFORE DAM": PRINT
17  NORMAL
20  PRINT ; TAB( 14);"SEASONAL MODEL": PRINT : PRINT "AUTUMN=1";"WINTER=2";"SPRING= 3";"SUMMER =
 4"
30  INPUT "WHICH SEASON(1-4)?";S: IF S = 1 THEN S = S - 1
32  IF S = 4 THEN S = S + 2
34  IF S = 3 THEN S = S + 1
40  REM  Q1=RESERVOIR DISCHARGE,Q2=NOE DISCHARGE,Q3=NOE CONFLUENCE DISCHARGE,Q4=LAND DRAINAGE DI
SCHARGE
50  REM  Q5=CHATSWORTH DISCHARGE,Q6=WYE DISCHARGE,Q7=SOUGH & EFFLUENT DISCHARGE,Q8=MATLOCK DISCH
ARGE
60  REM  CHEMICAL DATA FOR THE ABOVE SITES IS C WITH THE APPROPRIATE SUFFIX,I.E C1=RESERVOIR CON
CENTRATION
70  DIM SE(5,8): REM    SETS ARRAY DIMENSIONS,5 SITES(J),4*2 SEASONS
80  FOR I = 0 TO 7: FOR J = 0 TO 4: READ SE(J,I): NEXT J: NEXT I: REM  ARRAY VARIABLES (I=SEASON
S J=SITES)
90 Q1 = SE(0,S):Q2 = SE(1,S):Q4 = SE(2,S):Q6 = SE(3,S):Q7 = SE(4,S)
100 Q3 = Q1 + Q2:Q5 = Q3 + Q4:Q8 = Q5 + Q7 + Q6
200 C1 = SE(0,S + 1):C2 = SE(1,S + 1):C4 = SE(2,S + 1):C6 = SE(3,S + 1):C7 = SE(4,S + 1)
210 C3 = ((Q1 * C1) + (Q2 * C2)) / Q3: REM  NOE CONFLUENCE COND.
220 C5 = ((Q3 * C3) + (Q4 * C4)) / Q5: REM  CHATSWORTH COND.
230 C8 = ((Q5 * C5) + (Q7 * C7) + (Q6 * C6)) / Q8: REM  MATLOCK COND.
300 Q1 =  INT (Q1 * 100 + .5) / 100
310 Q2 =  INT (Q2 * 100 + .5) / 100
320 Q3 =  INT (Q3 * 100 + .5) / 100
330 Q4 =  INT (Q4 * 100 + .5) / 100
340 Q5 =  INT (Q5 * 100 + .5) / 100
345 Q6 =  INT (Q6 * 100 + .5) / 100
350 Q8 =  INT (Q8 * 100 + .5) / 100
352 C1 =  INT (C1 * 100 + .5) / 100
354 C2 =  INT (C2 * 100 + .5) / 100
356 C3 =  INT (C3 * 100 + .5) / 100
358 C4 =  INT (C4 * 100 + .5) / 100
360 C5 =  INT (C5 * 100 + .5) / 100
362 C6 =  INT (C6 * 100 + .5) / 100
364 C7 =  INT (C7 * 100 + .5) / 100
366 C8 =  INT (C8 * 100 + .5) / 100
```

```
500  PRINT "RES.DIS=";Q1; TAB( 16)"RES COND.=";C1: PRINT
510  PRINT "NOE DIS=";Q2; TAB( 16);"NOE COND.=";C2: PRINT
520  PRINT "NOE CONF.DIS=";Q3; TAB( 16);"NOE CONF.COND="C3: PRINT
530  PRINT "LAND DRAIN Q=";Q4; TAB( 16);"LAND DRAIN COND=";C4: PRINT
540  PRINT "CHATS.DIS=";Q5; TAB( 16);"CHATS COND=";C5: PRINT
550  PRINT "WYE DIS =";Q6; TAB( 16);"WYE COND=";C6: PRINT
560  PRINT "EFF.DIS.=";Q7; TAB( 16);"EFF.COND.=";C7: PRINT
570  PRINT "MATLOCK DIS.=";Q8; TAB( 16);"MATLOCK COND=";C8
1000  DATA    0.96,.82,2.33,1.72,.82,95,290,252,507,845: REM   AUTUMN DATA (DISCHARGE THEN CONDU
CTIVITY)
1010  DATA  0.89,.78,3.2,2.23,4.02,95,390,342,497,498: REM  WINTER DATA
1020  DATA   0.8,.87,1.67,2.4,1.5,105,352,340,503,642 : REM   SPRING DATA
1030  DATA     .8,.49,.92,1.32,.48,107,327,317,510,1825: REM  SUMMER DATA
```

Computer Model for Predicting the Effects of Reservoir Construction on the Water Chemistry Downstream on the river Derwent. (Apple soft Basic).

Appendix C.24. Computer model for the prediction of changing reservoir discharge or River Wye contribution on the seasonal pattern of conductivity on the River Derwent. SUMMER.

```
370  HOME
380  PRINT ; TAB( 16);"SUMMER"
390  PRINT : REM     MODEL BASED ON FLOW % CONTRIBUTIONS,DERIVED FROM LOW FLOW SURVEYS.
400  REM   :CONDUCTIVITIES DERIVED FROM COND. V FLOW REGRESSION CURVES,SEASONALLY BASED.
410  INPUT "DISCHARGE PRIOR TO RELEASE (BETWEEN 3 & 27  CUMECS)=  ";Q6
420  IF Q6 > 27 GOTO 410
425  IF Q6 < 3 GOTO 410
430  PRINT
440 Q1 = Q6 * 20 / 100: REM    RESERVOIR DISCHARGE
450 Q2 = Q6 * 12 / 100: REM    NOE DISCHARGE
460 Q3 = Q6 * 23 / 100: REM     LAND DRAINAGE
470 Q4 = Q6 * 12 / 100: REM     MATLOCK EFFLUENT AND SOUGH DRAINAGE
480 Q5 = Q6 * 33 / 100: REM    RIVER WYE
490 C6 = 410 - (4.07 * Q6): REM      REGRESSION FOR SUMMER FROM AUTOMATIC SITE AT MATLOCK
500 C5 = 530 - (14.9 * Q5): REM      REGRESSION ON R.WYE USING SUMMER MONTHLY SURVEY DATA.
510 C1 = 105: REM      CONDUCTIVITY OF RESERVOIR WATER DURING SUMMER
520 Q7 = Q1 + Q2 + Q3: REM   CHATSWORTH DISCHARGE
530 C7 = 261 - (1.94 * Q7): REM   CHATSWORTH CONDUCTIVITY
540 C2 = ((Q7 * C7) - (90 * Q1)) / (Q2 + Q3): REM   CONDUCT. OF NOE & LAND DRAIN.
550 C4 = ((Q6 * C6) - (Q5 * C5) - (Q7 * C7)) / Q4: REM   EFFLUENT CONDUCTIVITY
560 C4 = C4 + 100: REM  100 ENSURES THAT EFFLUENT CONDUCTIVITY REMAINS REALISTIC
570 C6 =  INT (C6 * 100 + .5) / 100:C5 =  INT (C5 * 100 + .5) / 100
580 C2 =  INT (C2 * 100 + .5) / 100:C7 =  INT (C7 * 100 + .5) / 100
590 C4 =  INT (C4 * 100 + .5) / 100
600  GOTO 690
610  PRINT "RES.Q="Q1; TAB( 16);"RESERVOIR COND=";C1
620  PRINT "NOE Q=";Q2; TAB( 16);"LAND DRAIN Q= ";Q3
630  PRINT "NOE & LAND DRAIN COND=";C2
640  PRINT "CHATS Q=";QC TAB( 16);"CHATS. C=";CC
650  PRINT "EFF.Q=";QE TAB( 16);"EFF.COND=";CE
660  PRINT "R.WYE Q=";Q5; TAB( 16);"R.WYE COND=";C5
670  PRINT "MAT.Q=";QM; TAB( 16);"MAT.COND=";CM
680  PRINT : PRINT
```

```
690 QR = Q1: REM    PUTS PREDICTED % RESERVOIR VALUE INTO MIXING EQUATIONS
700 N = N + 1
710 QC = Q3 + Q2 + QR: REM     NEW CHATSWORTH DISCHARGE
720 QM = QC + Q5 + Q4: REM   NEW MATLOCK DISCHARGE
730 CC = ((QR * C1) + ((Q2 + Q3) * C2)) / QC: REM   NEW CHATSWORTH CONDUCTIVITY
735 CM = ((QC * CC) + (Q4 * C4) + (Q5 * C5)) / QM: REM  NEW MATLOCK COND.
740 QE = QM - QC - Q5:CE = ((QM * CM) - (CC * QC) - (Q5 * C5)) / QE: REM  NEW EFF.VALUES.
750 CE =  INT (CE * 100 + .5) / 100:CC =  INT (CC * 100 + .5) / 100
755 CM =  INT (CM * 100 + .5) / 100
760  IF N = 1 THEN  GOTO 610
770  IF N = 3 THEN  GOTO 790
780  INPUT "NEW RESERVOIR DISCHARGE= ";QR: GOTO 700
790  PRINT "CHATS.Q=";QC; TAB( 16);"CHATS.COND=";CC
800  PRINT "MAT.Q=";QM; TAB( 16);"MAT. COND=";CM
810  PRINT : PRINT
820  INPUT "WYE DISCHARGE = ";QW: REM    NEW WYE DISCHARGE
830 CW = 530 - (14.9 * QW): REM    NEW WYE CONDUCTIVITY
840  IF CW < 200 THEN CW = 200
850 Q9 = Q4 + Q7 + QW: REM     NEW MATLOCK DISCHARGE
860 C9 = ((QW * CW) + (Q4 * C4) + (Q7 * C7)) / Q9: REM     NEW MATLOCK CONDUCTIVITY
870 C9 =  INT (C9 * 100 + .5) / 100
880 CW =  INT (CW * 100 + .5) / 100
890  PRINT "WYE Q= ";QW; TAB( 16);"WYE COND= ";CW
900  PRINT "MAT.Q=";Q9; TAB( 16);"MAT.COND=";C9
```

Appendix C.25. Computer model for the prediction of changing reservoir discharge or river Wye contribution on the seasonal pattern of conductivity on the River Derwent. SPRING.

```
370  HOME
380  PRINT ; TAB( 16);"SPRING"
390  PRINT : REM    MODEL BASED ON FLOW % CONTRIBUTIONS,DERIVED FROM LOW FLOW SURVEYS.
400  REM  :CONDUCTIVITIES DERIVED FROM COND. V FLOW REGRESSION CURVES,SEASONALLY BASED.
410  INPUT "DISCHARGE PRIOR TO RELEASE (BETWEEN 4 & 84  CUMECS)=  ";Q6
420  IF Q6 > 84 GOTO 410
425  IF Q6 < 4 GOTO 410
430  PRINT
440 Q1 = Q6 * 11 / 100: REM   RESERVOIR DISCHARGE
450 Q2 = Q6 * 12 / 100: REM   NOE DISCHARGE
460 Q3 = Q6 * 23 / 100: REM    LAND DRAINAGE
470 Q4 = Q6 * 21 / 100: REM    MATLOCK EFFLUENT AND SOUGH DRAINAGE
480 Q5 = Q6 * 33 / 100: REM   RIVER WYE
490 C6 = 430 - (3.37 * Q6): REM   REGRESSION FOR SPRING FROM AUTOMATIC SITE AT MATLOCK
500 C5 = 547 - (13.6 * Q5): REM    REGRESSION ON R.WYE USING SPRING MONTHLY SURVEY DATA.
510 C1 = 100: REM    CONDUCTIVITY OF RESERVOIR WATER DURING SPRING
520 Q7 = Q1 + Q2 + Q3: REM  CHATSWORTH DISCHARGE
530 C7 = 281 - (5.31 * Q7): REM   CHATSWORTH CONDUCTIVITY
540 C2 = ((Q7 * C7) - (90 * Q1)) / (Q2 + Q3): REM   CONDUCT. OF NOE & LAND DRAIN.
550 C4 = ((Q6 * C6) - (Q5 * C5) - (Q7 * C7)) / Q4: REM   EFFLUENT CONDUCTIVITY
560 C4 = C4 + 100: REM  100 ENSURES THAT EFFLUENT CONDUCTIVITY REMAINS REALISTIC
570 C6 =  INT (C6 * 100 + .5) / 100:C5 =  INT (C5 * 100 + .5) / 100
580 C2 =  INT (C2 * 100 + .5) / 100:C7 =  INT (C7 * 100 + .5) / 100
590 C4 =  INT (C4 * 100 + .5) / 100
600  GOTO 690
610  PRINT "RES.Q="Q1; TAB( 16);"RESERVOIR COND=";C1
620  PRINT "NOE Q=";Q2; TAB( 16);"LAND DRAIN Q= ";Q3
630  PRINT "NOE & LAND DRAIN COND=";C2
640  PRINT "CHATS Q=";QC TAB( 16);"CHATS. C=";CC
650  PRINT "EFF.Q=";QE TAB( 16);"EFF.COND=";CE
660  PRINT "R.WYE Q=";Q5; TAB( 16);"R.WYE COND=";C5
670  PRINT "MAT.Q=";QM; TAB( 16);"MAT.COND=";CM
680  PRINT : PRINT
```

```
690 QR = Q1: REM    PUTS PREDICTED % RESERVOIR VALUE INTO MIXING EQUATIONS
700 N = N + 1
710 QC = Q3 + Q2 + QR: REM     NEW CHATSWORTH DISCHARGE
720 QM = QC + Q5 + Q4: REM   NEW MATLOCK DISCHARGE
730 CC = ((QR * C1) + ((Q2 + Q3) * C2)) / QC: REM   NEW CHATSWORTH CONDUCTIVITY
735 CM = ((QC * CC) + (Q4 * C4) + (Q5 * C5)) / QM: REM  NEW MATLOCK COND.
740 QE = QM - QC - Q5:CE = ((QM * CM) - (CC * QC) - (Q5 * C5)) / QE: REM  NEW EFF.VALUES.
750 CE =  INT (CE * 100 + .5) / 100:CC =  INT (CC * 100 + .5) / 100
755 CM =  INT (CM * 100 + .5) / 100
760  IF N = 1 THEN  GOTO 610
770  IF N = 3 THEN  GOTO 790
780  INPUT "NEW RESERVOIR DISCHARGE= ";QR: GOTO 700
790  PRINT "CHATS.Q=";QC; TAB( 16);"CHATS.COND=";CC
800  PRINT "MAT.Q=";QM; TAB( 16);"MAT. COND=";CM
810  PRINT : PRINT
820  INPUT "WYE DISCHARGE = ";QW: REM    NEW WYE DISCHARGE
830 CW = 547 - (13.6 * QW): REM    NEW WYE CONDUCTIVITY
840  IF CW < 200 THEN CW = 200
850 Q9 = Q4 + Q7 + QW: REM     NEW MATLOCK DISCHARGE
860 C9 = ((QW * CW) + (Q4 * C4) + (Q7 * C7)) / Q9: REM     NEW MATLOCK CONDUCTIVITY
870 C9 =  INT (C9 * 100 + .5) / 100
880 CW =  INT (CW * 100 + .5) / 100
890  PRINT "WYE Q= ";QW; TAB( 16);"WYE COND= ";CW
900  PRINT "MAT.Q=";Q9; TAB( 16);"MAT.COND=";C9

]
```

Appendix C.26. Computer model for the prediction of changing reservoir discharge or River Wye contribution on the seasonal pattern of conductivity on the River Derwent. WINTER.

```
370  HOME
380  PRINT ; TAB( 16);"WINTER"
390  PRINT : REM     MODEL BASED ON FLOW % CONTRIBUTIONS,DERIVED FROM LOW FLOW SURVEYS.
400  REM   :CONDUCTIVITIES DERIVED FROM COND. V FLOW REGRESSION CURVES,SEASONALLY BASED.
410  INPUT "DISCHARGE PRIOR TO RELEASE (BETWEEN 10& 100 CUMECS)=  ";Q6
420  IF Q6 > 100 GOTO 410
425  IF Q6 < 10 GOTO 410
430  PRINT
440 Q1 = Q6 * 8 / 100: REM   RESERVOIR DISCHARGE
450 Q2 = Q6 * 7 / 100: REM   NOE DISCHARGE
460 Q3 = Q6 * 29 / 100: REM    LAND DRAINAGE
470 Q4 = Q6 * 36 / 100: REM    MATLOCK EFFLUENT AND SOUGH DRAINAGE
480 Q5 = Q6 * 20 / 100: REM   RIVER WYE
490 C6 = 421 - (2.46 * Q6): REM   REGRESSION FOR WINTER FROM AUTOMATIC SITE AT MATLOCK
500 C5 = 533 - (5.56 * Q5): REM    REGRESSION ON R.WYE USING WINTER MONTHLY SURVEY DATA.
510 C1 = 90: REM    CONDUCTIVITY OF RESERVOIR WATER DURING WINTER
520 Q7 = Q1 + Q2 + Q3: REM   CHATSWORTH DISCHARGE
530 C7 = 298 - (2.92 * Q7): REM   CHATSWORTH CONDUCTIVITY
540 C2 = ((Q7 * C7) - (90 * Q1)) / (Q2 + Q3): REM    CONDUCT. OF NOE & LAND DRAIN.
550 C4 = ((Q6 * C6) - (Q5 * C5) - (Q7 * C7)) / Q4: REM    EFFLUENT CONDUCTIVITY
560 C4 = C4 + 100: REM   100 ENSURES THAT EFFLUENT CONDUCTIVITY REMAINS REALISTIC
570 C6 =  INT (C6 * 100 + .5) / 100:C5 =  INT (C5 * 100 + .5) / 100
580 C2 =  INT (C2 * 100 + .5) / 100:C7 =  INT (C7 * 100 + .5) / 100
590 C4 =  INT (C4 * 100 + .5) / 100
600  GOTO 690
610  PRINT "RES.Q="Q1; TAB( 16);"RESERVOIR COND=";C1
620  PRINT "NOE Q=";Q2; TAB( 16);"LAND DRAIN Q= ";Q3
630  PRINT "NOE & LAND DRAIN COND=";C2
640  PRINT "CHATS Q=";QC TAB( 16);"CHATS. C=";CC
650  PRINT "EFF.Q=";QE TAB( 16);"EFF.COND=";CE
660  PRINT "R.WYE Q=";Q5; TAB( 16);"R.WYE COND=";C5
670  PRINT "MAT.Q=";QM; TAB( 16);"MAT.COND=";CM
680  PRINT : PRINT
```

```
690 QR = Q1: REM    PUTS PREDICTED % RESERVOIR VALUE INTO MIXING EQUATIONS
700 N = N + 1
710 QC = Q3 + Q2 + QR: REM     NEW CHATSWORTH DISCHARGE
720 QM = QC + Q5 + Q4: REM   NEW MATLOCK DISCHARGE
730 CC = ((QR * C1) + ((Q2 + Q3) * C2)) / QC: REM   NEW CHATSWORTH CONDUCTIVITY
735 CM = ((QC * CC) + (Q4 * C4) + (Q5 * C5)) / QM: REM  NEW MATLOCK COND.
740 QE = QM - QC - Q5:CE = ((QM * CM) - (CC * QC) - (Q5 * C5)) / QE: REM  NEW EFF.VALUES.
750 CE =  INT (CE * 100 + .5) / 100:CC =  INT (CC * 100 + .5) / 100
755 CM =  INT (CM * 100 + .5) / 100
760  IF N = 1 THEN  GOTO 610
770  IF N = 3 THEN  GOTO 790
780  INPUT "NEW RESERVOIR DISCHARGE= ";QR: GOTO 700
790  PRINT "CHATS.Q=";QC; TAB( 16);"CHATS.COND=";CC
800  PRINT "MAT.Q=";QM; TAB( 16);"MAT. COND=";CM
810  PRINT : PRINT
820  INPUT "WYE DISCHARGE = ";QW: REM    NEW WYE DISCHARGE
830 CW = 533 - (5.56 * QW): REM   NEW WYE CONDUCTIVITY
840  IF CW < 200 THEN CW = 200
850 Q9 = Q4 + Q7 + QW: REM     NEW MATLOCK DISCHARGE
860 C9 = ((QW * CW) + (Q4 * C4) + (Q7 * C7)) / Q9: REM     NEW MATLOCK CONDUCTIVITY
870 C9 =  INT (C9 * 100 + .5) / 100
880 CW =  INT (CW * 100 + .5) / 100
890  PRINT "WYE Q= ";QW; TAB( 16);"WYE COND= ";CW
900  PRINT "MAT.Q=";Q9; TAB( 16);"MAT.COND=";C9
```

Appendix C.27. Computer model for the prediction of changing reservoir discharge or River Wye contribution on the seasonal pattern of conductivity on the River Derwent. AUTUMN.

```
370  HOME
380  PRINT ; TAB( 16);"AUTUMN"
390  PRINT : REM     MODEL BASED ON FLOW % CONTRIBUTIONS,DERIVED FROM LOW FLOW SURVEYS.
400  REM   :CONDUCTIVITIES DERIVED FROM COND. V FLOW REGRESSION CURVES,SEASONALLY BASED.
410  INPUT "DISCHARGE PRIOR TO RELEASE (BETWEEN 3 & 85  CUMECS)=  ";Q6
420  IF Q6 > 85 GOTO 410
425  IF Q6 < 3 GOTO 410
430  PRINT
440 Q1 = Q6 * 17 / 100: REM    RESERVOIR DISCHARGE
450 Q2 = Q6 * 12 / 100: REM    NOE DISCHARGE
460 Q3 = Q6 * 34 / 100: REM     LAND DRAINAGE
470 Q4 = Q6 * 12 / 100: REM     MATLOCK EFFLUENT AND SOUGH DRAINAGE
480 Q5 = Q6 * 25 / 100: REM    RIVER WYE
490 C6 = 399 - (2.06 * Q6): REM    REGRESSION FOR AUTUMN FROM AUTOMATIC SITE AT MATLOCK
500 C5 = 513 - (3.58 * Q5): REM     REGRESSION ON R.WYE USING AUTUMN MONTHLY SURVEY DATA.
510 C1 = 95: REM     CONDUCTIVITY OF RESERVOIR WATER DURING AUTUMN
520 Q7 = Q1 + Q2 + Q3: REM   CHATSWORTH DISCHARGE
530 C7 = 263 - (1.26 * Q7): REM    CHATSWORTH CONDUCTIVITY IN AUTUMN.
540 C2 = ((Q7 * C7) - (90 * Q1)) / (Q2 + Q3): REM    CONDUCT. OF NOE & LAND DRAIN.
550 C4 = ((Q6 * C6) - (Q5 * C5) - (Q7 * C7)) / Q4: REM    EFFLUENT CONDUCTIVITY
560 C4 = C4 + 100: REM   100 ENSURES THAT EFFLUENT CONDUCTIVITY REMAINS REALISTIC
570 C6 =  INT (C6 * 100 + .5) / 100:C5 =  INT (C5 * 100 + .5) / 100
580 C2 =  INT (C2 * 100 + .5) / 100:C7 =  INT (C7 * 100 + .5) / 100
590 C4 =  INT (C4 * 100 + .5) / 100
600  GOTO 690
610  PRINT "RES.Q="Q1; TAB( 16);"RESERVOIR COND=";C1
620  PRINT "NOE Q=";Q2; TAB( 16);"LAND DRAIN Q= ";Q3
630  PRINT "NOE & LAND DRAIN COND=";C2
640  PRINT "CHATS Q=";QC TAB( 16);"CHATS. C=";CC
650  PRINT "EFF.Q=";QE TAB( 16);"EFF.COND=";CE
660  PRINT "R.WYE Q=";Q5; TAB( 16);"R.WYE COND=";C5
670  PRINT "MAT.Q=";QM; TAB( 16);"MAT.COND=";CM
680  PRINT : PRINT
```

```
690 QR = Q1: REM    PUTS PREDICTED % RESERVOIR VALUE INTO MIXING EQUATIONS
700 N = N + 1
710 QC = Q3 + Q2 + QR: REM     NEW CHATSWORTH DISCHARGE
720 QM = QC + Q5 + Q4: REM   NEW MATLOCK DISCHARGE
730 CC = ((QR * CR) + ((Q2 + Q3) * C2)) / QC: REM   NEW CHATSWORTH CONDUCTIVITY
735 CM = ((QC * CC) + (Q4 * C4) + (Q5 * C5)) / QM: REM  NEW MATLOCK COND.
740 QE = QM - QC - Q5:CE = ((QM * CM) - (CC * QC) - (Q5 * C5)) / QE: REM  NEW EFF.VALUES.
750 CE =  INT (CE * 100 + .5) / 100:CC =  INT (CC * 100 + .5) / 100
755 QE =  INT (QE * 100 + .5) / 100
760  IF N = 1 THEN  GOTO 610
770  IF N = 3 THEN  GOTO 790
780  INPUT "NEW RESERVOIR DISCHARGE= ";QR: GOTO 700
790  PRINT "CHATS.Q=";QC; TAB( 16);"CHATS.COND=";CC
800  PRINT "MAT.Q=";QM; TAB( 16);"MAT. COND=";CM
810  PRINT : PRINT
820  INPUT "WYE DISCHARGE = ";QW: REM    NEW WYE DISCHARGE
830 CW = 513 - (3.58 * QW): REM    NEW WYE CONDUCTIVITY IN AUTUMN.
840  IF CW < 200 THEN CW = 200
850 Q9 = Q4 + Q7 + QW: REM     NEW MATLOCK DISCHARGE
860 C9 = ((QW * CW) + (Q4 * C4) + (Q7 * C7)) / Q9: REM     NEW MATLOCK CONDUCTIVITY
870 C9 =  INT (C9 * 100 + .5) / 100
880 CW =  INT (CW * 100 + .5) / 100
890  PRINT "WYE Q= ";QW; TAB( 16);"WYE COND= ";CW
900  PRINT "MAT.Q=";Q9; TAB( 16);"MAT.COND=";C9
```

Computer model for the prediction of changing reservoir discharge or River Wye contribution on the seasonal pattern of Conductivity on the River Derwent.

APPENDIX D.

RIVER TRYWERYN ADDITIONAL DATA.

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DATE	Stge L	StgeH	WA-L	WA-H	HR-L	HR-H	QL	QH	nL	nH
1.6.84	5.0	49	2.6	15.18	0.10	0.39	1.2	13.2	0.05	0.06
2.6.84	6.0	50	2.7	15.18	0.10	0.39	1.2	13.2	0.05	0.06
29.5.84	6.0	48	2.7	15.18	0.09	0.39	1.2	13.2	0.05	0.06
30.5.84	5.0	49	2.6	15.18	0.10	0.39	1.2	13.2	0.05	0.06
31.5.84	5.0	49	2.6	15.18	0.10	0.39	1.2	13.2	0.05	0.06
5.2.84	17.0	45	6.4	15.18	0.18	0.37	3.0	12.9	0.07	0.06
3.2.84	15.0	43	5.4	13.48	0.15	0.35	2.6	11.5	0.06	0.06
2.2.84	20.0	47	8.0	15.18	0.20	0.39	3.8	13.0	0.07	0.06
1.2.84	11.0	40	4.8	13.48	0.13	0.35	1.7	11.1	0.08	0.06
31.1.84	12.0	40	4.8	13.48	0.13	0.35	1.9	11.1	0.08	0.06
30.1.84	15.0	40	5.4	13.48	0.15	0.35	2.6	11.1	0.06	0.06
23.4.83	14.5	40	5.4	13.48	0.15	0.35	2.6	11.1	0.06	0.06
24.4.83	11.0	40	4.8	13.48	0.13	0.35	1.6	11.1	0.08	0.06
25.10.82	10.0	40	3.8	13.48	0.10	0.35	1.6	11.1	0.05	0.06
4.9.82	8.0	47	3.0	15.18	0.08	0.39	1.2	13.0	0.05	0.06
5.9.82	8.0	46	3.0	15.18	0.08	0.39	1.2	13.0	0.05	0.06
15.5.82	22.0	40	8.7	13.48	0.23	0.35	4.4	11.1	0.07	0.06
16.5.82	8.0	40	3.0	13.48	0.08	0.35	1.2	11.1	0.05	0.06

Slope (from OS map 1:10000)=0.01 Distance from site 1=7.8km

Hydraulic paramtres at Site 6 on the River Tryweryn.

DATE	Stge L	StgeH	WA-L	WA-H	HR-L	HR-H	QL	QH	nL	nH
23.4.83	17	49	4.92	8.76	0.2	0.3	2.6	13.2	0.07	0.04
24.4.83	8	47	4.20	8.66	0.16	0.3	1.6	13.2	0.07	0.04
25.10.82	9	53	4.20	9.70	0.16	0.30	1.6	13.2	0.08	0.04
4.9.82	9	56	4.04	9.86	0.16	0.30	1.2	13.2	0.09	0.04
5.9.82	10	55	4.04	9.76	0.17	0.30	1.2	13.0	0.11	0.04
15.5.82	48	67	7.76	11.76	0.31	0.40	4.4	11.1	0.08	0.04
16.5.82	13	55	4.82	8.8	0.19	0.30	1.2	11.1	0.13	0.04
29.5.84	6	52	4.04	9.0	0.16	0.30	1.7	13.2	0.08	0.04
30.5.84	6	54	4.04	9.04	0.16	0.30	1.2	13.2	0.08	0.04
31.5.84	6	53	4.04	9.00	0.16	0.30	1.2	13.2	0.08	0.04
1.6.84	6	53	4.04	9.00	0.16	0.30	1.2	13.2	0.08	0.04
2.6.84	6	53	4.04	9.00	0.16	0.30	1.2	13.2	0.08	0.04

slope = 0.01   Distance from site 1 = 6.3 km.

Hydraulic dimensions at site 5. River Tryweryn.

DATE	Stge L	StgeH	WA-L	WA-H	HR-L	HR-H	QL	QH	nL	nH
4.6.83	15	46	2.96	10.0	0.16	0.46	1.6	13.2	0.05	0.05
5.6.83	10	46	2.16	10.0	0.12	0.46	0.8	13.2	0.07	0.05
23.4.83	24	47	4.56	10.0	0.25	0.46	2.6	13.2	0.07	0.05
24.4.83	16	46	2.96	10.0	0.16	0.46	1.6	13.2	0.05	0.05
29.5.84	28	53	2.5	12.0	0.15	0.5	1.2	13.2	0.06	0.05
30.5.84	22	53	2.5	12.0	0.15	0.5	1.2	13.2	0.06	0.05
31.5.84	20	52	2.5	12.0	0.15	0.5	1.2	13.2	0.06	0.05
1.6.84	21	53	2.5	12.0	0.15	0.5	1.2	13.2	0.06	0.05
2.6.84	22	51	2.5	12.0	0.15	0.5	1.2	13.2	0.06	0.05
3.2.84	23	53	4.3	12.0	0.25	0.5	2.6	12.6	0.06	0.05
1.2.84	20	50	3.8	12.0	0.20	0.5	2.0	12.0	0.06	0.05
5.2.84	25	53	4.7	12.0	0.27	0.5	2.7	12.7	0.05	0.05
31.1.84	21	50	3.9	12.0	0.2	0.5	2.0	12.0	0.06	0.05
30.1.84	24	50	4.56	12.0	0.25	0.5	2.6	12.6	0.05	0.05

Slope = 0.01 Distance from site 1 = 4.4.km.

The Hydraulic dimensions of site 4. River Tryweryn.

DATE	Stge L	StgeH	WA-L	WA-H	HR-L	HR-H	QL	QH	nL	nH
4.6.83	27	78	3.04	12.64	0.15	0.6	0.8	12.6	0.15	0.10
5.6.83	26	79	3.04	12.64	0.15	0.6	0.8	12.6	0.15	0.10
29.5.84	20	70	2.8	12.0	0.12	0.5	0.4	11.0	0.18	0.11
30.5.84	19	70	2.8	12.0	0.12	0.5	0.4	11.0	0.18	0.11
31.5.84	19	70	2.8	12.0	0.12	0.5	0.4	11.0	0.18	0.11
1.5.84	19	70	2.8	12.0	0.12	0.5	0.4	11.0	0.18	0.11
2.5.84	19	70	2.8	12.0	0.12	0.5	0.4	11.0	0.18	0.11

Slope = 0.02 Distance below site 1 = 3.3.km.

The hydraulic dimensions for site 3. River Tryweryn.

DATE	Stge L	StgeH	WA-L	WA-H	HR-L	HR-H	QL	QH	nL	nH
23.4.83	18	64	1.4	9.8	0.1	0.44	0.4	11.0	0.11	0.09
24.4.83	10	59	1.0	9.5	0.07	0.40	0.4	11.0	0.06	0.07
25.10.82	6	65	0.6	9.8	0.03	0.44	0.4	12.6	0.09	0.05
29.5.84	9	54	1.0	8.9	0.07	0.37	0.4	11.0	0.06	0.07
30.5.84	10	54	1.0	8.9	0.07	0.37	0.4	11.0	0.06	0.07
31.5.84	10	54	1.0	8.9	0.07	0.37	0.4	11.0	0.06	0.07
1.6.84	10	54	1.0	8.9	0.07	0.37	0.4	11.0	0.06	0.07
2.6.84	10	54	1.0	8.9	0.07	0.37	0.4	11.0	0.06	0.07

Slope = 0.02 Distance below site 1 = 1.3 km

The hydraulic dimensions at site 2. River Tryweryn.

DATE	Stge L	StgeH	WA-L	WA-H	HR-L	HR-H	Ql	QH	nL	nH
4.6.83	22	56	2.28	6.56	0.16	0.40	0.8	12.6	0.08	0.03
5.6.83	22	56	2.28	6.56	0.16	0.40	0.8	12.6	0.08	0.03
23.4.83	10	46	1.28	5.96	0.09	0.33	0.4	11.0	0.06	0.02
24.4.83	9	46	1.10	5.96	0.08	0.33	0.4	11.0	0.05	0.02
25.10.82	16	60	1.6	7.16	0.11	0.40	0.4	12.6	0.09	0.03
4.9.82	23	62	2.28	7.16	0.16	0.40	0.8	12.6	0.08	0.03
5.9.82	24	62	2.28	7.16	0.16	0.40	0.8	12.6	0.08	0.03
15.5.82	40	60	4.04	7.16	0.29	0.40	4.5	12.6	0.04	0.03
16.5.82	10	60	1.28	7.16	0.09	0.40	0.4	12.6	0.06	0.03
30.1.84	16	54	1.60	6.56	0.11	0.40	0.4	12.6	0.09	0.03
31.1.84	15	54	1.60	6.56	0.11	0.40	0.4	12.6	0.09	0.03
1.2.84	15	54	1.60	6.56	0.11	0.40	0.4	12.6	0.09	0.03
5.2.84	15	48	1.60	5.96	0.11	0.33	0.4	12.0	0.09	0.03
29.5.84	9	45	1.10	5.96	0.08	0.33	0.4	11.0	0.05	0.02
30.5.84	9	45	1.10	5.96	0.08	0.33	0.4	11.0	0.05	0.02
31.5.84	10	45	1.28	5.96	0.09	0.33	0.4	11.0	0.05	0.02
1.6.84	9	45	1.10	5.96	0.08	0.33	0.4	11.0	0.05	0.02
2.6.84	9	44	1.10	5.96	0.08	0.33	0.4	11.0	0.05	0.02

Slope = 0.01

The hydraulic dimensions of site 1. River Tryweryn.

Appendix D.2. Dimensions for the calculation of kinematic wave velocity.

SITE 1 - SITE 6 reach length 7.8km River Tryweryn

DATE	QL	QH	AL	AH	K	VL	Vob	Vk	T1	T2
15.5.82	4.5	12.6	9	15	1.18	.5	1.6	0.98	84	133
16.5.82	0.8	13	5.5	16	1.03	0.15	1.2	1.1	110	120
4.9.82	1.0	12.8	6.5	16	0.81	0.17	1.0	1.24	137	105
5.9.82	1.0	12.8	6.5	16	0.89	0.17	1.1	1.18	120	110
25.10.82	1.0	13.2	5.5	16	1.03	0.19	1.2	1.1	111	120
23.4.83	1.5	12.1	6.5	15	1.04	0.19	1.3	1.05	103	123
24.4.83	1.0	11.1	5.5	15	1.01	0.19	1.2	1.08	109	120
30.1.84	1.5	13.2	6.5	17	1.17	0.22	1.3	0.98	98	132

31.1.84	1.2	13.4	5.5	18	1.28	0.23	1.3	0.93	103	140
1.2.84	1.0	13.3	5.5	17	1.13	0.20	1.2	0.99	105	131
3.2.84	1.5	13.3	5.5	17	1.13	0.20	1.2	0.99	105	131
5.2.84	1.7	13.9	7	18	1.17	0.21	1.3	0.97	100	134
29.5.84	0.8	11.4	5.5	14.5	0.93	0.15	1.1	1.12	121	116
30.5.84	0.8	11.4	5.5	14.5	0.93	0.15	1.1	1.12	121	116
31.5.84	0.8	11.4	5.5	14.5	0.93	0.15	1.1	1.12	120	116
1.5.84	0.8	11.4	5.5	14.5	0.85	0.15	1.0	1.18	128	110
2.5.84	0.8	11.4	5.5	14.5	0.93	0.16	1.1	1.12	116	116

SITE 1 - SITE 5 reach length 6.3km River Tryweryn

DATE	QL	QH	AL	AH	k	VL	Vob	Vk	T1	T2
15.5.82	4.5	12.6	10.5	15.5	1.3	.45	2.1	0.96	49	109
16.5.82	0.8	13	7	16	1.10	0.11	1.5	1.1	71	97
4.9.82	1.0	12.8	8	16	0.75	.12	1.1	1.4	94	77
5.9.82	1.0	12.8	8	16	0.85	0.12	1.25	1.25	84	84
25.10.82	1.0	13.1	7.5	16	0.89	0.12	1.28	1.21	82	87
23.4.83	1.5	12.6	8	15	0.91	0.16	1.38	1.15	76	91
24.4.83	1.0	11.1	7.5	14.5	0.96	0.12	1.46	1.14	72	92

Dimensions for the calculation of kinematic wave movement. River Tryweryn.

QL= discharge at low flow QH = discharge at high flow
AL= wetted channel area at low flow AH= wetted channel area at high flow
K= Brady-Johnson roughness factor VL= velocity of water at low flow
Vob= observed velocity of wave peak Vk= kinematic water velocity
T1= observed time of travel of wave peak T2= calculated time of travel of water.

SITE 1 - SITE 4 reach length 4.4km River Tryweryn

DATE	QL	QH	AL	AH	K	VL	Vob	Vk	T1	T2
4.6.83	1.2	12.9	6.5	13.5	0.84	0.21	1.4	1.4	51	51
5.6.83	0.8	12.6	5	13	0.88	0.25	1.3	1.36	57	54
30.1.84	1.5	13	6	13.5	0.90	0.25	1.4	1.3	53	57
31.1.84	1.15	13.4	6	14	1.04	0.23	1.5	1.2	50	60

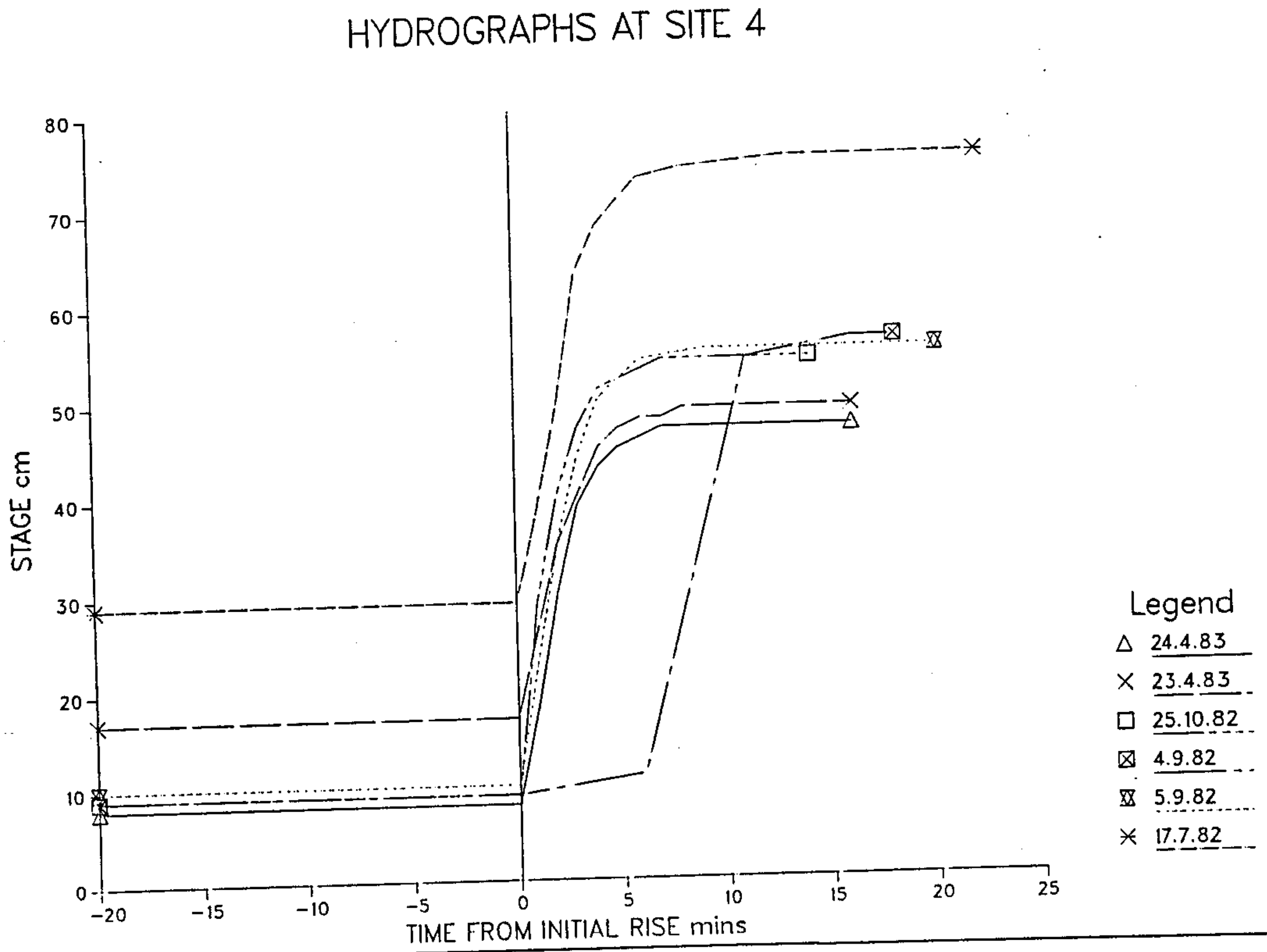
(CONTD)

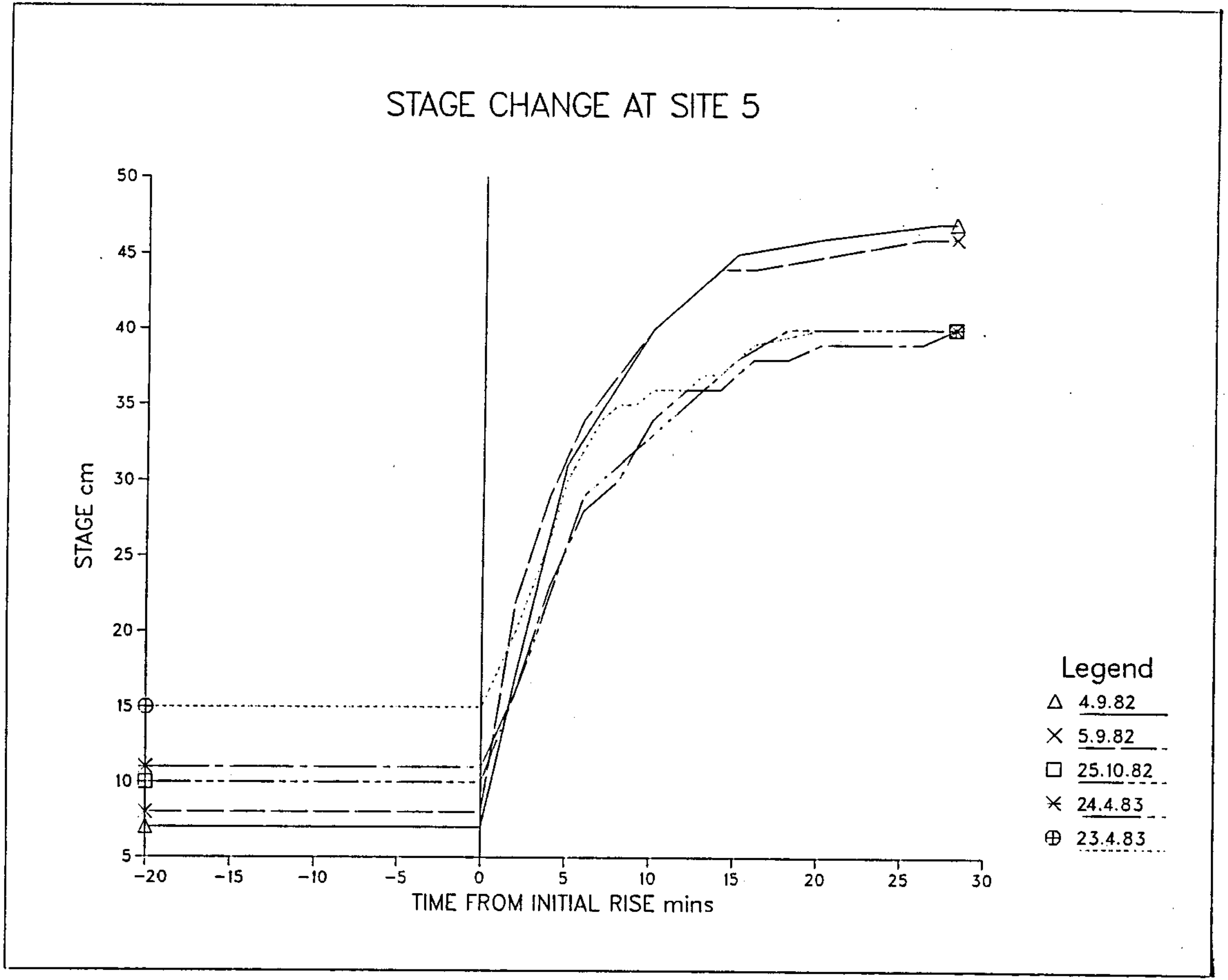
1.2.84	1.05	13.75	6	13.5	0.92	0.21	1.4	1.3	53	56
5.2.84	1.7	14	6.5	14.5	0.91	0.25	1.4	1.26	52	58
29.5.84	0.8	11.4	4.5	10.5	0.80	0.23	1.3	1.47	57	50
30.5.84	0.8	11.4	4.5	10.5	0.80	0.23	1.3	1.47	57	50
31.5.84	0.8	11.5	4.5	11	0.80	0.25	1.3	1.47	57	50
1.6.84	0.8	11.5	4.5	11	0.74	0.25	1.2	1.5	60	49
2.6.84	0.8	11.5	4.5	11	0.85	0.25	1.4	1.43	51	51.2
23.4.83	1.5	12	6	13	0.86	0.26	1.4	1.33	51	55
24.4.83	1.0	11.6	5.5	12	0.92	0.20	1.5	1.3	48	56

DATE	QL	QH	AL	AH	K	VL	Vob	Vk	T1	T2
SITE 1 - SITE 2 reach length 1.3km River Tryweryn										
25.10.82	0.4	12.6	4.5	12.5	0.89	0.1	1.55	1.46	14	14.9
23.4.83	0.4	11.0	4.5	10.0	0.80	0.1	1.44	1.59	15	14.0
24.4.83	0.4	11.0	4.5	10.0	0.80	0.1	1.55	1.54	14	14
29.5.84	0.4	11.0	4.5	10.0	0.80	0.1	0.99	1.54	22	14
30.5.84	0.4	11.0	4.5	10.0	0.80	0.1	0.99	1.54	22	14
31.5.84	0.4	11.0	4.5	10.0	0.80	0.1	1.03	1.54	21	14
1.6.84	0.4	11.0	4.5	10.0	0.80	0.1	1.55	1.54	15	14

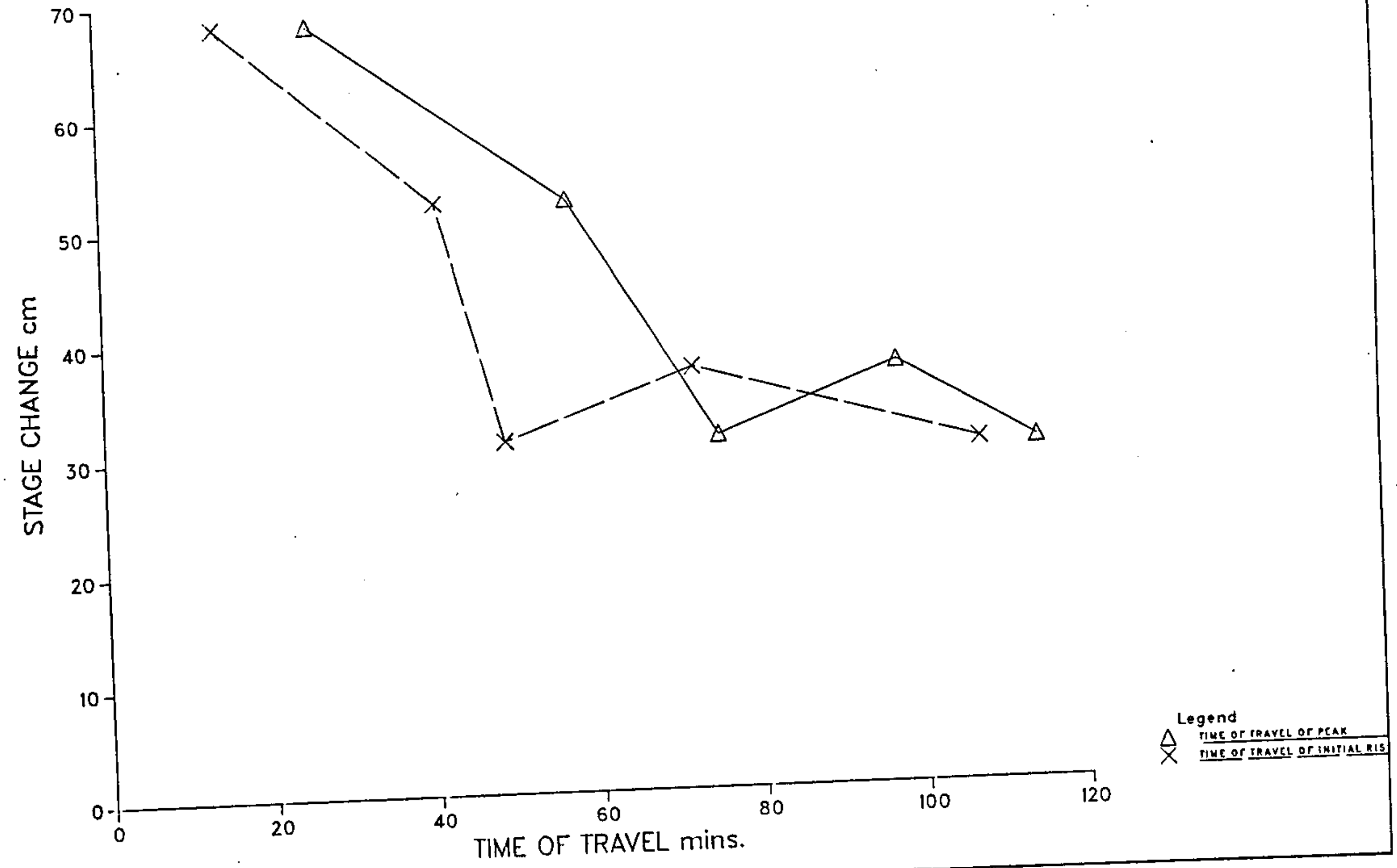
SITE 1 - SITE 3 reach length 3.3km River Tryweryn

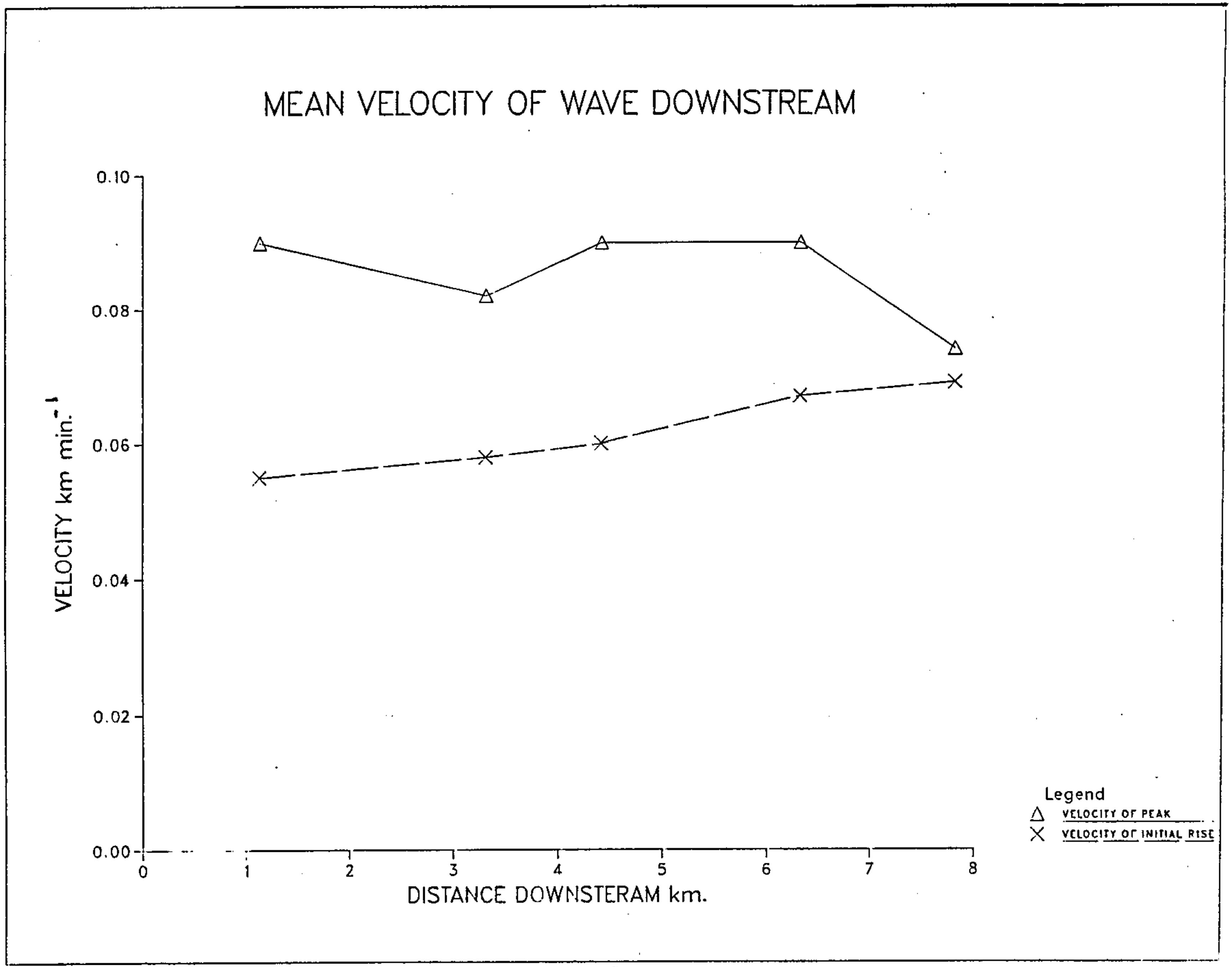
4.6.83	0.8	12.6	6.5	12.5	0.66	0.13	1.3	1.61	42	34
5.6.83	0.8	12.6	6.5	12.5	0.71	0.13	1.4	1.54	39	36
29.5.84	0.4	11	4.5	10.5	0.85	0.1	1.5	1.44	36	38
30.5.84	0.4	11	4.5	10.5	0.85	0.1	1.5	1.44	36	38
31.5.84	0.4	11	4.5	10.5	0.85	0.1	1.5	1.44	36	38
1.6.84	0.4	11	4.5	10.5	0.74	0.1	1.3	1.54	41	36
2.6.84	0.4	11	4.5	10.5	0.96	0.1	1.7	1.4	32	39


HYDROGRAPHS AT SITE 4
STAGE cm
0
10
20
30
40
50
60
70
80
TIME FROM INITIAL RISE mins
−20
−15
−10
−5
0
5
10
15
20
25
Legend
△ 24.4.83
× 23.4.83
□ 25.10.82
⊠ 4.9.82
⧖ 5.9.82
⋇ 17.7.82

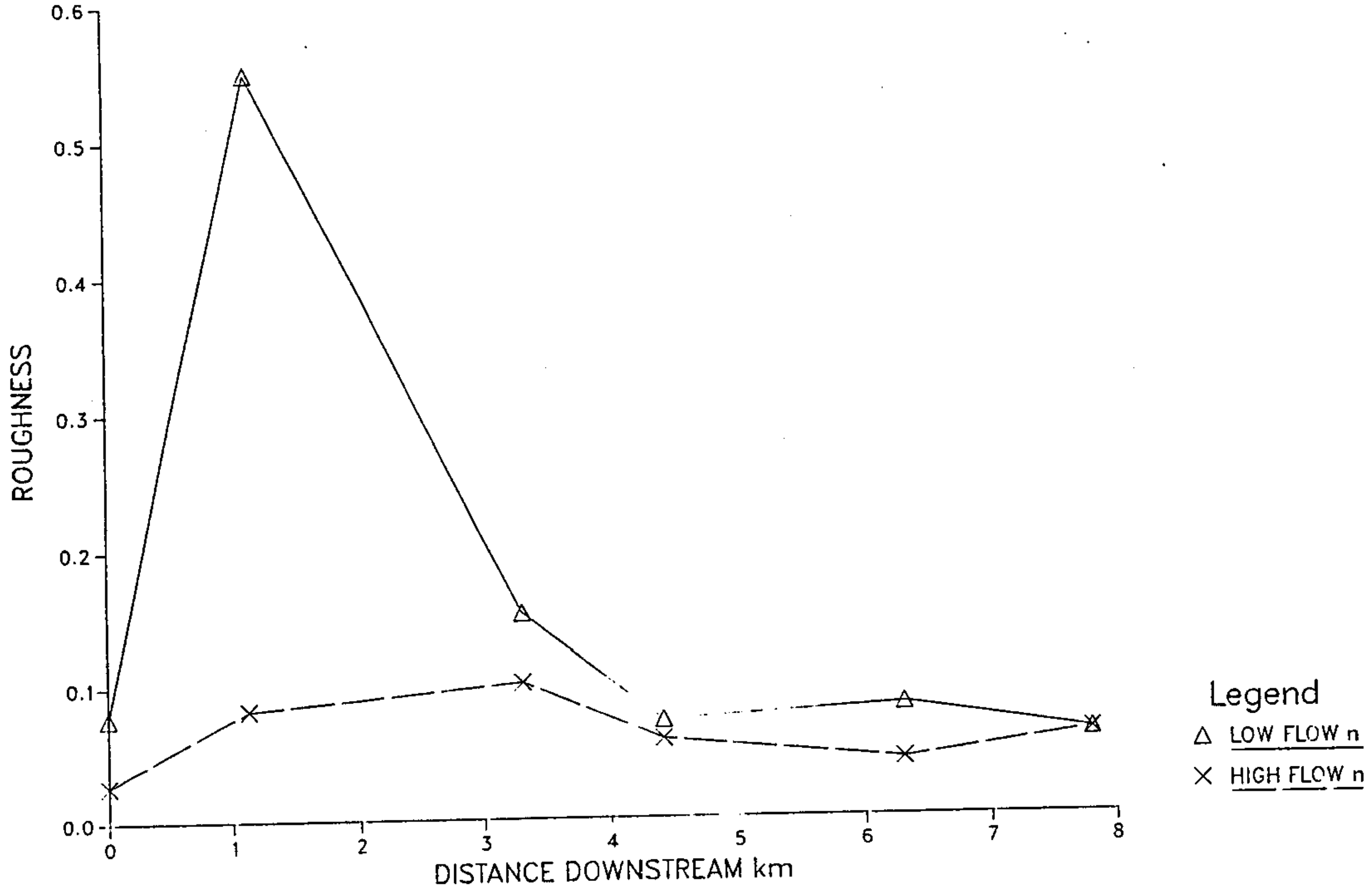

STAGE CHANGE AT SITE 5
STAGE cm
50
45
40
35
30
25
20
15
10
5
TIME FROM INITIAL RISE mins
−20
−15
−10
−5
0
5
10
15
20
25
30
Legend
△ 4.9.82
× 5.9.82
□ 25.10.82
⋇ 24.4.83
⊕ 23.4.83

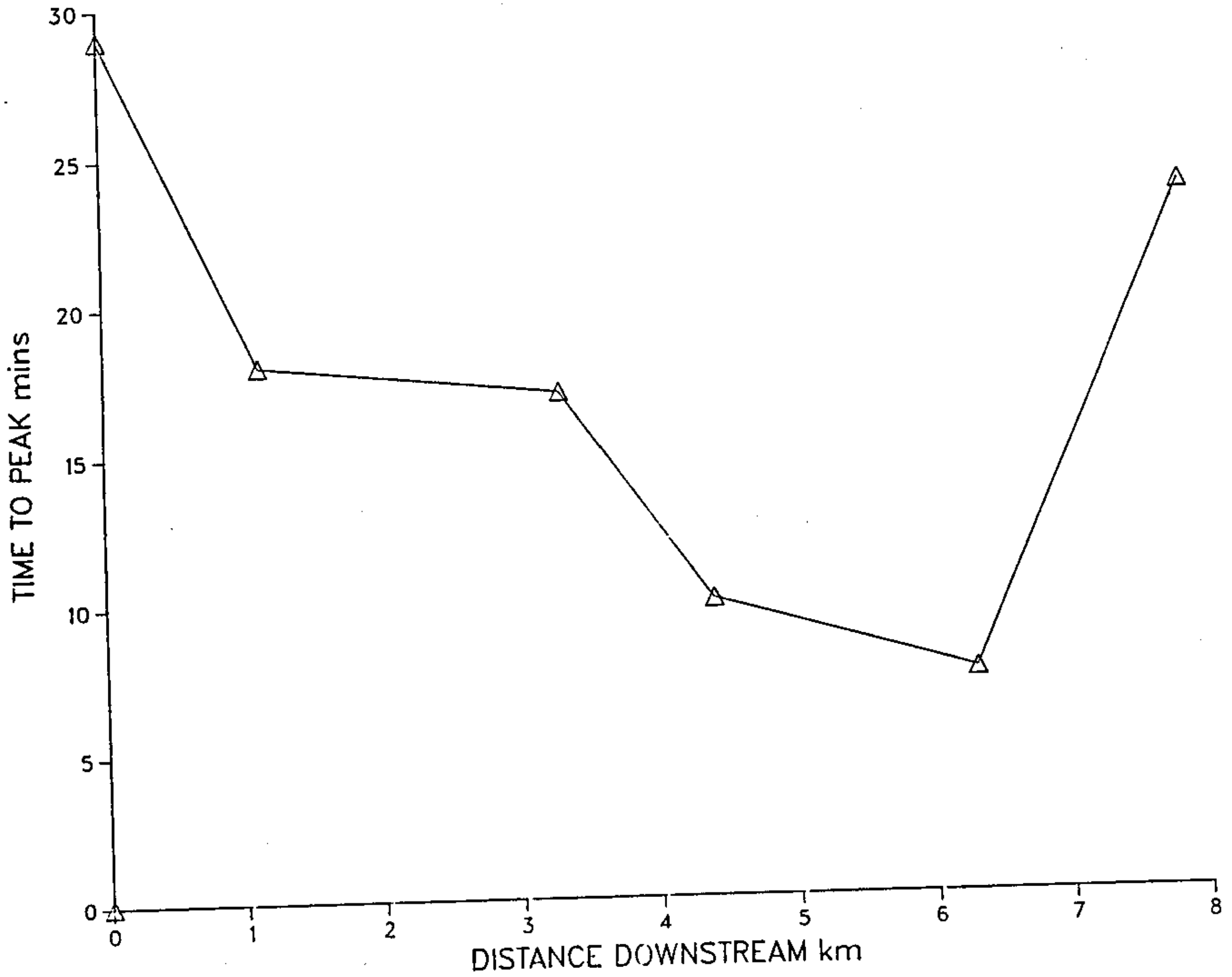
MEAN TIME OF TRAVEL OF WAVE AGAINST STAGE CHANGE




MEAN VELOCITY OF WAVE DOWNSTREAM
VELOCITY km min.⁻¹
0.00
0.02
0.04
0.06
0.08
0.10
0
1
2
3
4
5
6
7
8
DISTANCE DOWNSTERAM km.
Legend
△ VELOCITY OF PEAK
× VELOCITY OF INITIAL RISE

MEAN MANNINGS ROUGHNESS CHANGE DOWNSTREAM

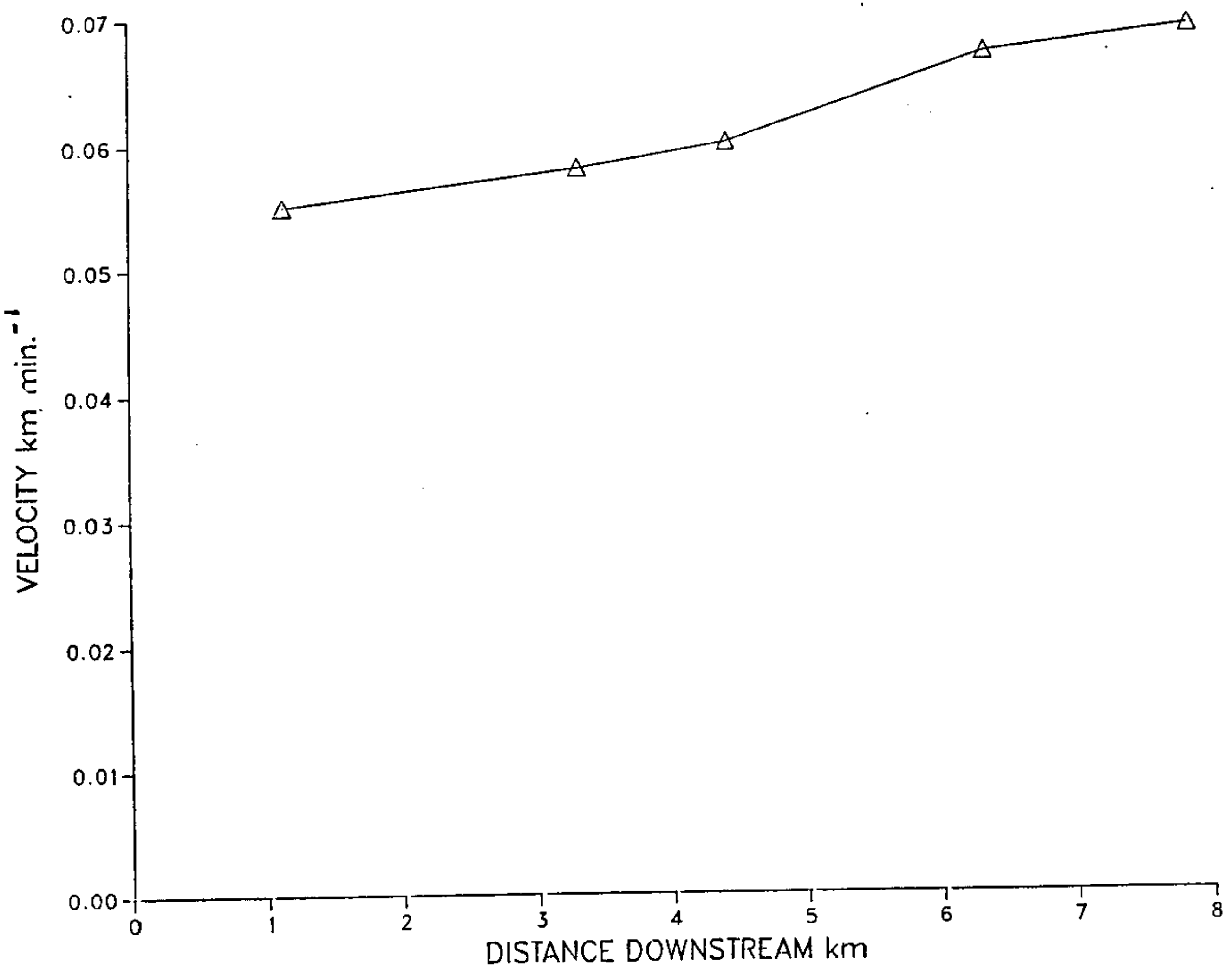




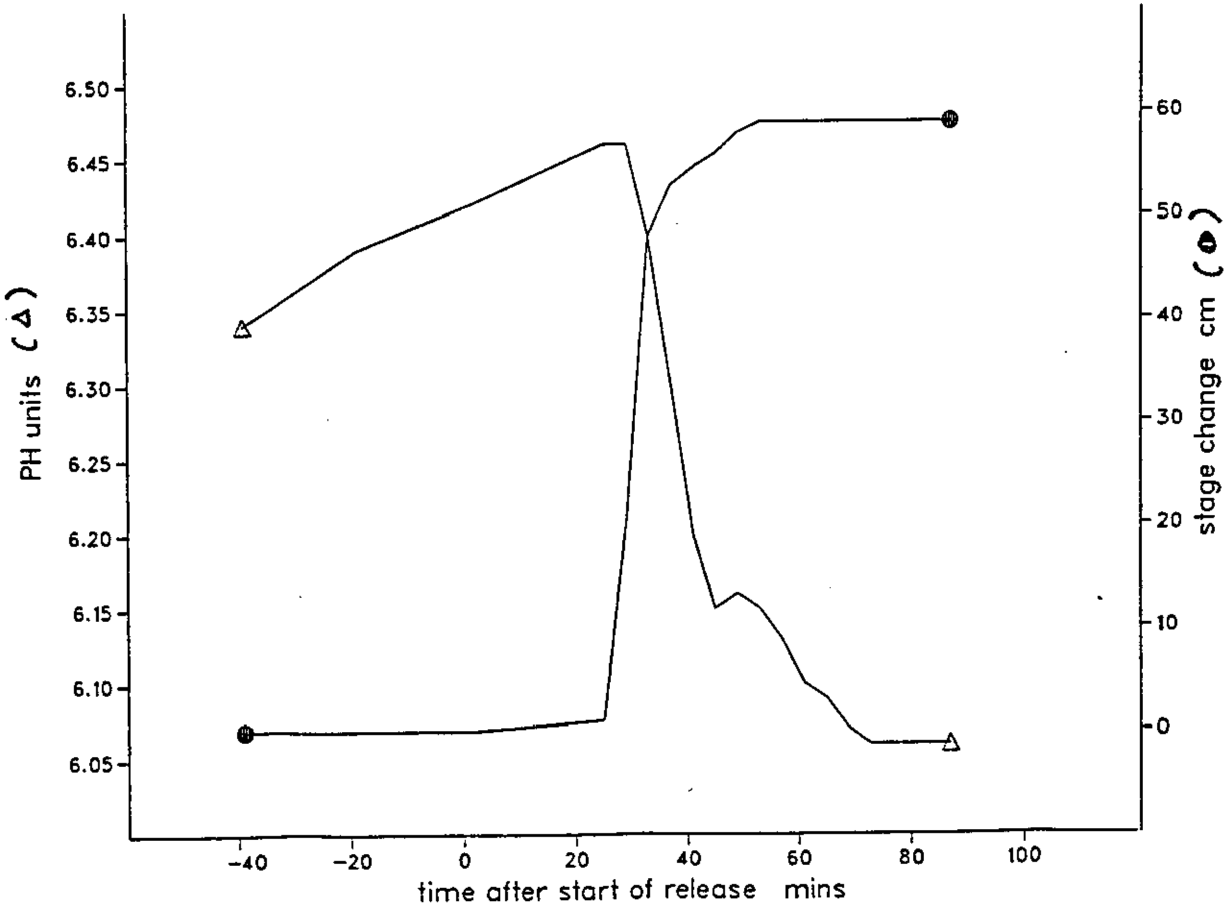
MEAN TIME TO PEAK AT A STATION,13 RELEASES

Appendix D.9

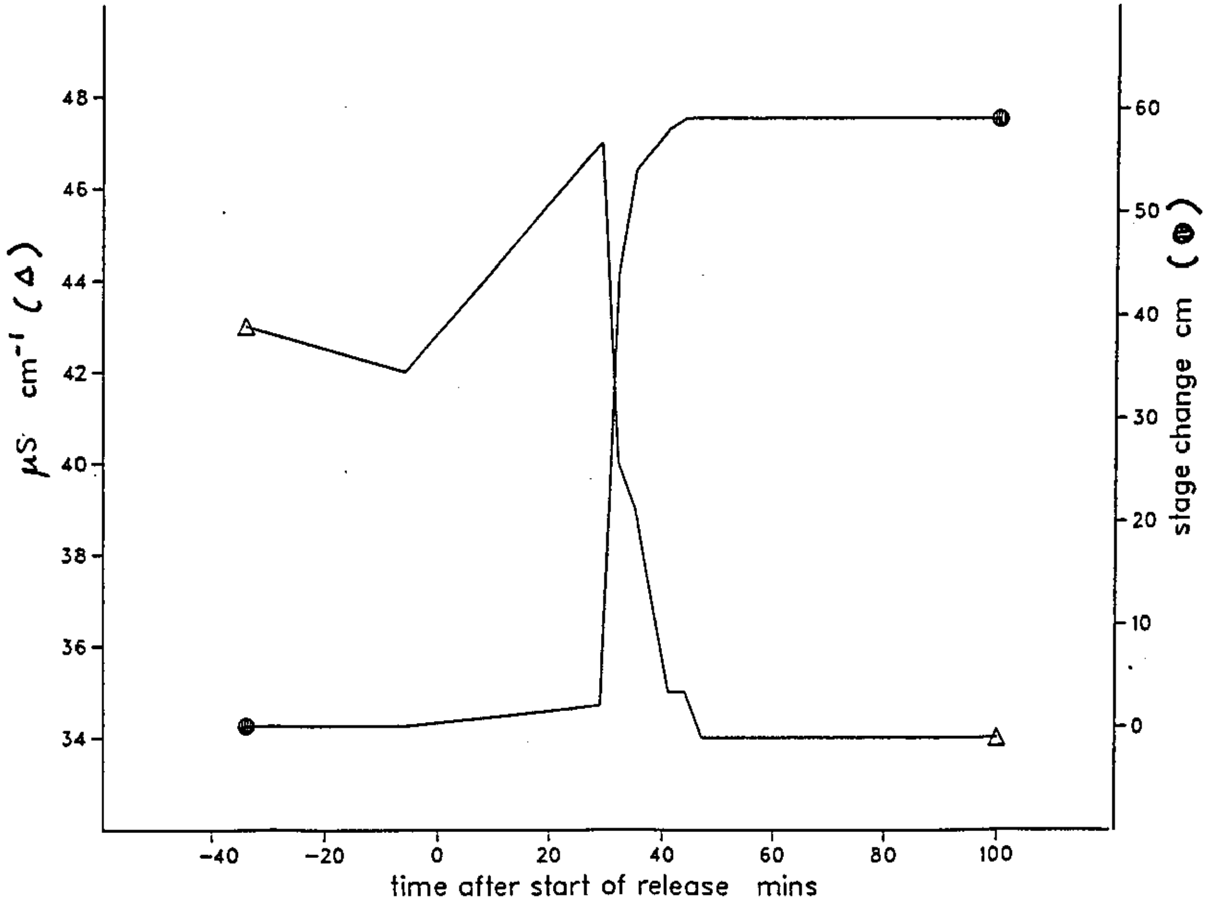
MEAN VELOCITY OF INITIAL RISE DOWNSTREAM

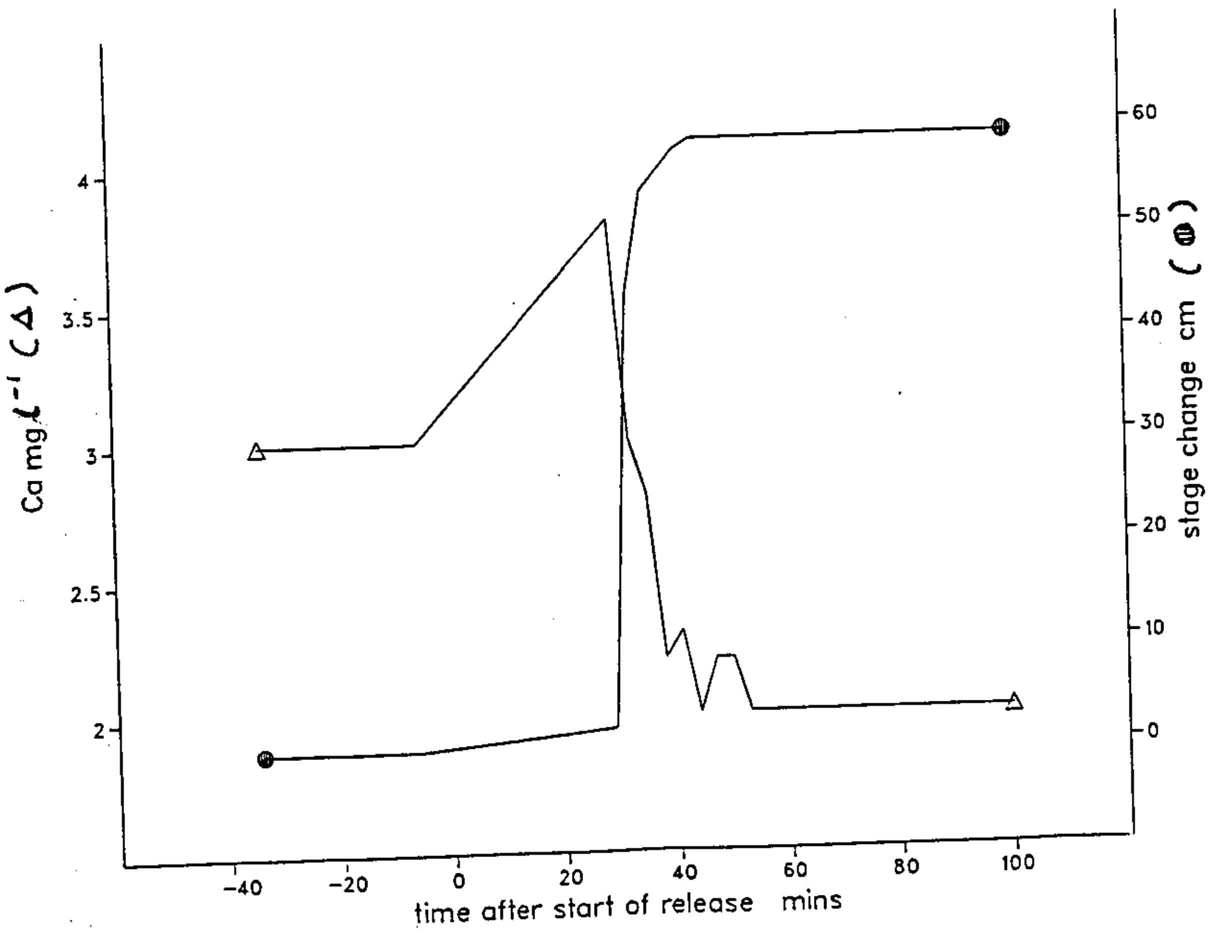


STAGE AND PH CHANGE, R.TRYWERYN, SITE 2, 24.4.83



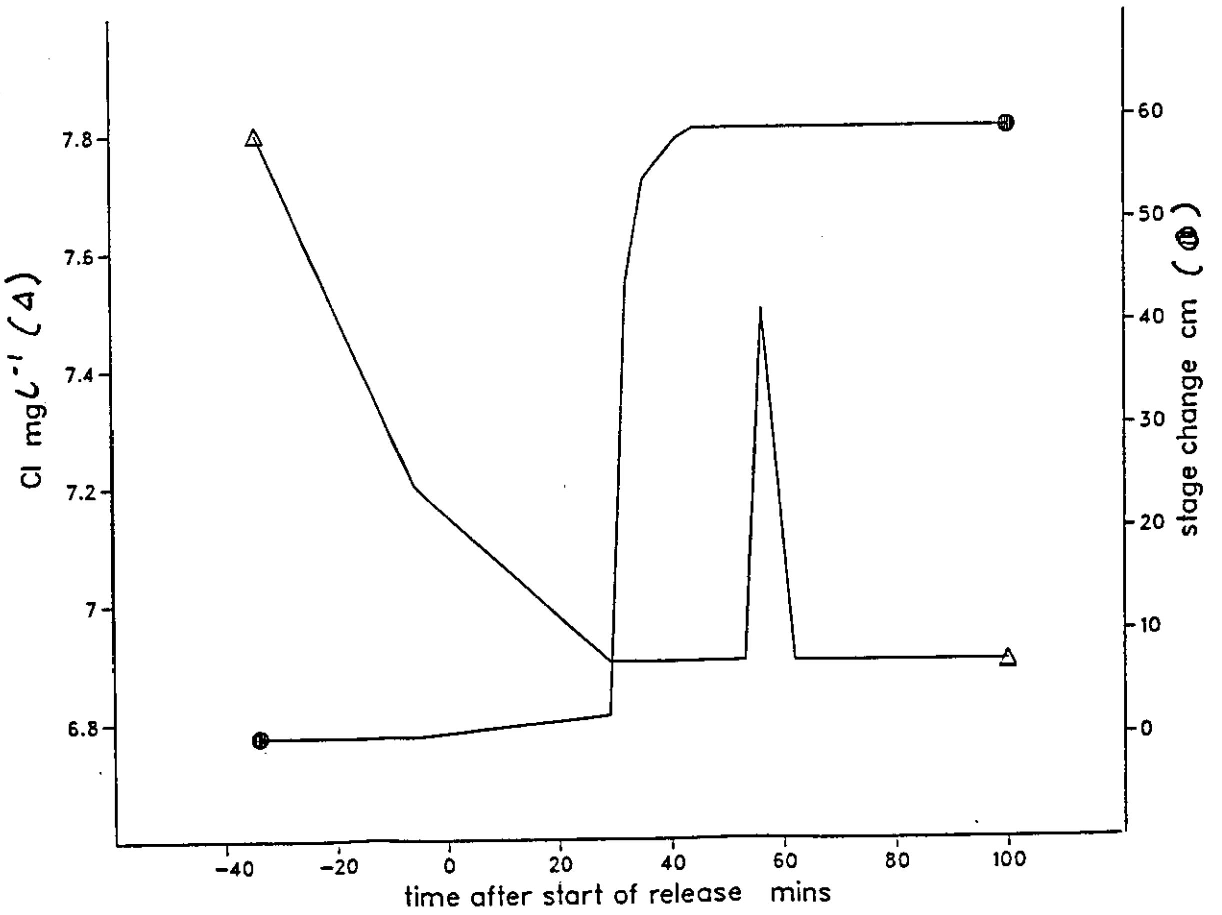
STAGE AND CONDUCTIVITY CHANGE, R.TRYWERYN,SITE 2, 25.10.82



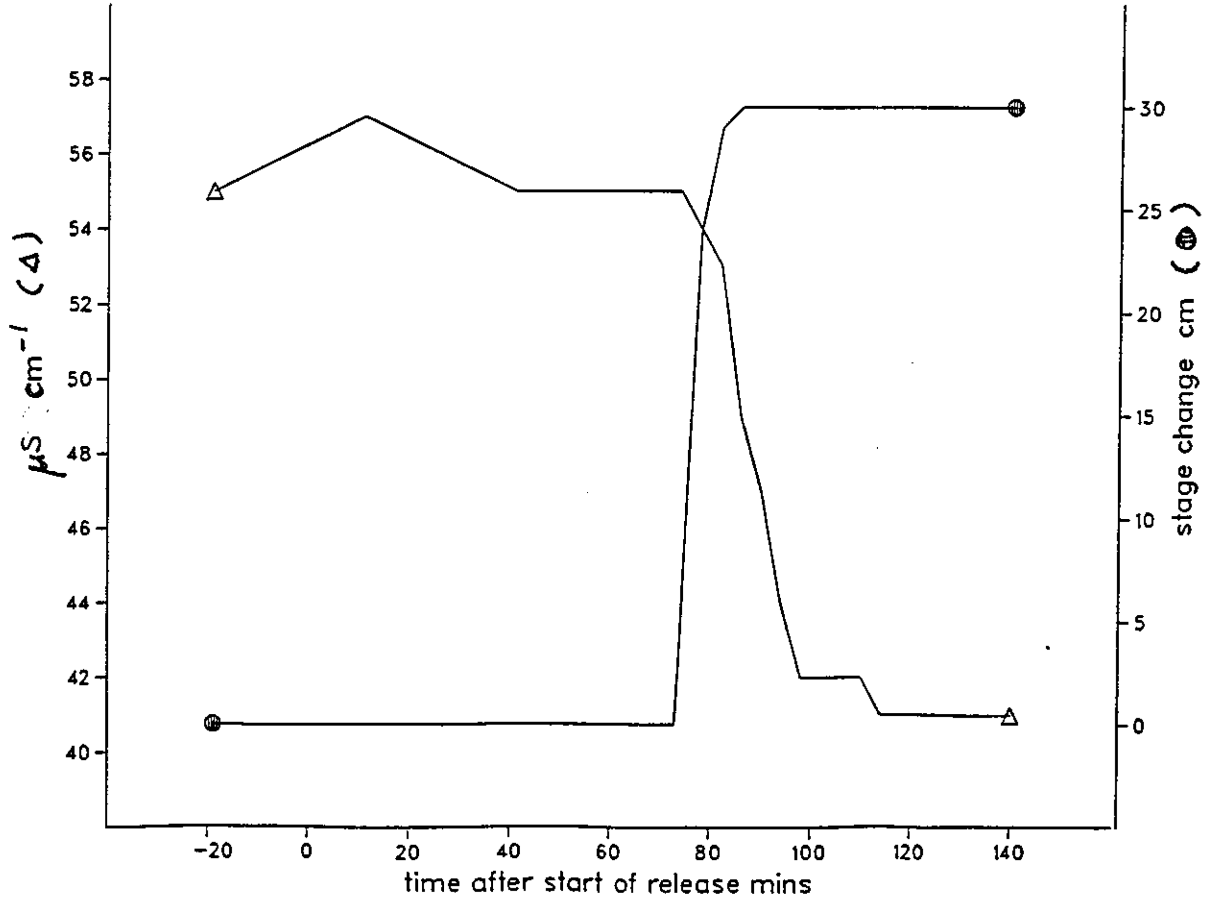


STAGE AND CALCIUM CHANGE, R.TRYWERYN, SITE 2, 25.10.82

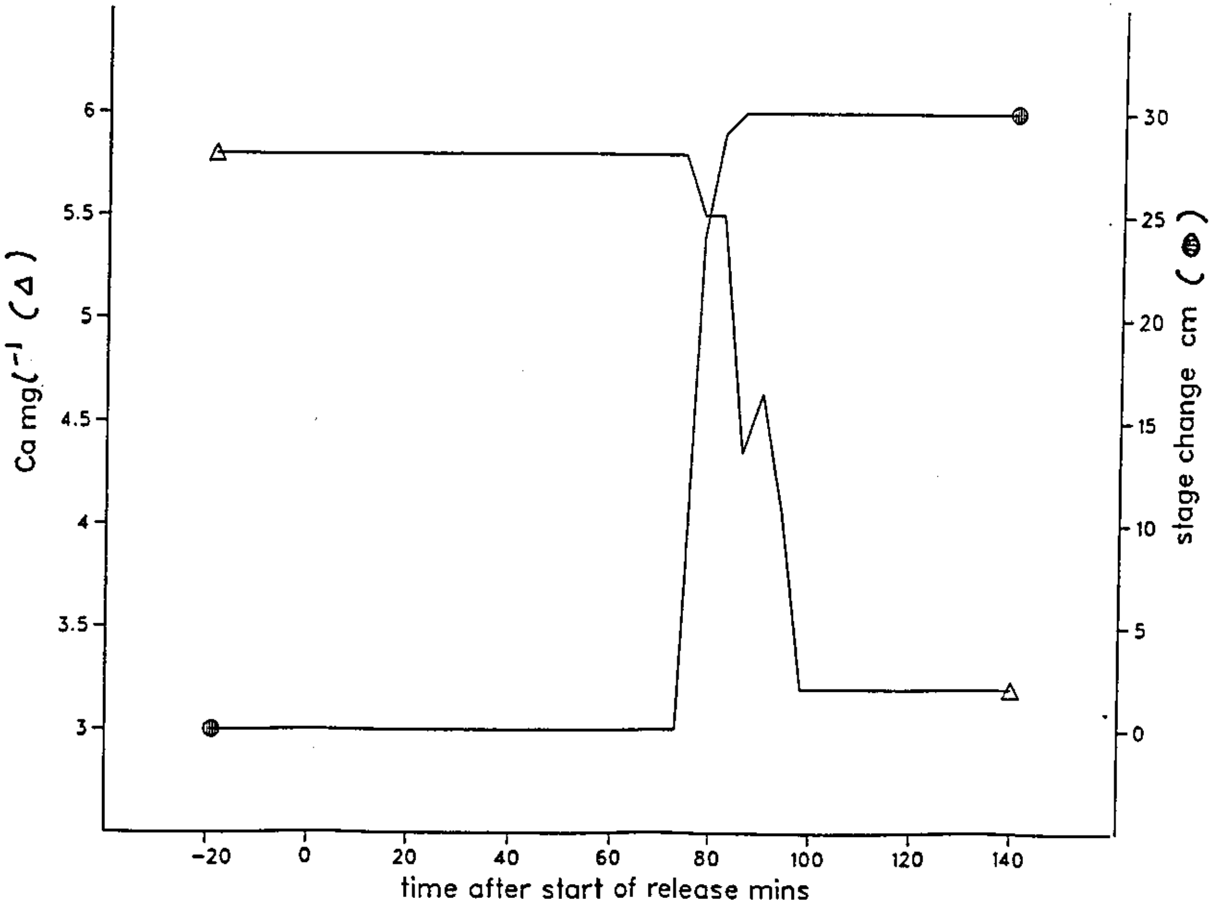
STAGE AND CHLORIDE CHANGE,R.TRYWERYN, SITE 2, 25.10.82



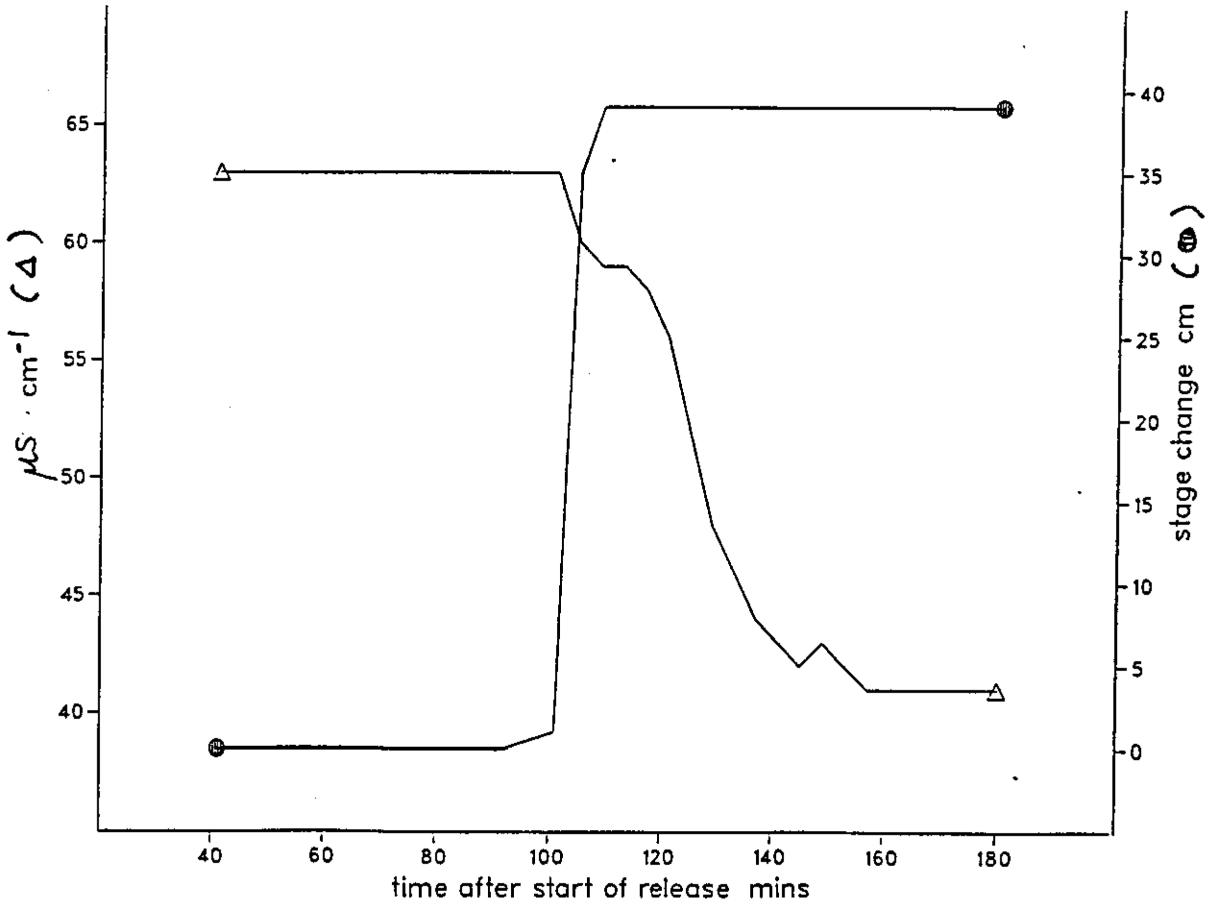
STAGE AND CONDUCTIVITY CHANGE, R TRYWERYN, SITE 4, 24.4.83

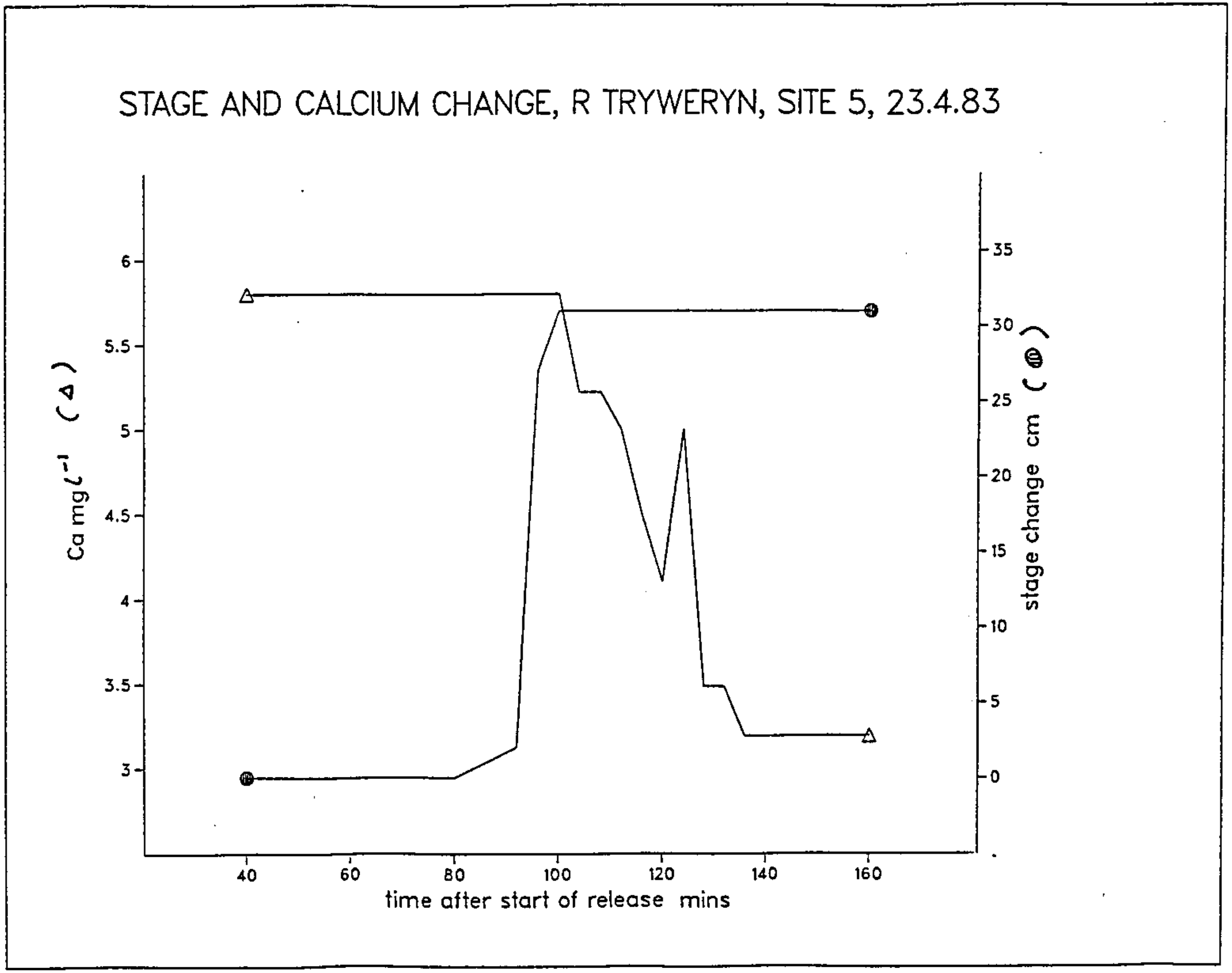


STAGE AND CALCIUM CHANGE, R TRYWERYN, SITE 4, 24.4.83



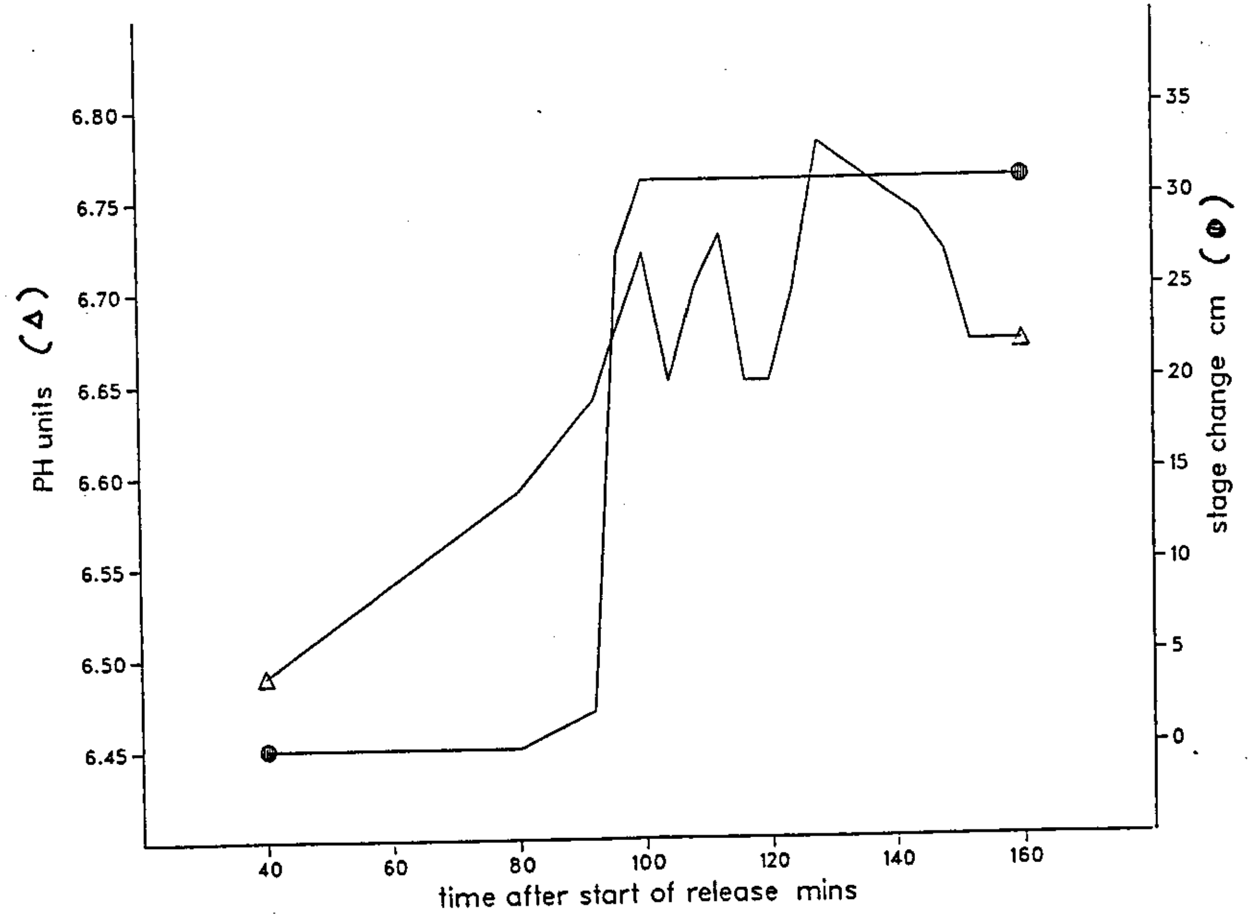
STAGE AND CONDUCTIVITY CHANGE, R TRYWERYN, SITE 5, 24.4.83

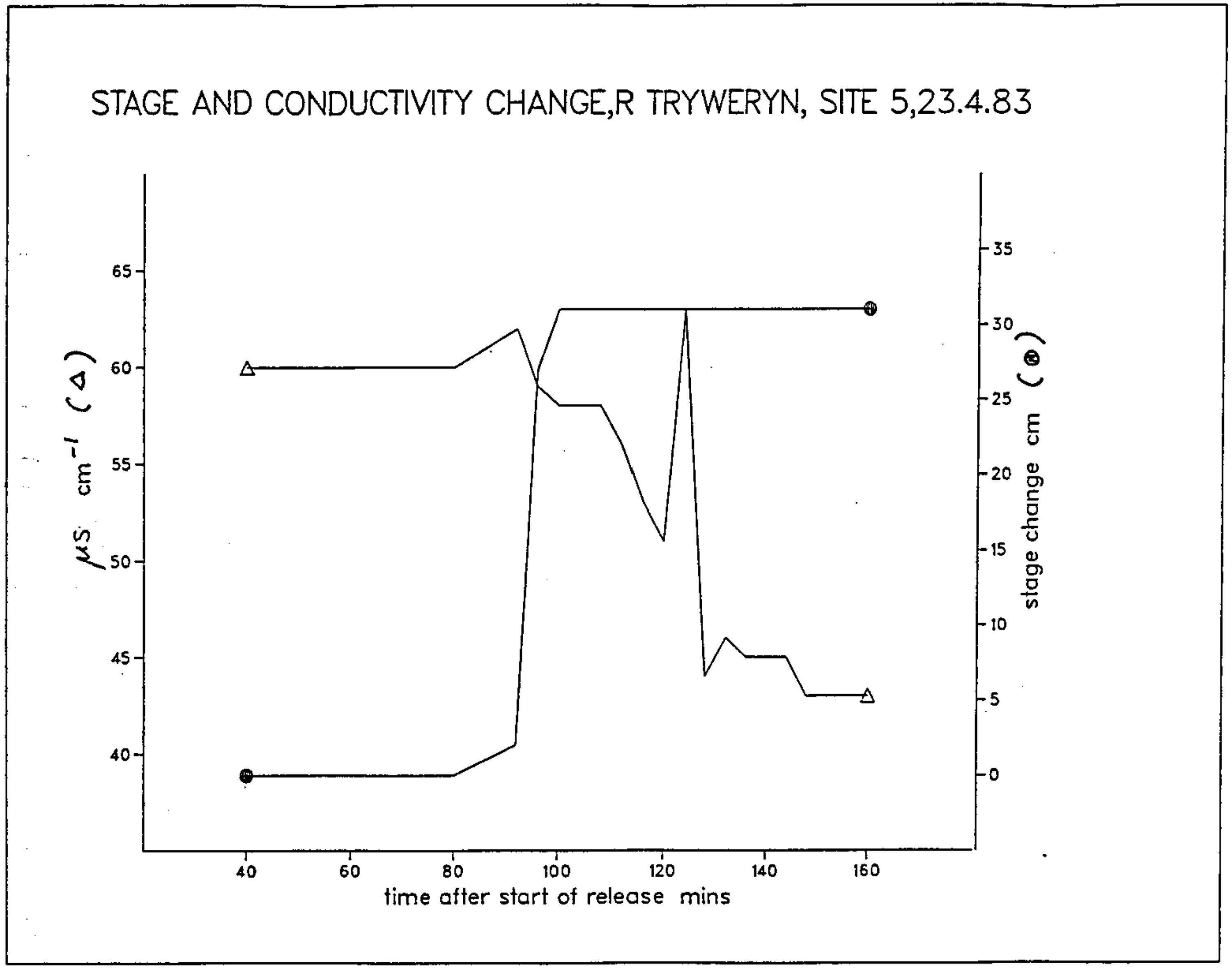




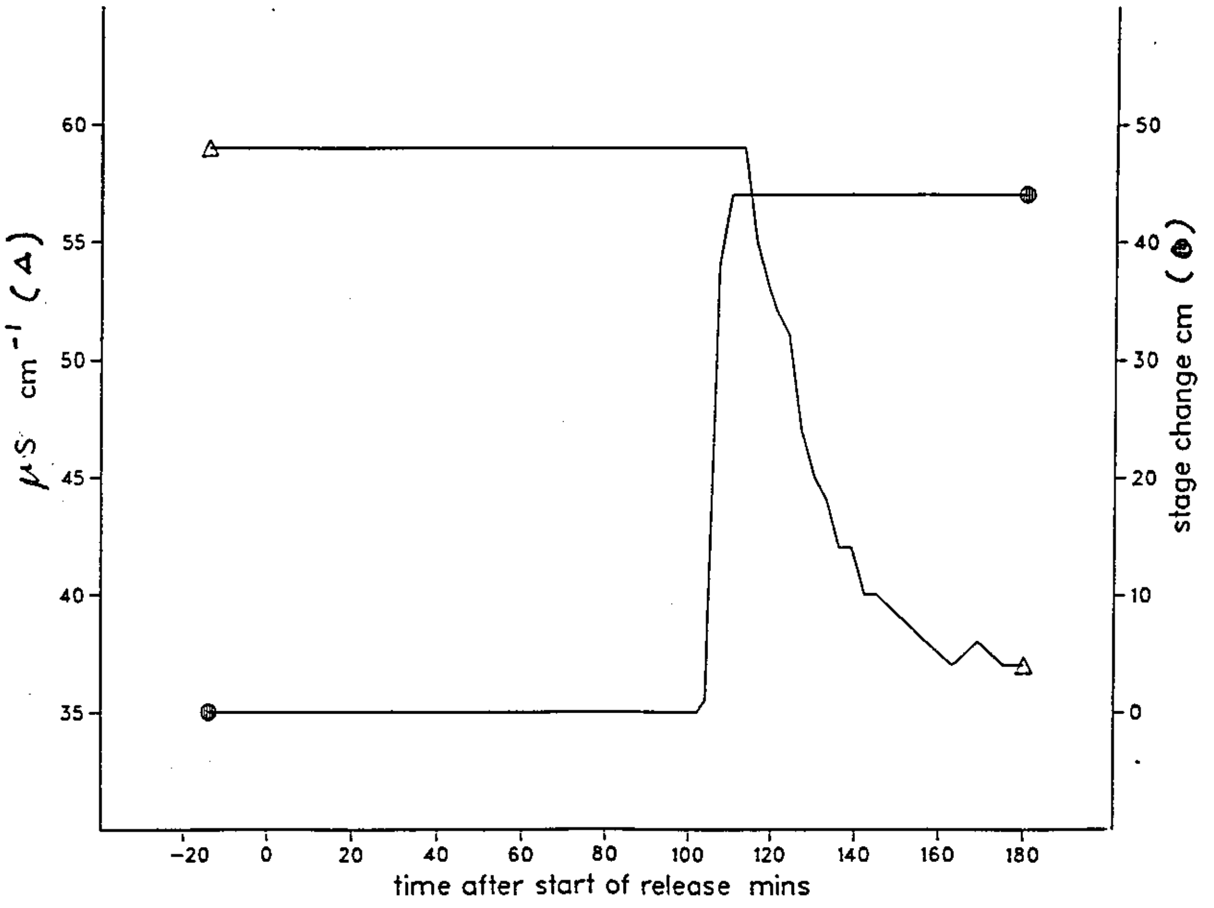
STAGE AND CALCIUM CHANGE, R TRYWERYN, SITE 5, 23.4.83

STAGE AND pH CHANGE,R TRYWERYN, SITE 5, 23.4.83



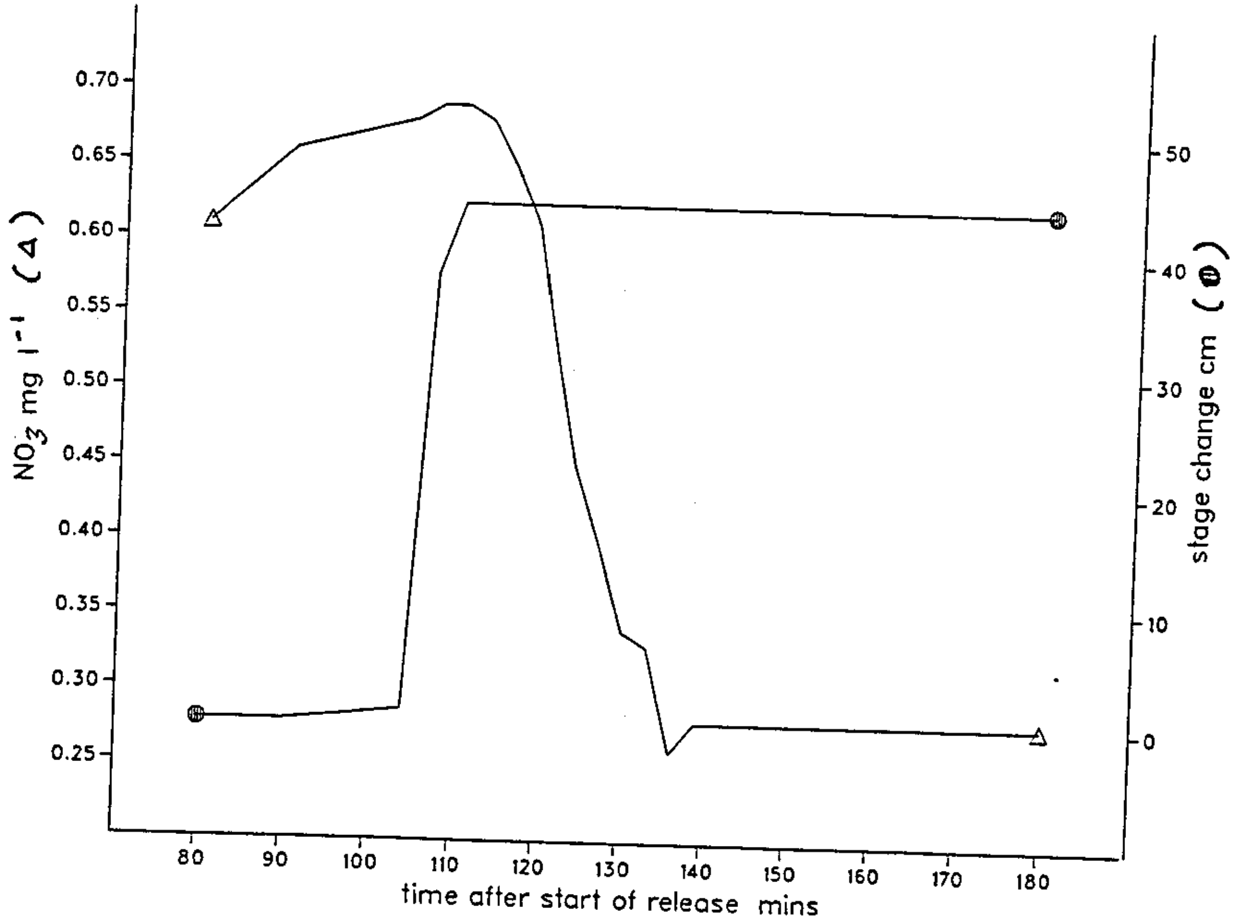


STAGE AND CONDUCTIVITY CHANGE,R TRYWERYN, SITE 5,23.4.83



STAGE AND CONDUCTIVITY CHANGE,R TRYWERYN, SITE 5, 25.10.82

STAGE AND NITRATE CHANGE, R TRYWERYN, SITE 5, 25.10.82



Appendix D.11

RIVER TRYWERYN WATER CHEMISTRY RESPONSE DURING RESERVOIR RELEASES - summary data.

22 reservoir releases in total were monitored on the River Tryweryn, of these 13 were examined for the chemical and hydrological changes created, and nine simply for hydrological variations induced downstream.

Summary chemical data for the 13 releases are presented. Although 6 sites were established it was not practical to moniter chemical variations at each site for every release. Sampling strategy was as described in 4.2.3.

TIME from release (mins) rise at site 1	stage (cm)	cond µScm^{-1}	NO_3^- mgl^{-1}	Cl^- mgl^{-1}	Ca^{2+} mgl^{-1}
-60	40	37	0.07	6.5	2.2
-50	40	36	0.07	6.6	2.3
-40	40	35	0.07	6.7	2.4
-30	40	34	0.06	6.8	2.5
-20	40	33	0.04	6.8	2.6
0	41	33	0.04	6.8	2.6
30	60	32	0.10	6.4	2.0
60	60	31	0.10	6.2	1.6
120	"	31	0.10	6.1	2.0
180	"	31	0.10	6.0	2.2
240	"	30.5	0.12	5.8	2.2
300	"	31	0.14	5.2	2.3
360	"	32	"	5.4	2.3
420	"	31	"	5.5	2.0
480	"	31	"	6.0	1.8
540	"	31	"	7.0	2.0
660	"	"	"	6.5	"
720	"	"	"	6.5	"

SITE 1 15.5.82.
n = 40

Time from initial rise at site 1 (mins)	stage (cm)	cond µScm^{-1}	NO_3^- mgl^{-1}	Cl^- mgl^{-1}	Ca^{2+} mgl^{-1}
-60	10	40	0.18	6.5	1.5
-50	10	40	0.20	6.0	1.7
-40	10	40	0.21	6.5	1.9
-30	10	38	0.22	6.0	2.0
-20	10	37	0.24	6.5	2.2
0	15	36	0.26	6.0	2.4
6	24	35	0.12	6.5	2.3
12	28	34	0.10	6.2	2.0
18	29	33	0.09	6.2	1.8
30	49	32	0.08	6.2	1.7
34	60	32	0.08	6.2	1.7
60	"	32	0.08	6.2	1.7
120	"	31	0.10	"	1.5
180	"	29	"	"	1.9
300	"	34	"	"	"
600	60	32	0.10	6.2	1.7

SITE 1. 16.5.82. n = 40

Time from stage rise at site 1 (mins)	stage (cm)	cond μScm^{-1}	NO_3^- mgl^{-1}	Cl^- mgl^{-1}	Ca^{2+} mgl^{-1}	PO_4^- mgl^{-1}
-60	10		0.11	7.14	2.7	0.013
-40	10		0.10	"	2.7	0.013
-20	10		0.10	"	2.5	0.013
0	15		0.10	"	2.5	0.009
6	24		0.13	"	2.7	"
12	28		0.16	"	2.5	"
18	39		0.15	"	2.5	"
24	43		0.14	"	2.5	"
30	49		0.15	"	2.3	"
84	49		0.15	7.14	2.7	0.013

SITE 1. 17.7.82
n = 40

Time from stage rise at site 1 (mins)	stage (cm)	pH units	NO_3^{-1} mgl^{-1}	Cl^- mgl^{-1}	Ca^{2+} mgl^{-1}
-60	24	6.19	0.12	7	2.9
-30	24	6.59	0.12	7	2.9
0	25	6.58	0.11	"	2.6
5	32	6.53	0.12	"	2.5
10	35	6.36	0.04	"	2.5
15	41	6.46	0.11	"	2.5
20	51	6.32	0.12	"	2.3
25	60	6.20	0.11	"	2.4
30	62	6.18	0.12	"	1.8
52	"	6.10	0.10	"	2.0
100	"	6.07	0.10	"	1.9
160	62	6.09	0.10	7	2.0

SITE 1. 5.9.82.
n = 40

Time from stage rise at site 1 (mins)	stage (cm)	pH units	NO$_3^{-1}$ mgl^{-1}	Cl$^-$ mgl^{-1}	Ca^{2+} mgl^{-1}	PO$_4^-$ mgl^{-1}
-80	10		0.19	7.14	2.27	0.014
-60	10		0.12	"	3.64	"
-40	10		0.14	"	2.95	"
-20	10		0.11	"	2.73	"
0	15		0.12	"	2.50	"
3	21		0.12	"	2.27	"
5	21		0.12	"	2.27	"
60	21		0.12	7.14	2.27	0.014

SITE 1. 18.7.82
n = 40

-60	23	6.63	0.09	7	2.5
-40	23	6.71	0.08	7	2.7
-20	23	6.71	0.10	"	2.7
0	24	6.83	0.09	"	2.8
5	29	6.86	0.10	"	2.5
10	35	6.89	0.09	"	2.5
15	47	6.81	0.11	"	3.4
20	52	6.81	0.11	"	2.9
25	61	6.83	0.11	"	2.8
30	62	6.84	0.10	"	2.8
35	62	6.70	0.11	"	2.4
45	"	6.63	0.10	"	2.2
115	62	6.25	0.09	7	2.3

SITE 1. 4.9.82.
n = 40

Time from stage rise at site 1 (mins)	stage (cm)	pH units	NO_3^- mgl^{-1}	Cl^{-1} mgl^{-1}	Ca^{2+} mgl^{-1}
-60	22	7.04	0.08	11.39	1.8
-30	22	7.03	0.07	"	"
0	23	7.00	0.09	"	"
4	27	6.99	0.07	"	"
12	37	6.87	0.08	"	"
20	46	6.81	0.08	"	"
28	56	6.73	0.08	"	"
36	56	6.64	0.07	"	"
40	56	6.64	0.07	"	"
80	56	6.64	0.07	11.39	1.8

SITE 1. 4.6.83
n = 40

-60	21	6.54	0.09	11.39	1.9
-30	21	6.54	0.09	11.39	1.9
0	22	6.55	0.09	"	"
4	25	6.57	0.08	"	"
8	30	6.58	0.09	"	"
12	30	6.54	0.09	"	"
16	40	6.55	0.09	"	"
20	45	6.51	"	"	"
24	46	6.48	"	"	"
28	54	6.46	"	"	"
32	56	6.46	"	"	"
40	56	6.43	"	"	"
100	56	6.43	0.09	11.39	1.9

SITE 1. 5.6.83.
n = 40

Time from start of release rise (mins) at site 1	stage (cm)	pH units	NO_3^- mgl^{-1}	Cl^- mgl^{-1}	Ca^{2+} mgl^{-1}
-55	27	6.64	0.09	11.39	1.8
-40	27	6.67	0.08	"	"
-25	27	6.71	0.08	"	"
20	27	6.73	0.08	"	"
51	28	6.75	0.07	"	"
54	30	6.80	0.07	"	"
58	73	6.75	0.08	"	"
62	76	6.75	0.08	"	"
66	77	6.72	0.05	"	"
70	78	6.73	0.08	"	"
74	78	6.71	0.05	"	"
78	"	6.65	0.09	"	"
102	"	6.52	0.08	"	"
130	"	6.47	0.08	"	"
158	"	6.42	"	"	"
186	"	6.22	"	"	"
230	78	6.22	0.08	11.39	1.8

SITE 3. 4.6.83.
n = 40

4	26	6.51	0.09	11.39	1.96
19	26	6.52	0.09	"	"
34	26	6.56	0.09	"	"
58	30	6.50	0.09	"	"
63	75	6.64	"	"	"
67	78	6.64	0.08	"	"
71	79	6.62	0.07	"	"
75	79	6.60	0.07	"	"
100	"	6.32	0.08	"	"
125	"	6.30	0.09	"	"
150	"	6.29	0.10	"	"
175	79	6.30	0.10	11.39	1.96

SITE 3. 5.6.83

n = 40

Time from start of release rise (mins) at site 1	stage (cm)	pH units	NO_3^- mgl^{-1}	Cl^- mgl^{-1}	Ca^{2+} mgl^-
-30	15	6.83	0.08	11.39	3.20
-10	15	6.80	0.08	"	3.01
-54	15	6.80	0.08	"	3.08
70	16	6.80	0.09	"	3.08
71	20	6.80	0.08	"	3.08
75	40	6.77	0.06	"	3.08
79	46	6.77	0.05	"	2.80
83	46	6.79	0.04	"	2.80
86	"	6.82	0.04	"	2.52
90	"	6.80	0.06	"	2.24
94	"	6.81	0.06	"	2.24
98	"	6.80	0.06	"	1.96
102	"	6.78	0.07	"	"
130	"	6.70	0.06	"	"
158	"	6.70	0.07	"	"
186	"	6.65	0.07	"	"
230	46	6.56	0.08	11.39	1.96

SITE 4. 4.6.83.
n = 40

-41	10	6.48	0.09	11.39	3.10
19	10	6.48	0.09	"	3.08
59	10	6.48	0.09	"	3.08
77	18	6.55	0.08	"	3.08
81	42	6.60	0.08	"	3.08
85	46	6.68	0.08	"	3.08
89	46	6.69	0.09	"	2.80
90	46	6.66	0.07	"	2.80
120	"	6.50	0.09	"	2.80
150	"	6.39	0.09	"	1.96
180	"	6.42	"	"	"
210	46	6.45	0.10	11.39	1.96

SITE 4. 5.6.83
n = 40

Time from start of release rise (mins) at site 1	stage (cm)	pH units	NO_3^- mgl^{-1}	Cl^- mgl^{-1}	Ca^{2+} mgl^{-}
-14	9	6.82	0.19	8.0	3.80
16	9	6.91	0.20	"	3.40
46	9	6.99	0.20	"	3.70
103	10	7.03	0.20	"	3.80
109	11	7.09	0.23	"	4.50
114	53	7.13	0.22	"	4.70
119	56	7.09	0.22	"	4.50
124	56	7.08	0.67	"	3.20
129	"	6.97	0.20	"	3.50
134	"	6.96	0.20	"	2.70
139	"	6.94	0.20	"	3.30
141	"	6.78	0.18	"	3.40
161	"	6.65	0.15	"	2.60
181	"	6.52	0.12	"	2.20
201	"	6.56	0.12	"	2.10
221	"	6.41	"	"	"
291	56	6.46	0.12	8.0	2.10

SITE 5. 4.9.82.
n = 65

10	10	6.80	0.20	8.0	3.10
45	10	6.88	0.22	"	3.08
105	11	6.88	0.22	"	3.08
107	35	6.90	0.22	"	3.08
108	44	6.90	0.22	"	3.08
109	50	6.86	0.24	"	3.08
110	52	6.88	0.22	"	2.80
111	54	6.88	0.23	"	2.80
114	55	6.88	0.22	"	3.5
119	"	6.82	0.21	"	1.96
129	"	6.69	0.19	"	"
139	"	6.46	0.14	"	"
149	"	6.40	"	"	"
159	"	6.38	"	"	"
169	"	6.38	0.13	"	"
179	"	6.38	"	"	"
254	55	6.29	0.13	8.0	1.96

SITE 5. 5.9.82
n = 65

Time from start of release *rise* (mins) *at site 1*	stage (cm)	pH units	NO$_3^-$ mgl^{-1}	Cl$^-$ mgl^{-1}	Ca^{2+} mgl^{-1}	cond µScm^{-1}
20	29	6.74	0.30	7.9	5.23	
50	29	6.91	0.30	"	5.23	
80	29	6.99	0.30	"	5.23	
99	38	7.03	0.28	7.1	4.77	
100	49	7.09	0.29	"	4.94	
101	63	7.13	0.30	"	5.00	
102	68	7.09	0.32	"	5.23	
104	73	7.04	0.30	"	4.59	
106	74	6.57	0.30	"	4.21	
111	75	6.96	0.30	"	3.89	
139	"	6.98	0.20	"	3.50	
141	"	6.78	0.18	"	3.15	
161	"	6.65	0.15	"	2.86	
181	"	6.52	0.19	"	2.73	
201	"	6.56	0.20	"	"	
221	"	6.51	"	"	"	
291	56	6.46	0.20	7.1	2.73	

SITE 5. 17.7.82.
n = 65

0	48	6.78	0.10	7.6	1.80	36
30	48	6.78	0.10	7.6	1.80	37
60	48	6.80	0.07	7.5	1.80	37
65	49	6.90	0.10	7.0	1.90	37
95	67	6.90	0.14	6.9	2.00	37
105	67	6.86	0.24	6.5	1.90	39
125	67	6.88	0.24	"	1.80	40
185	"	6.88	0.30	"	1.60	50
245	"	6.75	0.30	"	1.60	45
305	"	6.82	0.28	"	"	42
365	"	6.69	0.28	"	"	"
425	"	6.46	0.34	"	"	"
485	"	6.35	0.26	"	"	"
545	"	6.38	0.28	"	"	"
605	"	6.38	0.30	"	"	"
645	"	6.38	0.30	"	"	"
705	67	6.30	0.30	6.5	1.60	42

SITE 5. 15.5.82
n = 65

Time from start of release rise (mins) at site 1	stage (cm)	pH units	NO_3^- mgl^{-1}	Cl^- mgl^{-1}	Ca^{2+} mgl^{-1}	cond μScm^{-1}
10	19	6.74	0.25	8.0	4.23	
40	19	6.81	0.25	"	4.23	
70	19	6.99	0.25	"	4.85	
89	27	7.09	0.28	"	4.77	
92	38	7.09	0.29	"	4.94	
95	52	7.13	0.30	"	3.00	
97	54	7.07	0.32	"	3.23	
100	62	7.04	0.20	"	3.59	
106	63	6.54	0.20	"	4.11	
110	64	6.96	0.15	"	3.89	
140	"	6.88	0.20	"	3.50	
150	"	6.78	0.18	"	3.15	
160	"	6.65	0.15	"	2.86	
180	"	6.55	0.19	"	2.50	
200	"	6.56	0.15	"	"	
220	"	6.49	"	"	"	
300	64	6.48	0.15	8.0	2.50	

SITE 5. 18.7.82.
n = 65

0	13	6.58	0.57	10.0	4.50	60
30	13	6.48	0.43	10.0	5.00	60
60	13	6.50	0.60	9.5	4.40	57
65	17	6.80	0.43	9.0	4.00	47
95	65	6.89	0.55	9.0	3.80	58
105	65	6.86	0.45	8.5	3.60	45
125	65	6.78	0.05	8.0	1.80	37
185	"	6.88	0.03	"	1.75	35
245	"	6.78	0.04	"	1.80	30
305	"	6.78	0.03	"	"	28
365	"	6.69	"	"	"	"
425	"	6.46	"	"	"	"
485	"	6.25	"	"	"	"
545	"	6.38	"	"	"	"
605	"	6.40	"	"	"	"
645	"	6.38	"	"	"	"
705	65	6.48	0.03	8.0	1.80	28

SITE 5. 16.5.82
n = 65

Time from start of release rise (mins) at site 1	stage (cm)	pH units	NO_3^- mgl^{-1}	Cl^- mgl^{-1}	Ca^{2+} mgl^{-1}	cond μScm^{-1}
46	8	6.76	0.23	7.0	3.70	
66	8	6.85	0.23	7.0	3.60	
86	8	6.95	0.25	8.0	3.70	
122	9	6.93	0.24	7.0	3.60	
124	17	6.85	0.25	"	3.40	
129	31	6.79	0.23	"	3.40	
134	40	6.86	0.25	"	4.50	
139	45	6.86	0.24	"	5.05	
144	46	6.75	0.25	"	4.00	
149	47	6.76	0.23	"	3.70	
154	48	6.79	0.23	"	4.00	
159	"	6.69	0.22	"	3.60	
164	"	6.67	0.22	"	2.86	
169	"	6.81	0.19	"	2.50	
179	"	6.76	0.14	"	"	
229	"	6.59	"	"	"	
289	48	6.19	0.14	7.0	2.50	

SITE 6. 4.9.82.
n = 65

44	8	6.65	0.22	7.0	3.40	
74	8	6.77	0.23	"	3.60	
104	8	6.72	0.22	"	3.50	
119	8	6.80	0.22	"	3.60	
124	15	6.89	0.22	"	5.60	
126	22	6.86	0.24	"	4.20	
128	29	6.83	0.24	"	3.40	
130	34	6.75	0.21	"	3.70	
132	37	6.82	0.22	"	3.00	
134	40	6.83	0.22	"	2.60	
136	42	6.79	0.22	"	2.30	
138	44	6.74	0.22	"	2.50	
140	44	6.72	0.20	"	2.20	
142	46	6.70	0.15	"	2.00	
150	"	6.48	0.13	"	"	
200	"	6.28	0.12	"	"	
250	46	6.31	0.13	7.0	2.00	

SITE 6. 5.9.82
n = 65

Time from start of release rise (mins) at site 1	stage (cm)	pH units	NO_3^- mgl^{-1}	Cl^- mgl^{-1}	Ca^{2+} mgl^-	cond μScm^{-1}
0	22	6.80	0.10	8.0	2.50	
30	22	6.85	0.15	7.5	2.50	
60	22	6.95	0.13	8.0	2.50	
90	25	6.93	0.12	6.5	3.00	
105	25	6.85	0.10	6.8	2.50	
120	40	6.79	"	6.5	2.70	
150	40	6.86	"	7.8	2.50	
180	"	6.86	"	7.0	2.30	
240	"	6.75	"	"	"	
300	"	6.70	"	"	"	
360	"	6.59	"	"	"	
420	"	6.2	"	"	"	
480	"	"	"	"	"	
540	"	"	"	"	"	
600	"	"	"	"	"	
660	"	"	"	"	"	
720	40	6.26	0.10	7.0	2.30	

SITE 6. 15.5.82.
n = 65

60	8	6.45	0.90	7.5	5.50
90	8	6.77	0.90	8.5	5.90
110	9	6.65	0.90	9.5	5.00
120	12	6.70	0.90	9.2	5.20
130	25	6.79	0.80	9.5	5.60
140	38	6.78	0.70	9.0	4.20
150	39	6.53	0.60	8.0	3.00
180	40	6.75	0.18	7.6	2.50
240	"	6.82	0.10	"	2.50
300	"	6.73	"	"	2.00
360	"	6.79	"	"	"
420	"	6.74	"	"	"
480	"	6.72	"	"	"
540	"	6.69	"	"	"
600	40	6.69	0.10	7.6	2.00

SITE 6. 16.5.82
n = 65

time from start of rise at site I (mins)	stage (cm)	cond $\mu S cm^{-1}$	pH units	NO_3^- $mg l^{-1}$	Cl^- $mg l^{-1}$	Ca^{2+} $mg l^{-1}$
40	18	60	6.49	0.75	18.0	5.8
65	18	60	6.54	0.68	18.0	5.8
92	20	62	6.64	0.70	18.0	5.8
96	45	59	6.68	0.74	"	5.8
100	49	58	6.72	0.69	"	5.8
104	49	58	6.65	0.80	"	5.2
108	49	58	6.70	0.72	"	5.2
112	"	56	6.72	0.71	"	5.0
116	"	53	6.65	0.69	"	4.5
120	"	51	6.78	0.63	17.0	4.1
130	"	63	6.75	0.50	16.0	3.5
140	"	48	6.67	0.50	15.0	3.2
150	"	43	6.64	0.43	13.0	2.9
200	"	44	6.64	0.42	13.0	2.9
300	49	43	6.64	0.42	13.0	2.9

SITE 5. 23.4.83
n = 65

60	14	62	6.80	0.48	13.0	5.8
100	14	62	6.80	0.64	13.0	5.8
106	20	62	6.87	0.62	"	5.8
110	30	62	6.88	0.58	"	5.7
114	35	61	6.89	0.64	"	6.1
118	38	61	6.89	0.56	"	5.8
122	40	61	6.87	0.64	"	5.5
126	"	59	6.87	0.50	"	6.3
130	"	56	6.89	0.40	"	4.9
140	"	51	6.90	0.54	"	3.8
200	"	46	"	0.57	"	"
300	40	43	6.90	0.57	13.0	3.8

SITE 6. 23.4.83
n = 65

time from start of rise at site 1 (mins)	stage (cm)	cond μScm^{-1}	pH units	NO_3^- mgl^{-1}	Cl^- mgl^{-1}	Ca^{2+} mgl^{-1}
-60	10	56	7.08	0.15	12.0	2.3
-45	10	42	6.90	0.14	12.0	2.3
-30	10	40	6.80	0.55	"	"
0	11	41	6.77	0.64	"	"
4	17	40	6.75	0.29	"	"
8	20	38	6.67	0.25	"	"
12	27	37	6.29	0.40	"	"
16	35	37	6.31	0.20	"	"
20	40	38	6.26	0.40	"	"
24	46	39	6.18	0.49	"	"
32	46	37	6.06	0.48	"	"
36	"	37	5.98	0.47	"	"
60	"	36	5.93	0.50	"	"
80	46	36	5.98	0.47	12.0	2.3

SITE 1. 23.4.83
n = 45

-50	18	44	6.61	0.53	13.0	2.3
-40	18	42	6.68	0.53	13.0	3.1
-30	18	42	6.71	0.50	"	3.1
24	20	43	6.71	0.50	"	3.1
28	49	42	6.78	0.40	"	2.6
32	72	40	6.82	0.50	"	2.3
36	81	39	6.78	0.39	"	"
40	84	38	6.79	0.40	"	"
44	"	37	6.73	0.39	"	"
48	"	37	6.74	0.46	"	"
60	"	37	6.69	0.42	"	"
100	"	"	"	"	"	"
200	84	37	6.70	0.44	13.0	2.3

SITE 2. 23.4.83
n = 65

time from start of rise at site 1 (mins)	stage (cm)	cond $\mu S cm^{-1}$	pH units	NO_3^- $mg l^{-1}$	Cl^- $mg l^{-1}$	Ca^{2+} $mg l^{-1}$
-20	24	63	6.62	0.49	14.0	5.5
10	24	64	6.72	0.51	14.0	4.9
40	24	65	6.78	0.61	12.0	5.2
68	25	65	6.79	0.55	10.0	5.5
70	32	64	6.80	0.70	7.0	4.6
74	46	53	6.81	0.73	10.0	4.0
78	47	53	6.80	0.66	"	3.2
82	"	54	6.76	0.65	"	2.9
86	"	"	6.69	0.57	"	"
90	"	"	6.67	0.60	"	"
94	"	"	6.66	0.58	"	"
98	"	"	6.60	0.55	"	"
102	"	"	"	0.53	"	"
150	"	"	"	"	"	"
200	"	"	"	"	"	"
300	47	54	6.60	0.53	10.0	2.9

SITE 4. 23.4.83
n = 65

-60	9	47	6.32	0.44	12.0	3.5
-40	9	42	6.51	0.45	13.0	3.5
-20	9	41	6.55	0.40	"	3.8
0	10	43	6.62	0.43	"	4.1
3	16	40	6.60	0.44	"	3.5
7	19	39	6.54	0.40	"	2.9
11	22	40	6.48	0.39	"	2.3
15	32	38	6.40	0.40	"	"
19	37	37	6.39	0.38	"	"
23	37	"	6.20	0.39	"	"
31	44	"	6.11	0.38	"	"
43	45	"	"	"	"	"
63	"	"	"	"	"	"
83	45	37	6.10	0.38	13.0	2.3

SITE 1. 24.4.83
n = 45

time from start of rise at site 1. (mins)	stage (cm)	cond μScm^{-1}	pH units	NO_3^- mgl^{-1}	Cl^- mgl^{-1}	Ca^{2+} mgl^{-}
-10	10	45	6.34	0.42	14.0	3.4
10	10	44	6.39	0.47	14.0	4.3
20	10	44	6.42	0.38		4.0
24	11	44	6.46	0.46	10.0	3.8
28	30	43	6.40	0.43	14.0	3.2
32	58	40	6.30	0.40	"	3.0
36	63	39	6.20	0.41	"	2.3
40	65	38	6.15	"	"	2.9
44	75	37	6.02	"	"	2.3
48	78	"	"	"	"	"
52	79	"	"	"	"	"
74	"	"	"	"	"	"
80	"	"	"	"	"	"
100	"	"	"	"	"	"
200	"	"	"	"	"	"
300	79	37	6.02	0.42	14.0	2.3

SITE 2. 24.4.83
n = 65

-5	16	55	6.59	0.68	5.0	5.8
20	16	57	6.64	0.64	5.0	5.8
60	16	55	6.73	0.58	"	5.8
72	20	55	6.74	0.65	"	5.5
77	40	55	6.83	0.63	"	5.5
80	45	53	6.84	0.53	"	4.8
85	46	49	6.80	0.58	"	4.0
93	46	47	6.80	0.52	"	3.2
101	"	44	6.74	0.50	"	"
109	"	42	6.67	"	"	"
117	"	41	6.63	"	"	"
125	"	"	6.49	"	"	"
133	"	"	6.20	"	"	"
145	"	"	"	"	"	"
160	"	"	"	"	"	"
300	46	41	6.15	0.50	5.0	3.2

SITE 4. 24.4.83
n = 65

time from start of rise at site 1. (mins)	stage (cm)	cond μScm^{-1}	pH units	NO_3^- mgl^{-1}	Cl^- mgl^{-1}	Ca^{2+} mgl^{-1}
-10	8	63	6.62	0.62	16.0	7.5
30	8	63	6.66	0.62	14.0	7.5
60	8	63	6.68	0.62	"	7.3
100	9	63	6.77	0.58	10.0	6.9
104	43	60	6.81	0.55	14.0	6.4
108	46	59	6.88	0.55	"	7.0
112	47	59	6.70	0.52	"	5.5
116	"	58	6.75	0.50	"	4.6
120	"	56	6.70	0.42	"	3.5
124	"	48	"	0.40	"	"
132	"	46	"	"	"	"
140	"	43	"	"	"	"
160	"	41	"	"	"	"
200	"	"	"	"	"	"
300	47	41	6.70	0.40	14.0	3.5

SITE 5. 24.4.83
n = 65

10	11	63	6.76	0.68	16.0	7.8
20	11	63	6.84	0.64	"	8.1
60	11	63	6.90	0.58	"	7.5
116	12	62	6.92	0.65	"	7.8
122	28	61	6.94	0.63	"	8.4
126	34	50	6.93	0.53	"	7.8
128	36	59	6.91	0.58	"	6.7
134	38	58	6.80	0.52	"	5.6
140	39	56	6.50	"	"	5.9
146	40	52	6.31	"	"	4.8
152	"	49	6.26	"	"	3.8
200	"	42	6.20	"	"	"
260	"	"	6.30	"	"	"
320	40	42	6.30	0.52	16.0	3.8

SITE 6. 24.4.83
n = 65

time from start of rise at site 1. (mins)	stage (cm)	cond μScm^{-1}	pH units	NO_3^{-1} mgl^{-1}	Cl^- mgl^{-1}	Ca^{2+} mgl^-
-20	24	62	6.75	0.49	14.0	5.5
10	24	64	6.72	0.51	14.0	4.9
40	24	65	6.78	0.61	12.0	5.2
116	25	65	6.79	0.55	10.0	5.5
122	32	64	6.80	0.70	11.0	4.6
126	46	53	6.81	0.73	11.0	4.0
130	47	53	6.80	0.66	"	4.2
134	"	55	6.76	0.65	"	3.9
138	"	"	6.69	0.57	"	"
142	"	"	6.67	0.60	"	"
146	"	"	6.66	0.58	"	"
150	"	"	6.70	0.55	"	"
160	"	"	"	0.53	"	"
200	"	"	"	"	"	"
300	"	"	"	"	"	"
400	47	55	6.70	0.53	11.0	3.9

SITE 6. 1.6.83
n = 65

-60	9	37	6.22	0.44	11.0	4.5
-40	9	42	6.41	0.45	11.0	4.5
-20	9	41	6.45	0.40	"	4.8
0	10	43	6.42	0.43	"	5.1
3	16	40	6.70	0.44	"	4.5
7	19	39	6.44	0.40	"	4.9
11	22	40	6.38	0.39	"	3.3
15	32	38	6.40	0.40	"	"
19	37	37	6.39	0.38	"	"
23	37	"	6.20	0.39	"	"
31	44	"	6.21	0.38	"	"
43	45	"	"	"	"	"
63	"	"	"	"	"	"
83	45	37	6.21	0.38	11.0	3.3

SITE 1. 1.6.83
n = 45

time from start of rise *at site 1* (mins)	stage (cm)	cond μScm^{-1}	pH units	NO_3^- mgl^{-1}	Cl^- mgl^{-1}	Ca^{2+} mgl^{-1}
50	5	47	7.13	0.05	11.0	3.0
75	5	47	7.14	0.03	"	3.0
132	6	46	7.03	0.05	"	3.1
134	20	"	7.00	0.04	"	2.9
136	27	"	6.97	0.03	"	3.0
138	31	"	6.92	0.04	"	2.8
142	35	"	6.85	0.05	"	2.6
146	45	"	6.80	0.04	"	2.7
150	50	"	6.81	0.05	"	2.8
200	50	46	6.80	0.05	11.0	2.8

SITE 6. 2.6.84
n = 65

60	6	47	6.74	0.05	10.0	3.3
100	6	47	6.80	0.08	10.0	3.5
110	7	48	6.81	0.05	"	3.0
112	30	53	6.90	0.05	"	2.9
114	46	50	6.89	"	"	3.2
116	51	47	6.89	"	"	3.0
118	53	47	6.87	"	"	3.7
120	53	48	6.84	"	"	3.8
130	"	45	6.86	"	"	3.6
140	"	55	7.18	"	"	6.6
200	53	48	6.90	0.05	10.0	3.7

SITE 5. 2.6.84
n = 65

time from start of rise at site 1 (mins)	stage (cm)	cond μScm^{-1}	pH units	NO_3^- mgl^{-1}	Cl^- mgl^{-1}	Ca^{2+} mgl^{-1}
10	19	42	6.73	0.05	9.0	3.0
20	19	42	6.73	0.03	9.2	3.0
58	20	42	6.77	0.05	8.5	3.1
60	48	"	6.75	0.04	8.9	2.9
62	62	"	6.73	0.03	8.9	3.0
64	65	"	6.89	0.02	8.9	2.8
66	68	"	6.74	0.05	8.9	2.6
68	70	"	6.80	0.04	8.8	2.7
100	70	42	6.70	0.05	9.0	2.7

SITE 3. 2.6.84
n = 40

60	6	47	6.74	0.05	10.0	3.3
100	6	47	6.80	0.08	10.0	3.5
110	7	48	6.81	0.05	"	3.0
112	30	53	6.90	0.05	"	2.9
114	46	50	6.89	"	"	3.2
116	51	47	6.89	"	"	3.0
118	53	47	6.87	"	"	3.7
120	53	48	6.84	"	"	3.8
130	"	45	6.86	"	"	3.6
140	"	55	7.18	"	"	6.6
200	53	48	6.90	0.05	10.0	3.7

SITE 5. 2.6.84
n = 65

time from start of rise at site 1 (mins)	stage (cm)	cond μScm^{-1}	pH units	NO_3^- mgl^{-1}	Cl^- mgl^{-1}	Ca^{2+} mgl^{-}
10	6	43	6.48	0.31	7.8	3.0
20	6	42	6.61	0.23	7.2	3.0
30	6	42	6.75	0.29	7.5	3.1
31	8	47	6.55	0.14	6.9	3.8
34	65	40	6.53	0.23	6.9	3.0
37	76	39	6.53	0.22	6.9	2.8
40	82	37	6.56	0.22	6.9	2.2
43	84	35	5.98	0.22	6.9	2.2
46	85	35	6.30	0.24	7.2	2.0
70	85	34	6.24	0.21	6.9	2.0
90	"	34	6.18	0.20	6.9	2.0
130	"	"	"	"	"	"
200	85	34	6.18	0.20	6.9	2.0

SITE 2. 25.10.82
n = 40

30	9	45	6.98	0.05	9.0	3.3
15	9	45	6.80	0.08	9.0	3.5
0	10	43	6.85	0.05	"	3.0
4	15	42	6.76	0.05	"	2.6
8	20	56	6.85	"	"	6.2
12	23	42	6.71	"	"	3.0
16	34	42	6.76	"	"	2.7
20	36	42	6.74	"	"	3.3
24	37	45	6.76	"	"	3.6
28	37	55	7.18	"	"	3.3
38	37	44	6.90	"	"	3.3
60	37	44	6.90	0.05	9.0	3.3

SITE 1. 2.6.84
n = 40

APPENDIX E.

RIVER WASHBURN ADDITIONAL DATA.

E.1 Hydraulics parameters of the River Washburn 418
E.2 Stage v chemistry change at the dam site:-
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- pH (23.10.82) 420
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- Conductivity (23.10.82) 422
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- Conductivity (9.4.83) 432
- Conductivity (5.11.83) 433
- Stage v calcium change at site 2 (5.11.82) 434

Appendix E.1

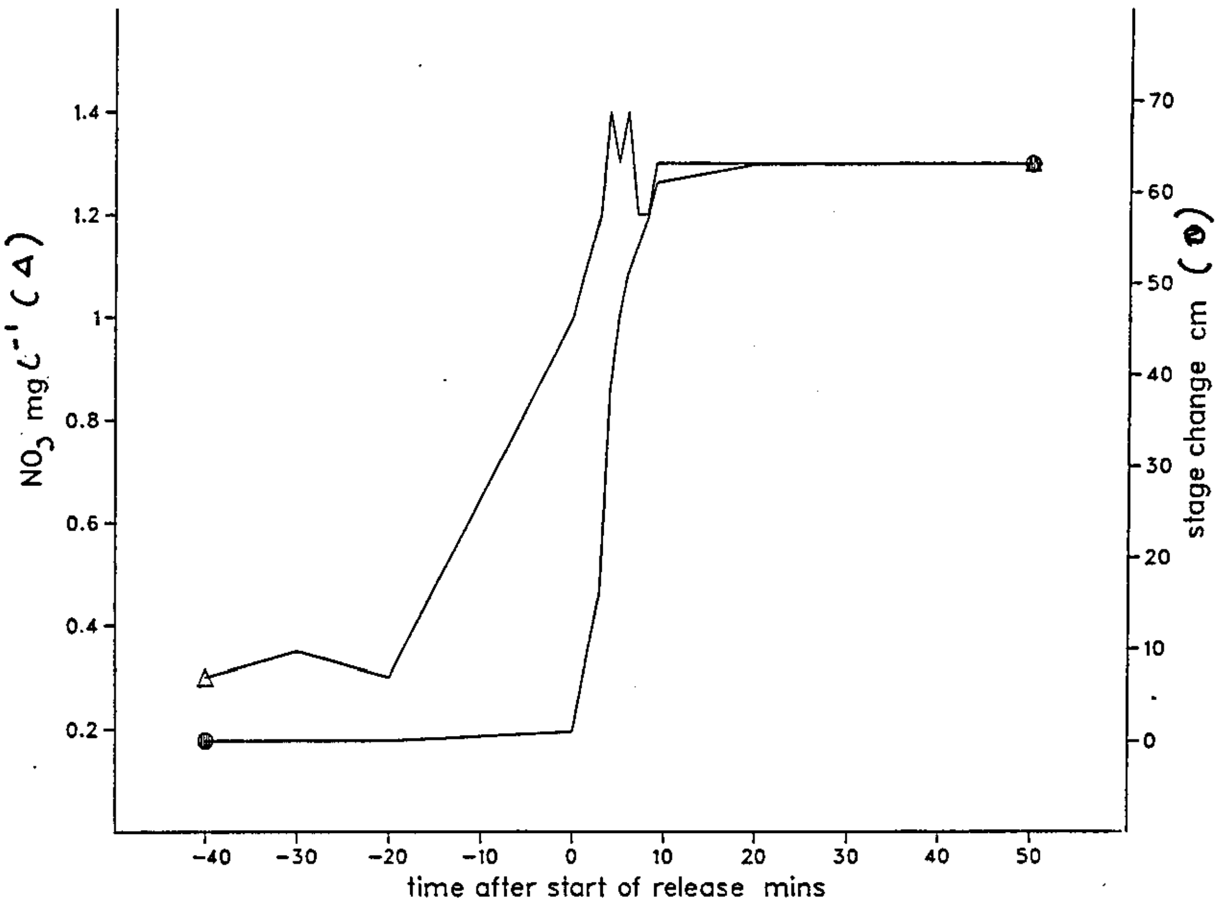
DATE	QL	QH	AL	AH	K	VL	Vob	T1	T2
23.10.82	0.10	4.0	1.1	7.1	2.0	0.9	1.2	32	65
9.4.83	0.20	3.0	1.53	5.8	2.6	0.13	1.2	24	71
10.4.83	0.05	4.20	0.9	7.3	2.3	0.07	1.2	27	65
5.11.83	0.15	4.30	1.1	7.2	2.7	0.12	1.4	23	68

QL = low flow discharge QH = high flow discharge AL = wetted channel area at low flow AH = wetted channel area at high flow K = Brady-Johnson roughness factor VL = low flow velocity Vob = observed velocity of wave peak T1 = time of travel of observed wave peak T2 = calculated time of travel of water

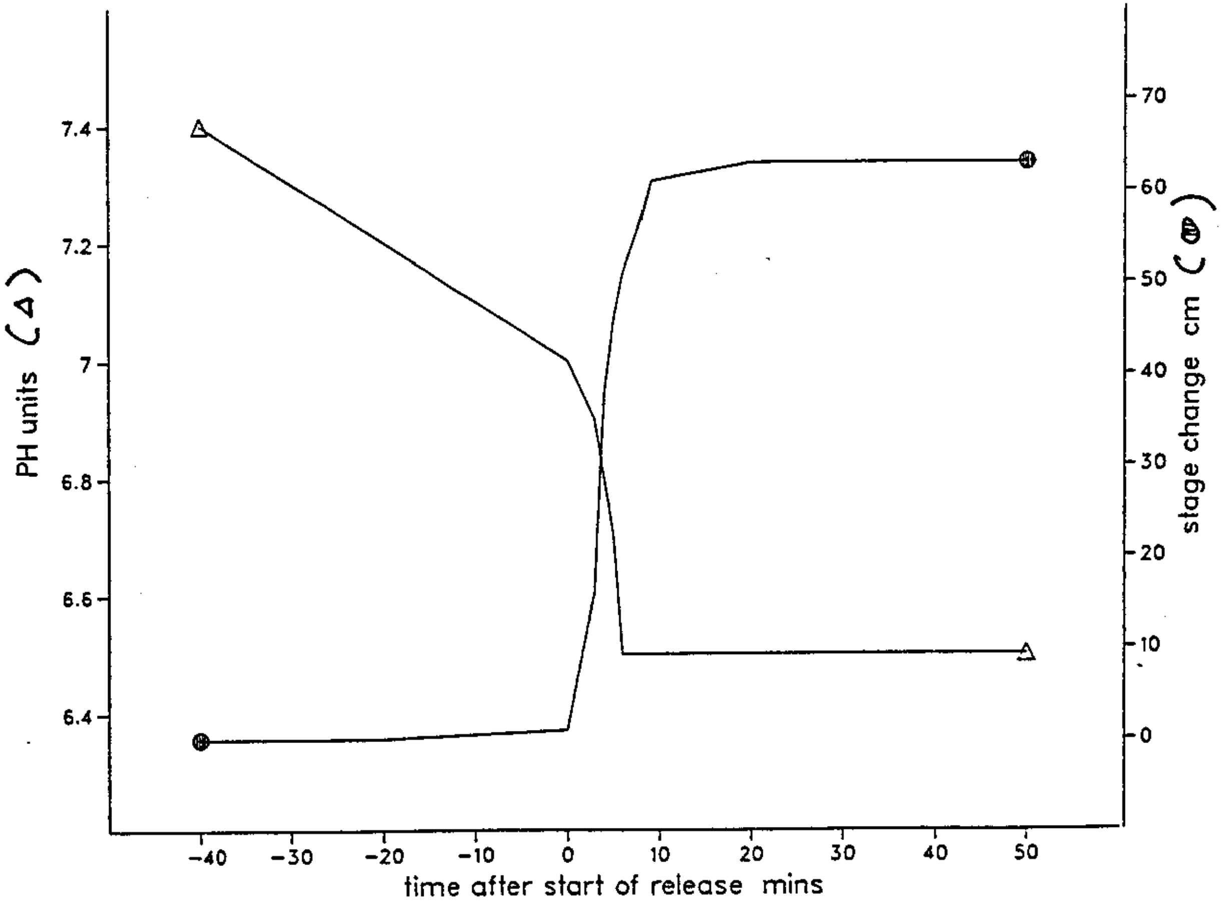
Site 1 - site 2 on the River Washburn. Reach length 2.45 km.

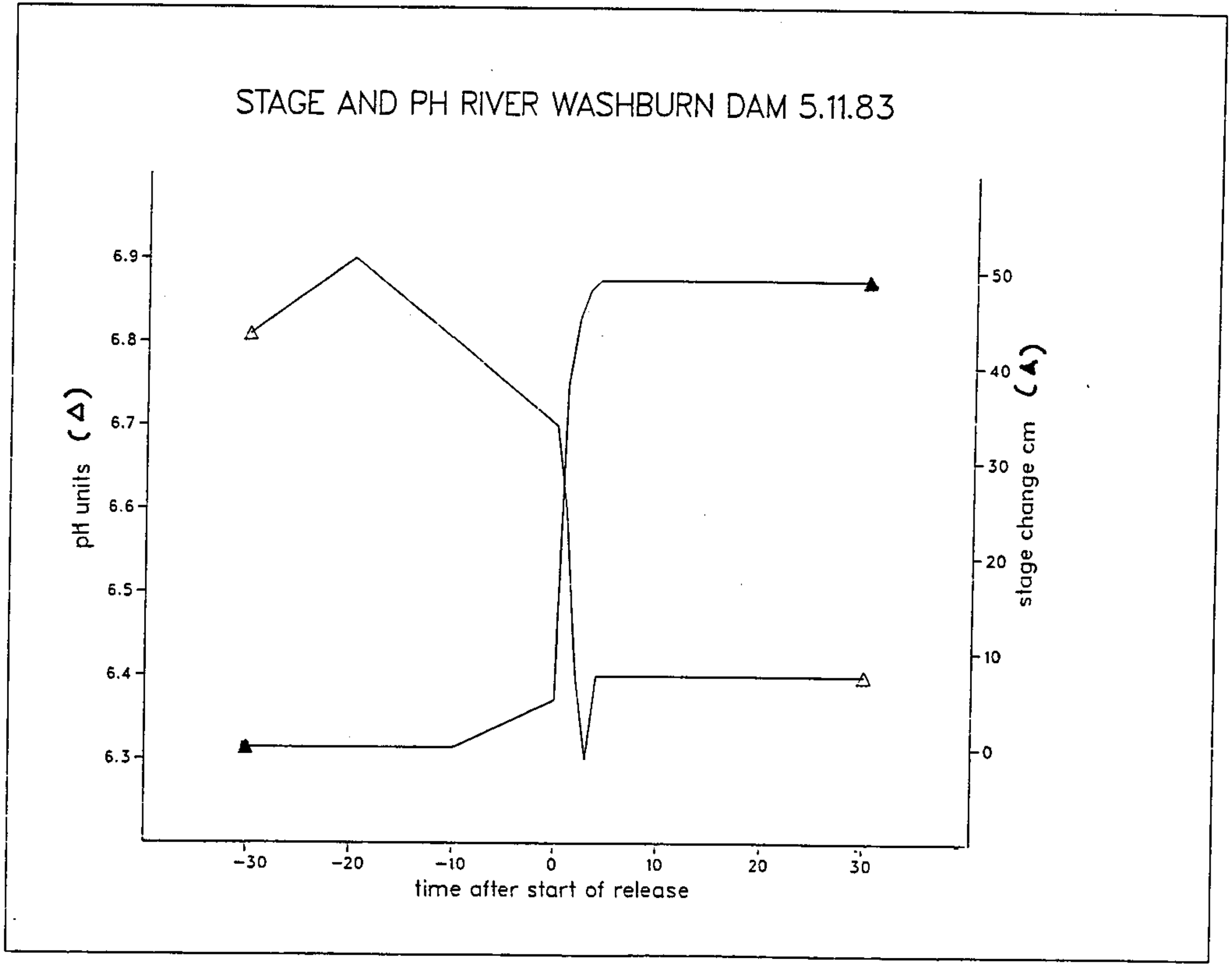
Hydraulic parametres on the River Washburn.

STAGE AND NITRATE, RIVER WASHBURN, DAM SITE, 23.10.82



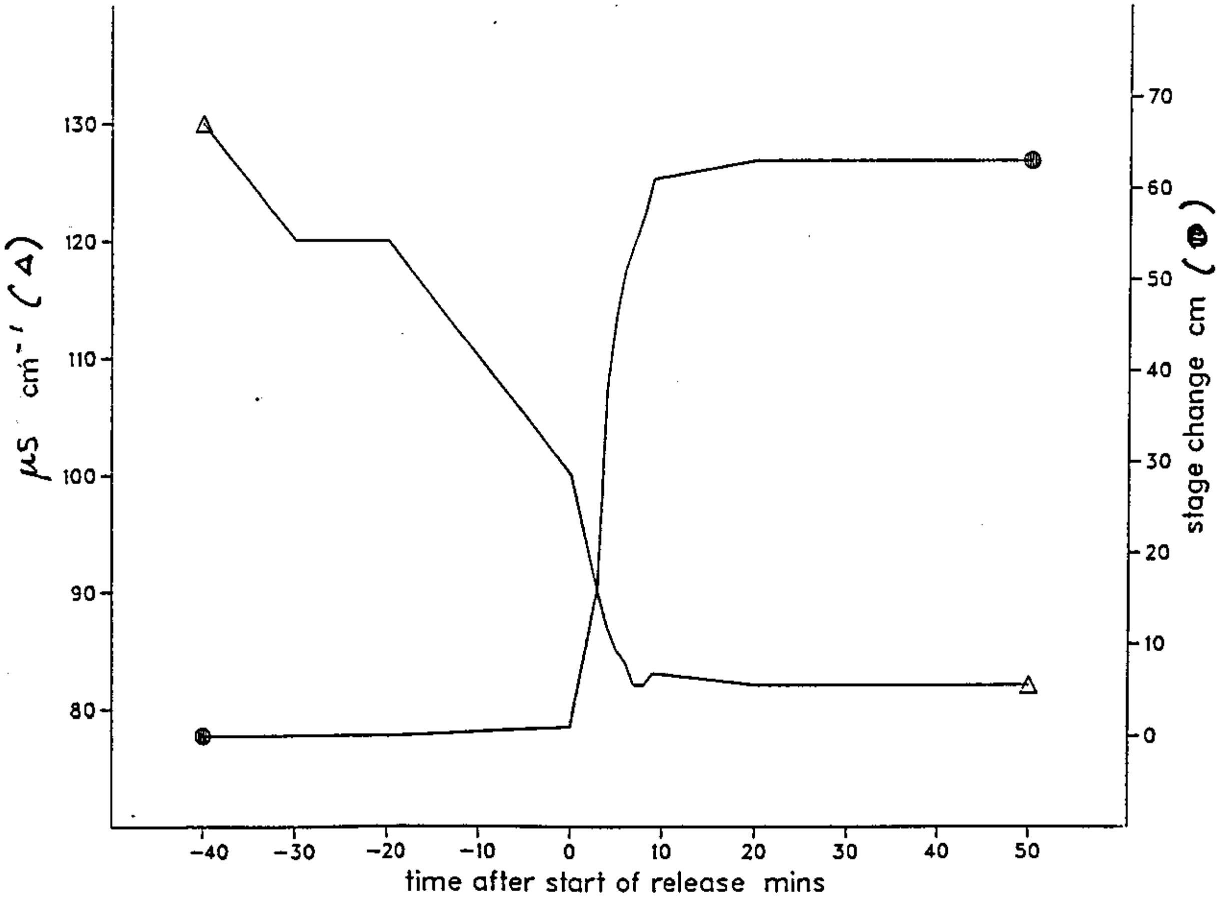
STAGE AND PH, RIVER WASHBURN, DAM SITE, 23.10.82

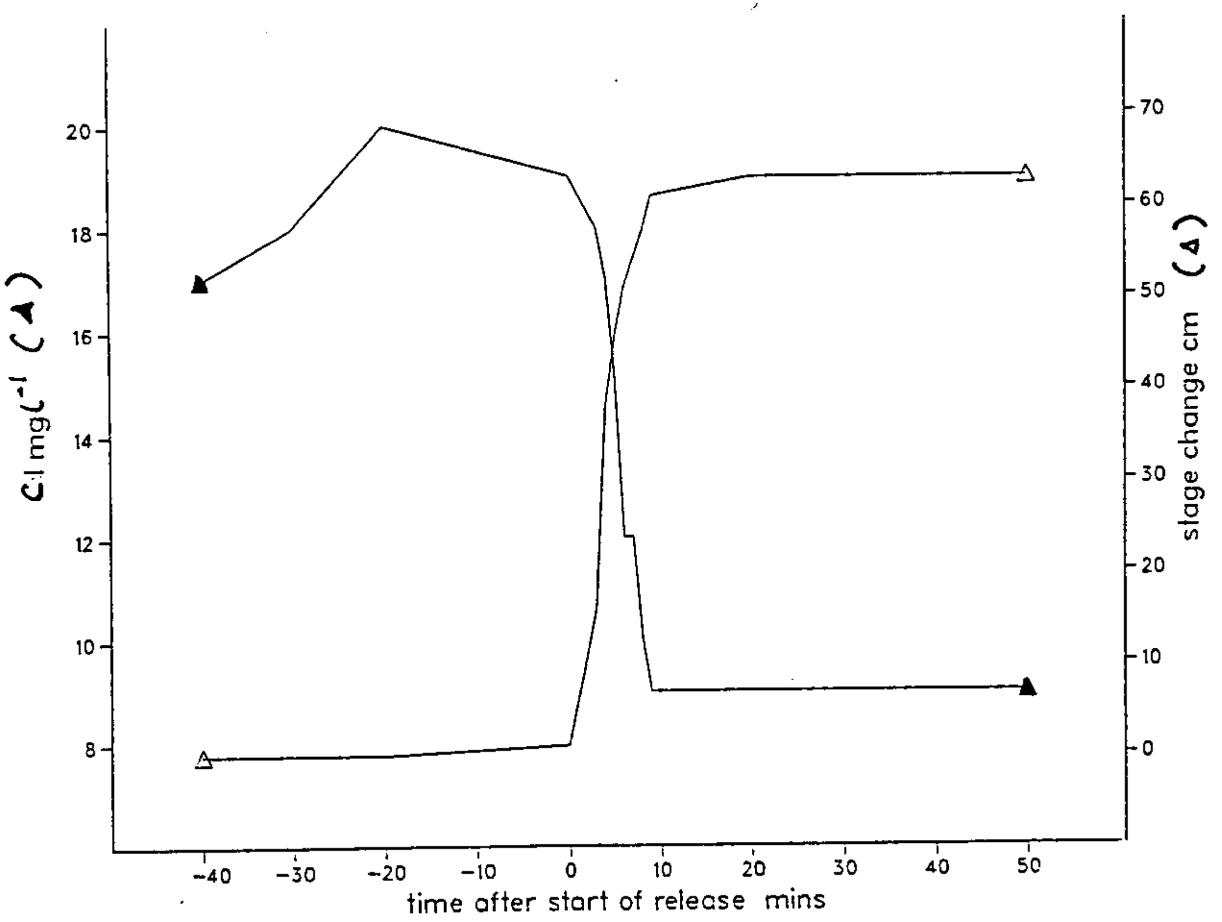




STAGE AND PH RIVER WASHBURN DAM 5.11.83

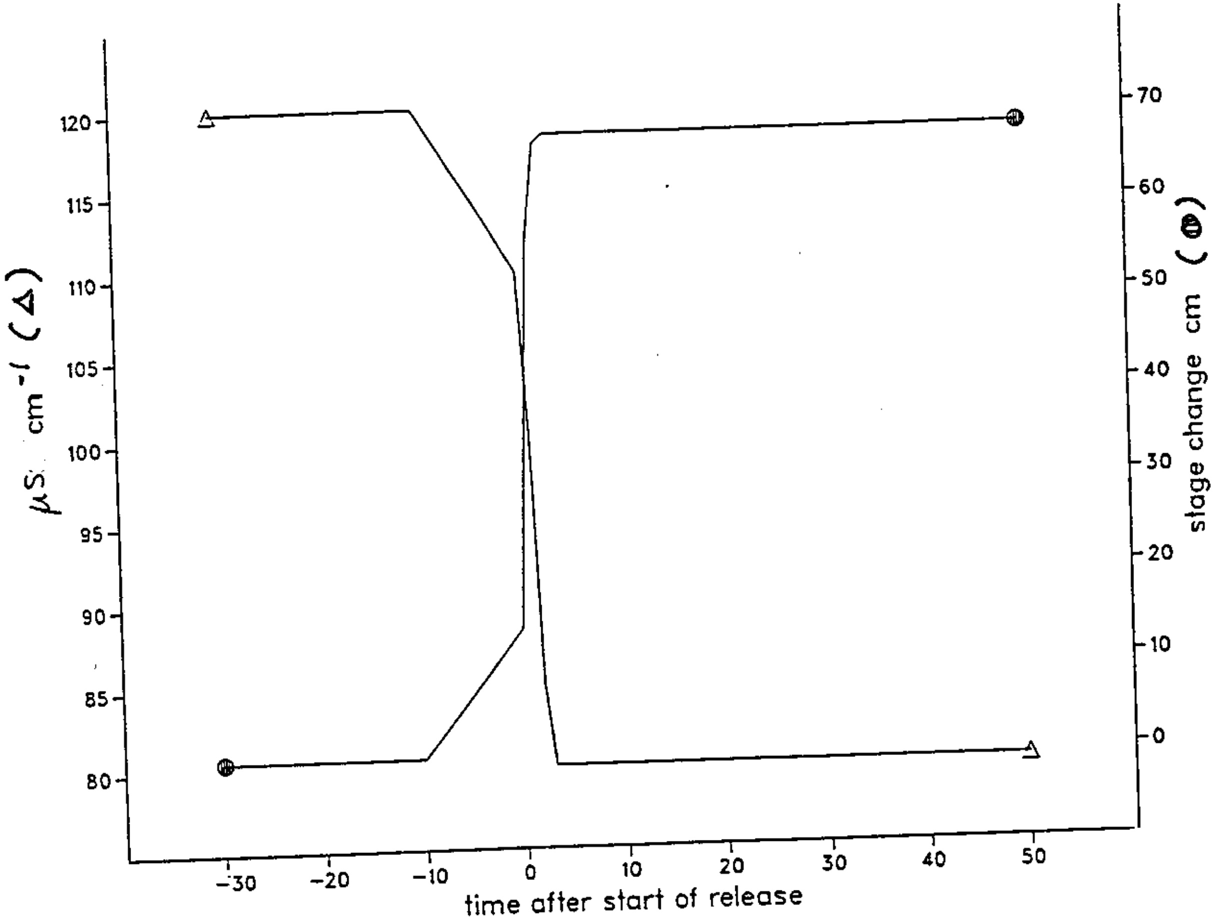
STAGE AND CONDUCTIVITY, RIVER WASHBURN, DAM SITE, 23.10.82



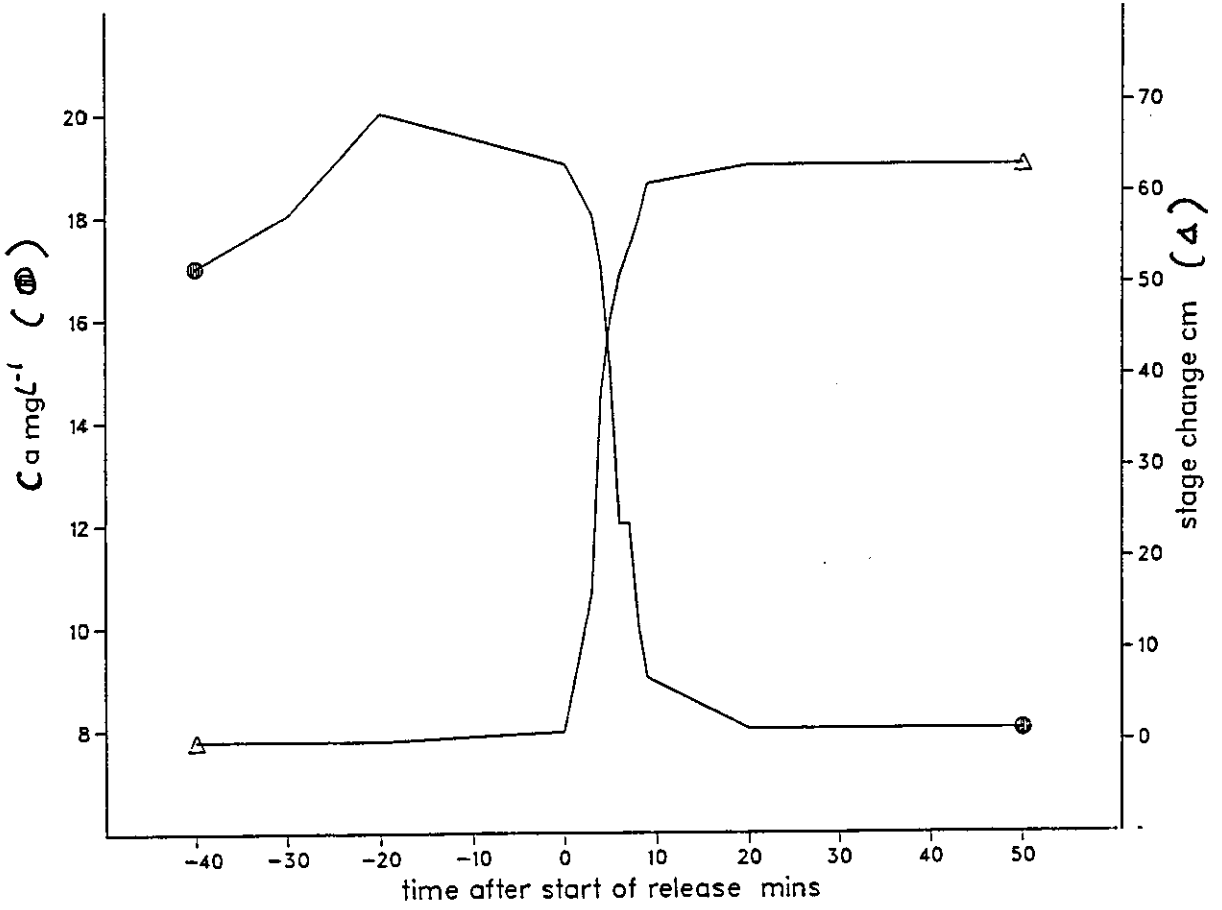


STAGE AND CHLORIDE CHANGE, RIVER WASHBURN, DAM SITE, 23.10.82

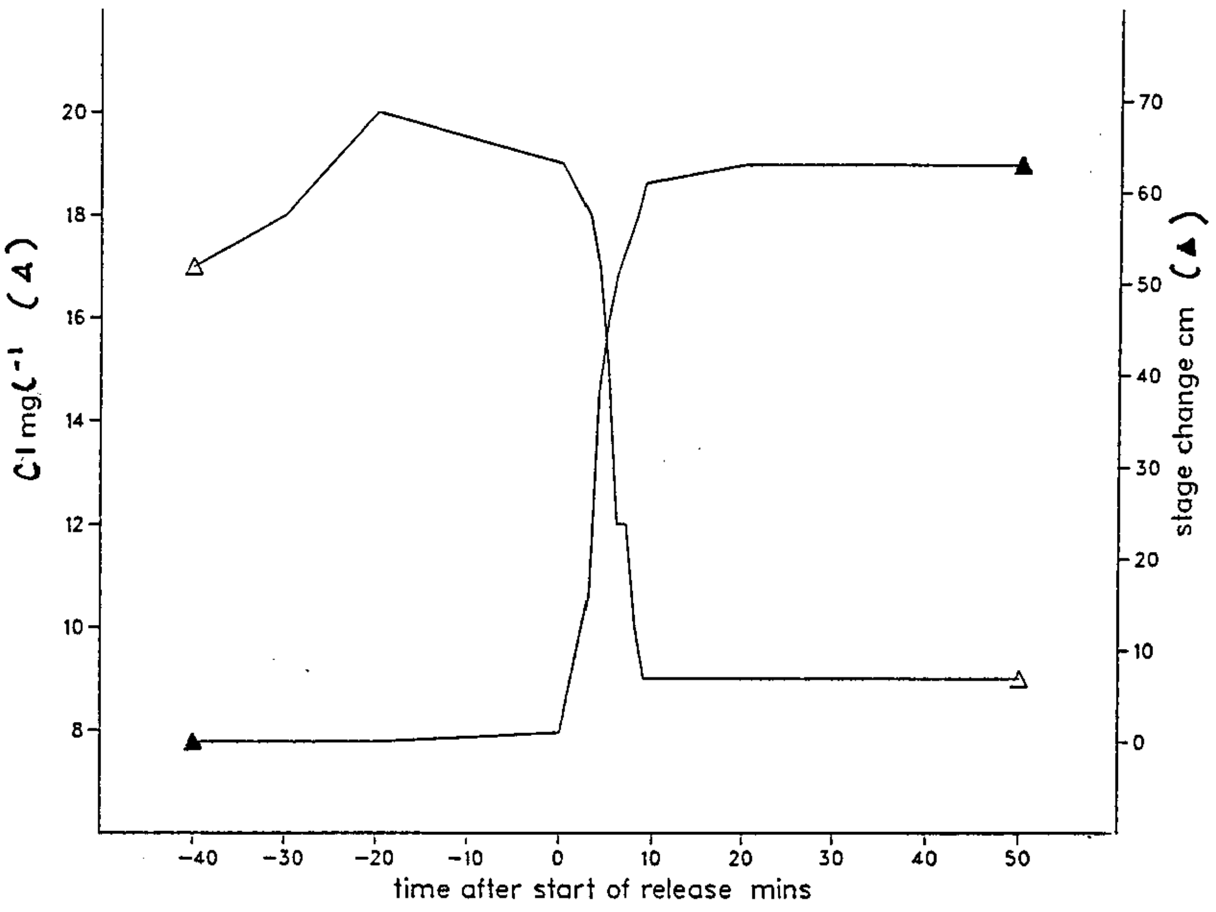
STAGE AND CONDUCTIVITY CHANGE,RIVER WASHBURN,DAM SITE,10.4.83



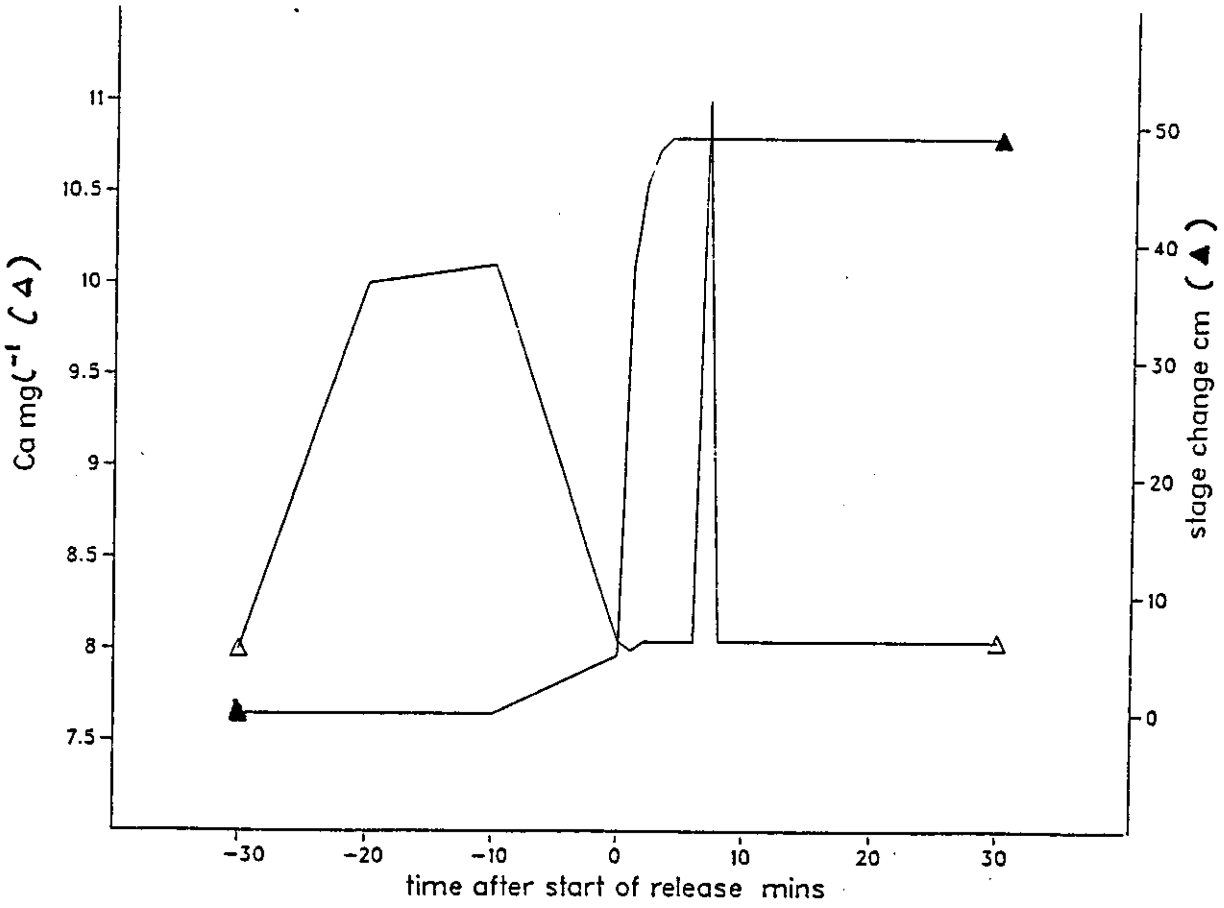
STAGE AND CALCIUM CHANGE, RIVER WASHBURN, DAM SITE, 23.10.82



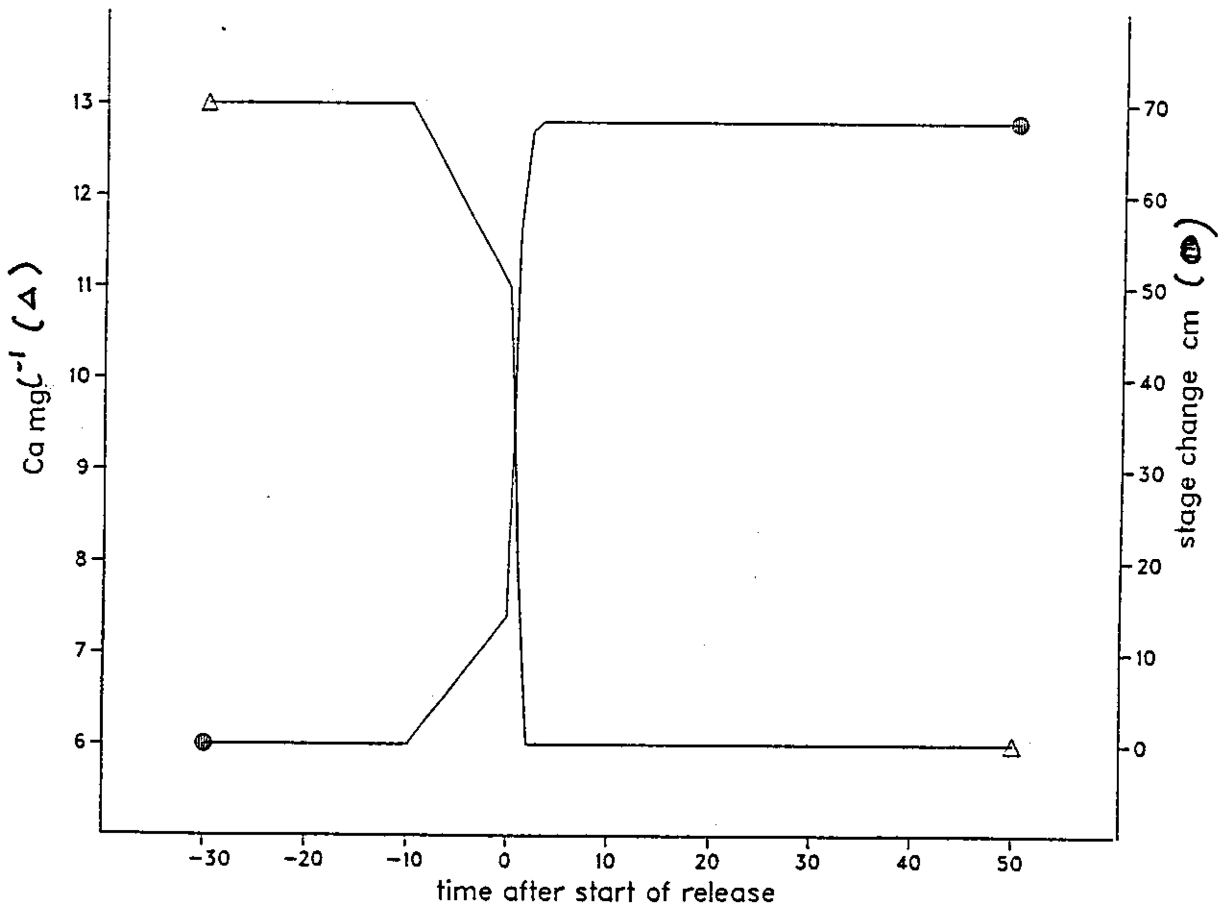
STAGE AND CHLORIDE CHANGE, RIVER WASHBURN, DAM SITE, 23.10.82



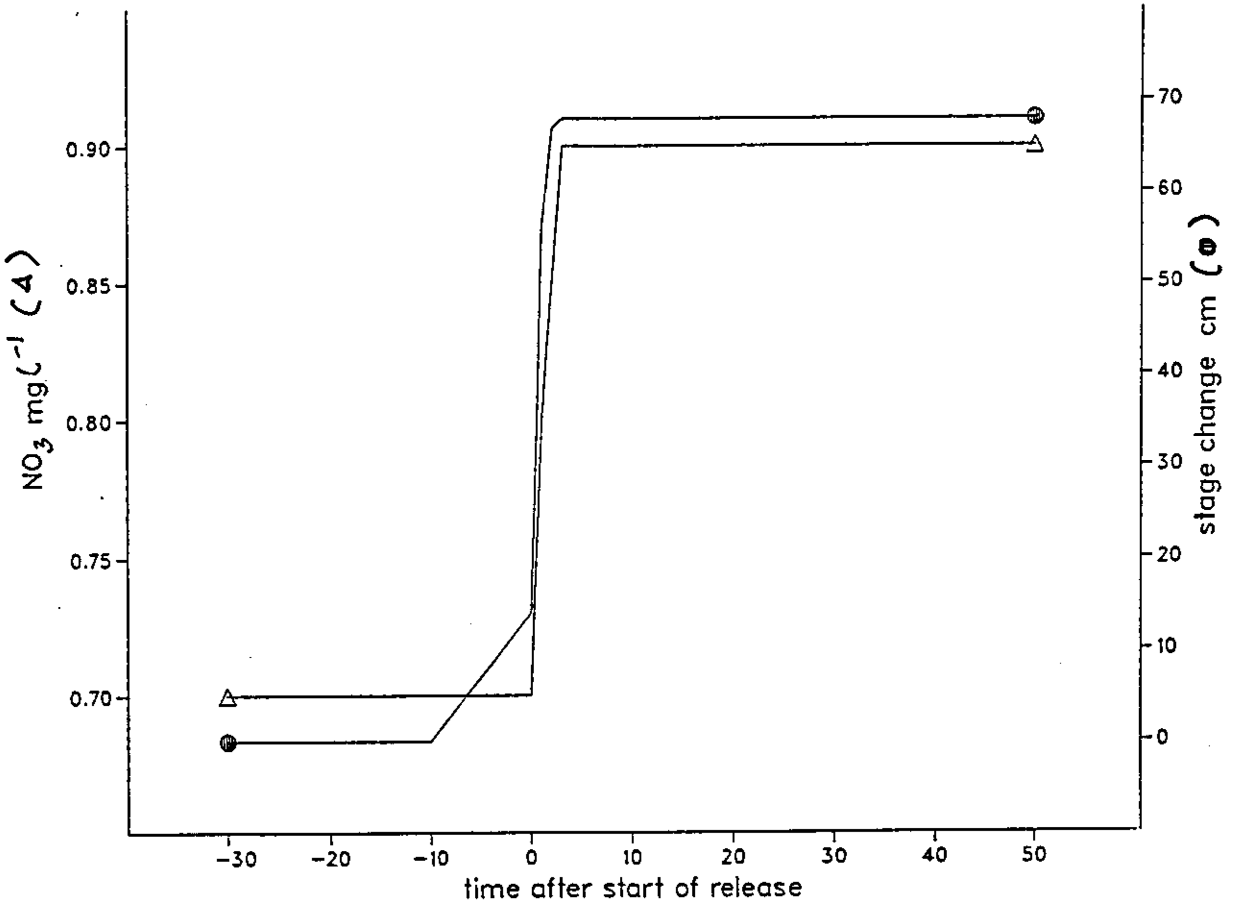
STAGE AND CALCIUM CHANGE RIVER WASHBURN DAM SITE 5.11.83.

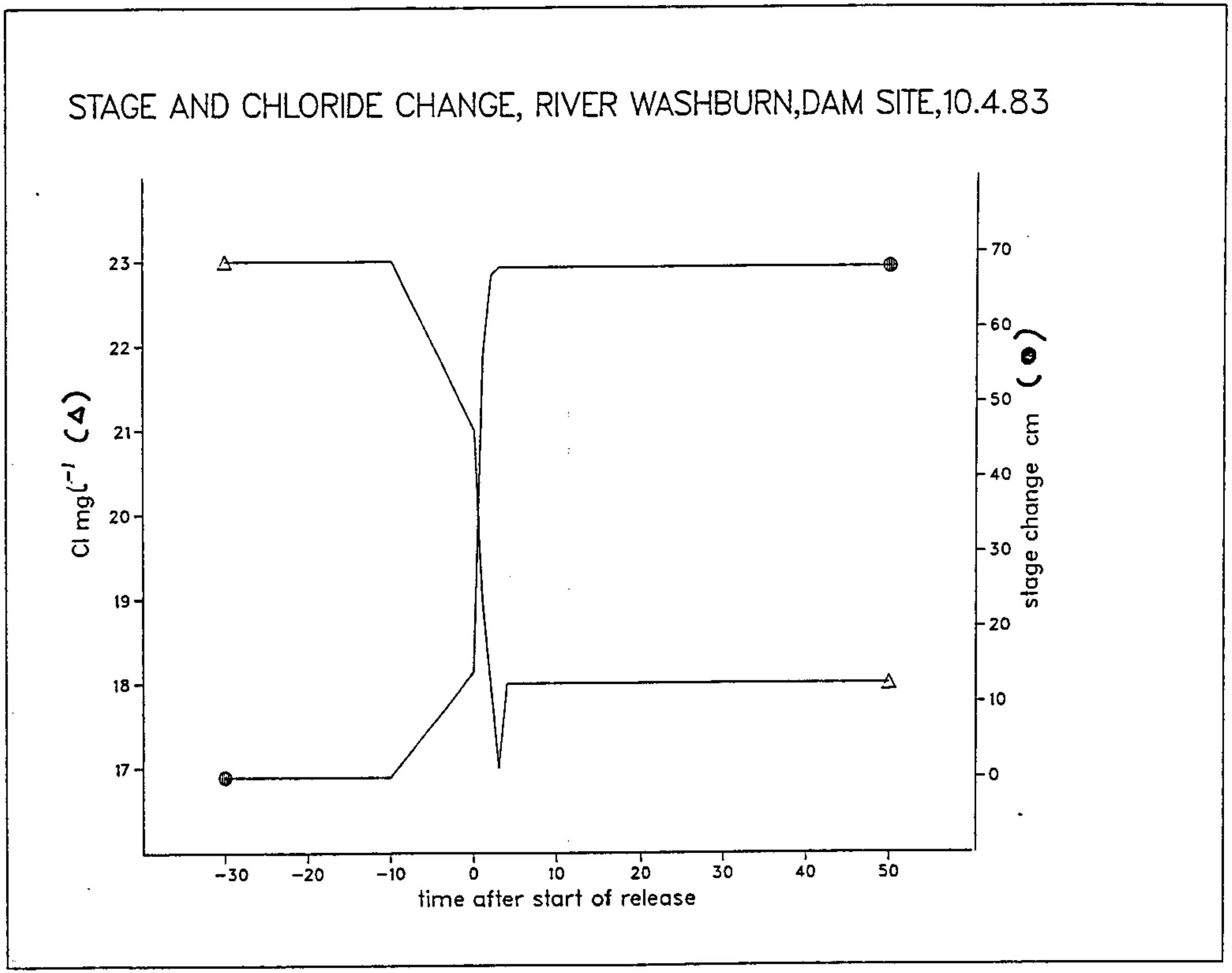


STAGE AND CALCIUM CHANGE, RIVER WASHBURN, DAM SITE, 10.4.83



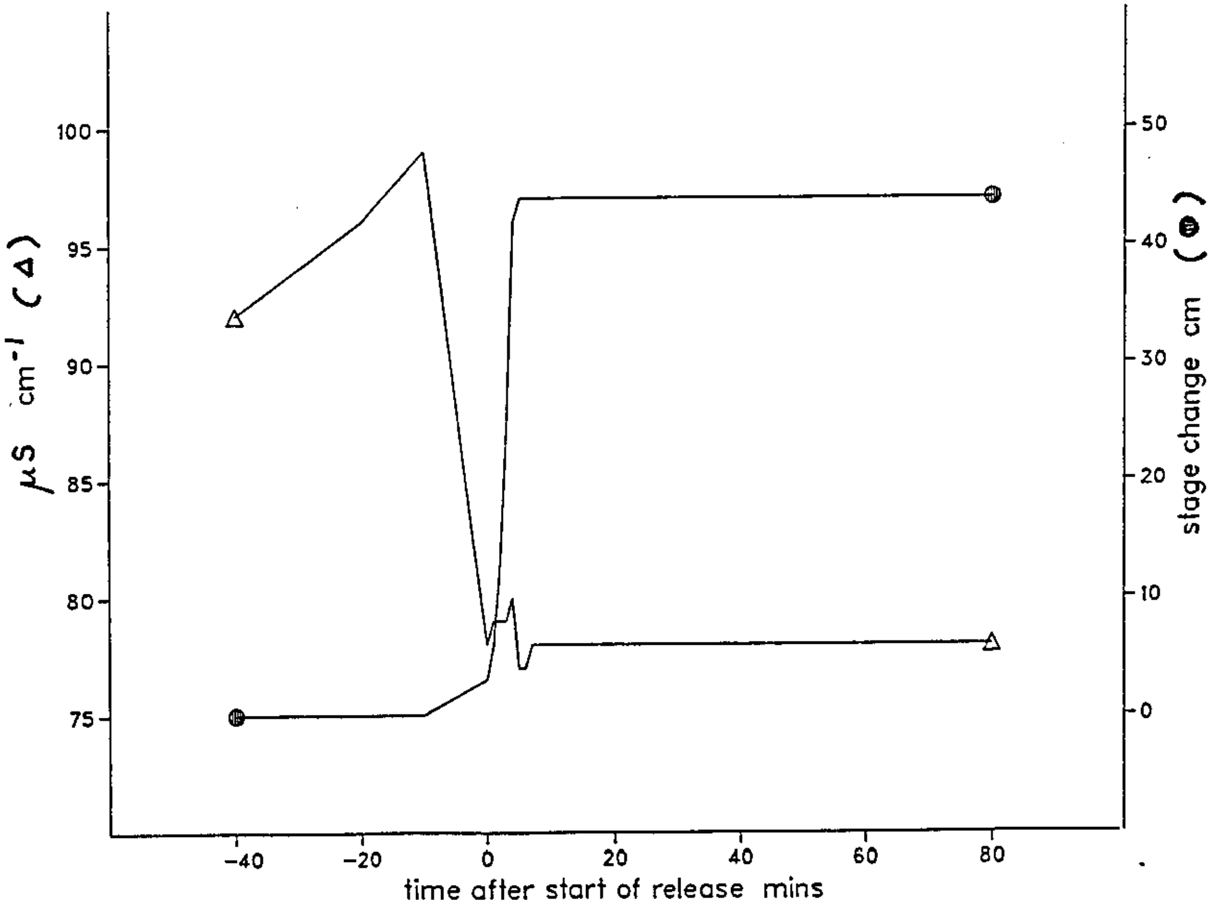
STAGE AND NITRATE CHANGE, RIVER WASHBURN, DAM SITE, 10.4.83



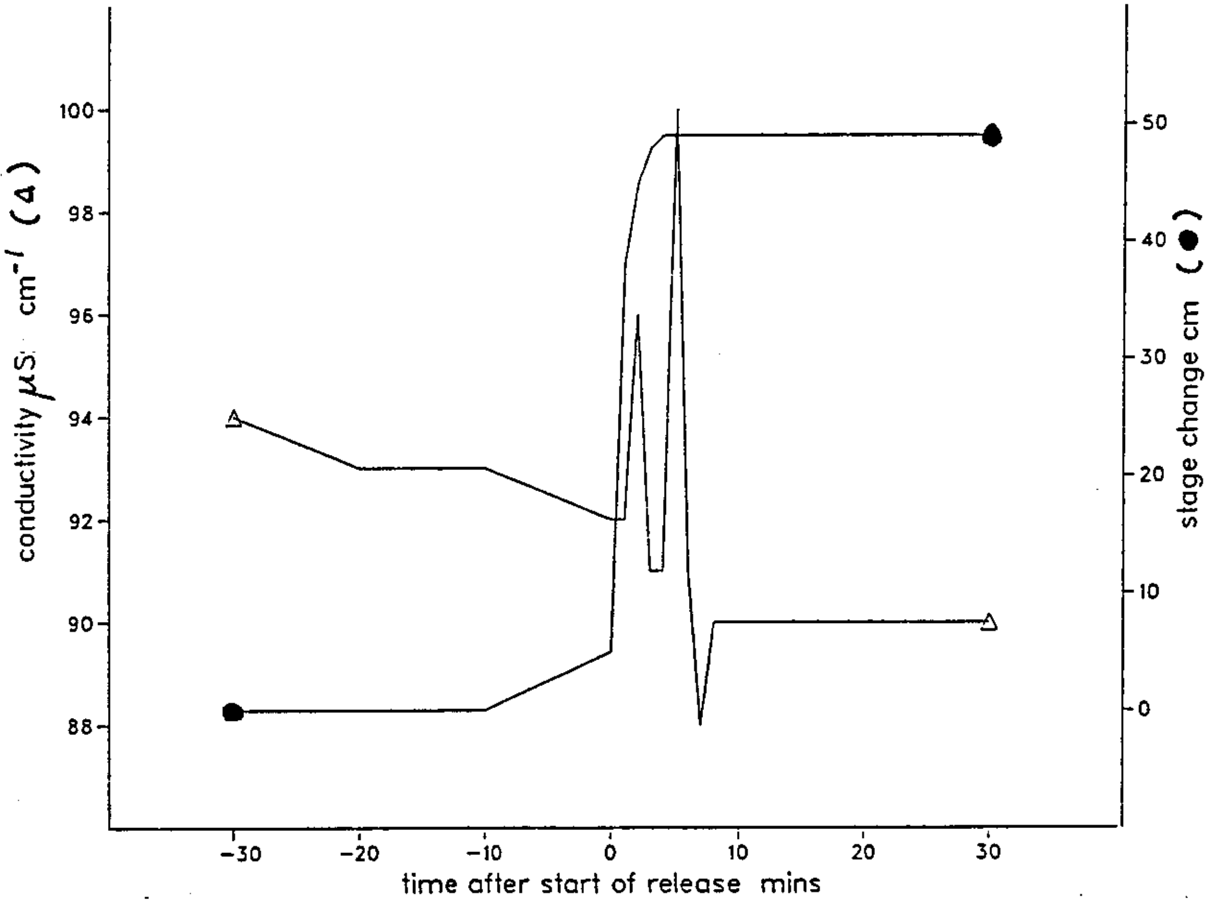


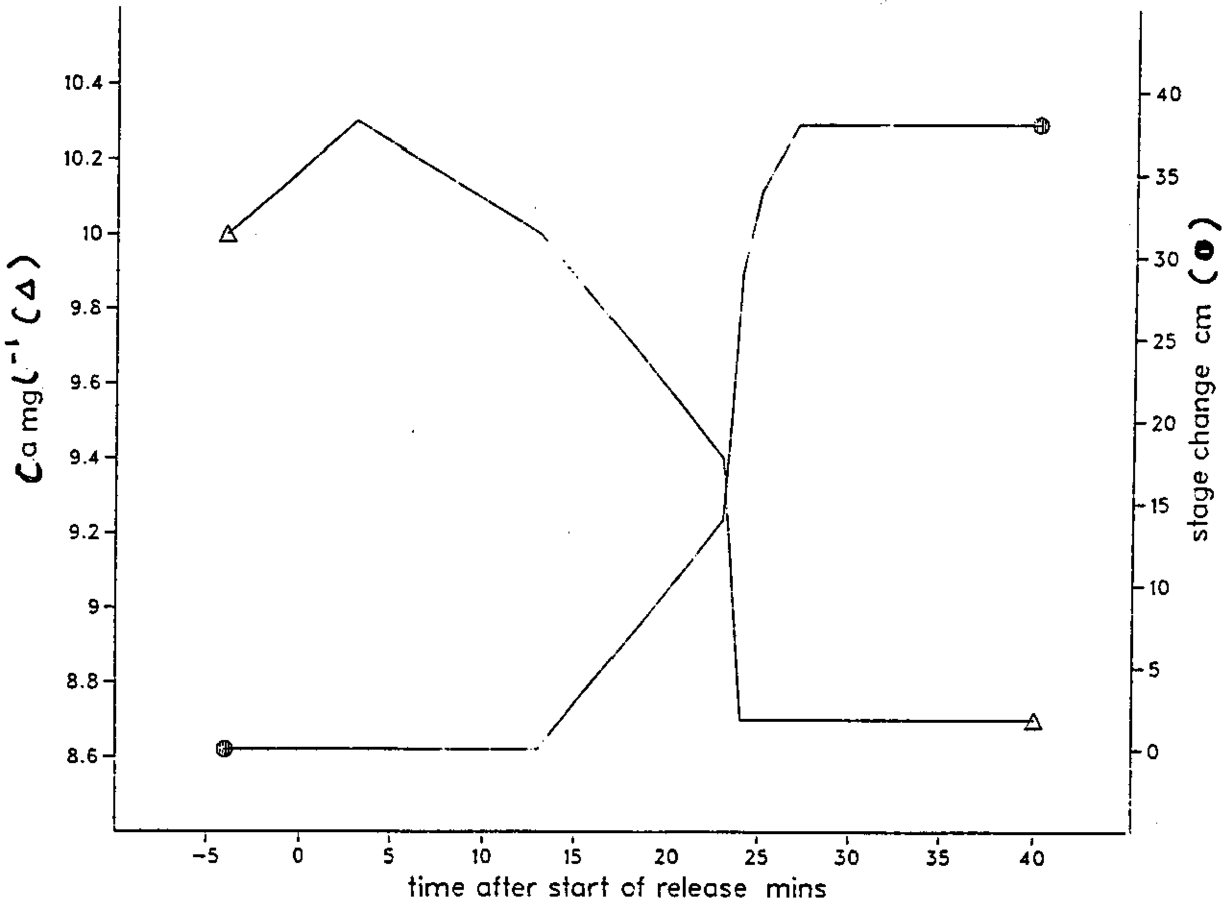
STAGE AND CHLORIDE CHANGE, RIVER WASHBURN,DAM SITE,10.4.83

STAGE AND CONDUCTIVITY CHANGE, RIVER WASHBURN,DAM SITE, 9.4.83



STAGE AND CONDUCTIVITY CHANGE ,RIVER WASHBURN DAM SITE 5.11.83.





STAGE AND CALCIUM, RIVER WASHBURN , 5.11.83

APPENDIX F.

RIVER NORTH TYNE ADDITIONAL DATA.

F.1 Hydraulic details for the calculation of kinematic wave movement on the River North Tyne. A release of 50 m^3s^{-1} on a low flow of 25 $m^3 s^{-1}$. 436
F.2 Hydraulic details for the calculation of kinematic wave movement on the river North Tyne. A release of 50 m^3s^{-1} on a low flow of 2.5 m^3s^{-1}. 437
F.3 Hydraulic details for the calculation of kinematic wave movement on the river North Tyne. A release of 25 m^3s^{-1} on a low flow of 2.5. m^3s^{-1}. 438
F.4 Variation of water quality parameters with stage change caused by reservoir releases:-
Conductivity, at site 1 439
Calcium, at site 4 440
pH, at site 4 441
Nitrate, conductivity and calcium at site 3. 442

REACH	length km	QL $m^3 s^{-1}$	QH $m^3 s^{-1}$	AL m^2	AH m^2	K	VL $m\ s^{-1}$	Vob $m\ s^{-1}$	Vk $m\ s^{-1}$	T1 mins	T2 mins
0-1	0.25	25	50	32.5	46.4	0.46	0.60	0.83	0.90	5	4.6
1-2	1.75	25	50	32.5	46.4	0.68	0.77	1.22	1.10	24	27.0
2-3	2.35	25	50	25.0	44.1	0.90	1.30	1.36	1.40	29	28.0
0-3	4.35	25	50	28	45	0.84	0.97	1.25	1.17	58	62.0
3-4	5.70	31	56.3	35	43	1.05	1.19	1.94	1.40	51	66.3

Hydraulic details for the calculation of kinematic wave movement on the River North Tyne. A release of 50 $m^3 s^{-1}$ on a low flow of 25 $m^3 s^{-1}$.

REACH	length km	QL $m^3 s^{-1}$	QH $m^3 s^{-1}$	AL m^2	AH m^2	K	VL $m\ s^{-1}$	Vob $m\ s^{-1}$	Vk $m\ s^{-1}$	T1 mins	T2 mins
0-1	0.25	2.5	50	15.9	46.4	0.32	0.16	0.5	0.94	5	10.6
1-2	1.75	2.5	50	15.9	46.4	0.78	0.16	1.18	1.10	24.7	26.9
2-3	2.35	2.5	50	10.0	44.1	0.98	0.16	1.35	1.14	29	37.5
0-3	4.35	2.5	50	13	45	0.84	0.16	1.25	1.05	58.7	69.1
3-4	5.70	9.0	56.3	15.2	43	1.09	0.59	1.86	1.22	51	77.8
4-5	4.80	15.7	62.7	17.5	39.3	0.60	0.87	1.31	1.49	61	53.7

QL = low flow discharge QH = high flow discharge AL = wetted area at low flow AH wetted area at high flow VL = vlocity at low flow Vob = observed velocity of wave peak Vk = calculated velocity of water peak T1 = time of travel of wave T2 = calculated time of travel of water.

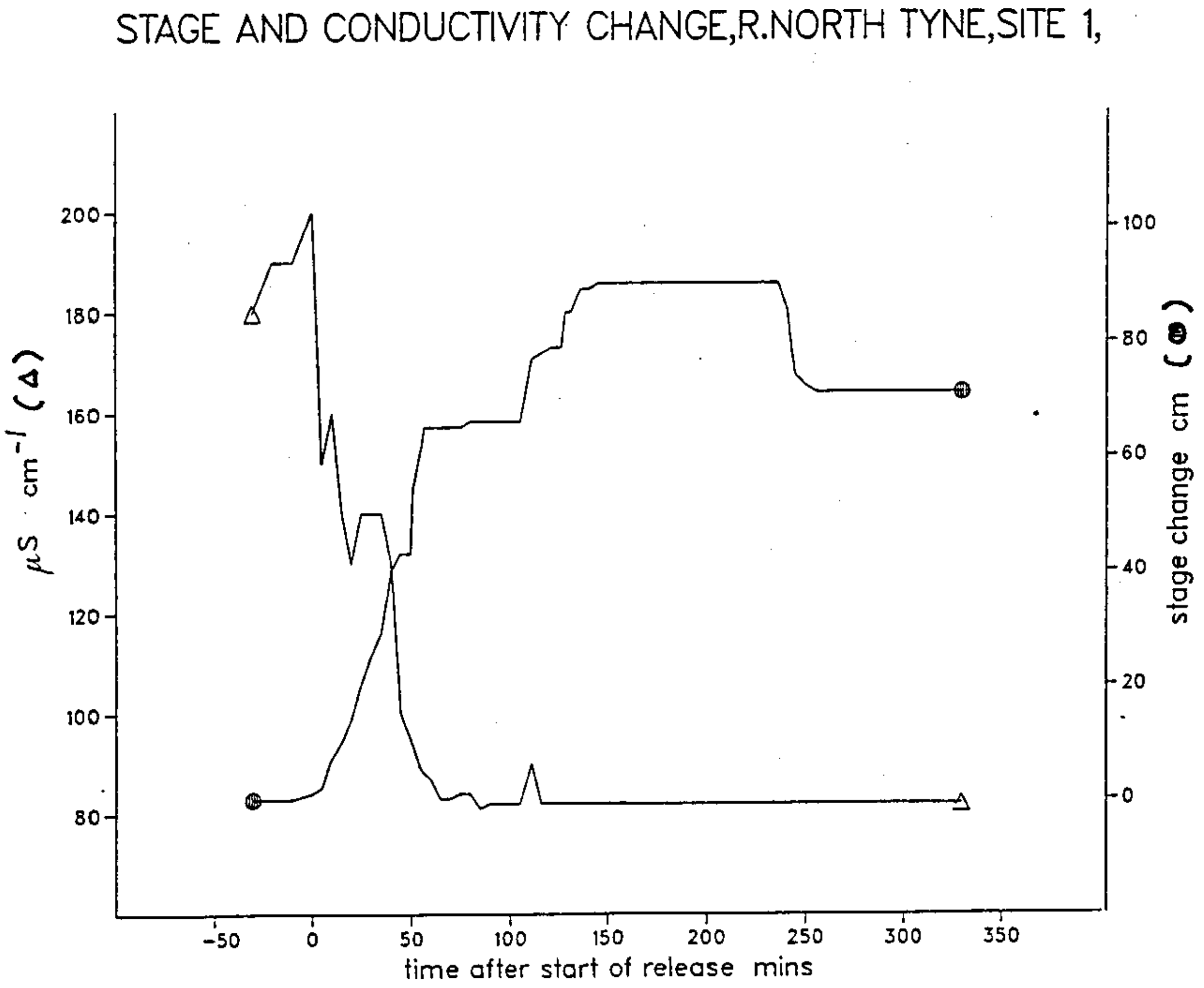
<u>Hydraulic details for the calculation of kinematic wave movement on the River North Tyne. Release of 50 $m^3 s^{-1}$ on a low flow of 2.5 $m^3 s^{-1}$.</u>

REACH	length km	QL m^3s^{-1}	QH m^3s^{-1}	AL m^2	AH m^2	K	VL $m\ s^{-1}$	Vob $m\ s^{-1}$	Vk $m\ s^{-1}$	T1 mins	T2 mins
0-1	0.25	2.5	25	15.9	32.5	0.44	0.16	0.60	0.78	7	5.4
1-2	1.75	2.5	25	15.9	32.5	0.57	0.16	0.77	0.78	38	37.6
2-3	2.35	2.5	25	10.0	25.0	0.91	0.16	1.30	0.80	30	49.2
0-3	4.35	2.5	25	13	28.0	0.65	0.59	0.97	0.82	75	88.8
3-4	5.70	9.0	31.5	15.2	35.0	0.90	0.59	1.19	1.01	80	91.3

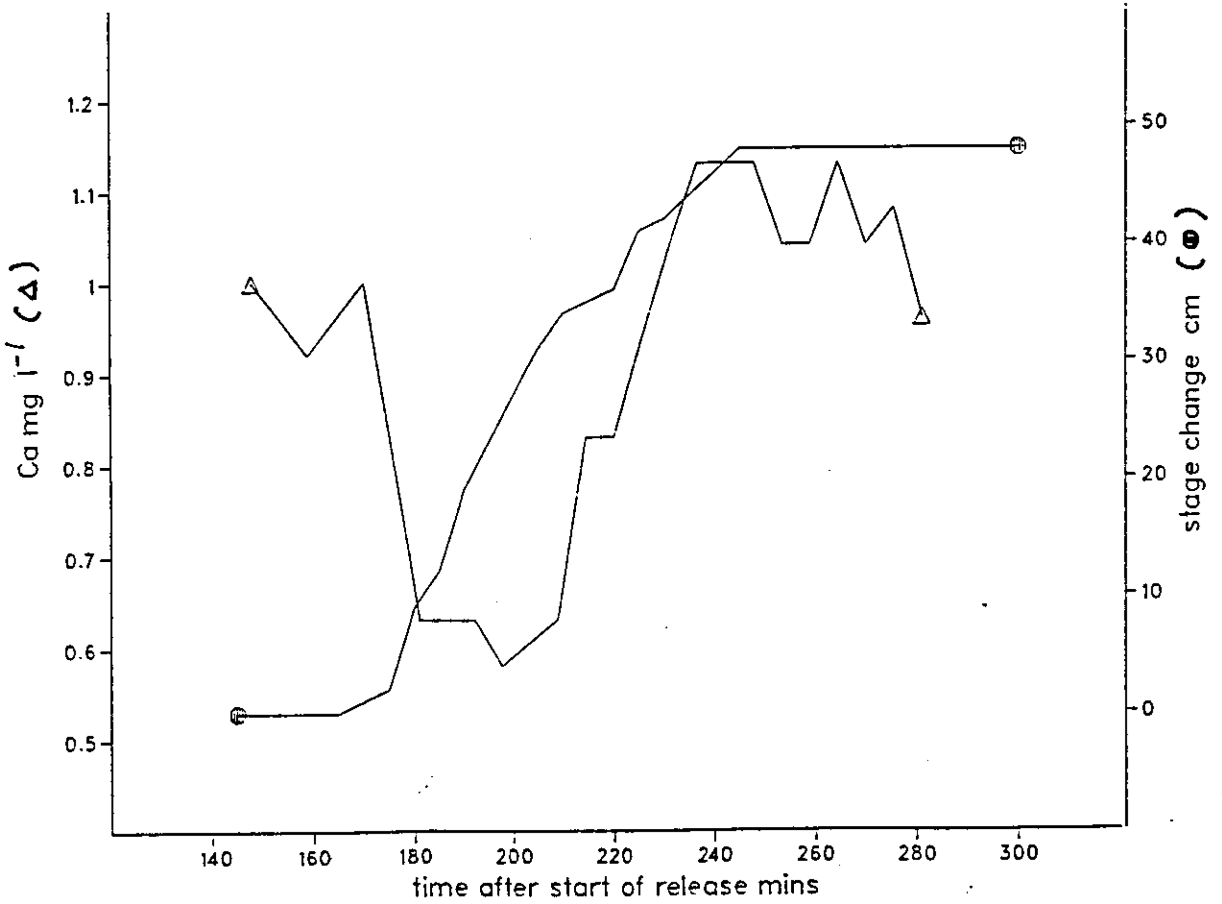
Hydraulic details for the calculation of kinematic wave movement on the River North Tyne. Release of 25 m^3s^{-1} on a low flow of 2.5 m^3s^{-1}.

Appendix F.4

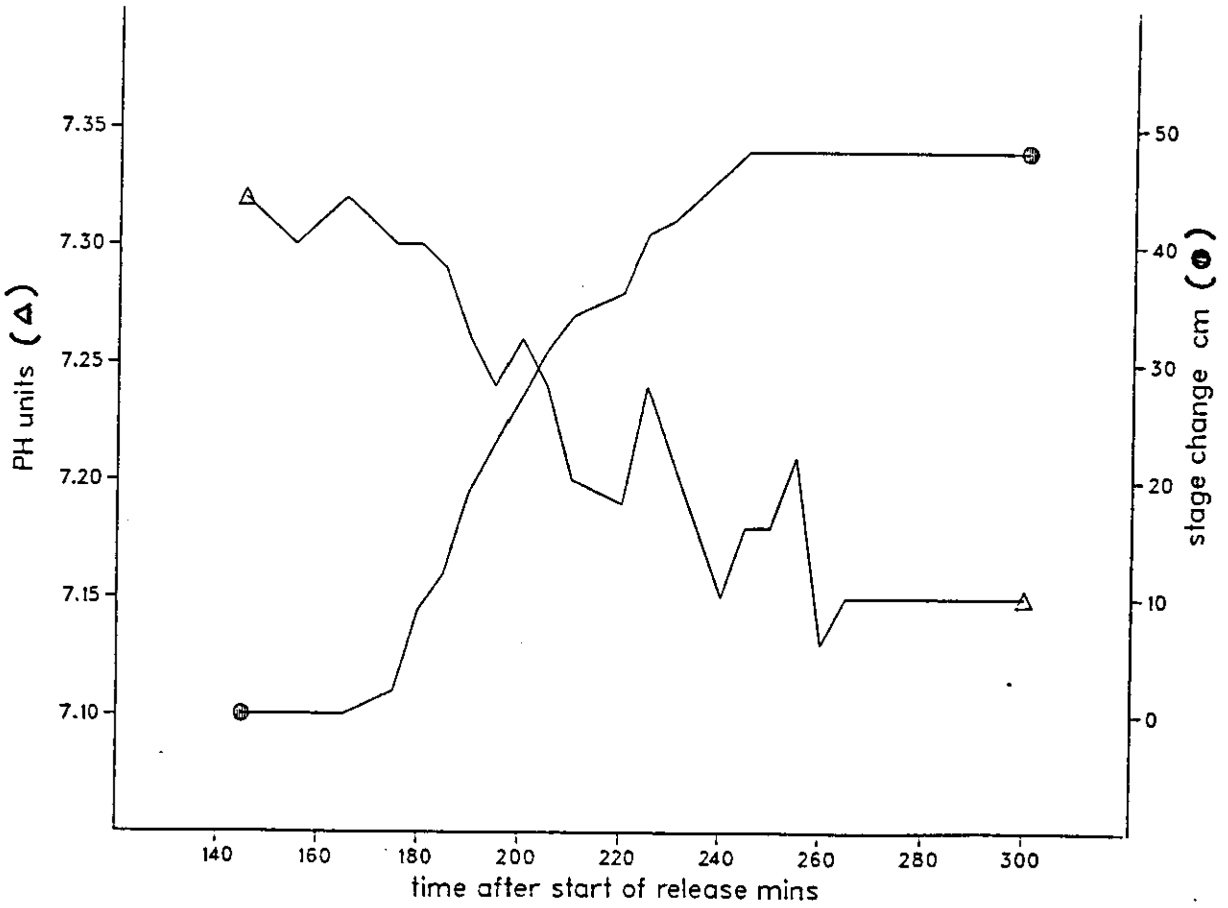
Chemical variation with stage change.

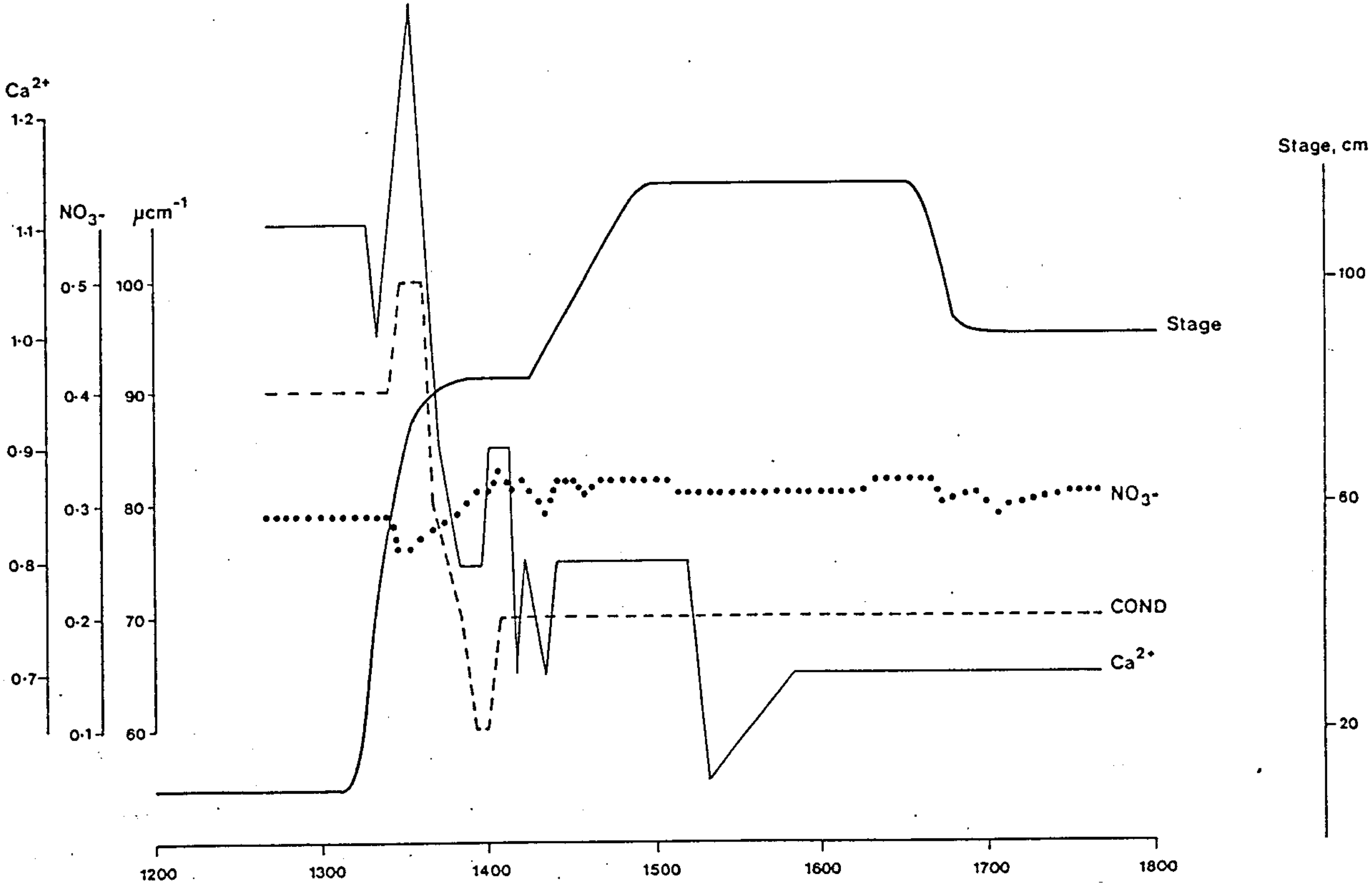


STAGE AND CALCIUM CHANGE, R.NORTH TYNE, SITE 4.



STAGE AND PH CHANGE, R.NORTH TYNE, SITE 4.





Variation of water quality parameters with stage change, caused by a reservoir release, at site 3, 10.05 km below Kielder Dam.

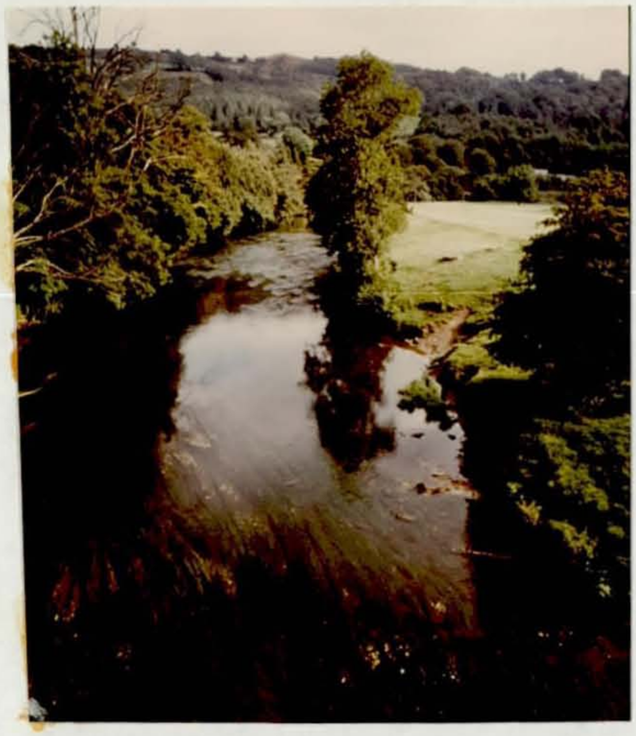
APPENDIX G.

PHOTOGRAPHS OF THE STUDY RIVERS.

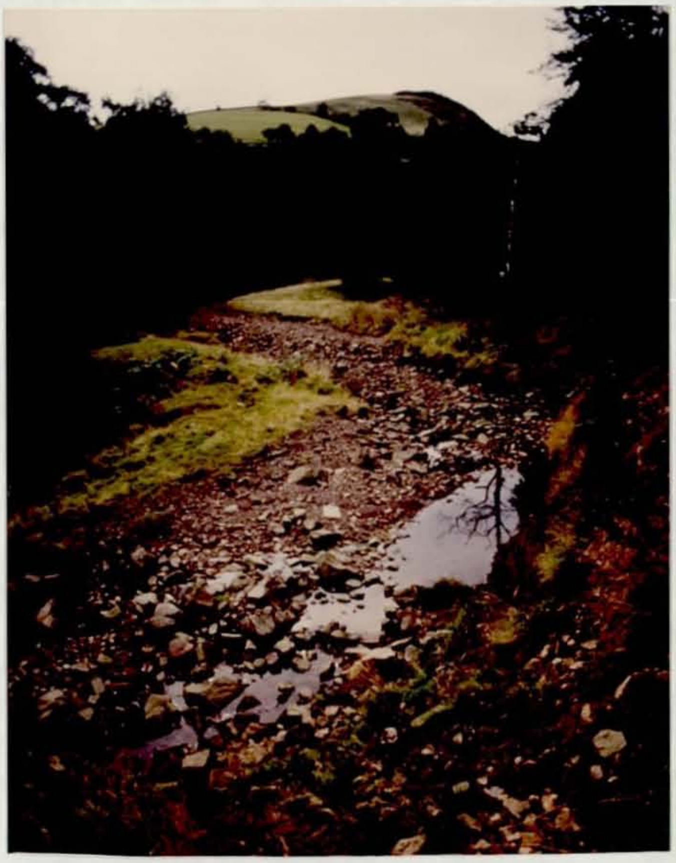
G.1 Selected sites on the River Derwent 444
G.2 Selected sites on the River Tryweryn 446

Appendix G.1

RIVER DERWENT.



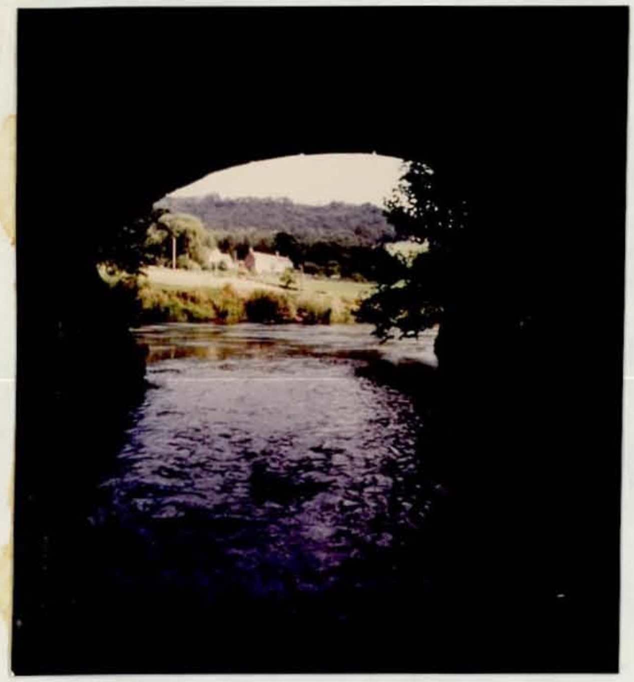
Below Matlock Bath.



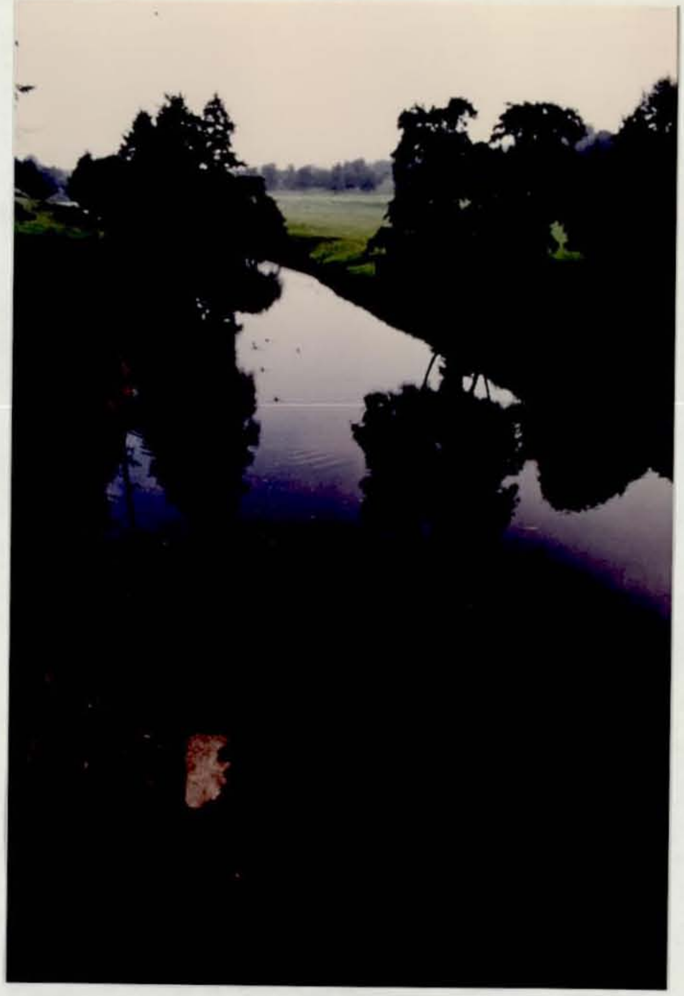
Above the Reservoir.

Ladybower Reservoir.

RIVER DERWENT.



Merebrook Sough.

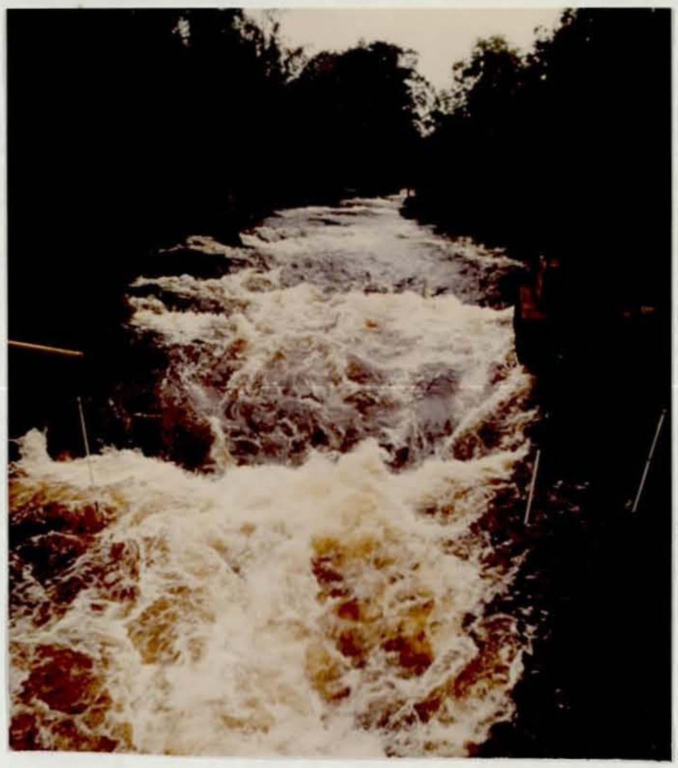


Chatsworth.

The Derwent/Amber Confluence - Ambergate.

Appendix G.2

RIVER TRYWERYN.

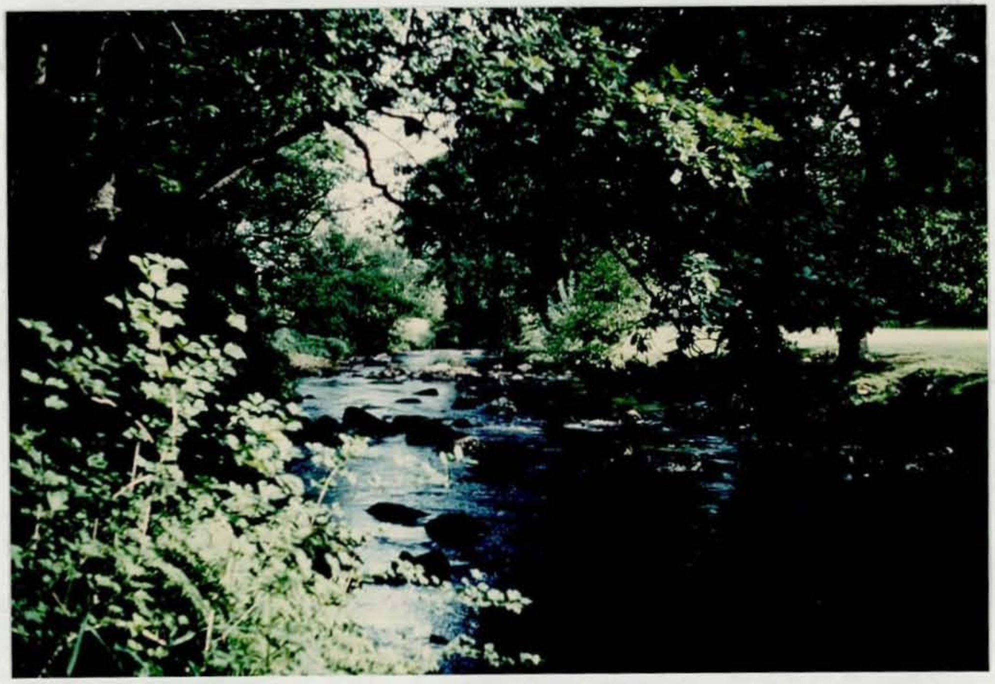


Site 2 (International Canoe Slalom course) - high flow.

The Tryweryn/Mynach Confluence (immediately below Site 3) - both in flood.

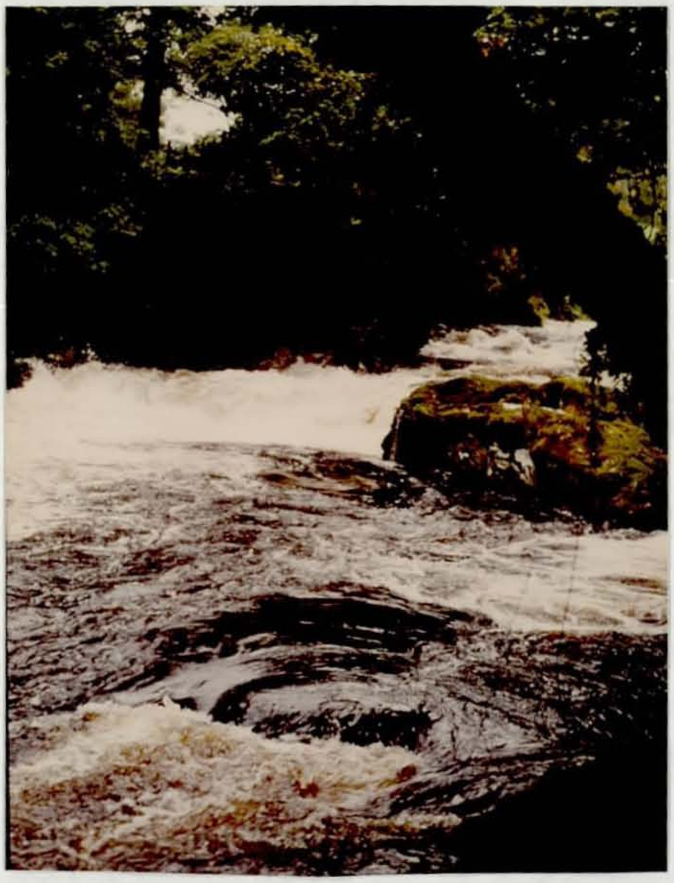
RIVER TRYWERYN.

Site 5 - high flow.



Site 5 - low flow.

RIVER TRYWERYN.



Bala Mill Falls (between Sites 5 and 6), at high flow.

Site 6 - the lowest and least turbulent site (high flow).