Water quality modelling of a grossly polluted stream using continuous monitoring.

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Thesis for the degree of

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WATER QUALITY MODELLING OF A GROSSLY POLLUTED STREAM USING CONTINUOUS MONITORING

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"We seek for slumbering trout
And whispering in their ears
Give them unquiet dreams."

<u>William Butler Yeats</u>

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Postgraduate Study and Scientific Meetings Attended

1974-75	Modern methods of analysis module of the MSc course in 'Instrumental Chemical Analysis' Department of Chemistry, Sheffield Polytechnic.
1974-75	Statistics module of the postgraduate diploma in Water Engineering and Pollution Control, Department of Civil Engineering, Sheffield Polytechnic.
1974-76	Various staff courses in computer programming in Fortran IV and the use of statistical routines on the IBM 370.
1974-77	Various research colloquia within the Department of Chemistry, Sheffield City Polytechnic. Various meetings of the Modern Methods of Analysis group, Sheffield Metallurgical and Engineering Association.
1975 February 4.	Meeting of the Society of Chemical Industry; 'Entry and distribution of pollutants in ground waters and rivers', 14 Belgrave Square, London.

1975 February 19.	Joint meeting of the Analytical Division of the Chemical Society and the Society for Water Treatment and examination; 'Pollution and Water Chemistry'; University of Newcastle, Newcastle upon Tyne.
19-20 June	Symposium of The Analytical Division of the Chemical Society. 'The Application of New Techniques in Environmental Analysis'. St Andrews University, St Andrews.
1-2 July	Anglian Water Authority Symposium 'Water Quality Modelling of the Bedford Ouse', Churchill College, Cambridge.
15-17 Sept	Water Research Centre Conference ' Instruments and Control systems for the Water Industry', University of Reading, Reading.
1976 6 May	Water Research Centre Open Day, Stevenage Laboratory, Stevenage.
23 November	The Chemical Society Industrial Division of the Environment Group Symposium 'Pollution Monitoring', The Scientific Societies Lecture Theatre, Saville Row, London
1977 15 April	Water Research Centre regional meetings, 'Flow Measurement by means of tracers, Hallam Towers Hotel, Sheffield.

1977	8 May	The Chemical Society, Analytical Division, 'Research and Development topics in Analytical Chemistry'. Chelsea College, University of London, London. Paper presented on 'The Application of Continuous Monitoring to the Study of a Grossly Polluted Stream'.

Abstract

The development of a statistical water quality model for a grossly polluted stream in an industrial environment, is examined. The data used for model development was obtained from a continuous water quality monitoring station (WQMS), which recorded five quality determinands each quarter hour. The continuous monitoring was performed in conjunction with a discrete sampling and analysis programme, which covered eight sites upstream of the WQMS. Continuous flow gauging was also performed, with a stream flow model based on unit hydrograph theory being developed for the period prior to flow gauge installation. The applications of continuous water quality monitors are discussed and necessary precautions for the operation of the WQMS in a grossly polluted environment are described. The literature concerning water quality monitoring has been surveyed, particularly that appertaining to continuous monitoring.

The monitored data was subjected to various handling techniques, with subsequent statistical analyses being performed by computer. The analyses indicated various interrelationships within the determinands, which were quantified and upon which the model was built. Multiple regression was found to be most effective at describing the system under study. The model has been evaluated and it is shown that grossly polluted systems can be effectively monitored by continuous techniques. The increased reliability and utility of the model, built upon large volumes of continuous monitored data, is illustrated. Conclusions are given, with suggestions for future work being made.

CONTENTS

Appendices

A major problem with respect to the use of such indices is the diverse nature of the users of water within our society. The quality requirements for water utilization vary widely e.g. a high dissolved oxygen concentration is essential if good fishing is to be found but is only of marginal value in a potable water supply, while it is highly undesirable in boiler feed water[2]. The fact that water quality is a very subjective concept and is directly linked to the utility of the water is further emphasised by the definitions of water pollution. One such definition states that "pollution occurs when the water is altered in composition or condition rendering it less suitable for any or all, of the purposes for which it would be suitable in its natural state"[3]. Therefore when attempting to detect pollution within a water system different users adopt different criteria. It is generally accepted that provided public health and amenity are safeguarded it is the responsibility of the users to alter the water composition at their own expense to suit their own individual requirements[4].

1.3 Historical aspects of water quality

Modern water treatment began in the 19th century in England, with the use of slow sand filters. This development was coincident with the industrialisation of the country and the realisation that many diseases, which had ravaged townspeople, were directly linked to the presence of highly polluted watercourses. Industrialisation saw river water being used for many new purposes such as cooling, washing and power generation. These watercourses often acted as the sewers of the towns[5]. Treatment plants were developed because of this unhealthy and highly objectionable method of sewage disposal. Thus the river systems became the conduits for carrying treated, instead of raw, sewage out to the sea. This unfortunately did not solve the problem as indiscriminate discharges of wastewaters from expanding industries and growing cities continued to render entire waterways unfit for any use other than that of open sewers. This industrial scar was looked upon by many as being the price of progress. With the evolution of governments more susceptible to popular opinion water quality became the subject of parliamentary legislation. Some of the relevant acts are listed in table T-1-2.

Table T-1-2

Rivers (Prevention of Pollution) Act	1876	Never very effective
Rivers (Prevention of Pollution) Act	1893	Amendments to the 1876 Act
Salmon and Freshwater Fisheries Act	1923	Now illegal to kill fish by pollution
Public Health Act	1936	Dealt with sewers
Public Health (Drainage of Trade Premises) Act	1937	Amendments to the 1936 Act
River Boards Act	1948	Establishment of the river boards
Rivers (Prevention of Pollution) Act	1951	Repeated the 1876 and 1898 Acts
Rivers (Prevention of Pollution) Act	1961	Consents needed for pre-1951 discharges
Public Health Act	1961	Dealt with trade effluents
Water Resources Act	1963	River Authorities were set up as was the Water Resources Board
Water Act	1973	Re-organisation of the water industry
Control of Pollution Act	1974	Not yet fully implemented

1.4 The Project

It was in an attempt to ascertain whether the water quality of a grossly polluted stream could be successfully mathematically modelled that this project was undertaken. A great many models have been produced for potable water-courses and estuarine systems but the need to model polluted streams seems to have been somewhat neglected. Many polluted streams have potentially great industrial and recreational utility but because of their poor quality do not fulfil this potential.

In order that the model developed fully reflected the water system studied, a continuous as well as a discrete water quality and quantity monitoring programme was performed.

CHAPTER 2

Water Quality Monitoring

2.1 Introduction

The increased awareness of environmental pollution along with the rising demand for water for industrial, recreational and domestic purposes, has led to a greater emphasis on the study of the quality of water. The importance of water quality, especially that of potable supply, has led to discrete sampling programmes being instigated by many Water Authorities. In such programmes Water Authority officials sample and analyse the water both chemically and biologically to determine whether the quality indices are within the pre-determined limits.

2.2 Disadvantages of discrete monitoring

The sampling has traditionally been performed by the 'grab' sampling technique with subsequent analysis by 'wet chemical' methods, in the laboratory. This method of sampling and production of water quality data, known as discrete monitoring, has some inherent faults[6,7] as outlined in table T-2-1.

Table T-2-1

i) Samples taken with a monthly frequency, as is normal, only represent a minute part of the river flow for that month.

ii) No information is obtained about sporadic discharges whether deliberate or accidental.

iii) No information is obtained about periodic variations in water quality, particularly about diurnal variations, for example in dissolved oxygen.

iv) No warning of the deterioration of water quality is obtained, this is especially important in potable water supplies.

Recent developments in instrumental analytical chemistry have made it possible for continuous automatic water quality monitors to be produced.[8,9,10,11,12,13] These instruments have the capability of overcoming most of the inadequacies of discrete sampling as shown in table T-2-I.

2.3 The development of water quality monitoring systems

This started before the second world war, with the introduction of the pH meter and facilities for controlling the addition of acid or alkali to neutralise effluents discharged to sewers. By 1963 the Trent River Board had installed simple thermometers to measure and record water temperatures at a number of points below a large direct cooled power station on the river Trent.

In the United States of America (USA), the need for a more sophisticated approach to water quality monitoring was realised by 1962. Mentick[14] produced specifications for an integrated water quality data acquisition system which, mainly due to the Orsanco project, were later revised.

2.3.1 The Orsanco system[15] is still regarded as perhaps the best proven of all the American systems. It comprises fourteen field stations, eight of which are on the Ohio river and six on tributaries, a central receiving station, and a data processing centre. All field stations are equipped with transmitters for telemetering data to headquarters, and are connected in series with one another. They are mains powered and are equipped to monitor some or all of the following parameters: pH value, redox potential, chloride-ion concentration, dissolved-oxygen concentration, conductivity, temperature and solar radiation. The monitoring stations are sited either in municipal water-treatment plants or in power-generating plants on the river bank. This has a number of advantages including the ability of tapping intake lines to obtain a representative sample and the reduced threat of vandalism. Maintenance of the equipment is carried out on a fortnightly basis with the calibration of the sensing system being performed at the same time. It has been found that with the incorporation of the telemetry network, the percentage of usable data has increased from less than 50% to more than 90%. This has been achieved by the inclusion of test signals, the elimination of data outside a given tolerance limit and the provision of alarm, standardisation and sampling facilities which telemetry allows.

2.3.2 <u>Research and development within the United Kingdom (UK)</u> has tended to concentrate upon the self contained water quality monitors. The development of such complex systems has been directly linked to the development of the sensors used in them. An example of this is the way in which the development of the Mackereth dissolved oxygen electrode in 1964[8], stimulated interest within the UK, into the continuous monitoring of water quality. This was further reinforced by the development in 1966 of a suspended solids

(SS) monitor. By 1968 a multiparameter water quality monitoring unit had been completed.[16] This incorporated sensors for dissolved oxygen (DO), electrical conductivity (EC), suspended solids (SS), temperature (T) and pH, (the five standard quality determinands). An autoanalyzer was also under evaluation, around the same time, for the automatic measurement of ammonia concentrations. Monitors were sited on both the River Trent[17,18] and the River Lee[19] the data being recorded on a six point multichannel recorder. One of the two monitors installed on the River Lee, at Kings Weir in 1968, also monitored nitrate concentration,[20] by means of an autoanalyzer.

These initial water quality monitoring systems were exclusively manufactured by Electronic Instruments Ltd (EIL) although it was not long before other monitors were marketed. With the rapid advances in sensor development one or more of the parameters listed in table T-2-2 are now capable of being monitored by a wide range of discrete instruments and integrated monitors. For example, the monitors manufactured by Electronic Instruments Ltd, Plessey Radar Ltd, and Philips Pollution Monitoring, among others, measure the five standard quality determinands, with the Philips monitor also measuring redox potential and chloride-ion concentration in its standard form. Table T-2-2 outlines the relatively few parameters which can be monitored at present with meaningful accuracies and at reasonable cost, by automatic water quality monitors.[21] Table T-2-3 outlines a comparison of three popular monitors.

Table T-2-2

Parameter	Units	Range	Accuracy
Temperature	°C	(-10) - 40	± 0.5°C (linear)
Dissolved oxygen	% saturation	0 - 100	± 1% (linear)
		0 - 200	± 2% (linear)
Oxidized Nitrogen	mg N dm^{-3}	0 - 50	± 5% (log scale)
Ammoniacal Nitrogen	mg N dm^{-3}	0 - 5	± 5% (log scale)
		0 - 10	
		0 - 50	
Organic matter	mg C dm^{-3}	0 - 10	± 5% (log scale)
		0 - 100	
Suspended matter	mg dm^{-3}	5 - 500	± 5% (log scale)
		50 - 5000	
Conductivity	μ S cm^{-1}	5 - 5000	± 5% (log scale)
		50 - 50000	
Chloride	mg dm^{-3}	0.5 - 500	± 5% (log scale)
		25 - 25000	
Hardness	mg dm^{-3} $CaCO_3$	10 - 1000	± 5% (log scale)
pH value	pH value	2 - 11	± 0.1 (linear)
Sunlight intensity	$cal.cm^{-2}h^{-1}$	0 - 120	± 1.2 (linear)
Dissolved carbon dioxide	mg dm^{-3}	0 - 100	± 5% (log scale)

T-2-3

MONITORING FACILITIES	E.I.L. 7.9.7.2.	PLESSEY M.M.5.	PHILIPS A.W.M.S.
DISSOLVED OXYGEN	✓	✓	✓
SUSPENDED SOLIDS	✓	✓	✓
pH	✓	✓	✓
ELECTRICAL CONDUCTIVITY	✓	✓	✓
TEMPERATURE	✓	✓	✓
OPTIONAL SENSORS	✓	✓	✓
AUTOMATIC CLEANING	12 or 24 HOURLY	12 or 24 HOURLY	HOURLY (ULTRASONIC)
MAINS POWERED	✓		✓
MAINS CHARGED, BATTERY POWERED		✓	
FLOW FAILURE INDICATOR	✓		
PORTABLE	✓	✓	
AUTOMATIC SAMPLING		✓	
OUTPUT ONTO CHART RECORDER	✓	✓	✓
OUTPUT ONTO MAG. TAPE	OPTIONAL	✓	
HYDRAULIC SYSTEM	SUPPLIED BY USER	EITHER LAND BASED OR SUBMERSIBLE	VARIABLE STAGE PUMPING
TELEMETRY OPTION	✓	✓	✓

2.3.3 A summary of water quality monitoring in the rest of the world

Water quality monitoring has lagged slightly behind the UK and hence considerably behind the USA. Even so, rapid advances are being made in many of the continental countries especially West Germany.[22] One factor which has to be remembered when considering the development of continuous monitoring abroad, is that a lot of countries do not yet have the strict pollution legislation found in this country. Thus our foreign colleagues may not yet be under the same legal obligations to monitor their watercourses with the same vigour.

The French Government is currently engaged in the establishment of a network of sampling and analysing stations. A prototype station was commissioned in 1972 at Boran to the north of Paris. Water pollution monitoring in Japan is on a much smaller scale than air pollution monitoring. For example, in Tokyo there are only ten riverside measuring points where the condition of the river water is assessed. These measurements are made off line using standard chemical techniques.[23]

2.4 Water Quality Sensors

As already stated, the effectiveness of any water quality monitoring system is dependent ultimately upon the reliability and precision of its sensors. The development of multiparameter monitors has thus been governed by the development of the individual sensors associated with them.

2.4.1 The sensors for the five common determinands, (DO, SS, pH, EC and T), illustrate this point.

2.4.1.1 Measurement of Dissolved Oxygen Concentration

Dissolved oxygen concentration is regarded as being an extremely good indicator of pollution. Figure 2 -1 shows a diagramatic representation of how a river reacts to the commonest type of water pollution, that is, a discharge of organic matter such as sewage. The diagram illustrates the oxygen sag curve[24] where the relationship between Biochemical oxygen demand (BOD) and the oxygen concentration can be clearly seen. Figure 2 -2 shows the great effect the drop in DO level has upon the micro-organisms present within the water, it also drastically affects the quantity and type of fauna present.[25] Thus the usefulness of dissolved oxygen as a pollution detector can clearly be seen.

The classical method of measurement is the Winkler titrimetric test, the reported precision of which is ± 0.1 mg dm^{-3} of DO.[26] Electrochemical detection of the end point increases the sensitivity, accuracy and precision of this technique. Other methods of DO determination may be employed, these include;[27]

(i) dc potentiometric,
(ii) coulometric,
(iii) gas exchange,
(iv) gas chromatographic,
(v) radiometric,
(vi) conductometric,
and (vii) voltammetric.

Effects of an organic effluent on a river

Fig.2-1

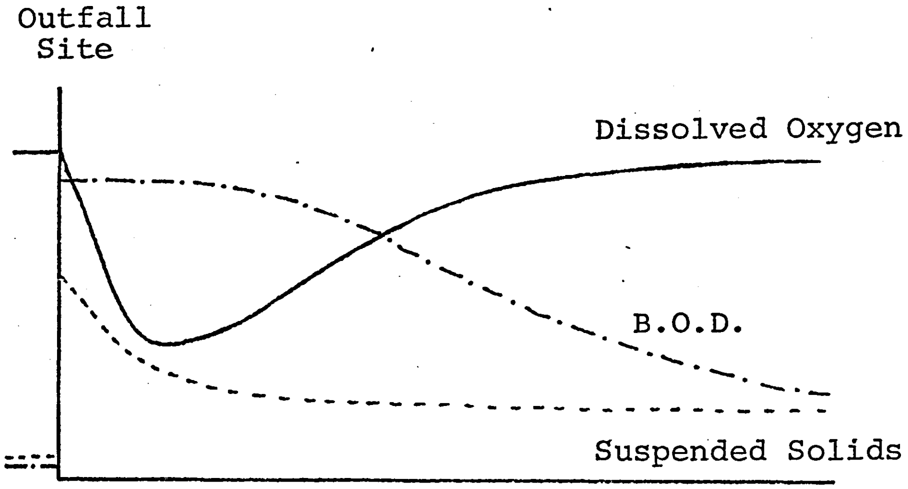


Fig.2-2

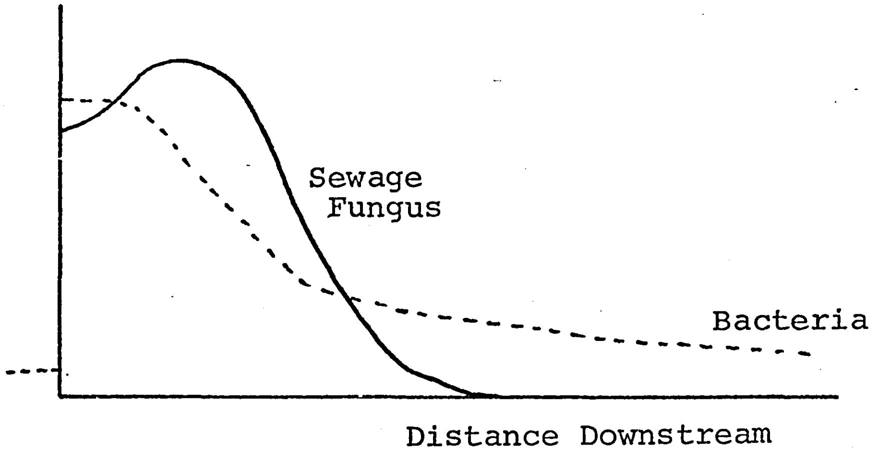


Fig. 2-3 Section through a Mackereth electrode

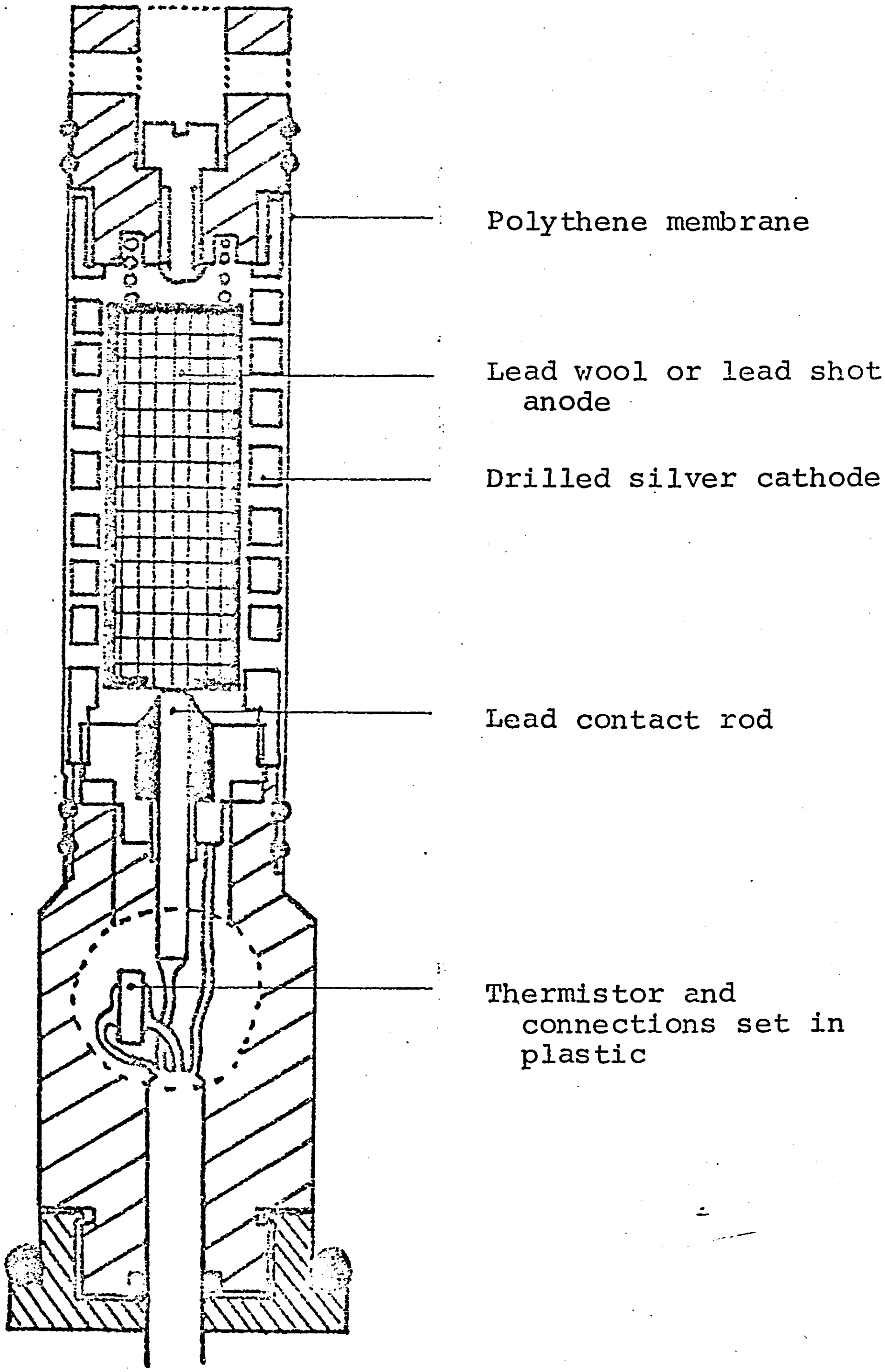
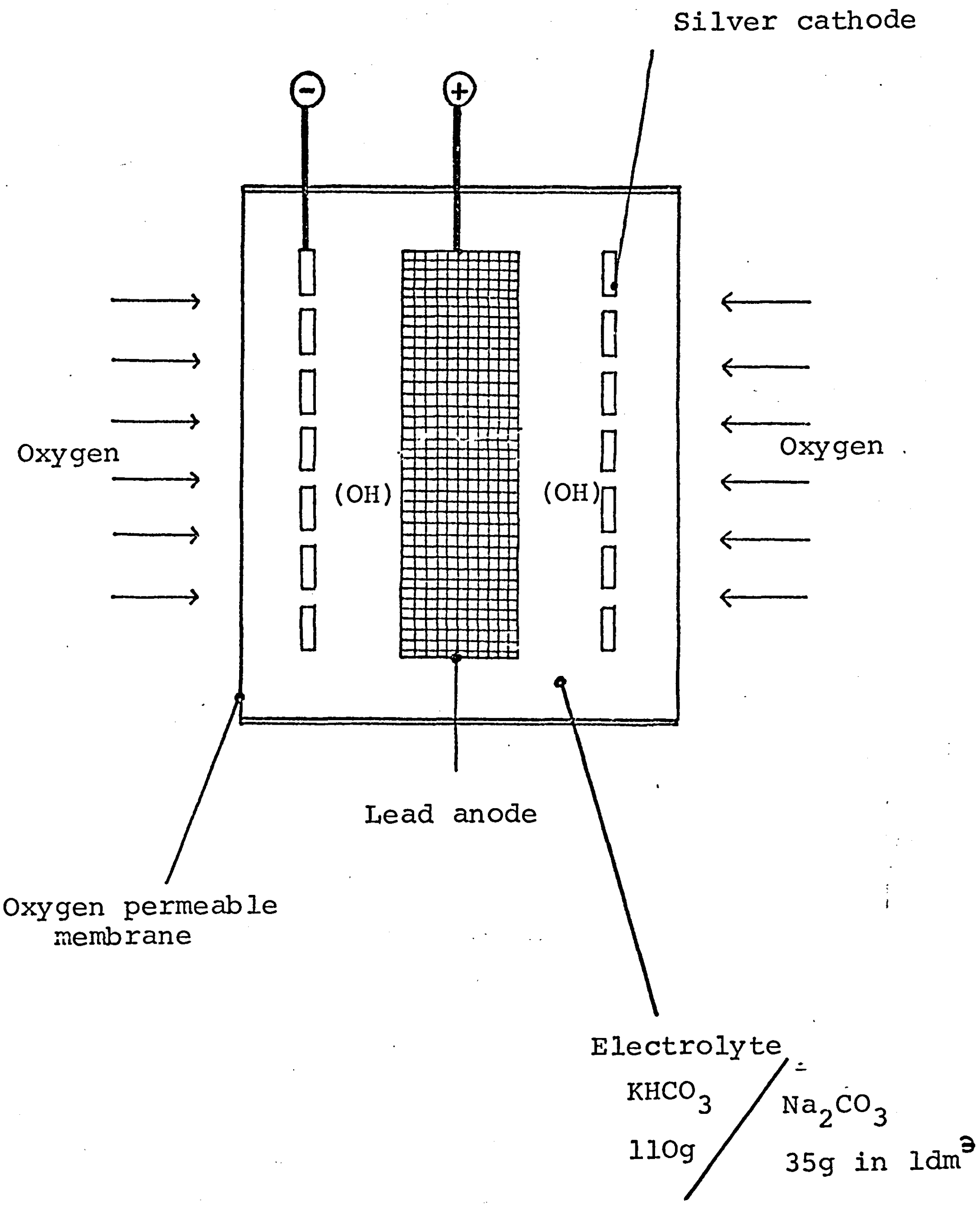


Fig.2-4 Principle of Mackereth cell



Voltammetric methods of DO analysis have, along with others, been the subject of a considerable amount of research. Continuous monitoring systems for dissolved oxygen have been developed using a dropping mercury electrode (DME) with reported sensitivities in the range 0.05 - 0.1 mg dm^{-3} DO.[28,29] The development of the voltammetric membrane electrodes have had the most invigorating effect upon dissolved oxygen analysis. These electrodes are particularly suitable for work in natural and waste waters due to their rugged nature.

The Mackereth galvanic electrode in the UK, and the improved Clark voltammetric cell in the USA, have both been found to be highly satisfactory.[30,31,32] A linear response and a reproducibility of ± 1% full scale deflection is normally obtainable from sensors operating in specially designed flow cells. The Mackereth galvanic electrode most commonly used is the temperature compensated modification of the original cell.[33] The electrode, Fig. 2-3 comprises a perforated cylindrical silver cathode surrounding and insulated from a porous lead anode. A small quantity of electrolyte is retained by an external tubular polythene membrane 0.063mm thick. This is seated to the body of the electrode at both ends by means of two O rings. The electrolyte is a mixture of equal volumes of saturated potassium bicarbonate and sodium carbonate. The temperature compensating thermistor is housed at the upper end of the electrode. Fig. 2-4 is a diagrammatic representation of how the electrode functions. The electrochemical reactions taking place within the electrode are:

$$O_2 + 2H_2O + 4e \longrightarrow 4OH^-$$

$$2Pb + 4OH^- - 4e \longrightarrow 2Pb(OH)_2$$

It must be remembered that just as the pH electrode measures hydrogen ion (H^+) activity so the DO electrode essentially measures the activity of molecular oxygen in solution. Thus care concerning the atmospheric pressure and salinity of the water must be exercised, but it is more critical that an appreciation of the temperature of the water be known when recording and interpreting the DO electrode results. Dissolved oxygen electrodes of this type have reputedly operated for several months, in pollution monitoring conditions, without needing any attention other than routine cleaning.[33] Recently a teflon coated membrane electrode has been developed for use primarily in the monitoring of the aeration process in activated sludge plants.[34] This electrode has the advantage of being inexpensive, small and easily made and should prove a most useful advance.

2.4.1.2 The measurement of suspended solids

The method first used to measure this parameter was to filter the sample and then weigh the filtrate. This was not capable of being automated successfully and hence the most practical automatic methods now rely upon the measurement of transmitted or scattered light.[35,36] The degree of scattering or transmission being related to the concentration of suspended solids within the sample

According to the theory developed by Rose,[37] the intensity I of beam of light, originally of intensity I_o, after passing through a length l of sample is given by the equation

$$\ln (I_o/I) = l.c.\pi/4 \sum_{o}^{n} K_z n d_z^2$$

where c is the concentration of suspended matter, K_z is the ratio of the light absorbed by a particle of size d_z, to that which would have been absorbed had the laws of geometric optics held, (this is a correction for the effects of diffraction) n is the number of particles of size d_z per gram of suspended matter. The equation shows that the optical properties of the suspension are dependent upon both the concentration and the nature of the suspended matter.

The main disadvantage with monitors which operate by means of transmission measurements is the fact that they fail to distinguish between soluble colour and suspended matter,[39] the measurement being purely one of optical density. To overcome this many monitors have been developed to measure scattered light.[40] Unfortunately not all of these compensate entirely for the presence of soluble colour, the scattered light being absorbed by the colour before it reaches the photo cell.

One popular commercially available instrument uses two coherent beams of light from the same tungsten filament bulb, which have different sample path lengths. The ratio of the optical densities of the two sample gaps being the variation recorded. Compensation is thus provided for uniform fouling of optical surfaces and for variations in lamp output. The instrument sensitivity can be varied from 100 to 100,000 mg dm^{-3} full scale. This monitor has the disadvantage that at low SS concentrations errors can be caused by the varying amounts of soluble colour within the sample.[41] There is another instrument which compensates for this by recording the ratio of scattered to transmitted light. This has a range of 10 mg dm^{-3} to 2,000 mg dm^{-3} full scale. Non-uniform fouling of the optical surfaces can unfortunately still cause great problems.[42]

A recent development[43] uses two lamps energised alternately (thus transposing the functions of the photocells used to measure scattered or transmitted light or the light transmitted through sample gaps of different length) and averaging the two outputs so obtained.

2.4.1.3 The measurement of pH

The glass electrode, is an established and useful analytical tool and as such is ideally suited for automatic monitoring systems.[31] The theory of operation of the glass electrode is well known and extensively covered in the literature.[44] The manufacturers of the more popular electrodes claim that with regular weekly cleaning the electrode will produce results to an accuracy of ± 0.1 pH units. This claim is challenged somewhat by various workers who found only a ± 0.3 pH unit accuracy with regular cleaning.[45] One particular worker[46] did not even obtain this accuracy although his situation does not seem typical.

2.4.1.4 The measurement of electrical conductivity

The dc conductivity cells now in use with the various monitors have been shown to be reasonably reliable under pollution monitoring conditions.[47] The theory of operation of conductivity cells is well covered in the literature.[48] The initial problems of calibration seem now to have been solved. The electrodes are unaffected by slime growth and this is one of the main reasons why they are regarded as one of the more reliable of water quality sensors. Even so, as with all the sensors, the sensors precision and the accuracy of its data are both directly related to the amount of cleaning and servicing the monitor receives.

2.4.1.5 The measurement of temperature

This operation has been automated by the utilisation of thermistors. Although these are more practical than thermometers their precision, according to some workers,[49] is not always up to the manufacturers specifications. One particular worker[50] has shown that only approximately 66% of the readings taken by the thermistor in his monitoring station were within the required accuracy of ± 0.5°C. This disadvantage can be in some part remedied by regular calibration checks and if necessary suitable adjustments.

2.4.2 Ion selective electrodes

The development of ion selective electrodes (ISE's) has added a new dimension to water quality monitoring. The ability to monitor specific ions within a watercourse, without the expensive and often inconvenient discrete sampling/ laboratory analysis, is a great step forward. The specific ions now capable of being measured using ISE's include Fluoride F^-, Chloride Cl^-, Cyanide CN^-, Nitrate $NO_3^=$ and Calcium CA^{++}.

There are five main types of ISE's[12] as shown in table T-2-4.

Table T-2-4

Electrode	Composition	Example
(a) Glass	Depends upon specialised glass	pH electrode (H^+)
(b) Solid State	With either membranes of single crystalls or pressed discs of appropriate material	Cyanide, Fluoride, Chloride, Sulphide, Lead
(c) Heterogeneous Membrane	Active constituent is disposed in an inert binder such as silicone rubber	Chloride, Sulphide
(d) Liquid ion-exchange Membrane	Three separate liquids form an interface within a rigid hydrophobic porous plastic support	Nitrate
(e) Sensitized	A sensitizing layer surrounds an ISE of one of the above types	Carbon dioxide, Ammonia, Sulphur dioxide and enzyme electrodes

Many ISE's have been utilised in monitoring situations due to their ease of automation.[51] It has been found that provided samples are maintained at constant temperatures and the samples and standards are measured alternately, a precision better than ± 10% can be achieved.[12] Table T-2-5 shows the advantages and disadvantages of ion selective electrodes in continuous monitoring.

Table T-2-5

(a) Electrode measurements are rapid.

(b) Coloured or viscous samples can be measured directly.

(c) In some cases, no sample pre-treatment is necessary.

(d) Electrodes can measure over wide ranges, in excess of ten orders of magnitude in some cases.

(e) Although the precision of electrode measurements is not as high as that of other analytical techniques the order of precision normally achieved i.e. ± 5 - 10% is normally adequate for pollution monitoring.

(f) ISE's measure activity, though they can be used to determine total and free ion concentrations.

Concentration values are usually of more significance than activity but in certain situations where the positions of chemical equilibria are required, activity measurements are much more useful. Such a case would be in the determination of the hardness of water.

2.4.2.1 The mode of operation of ion selective electrodes is dependent upon the development of a potential between the electrode and its reference electrode. This potential is in the order of millivolts hence usually necessitating the use of an extended range pH meter for accurate measurements. A more detailed account of the operation of an ion-selective electrode will be found later, in the section relating to the ammonia automatic monitor (2.5.3)

2.5 Types of monitoring systems available

There are two main types of continuous monitoring systems:

1) one which makes measurements without chemical modification of the sample;
2) one which makes measurements after suitable chemical reactions have taken place.

2.5.1 The land based multiparameter monitor is the major kind of instrument of the type 1 variety in use. This monitor receives water from the watercourse via a pump which can either be of a landmounted or submersible type.

Table T-2-3 outlines the attributes of the three most popular water quality monitors according to the manufacturer's specifications.

The monitoring stations are normally housed in vandal proof buildings with mains electricity.[31] Mains power is also a practical necessity for the continuous operation of the so called battery operated Plessey system.

There are more than fifty water quality monitoring stations in the UK,[21] the largest proportion of these being installed by the Severn Trent Water Authority. Only a very small number of installations are privately owned rather than Water Authority property. There are approximately seven stations in Wales with only four reported in Scotland. The most popular monitor is the EIL 7972 which accounts for more than half the total within the UK, closely followed by the Plessey MM5. The performance of these commercial monitors, within relatively unpolluted river systems, has been assessed by various workers,[31,45,52,53,54,55] the main conclusions being that provided maintenance and calibration work is performed on a regular basis the results obtained can be of reasonable reliability and reproducibility.

These conclusions, along with the obvious advantages of continuous monitoring, as mentioned previously, would seem to vindicate the initial capital expense incurred in setting up such monitoring systems, particularly within catchments where the water is used for potable supply.

2.5.2 The submersible water quality monitor is the obvious alternative to the land based variety when this has proven impractical, for example in an estuarine or reservoir situation. A two parameter submersible monitor has been developed[56] which will monitor temperature and dissolved oxygen. This is most suitable for work in remote areas where light-weight self-contained equipment, which can be easily camouflaged to prevent malicious damage, is required.

The monitor is fully automatic with a maximum battery life of six weeks before re-charging is required. It can operate at depths of up to 30 metres the data being stored within the instrument as a digital printout (in degrees Centigrade and percentage saturation) in real values on paper tape. This type of monitor has a number of particularly useful capabilities an example of one is the determination of oxygen and temperature profiles within estuaries and reservoirs.

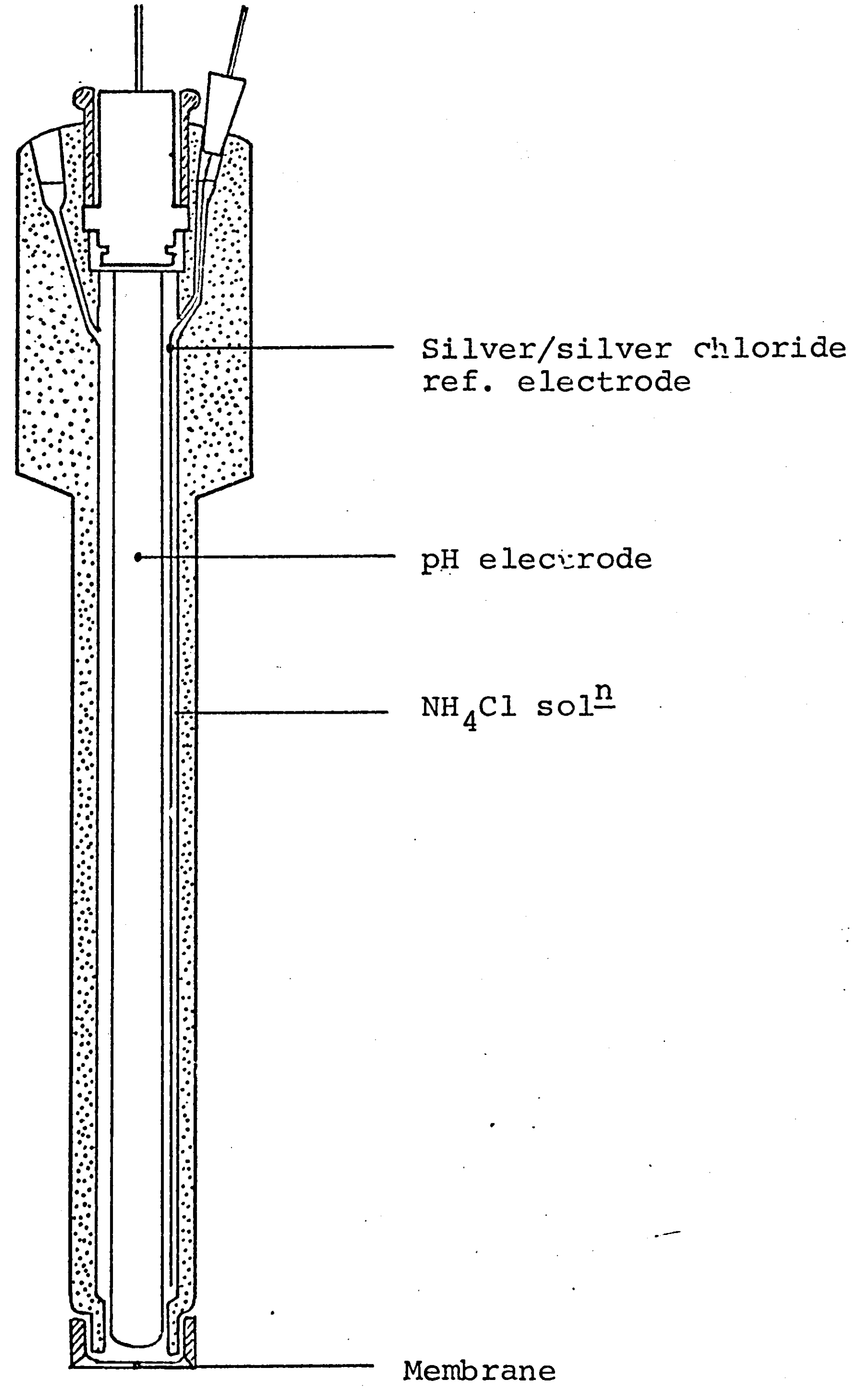
Development work has also taken place on a multiparameter submersible unit.[57] This includes sensors for the measurement of the five common water quality determinands (DO, T, SS, pH, and EC). The data from this monitor is recorded in serial ten-bit binary form on ¼" magnetic tape.[56,58.] Satisfactory performance has been reported in respect of three such prototype monitors installed in Lake Erie and Lake Ontario in Canada.[57]

2.5.3 Ammonia Monitor

Several methods for the continuous determination of ammoniacal nitrogen have been developed and tried in the UK.[59,60] Autoanalyser as well as coulometric techniques have been used with success,[16] but work is now being concentrated on the ammonia ion selective electrode monitoring systems.[61]

The Ammonia ISE, Fig.2-5 measures the undissociated ammonia within the sample. It develops a potential which is proportional to the logarithm of the activity of ammonia present. Dissolved ammonia in the sample solution diffuses

Fig. 2-5 An Ammonia electrode



through the membrane until the partial pressure of ammonia is the same on both sides of the membrane. In any given sample the partial pressure of ammonia will be proportional to its concentration. Having diffused through the membrane the ammonia dissolves in the internal filling solution and, to a small extent, reacts reversibly with water in the filling solution:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad \ldots\ldots\ldots(1)$$

The relationship between ammonia, ammonium ion and hydroxide is given by:

$$\left[NH_4^+\right] + \left[OH^-\right] \Big/ \left[NH_3\right] = \text{equilibrium constant K}$$

The internal filling solution contains ammonium chloride at a sufficiently high level so that the ammonium ion concentration can be considered fixed. Thus:

$$\left[OH^-\right] = \left[NH_3\right] \text{ x K}$$

The potential of the electrode, with respect to the internal reference electrode, varies in a Nernstian manner with changes in the hydroxide level:

$$E = E_o - S \log \left[OH^-\right]$$ where S is the Nernstian slope.

The sensing electrode is a modified glass electrode, its response to ammonia being given by:

$$E = E_1 - S \log \left[NH_3\right]$$

One major disadvantage of this electrode is that the samples have to be buffered to about pH 11, as below this, little or no free ammonia would be present within the sample solution. This buffering is beneficial, however, in that it removes the effects that other dissolved gases may have on the electrode. Results show that the ammonia electrode shows a precision and accuracy comparable with other accepted methods of analysis.[62]

2.5.4 Heavy Metal Monitoring

Recent work has indicated the possibility of the monitoring on a continual basis, of the heavy metal content of natural waters. One technique, based on anodic stripping voltammetry (ASV), is claimed to be able to reach concentrations as low as 10^{-10} molar.[63]

A different technique, based on the titration of sulphide ion with the heavy metal, followed by the highly sensitive and specific sulphide ISE, has shown promising results and could possibly lend itself to automation. Unfortunately at the present time metal ISE's have proven to be most unreliable as far as continuous monitoring systems are concerned. The need for frequent standardisation to achieve reasonable accuracy means that they cannot be left unattended for any length of time.[53]

An automatic ion selective monitor has been developed[64] for ions which can be determined quantitatively by an electrode. This monitor has the features listed in Table T-2-6.

Table T-2-6

(a) Peristaltic pump feeds sample to flowcell.

(b) The signal produced by the amplifier is continuous to a meter and a remote recorder output socket.

(c) Isolated output for telemetry or control can be provided.

(d) Automatic standardisation eliminates drifting.

(e) A manual standardisation facility is fitted.

(f) Process time of 30 minutes.

(g) Minimum maintenance required, weekly inspection and refilling of reservoirs.

(h) The monitor is adaptable to changing the electrode if a different parameter is to be monitored.

Much research into improving the performance of ISE's and the development of new ones is presently being undertaken worldwide. Research into the use of ISE's in water quality monitoring situations is being performed not only in Britain[51] but in Europe[10] and in the USA[9]. An example is the development in Belgium of a method of determining nitrate concentrations by means of an ammonia ISE. This was developed due to the unsatisfactory performance of the nitrate ISE.[31,65].

2.5.5 Organic pollution monitoring has been the subject of much recent research and development work.[66] Traditionally the analysis used to measure of the concentration of organic matter within a stream, was the biochemical oxygen demand test (BOD). This was originally devised as a means of assessing the quality of sewage effluents but has since been used almost universally for quantifying organic pollution.

In this test a sample is taken and diluted with oxygenated water, which in some cases has to be specially prepared[67], its dissolved oxygen concentration is then determined. The sample is then incubated at 20°C for five days after which the dissolved oxygen concentration is once again measured. The difference in dissolved oxygen concentrations being that quantity of oxygen used in the oxidation of organic matter by the micro-organisms present. This quantity of oxygen being then known as the BOD in mg dm^{-3}. Thus from the BOD of a sample, general information regarding the organic and microbiological content of the water, may be obtained. Although the BOD test is one of the most important water quality analyses it suffers from some unfortunate disadvantages.[68] These are outlined in table T-2-7 .

Table T-2-7 Disadvantages of the BOD_5 test

(i) On average only 70% of the organic matter is broken down in the five day period.

(ii) An incorrect indication of BOD is given if the concentration of dissolved oxygen and not the micro-organisms is the limiting factor. This is corrected for by dilution with oxygen rich water, which means that the oxygen demand must be known approximately beforehand.

(iii) If the water contains toxic substances, the analysis may fail owing to poisoning of the micro-organisms. The same poisoning can of course occur in nature.

(iv) If the appropriate micro-organisms are absent or deficient, they have to be introduced.

(v) The need to determine the dissolved oxygen concentration twice necessitates the use of much laboratory time and of skilled labour.

(vi) The test is not suitable for the control of treatment process due to its long time lag. The result of any analysis being reported too late in the event of any accidents.

(vii) The inability of the test to be successfully automated.

Although respirometry equipment is now available for the BOD analysis[69] the inherent disadvantages of the test have not been removed. It has been this inability to solve all the problems of the BOD test which has led to the development of alternative organic monitoring techniques and instrumentation.[68,70]

These recent advances include equipment to monitor total organic carbon (TOC), total oxygen demand (TOD) and chemical oxygen demand (COD).[68,71] These instruments have been shown to be extremely useful in the automatic monitoring of organic pollution,[72] some being capable of being used in an on-line mode, but due to the large capital expense involved and their need for considerable maintenance they are not at present widely used. There is however, one instrument, which assesses organic pollution by means of ultra-violet light (UV) absorption, which may be more practical in terms of cost and reliability for the continuous monitoring situation. This instrument, the WRC Organic Pollution Monitor (OPM) (H Tinsley & Co Ltd) was developed after much early work by Hoather[73] and later Bramer, Walsh and Caruso[74] where it was demonstrated that the optical density of samples at 275nm was closely proportional to the permanganate value (PV). Various other workers have compared UV light absorption with total organic carbon content, obtaining high correlations.[75] The performance of the OPM has been tested on sewage effluents, the results indicating reasonably high correlations of TOC, BOD and COD with the UV light absorption.[53]

2.5.6 Monitors which require chemical modification of the sample have proven to be most useful where repetitive measurements of natural and wastewaters are required.[76] In the USA water quality monitoring using a system monitoring twelve determinands sequentially has been in operation since 1967. The results are obtained colourimetrically after wet chemical reactions have been made. The initial results of this monitoring system were poor, due mainly to the presence of suspended solids which were not easily removable. This led to modificationsbeing made, with a subsequent analytical improvement.[58]

Chemical oxygen demand (COD) is a determinand the analysis of which has been subjected to much research, with a view to automation. The result being that a number of monitors are now available for its automatic determination.[77,78] The most popular one being the Auto-Analyzer which utilises the standard chemical analysis with colourimetric end point determination.[79]

COD has been regarded, for some time, as being a most important determinand for assessing organic pollution. It is a natural addition to the BOD, measuring the oxygen requirement of all the organic matter present rather than only that which can be oxidised by the micro-organisms. The test involves the boiling under reflux of the diluted sample with potassium dichromate and silver sulphate catalyst in concentrated sulphuric acid. The excess dichromate after two hours of refluxing is determined by titration with ferrous sulphate. Interference from chloride is suppressed by the addition of mercuric sulphate.

The great difference in the time necessary for a COD analysis when compared to a BOD test is one of the major reasons for its recent automation. Although it does not give the same information, it can be most useful when run in conjunction with the BOD test, in ascertaining an approximation of the degree of industrial organic pollution, by means of the COD/BOD ratio.[80]

Other important determinands capable of being monitored using auto-analysers include nitro-compounds for which a monitor has been developed by the US Army Environmental Health Agency.[81] Continuous monitoring of phenols and detergents is also possible using similar instrumentation. An autoanalyser has recently been developed which can perform seven different analyses simultaneously with a throughput of 40 samples per hour.[82] Work is presently being performed in the USA on the computerisation of multichannel auto-analysers to increase the productivity, accuracy and quality control in water samples.[83,84]

2.6 Conclusion

It appears that, even though there are many useful automatic monitors based on wet chemical methods, the major advances in continuous water quality monitoring will and have already come from the utilisation of electrochemical techniques. One such recent advance has been made in the electrochemical monitoring of cyanide, with the need for distillation of the sample to ensure specificity now no longer necessary.[85]

The electrochemically based monitors have the advantages of increased speed of analysis, precision and added suitability for on-line monitoring, a factor which will undoubtedly become more important with the inevitable increase in computerisation within the water industry.

CHAPTER 3

The Blackburn Brook Catchment

3.1 The Blackburn Brook is a tributary of the River Don, Fig. 3-1, rising to the north of Sheffield and flowing for approximately 13 km, until it meets the River Don at Tinsley. The Brook drains a catchment area of 41 km^2 with the aid of two major tributaries, Charlton Brook and Sheffield Lane Dike, and numerous minor ones. The catchment is essentially urbanised with heavy industry situated around the Chapeltown and Ecclesfield areas. It has a population of 27,700 persons with 11,090 dwellings,[86] it is estimated that by 1981 this will have risen to 18,000. There is considerable industrial and private housing expansion planned especially in the High Green and Chapeltown areas. The main development within the area over recent years has been the M1 motorway. It runs down the whole length of the catchment from Chapeltown to Tinsley. A major influence of the M1 upon the catchment is due to the fact that its drains run directly into the brook. Thus motorway effluents such as petrol, oil, lead and rubber all contribute to the overall pollution loading of the brook. In frosty weather a large amount of road salt is spread across the carriageways and eventually this also finds its way into the brook.

3.2 The reasons why the brook was chosen for study were numerous, the main ones being outlined in table T-3-1.

Fig. 3-1 The Blackburn Brook River System

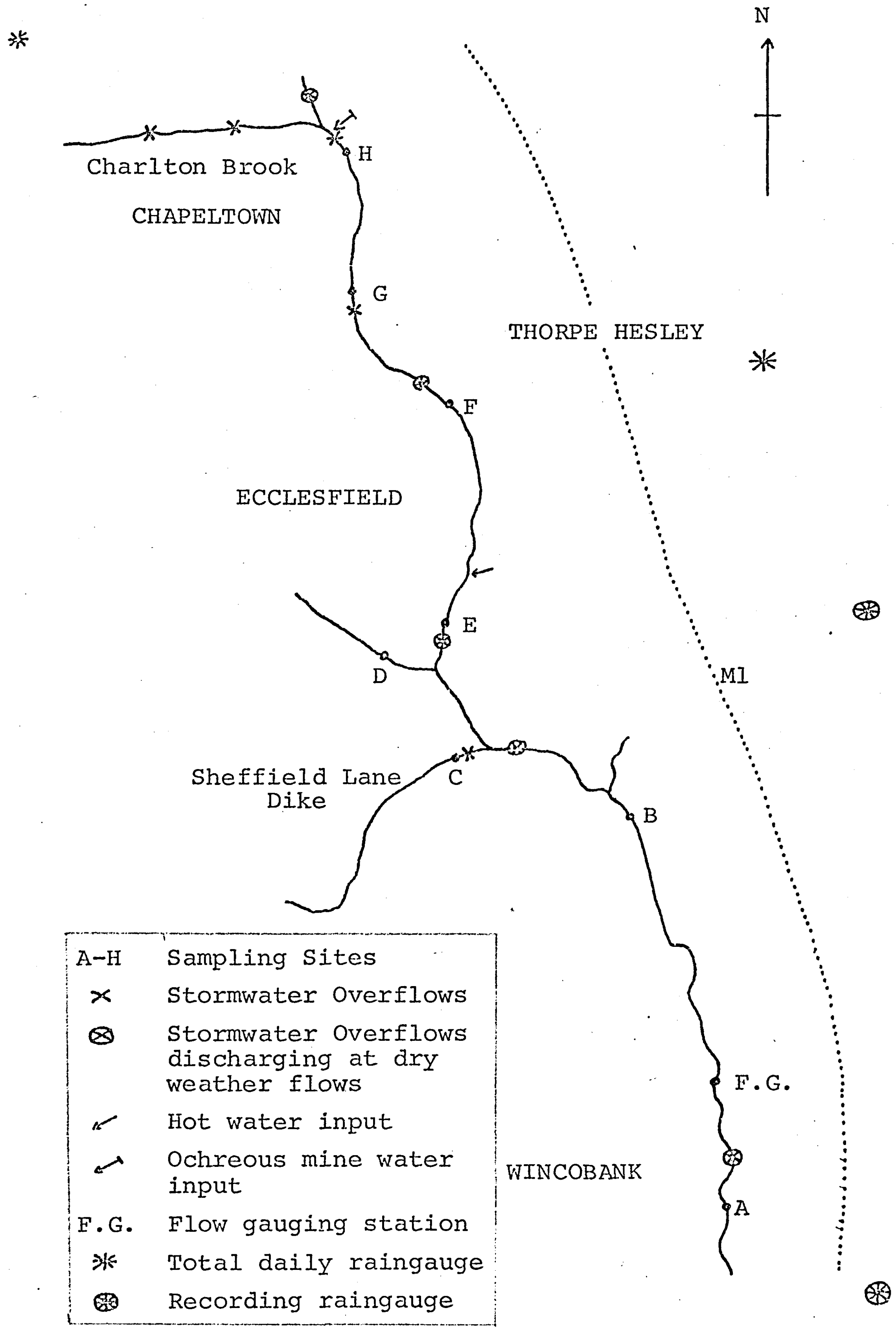
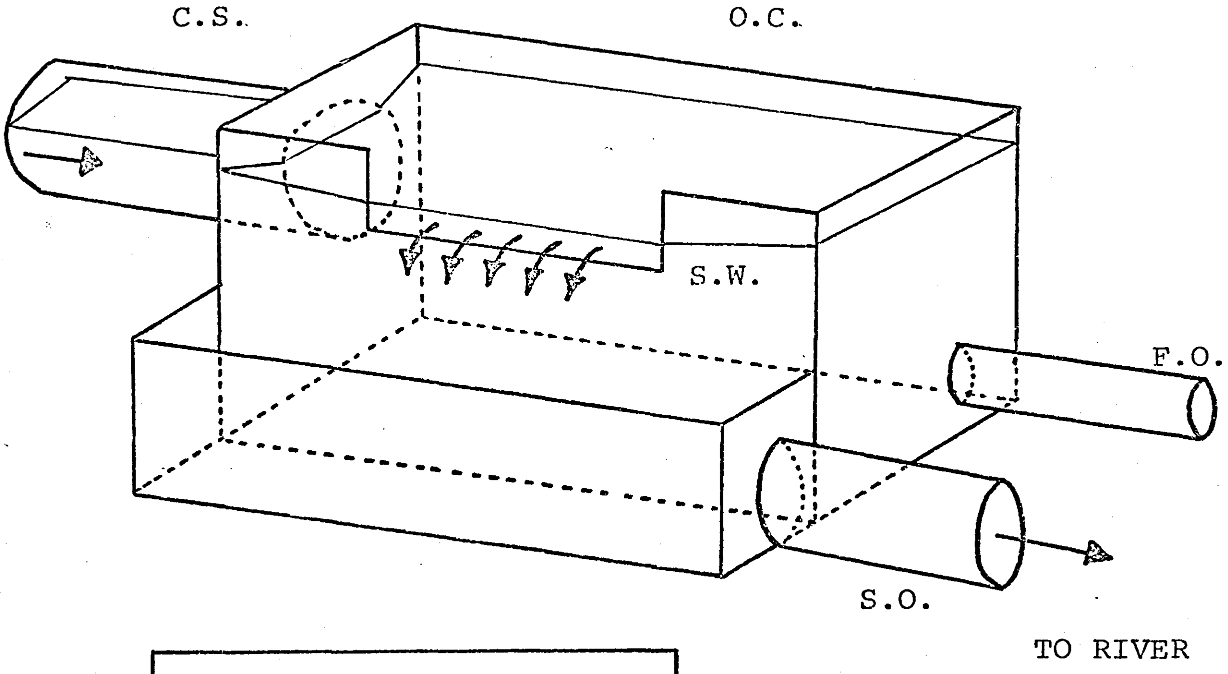


Table T-3-1 The main reasons for studying Blackburn Brook

i)	The presence of critical levels of both domestic and industrial pollution.
ii)	The suitability, with respect to size and type of the catchment, for possible water quality modelling.
iii)	The opportunity to site the monitoring station within the relatively secure confines of a downstream steelworks.
iv)	The availability within the monitoring site of an electricity supply and running water.

3.3 Pollution within the brook originates from two main sources, industrial discharges and sewage overflow. The domestic pollution enters the brook as raw sewage from grossly overloaded and in some parts damaged sewers, via storm water overflows (SWO's), Fig. 3-2. As would be expected from their name, SWO's are designed to discharge excess sewage flow during storm conditions, to the river or stream. The situation in this particular case is so bad that some of the overflows are discharging even during dry weather. The drainage area was originally sewered at the beginning of the century and was drained to sewage disposal works at Ecclesfield. The works were constructed in 1894 being extended in 1919, 1921 and 1924.[87] As a result of development in the area the works at Ecclesfield became inadequate to deal with the additional load. By 1940 the Authorities had to choose between expanding the existing works or abandoning them and conveying the sewage to the Sheffield works at Blackburn

Fig.3-2 DIAGRAM OF THE OPERATION OF A TYPICAL STORM WATER OVERFLOW



C.S.	COMBINED SEWER
O.C.	OVERFLOW CHAMBER
S.W.	SIDE WEIR
F.O.	FOUL OUTLET
S.O.	STORM OUTLET

meadows. On economic grounds it was decided to adopt the latter policy and a new trunk sewer was laid. This functioned as calculated until the present decade when due to large scale residential and industrial development numerous sections of the system became surcharged and SWO's began to operate prematurely. As an example, during storms it is not uncommon to see raw sewage oozing from the manholes in the centre of Chapeltown.[88] Raw sewage entering the Charlton Brook, a tributary of the Blackburn Brook, was claimed to have been an important factor in the unusually high incidence of Hodgkins disease within the area.[89] Hodgkins disease is a type of blood cancer the cause and transmission of which are still unknown. An enquiry[90] carried out by the Sheffield Health Department concluded that the overloaded sewage system and the polluted brook were not the cause of the high cancer figures as previously suspected, but it failed to ascertain what was.

The surcharging of the SWO's also leads to problems of industrial waste pollution. There are many diverse industrial complexes within the catchment which have Water Authority consents to discharge their wastes to sewer, but due to the state of the sewage system the wastes which have been legally discharged to sewer enter the brook in varying amounts via the surcharging overflows. This is not only a problem for the environmentalists, but due to the Brook water's natural utility, for the industrialists also. The brook waters are used for such industrial purposes as tank washing and cooling. The large pollution loading of the water means that expensive pre-treatment is usually necessary prior to use. As the pollution loadings increase so the cost of industrial pre-treatment increases, not to mention the increased hazard to public health.

In an attempt to alleviate these problems a new sewerage system is being constructed within the Blackburn valley. It will consist of a combined trunk sewer from Chapeltown to Blackburn Meadows Sewage Works, with various side sewers linking into it. It is not to take the place of the existing sewer but will operate in conjunction with it. Even though the new sewer will take sewage from areas not sewered by the existing system it is envisaged that its operation will remove the problem of water pollution caused by surcharging SWO's. The new sewer is expected to be in operation by late 1978.

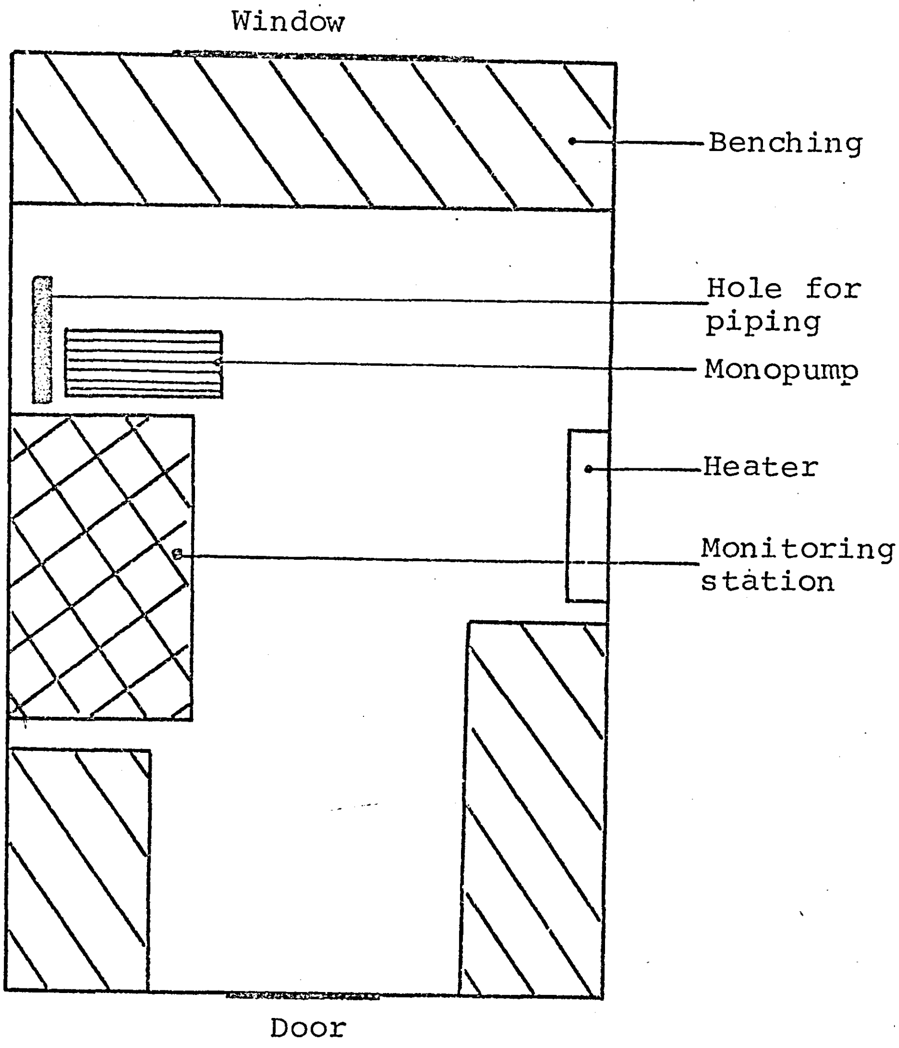
3.4 The water quality monitoring of the brook was performed by the use of two separate monitoring programmes. One programme was designed around a continuous water quality monitor, the other consisted of discrete sampling and analysis taking place at a number of preselected sites.

3.4.1 The continuous monitoring apparatus used throughout the project was a Plessy MM5, Land-based Continuous Water Quality Monitoring station,(WQMS) (The Plessey Co Ltd, Plessey Radar, Weybridge, Surrey, England). This was a self-contained piece of equipment which conbined all the hydraulic and electronic systems necessary to provide a monitoring station capable of being sited within any suitable shelter. In this particular case the monitor was installed inside a suitably modified site caravan, shown in Fig.3-3. The caravan was fitted with work tops and cupboards as well as wired for mains electricity, convector heating equipment was also installed. The monitor was installed over the wheel arches by means of special rubber shock mountings. In an attempt to prevent vandalism the only window in the caravan was fitted with a removable lockable wooden panel on the outside and the thin plywood door was covered with a solid piece of aluminium sheeting.

3.4.1.1 The monitoring site on the Blackburn Brook was obtained within the premises of Arthur Lee and Sons Trubrite works at Tinsley, Fig. 3-1. The brook flows in an open culvert at this point, the monitoring station being sited immediately below where the brook first enters the works. The water in the culvert is used by Lee's for acid tank wash purposes and so as to aid abstraction they dam the culvert by means of a Penstock sluice gate. This means that the water at the sampling point is usually at an artificial depth of approximately 2 metres.

3.4.2 The discrete sampling and analysis programme was undertaken to supplement the continuous one. It was thought that its operation would lead to a greater understanding of the water system as well as possibly quantifying and identifying the sites of major pollution. The programme consisted of the sampling and analysis of water taken from seven different sites upstream of the WQMS, Fig. 3-1. The sampling was performed with a weekly frequency throughout most of the monitoring period. Dissolved oxygen, temperature,

Fig. 3-3 Plan of Caravan and contents



pH and conductivity were all monitored in situ, with portable apparatus, the collected sample of approximately 250 cm^3 being later analysed in the laboratory for the other relevant determinands.

3.4.2.1 The discrete sampling stations were selected because of their position with regard to the major tributaries of the Brook, the main industrial complexes and the various access roads and pathways available.

1) Station H

This was situated in Chapeltown downstream of where the brook emerged from an underground culvert. The Brook at this point flows through a wooded area containing an old rubbish tip. A mine drainage pipe emerged from beneath this tip and ochreous water was seen to drain into the Brook immediately above H. Although the Brook flowed through the large Newton Chambers industrial complex before it reached station H, there were no major inputs into it from this factory. The Brook was quite shallow here with many rocks and domestic rubbish within it.

2) Station G

This also was situated in Chapeltown but unlike H was within a park, in the centre of the town. At this point the Brook was approximately three metres wide, quite shallow and relatively fast flowing. The

Brook flowed out of Chapeltown through agricultural land to station F.

3) Station F

By the time the Brook reached this site, six storm water overflows (SWO's) two continually discharging, had contributed to its flow. The water takes on a grey-brown colour and for the first time gives the appearance of being badly polluted. There were a few large rocks within the Brook, at this point, which became visible during low flow conditions. Usually the water was much deeper than it had been upstream and flowing with a reduced velocity. The rocks, when visible, were seen to be covered with a grey slime and at this point the Brook had a distinctive odour. Below station F the Brook entered Smithy Wood coking plant, where in the past stream water was used for washing the coal, the waste water being put straight back into the Brook. This practice is said to have stopped some years ago. The Brook flowed in underground culverts for most of its journey through the coking plant, emerging just prior to reaching A Lee & Sons, Ecclesfield. The seventh SWO was situated here and by the time the Brook reached station E it was classifiable as grossly polluted.

4) Station E

A rubbish tip was again sited next to the Brook, with A Lee & Sons, Ecclesfield on the other side. There were two SWO's immediately downstream one of these discharging continually even under conditions of dry weather flow. The water at this point was usually darker than upstream and it always was much warmer than at any other of the sampling stations. This fact led to an investigation upstream, which revealed a high temperature input from Smithy Wood coking plant. When conditions of low flow prevailed the bed of the Brook was seen to comprise layers of oily mud up to 0.75m in depth. The Brook then flowed past one or two smaller factories, one of these being Moorwood Vulcan.

5) Station D

This was situated on a small tributary of the Brook, it was narrow and usually fast flowing. The stream is biologically active in that weed and algae were seen to grow and thrive within its waters.

6) Station C

This was sited on the Sheffield Lane Dike. This stream had a number of land drains running into it and one major SWO. It was shallow and fast flowing, although its banks tended to be strewn with domestic rubbish as it flowed through the large housing estate of Shiregreen before reaching C. The confluence of this tributary with the Blackburn Brook showed how cloudy and polluted the Brook was. There was a distinctly visible clear-cloudy boundary between the two streams. The Brook at this stage was again flowing through agricultural land. Below the confluence with the Sheffield Lane Dike the Brook flowed over a weir of about two metres in height; foaming was seen to occur frequently at this point. The colour of the Brook was also subject to change from station E onwards; it has been known to be bright orange for quite some distance around this point. Below the weir there was an inlet from a tip drain, the effluent from which was black and highly noxious in nature. Immediately below this was another continually discharging SWO.

7) Station B

This station was at the site of an old weir which was only removed towards the end of the monitoring period. The water here was fast flowing and flowed over reasonably large rocks and the usual domestic rubbish. There was an input from a plating works, the colour of which ranged from bright red to blue. A SWO was also sited just below B, immediately above a scrapmetal works. The Brook flowed through the works down past GKN Shardlow, where it passed over two weirs, and finally through A Lee & Sons, Tinsley.

8) Station A

This was the site of the WQMS. At this point the water had been affected by three SWO's below station B and numerous drains, many leading directly from the motorway. The Brook at this point had a very low velocity, due to it being kept artificially deep by means of the penstocks downstream. It was always grey-brown in colour and the contents of the sewers were regularly seen to be present floating on and suspended in the water. The positioning of station A enabled a crosscheck to be made with respect to the WQMS data. It also meant that, as many more determinands were monitored in the discrete programme, a more detailed account of the water quality at this most important monitoring site could be obtained.

CHAPTER 4

Flow Gauging

4.1 Introduction

To fully appreciate the quality data obtained from both the discrete and continuous monitoring programmes, it is essential that the quantity of water involved is known.

4.2 Methods of flow gauging

There are various methods available for the determination of the flow within a stream[91] but there are only few capable of being used in a continuous mode.[92] All the methods utilise the relationship of flow to area and velocity. Since stream flow is measured in $m^3 s^{-1}$ it can easily be seen that it is a product of the cross sectional area of the water m^2 and its velocity ms^{-1}.

The velocity of the water can be measured by such techniques as:

(i) dilution gauging, where a dye or some other non-conservative substance is introduced into the water and its time of travel between two points is monitored;

(ii) velocity metering, where the velocity is measured across the stream by means of a mechanical water velocity gauge, the propeller of the gauge being inserted into the stream to approximately one third of the total depth, in order that a representative measurement may be taken.[93]

The method of flow gauging using the mechanical water velocity gauge involves measuring the depth of the water at each point across the stream where the velocity readings are taken. Thus, providing enough measurements are made, a profile of the stream can be produced. It is from this profile that the cross-sectional area of the stream is estimated and hence ultimately the stream flow determined. It can thus be seen that although this method provides a measure of the stream flow, it is not adaptable for use in any continuous survey of stream flow and its accuracy and precision is somewhat limited by the nature of natural stream beds and banks.

To overcome these disadvantages, especially with regard to the need for continuous flow measurements, much research has been performed.[94] One development from this research has been the ultra-sonic flow gauge,[91] this in theory is a great step forward although in practice the expense involved in purchasing and operating them, may be prohibitive to all but the larger Water Authorities.

The more common method of continuous flow gauging is the method involving the monitoring of the stage height of the water as it flows over a weir of regular dimensions. This monitoring of the height may be made intermittently by reading the height from a staging post within the stream or continuously by means of some form of water level indicator.[95]

If for some reason continuous flow monitoring is impractical or impossible to perform there is a technique, involving the use of unit hydrograph theory and the monitoring of rainfall, which can be used to produce stream flow estimates.

4.3 Unit Hydrograph Theory

Unit hydrograph theory is the most widely used method of predicting runoff from rainfall on natural catchments. The basic assumption is that a drainage area fed with a unit depth of effective rain, usually taken as 10cm, uniformly spread in time and space, produces a discharge hydrograph of a certain shape.[96] This is the T hour unit hydrograph where T is the effective rain duration. The system is linear and time invariant.

Other assumptions are that:

(i) the same rainfall, whenever applied, will produce the same hydrograph;

(ii) the runoff due to two or more different effective rainfalls is the arithmetic sum of the separate runoffs that would be obtained if the rainfalls were applied separately.

4.3.1 The production of a T hour unit hydrograph can be summarised as shown in table T-4-1.[97,98]

Table T-4-1

1.	Obtain hydrographs for fairly uniform storm intensities of the same duration.
2.	Separate the base flow from the surface runoff.
3.	Calculate runoff as mm depth on the catchment area.
4.	Divide the hydrograph ordinates by this value.

4.3.1.1 Storm hydrographs are produced by either monitoring the flow within the river system under various storm conditions, or by utilising past flow and precipitation records for the catchment under study.

4.3.1.2 Base flow separation is commonly achieved by drawing a straight line, AC, which begins when the hydrograph starts an appreciable rise and ends where the recession curve intersects the base flow curve, fig. 4-1. As this is an approximate method of separation it is important to be consistent when separating the base flows for different storms, so as to minimise the errors.

4.3.1.3 Effective rainfall volume is equivalent to the volume of direct surface runoff. This is determined by integrating the hydrograph curve after base flow separation, as shown in fig. 4-1. Usually the unit time of effective

Fig.4-1 Baseflow separation and Unit Hydrograph lagging procedure

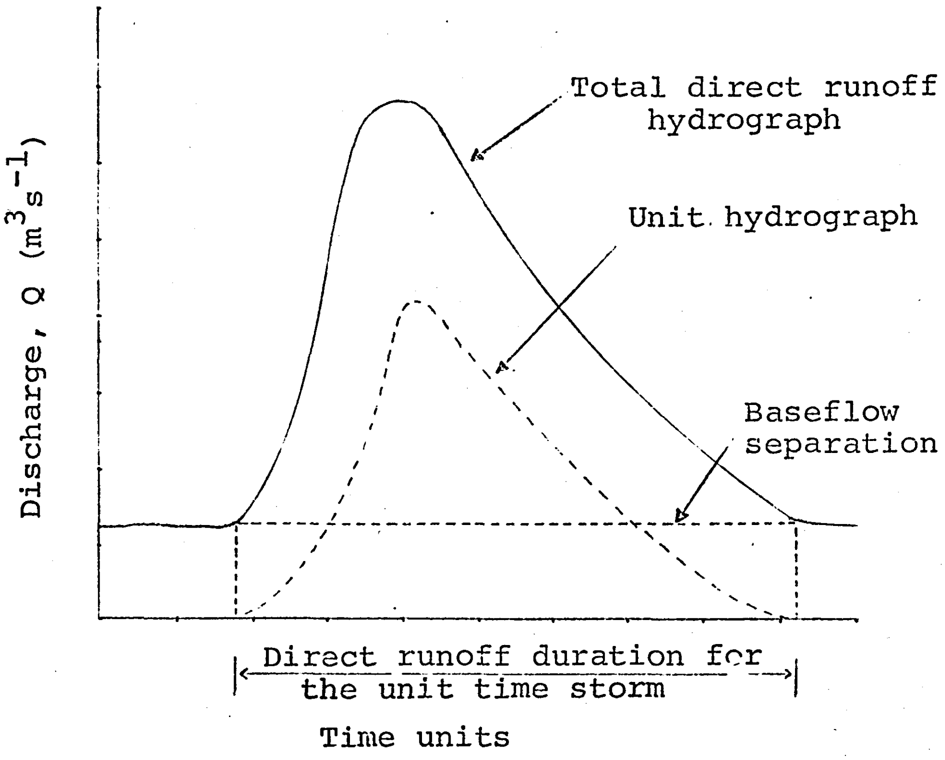
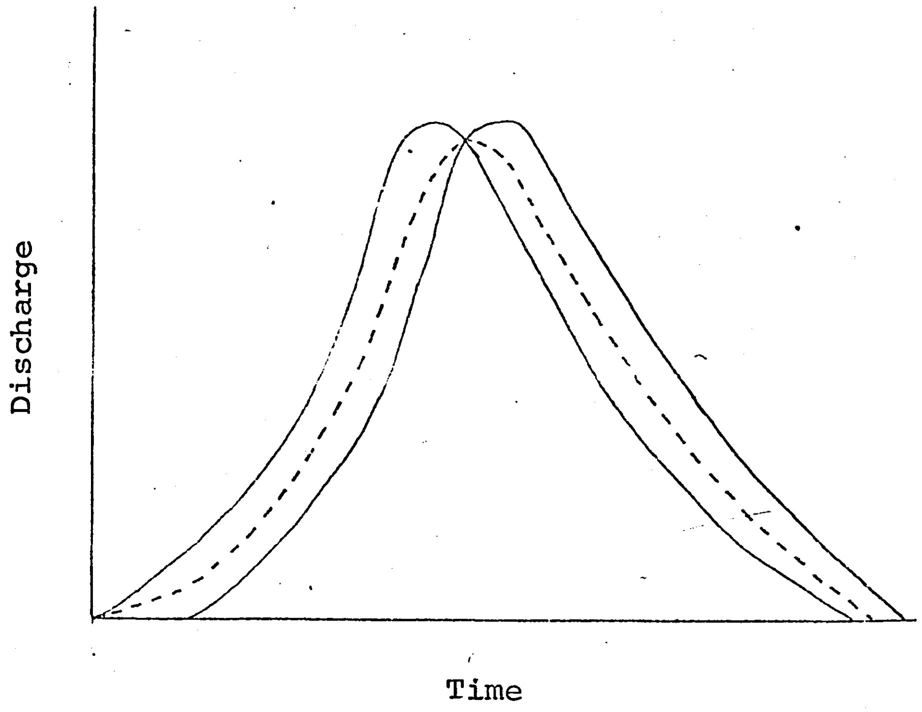


Fig.4-2



rainfall will be 1 day, 1 hour, 12 hours, or some other interval appropriate for the size of the drainage area studied.

4.3.1.4 Unit hydrograph construction is achieved by dividing the direct runoff ordinates (that is, total runoff - baseflow) by the effective rainfall volume. These values are then plotted to produce the T hour unit hydrograph. This then represents 10cm of direct runoff resulting from the rainfall occurring in T hours.

4.3.2 The utility of unit hydrograph theory may be summarised as:

(i) the synthesis of flow hydrographs for periods of increased storm duration;

(ii) the prediction of how a particular catchment reacts to a particular storm.

4.3.2.1 Flow hydrograph synthesis is usually performed by using either lagging or S-hydrograph methods.

4.3.2.1.1 The unit hydrograph lagging technique is based on the assumption that the linear response of the watershed is not influenced by previous storms. Thus it is possible to superimpose storms with the results being directly additive. For example, if a 1-hour unit hydrograph is available for a given watershed, a unit hydrograph resulting from a 2-hour storm can be obtained. The two 1-hour unit hydrographs are plotted with the second being lagged by 1 hour, the ordinates are added and then divided by two. Fig. 4-2 shows this technique and the resultant 2-hour unit hydrograph. This process can be performed ad-infinitum provided it is restricted to multiples of the original duration according to the expression

$$D^1 = 2^n D$$

where D^1 = possible durations of unit hydrograph

D = original duration of unit hydrograph

n = 1, 2, 3, ...

Thus it is not possible to mix a 1 h with a 2 h to produce a 3 hour unit hydrograph.

4.3.2.1.2 <u>The S-hydrograph method</u> overcomes the restrictions of the lagging techniques so allowing construction of any duration-unit hydrographs.[97] It is apparent that for a 1 hour unit hydrograph, the 10cm rainfall excess has an intensity of 10cm/h, whereas the 2 h unit hydrograph is produced by a rainfall intensity of 5cm/h. Continuous lagging of either one of these unit hydrographs is comparable to a continually applied rainfall at either 5cm/h or 10cm/h intensity, depending upon which unit hydrograph was chosen. For example, using the 1 h unit hydrograph, continuous lagging represents direct runoff from a constant rainfall of 10cm/h, as shown in Fig. 4-3. Cumulative addition of the initial unit hydrograph ordinates at time intervals equal to

Fig. 4-3 S-hydrograph lagging procedure and Unit hydrograph production

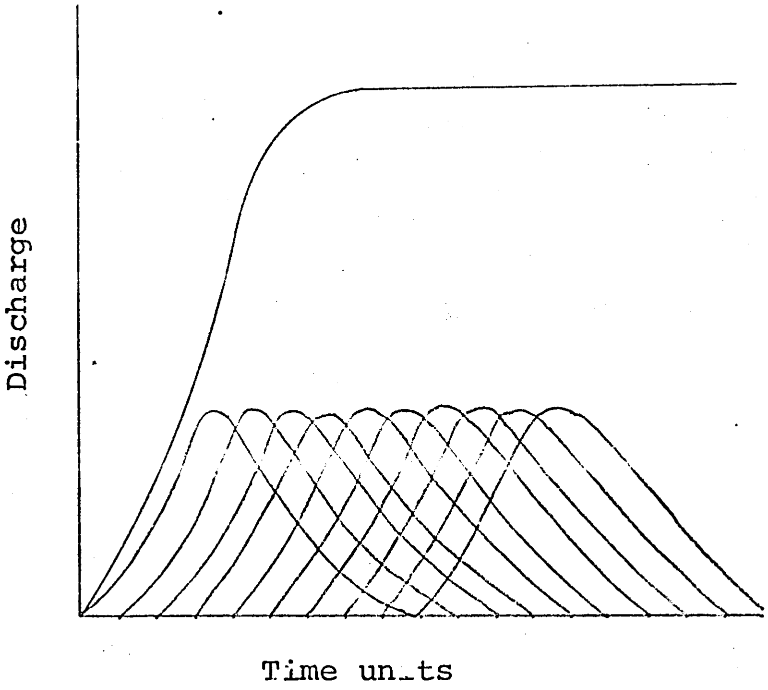
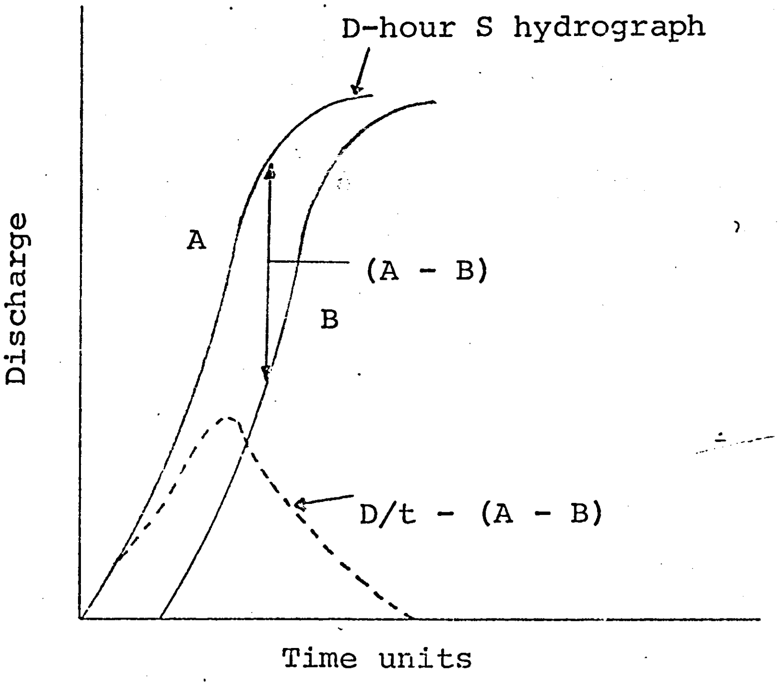


Fig.4-4



the unit storm duration results in an S-hydrograph. Once the S-hydrograph has been constructed, Fig. 4-4, a synthetic unit hydrograph can be produced by simply lagging the first S-hydrograph by a second, the time interval, t, being equal to the time of the desired duration. The difference in S-hydrograph ordinates is then multiplied by D/t, where D is the duration of the initial S-hydrograph.

With the advent of the digital computer an increased number of unit hydrograph syntheses are being performed by means of Matrix algebra methods.[99]

4.3.2.2 The estimation of stream reaction to a given storm may be achieved by utilising unit hydrograph theory. The procedure necessary to obtain estimates of river flows can be summarised as in Table T-4-2.

Table T-4-2

i) Obtain unit hydrographs of the particular watercourse for a variety of storms of differing intensities and duration.

ii) Monitor the rainfall within the catchment.

iii) Calculate the effective rainfall for the particular storm under study, using the equation defined in the Flood Studies Report.[100]

iv) The particular unit hydrograph corresponding to the conditions of the storm under study is selected. The ordinates of this hydrograph are multiplied by the effective rainfall. The base flow prevalent at the particular time is then added, resulting in the production of the synthetic storm hydrograph.

4.4 The flow gauging of Blackburn brook

Although velocity metering was performed at various sites on the brook it was decided that a continuous record of stream flow was necessary to compliment the continuous water quality record. Thus a continuously recording flow gauging station was constructed and sited on the brook. It comprised of an Ott type R16 continous vertical water level indicator (Smail Sons and Co Ltd, Glasgow) mounted upon a 30cm diameter plastic tube, upstream of a double crested rectangular weir. The station was sited within the premises of G K N Shardlow, (Fig. 4-5). The recorder operated by means of a 32 day clockwork motor, the trace being recorded on chart paper, the whole mechanism being enclosed in a weather and vandal proof case. The weir was chosen as the station's site because of its hydraulic characteristics and its proximity to the monitoring station.

4.4.1 The transposition of gauge heights into flows

was initially performed by means of a calibration curve. Six gauge heights were selected, the respective flows being calculated by means of the standard hydraulic equation,[101]

$$Q = \frac{2}{3}\sqrt{\frac{2}{3}g}\, b\, C_D C_V H^{\frac{3}{2}} \quad \text{.........} \quad (4\text{-}1)$$

where Q = stream flow m^3s^{-1}

H = gauge height m

g = acceleration due to gravity, 9.81 ms^{-1}

b = total width of weir, m

C_D, C_V = coefficients calculated from the weirs dimensions.

Fig. 4-5 Recording Depth Gauge and Position in Brook

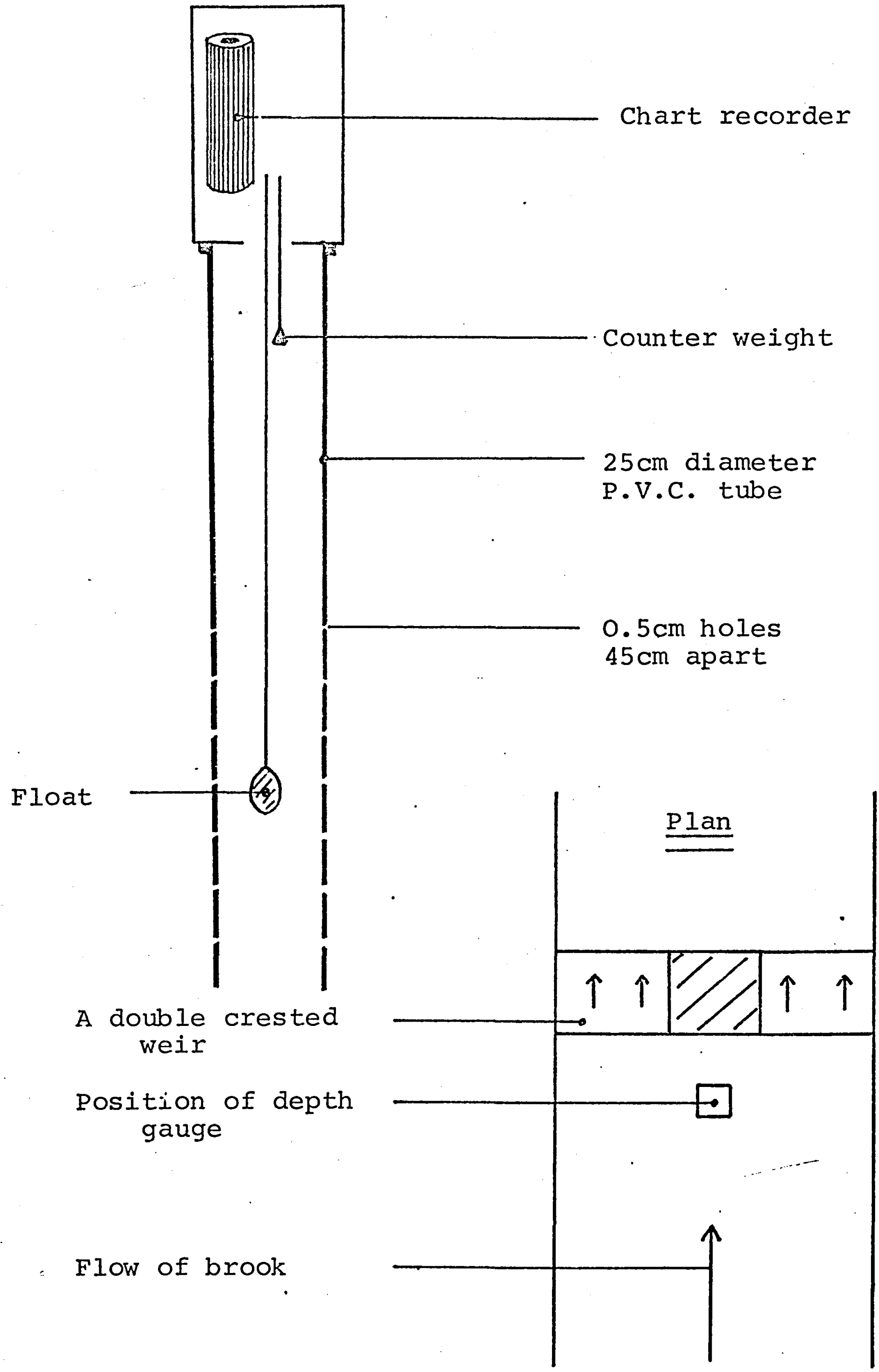
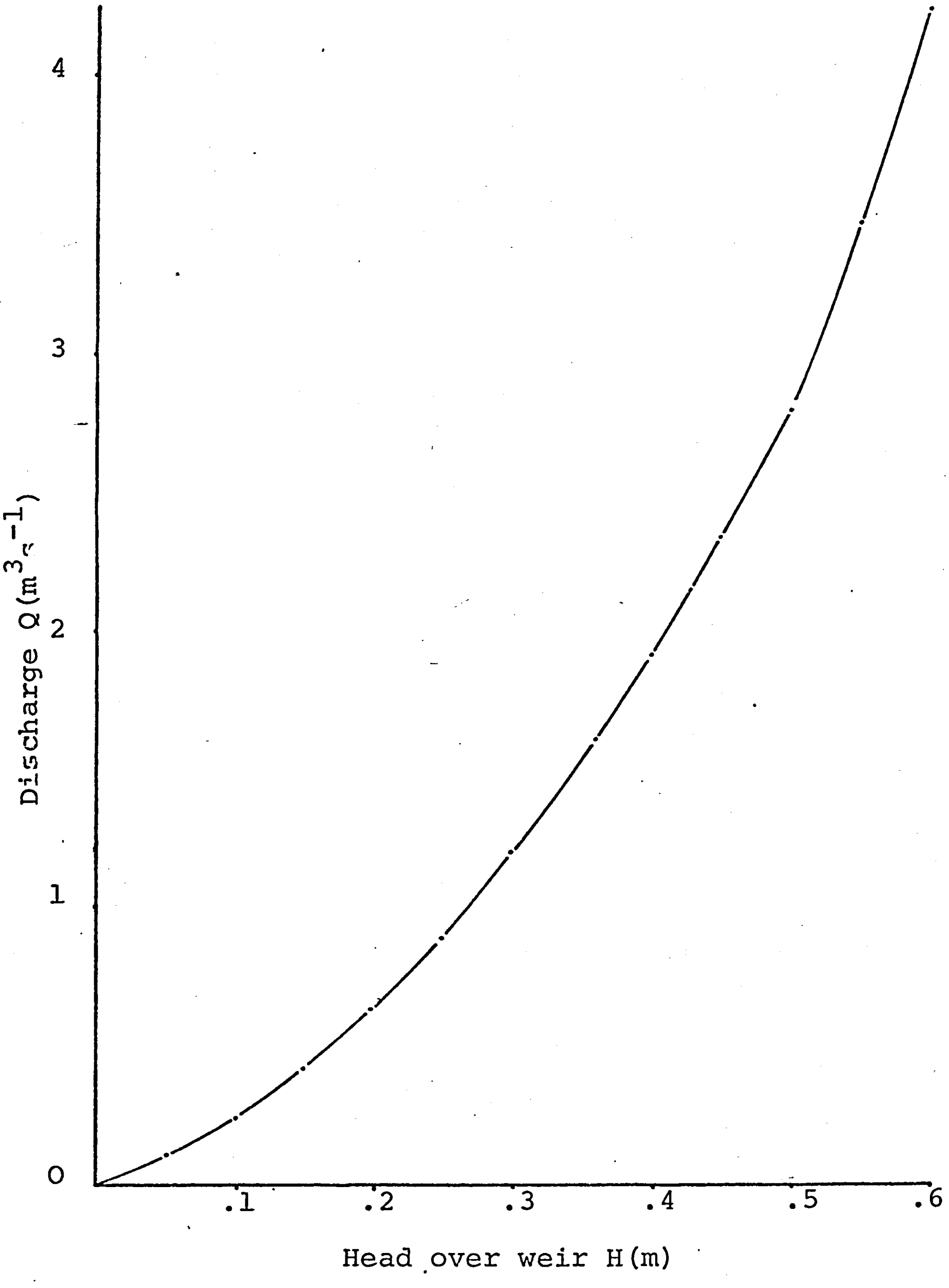


Fig.4-6 Calibration curve for the double crested weir



The calibration curve obtained, Fig. 4-6, proved to be exponential hence its utility was somewhat limited. It was decided that the most efficient way of transposing the gauged heights into flow measurements, was by means of a computer program. This would enable large numbers of transposed flow measurements to be obtained quickly and with a high degree of precision. The use of equation (4-1) within the program was justified by comparing its performance with that of another method of flow measurement.

4.4.2 <u>The testing of the transposition method</u> was achieved by comparing flow data obtained using equation (4-1) with data obtained from velocity measurements over one section of the double crested weir. Table T-4-3 outlines the results of the comparison of the two methods. It was decided that although the equation method tended to give slightly higher flow readings, the correlation between the two sets of results was sufficiently high for the required comparison. The main errors inherent in the velocity gauging technique are:

i) the inability to accurately measure the stream velocity for the whole cross sectional area of the flow over the weir;

ii) the velocity measurement under low flow conditions when the head over the weir is small;

iii) 'systematic' errors in either the velocity gauge or its use, or both;

iv) any factors, such as debris upstream, which affect the velocity distribution across and through the stream.

The 13.3% difference in the lowest flow readings was explained by the increased error involved in obtaining velocity readings under conditions of small stage height.

The equation method of flow measurement also, as would be expected, has some sources of error. The most important being the precision of the head measuring device and the determination of the gauge zero. Thus since the equation method compared favourably with the standard velocity gauging technique and as it was more compatible with the computer techniques being used, it was chosen as the flow gauging method.

4.5 Flow estimation for the period prior to flow gauge installation

The flow gauge was not commissioned until January 1975, thus there was an eleven months gap inbetween the beginning of quality monitoring and that of quantity monitoring. In order that the stream flows would be available for this period a method of flow prediction based on the unit hydrograph theory[97] was employed.

Table T-4-3

Comparison of equation method and velocity gauging method for flow estimation

Date	Velocity ms^{-1}	Mean height m	Flow (V) m^3s^{-1}	Flow (eq) m^3s^{-1}	% difference
24.3.76	0.75	0.05	0.094	0.10	6.25
2.4.76	1.00	0.125	0.313	0.325	3.85
23.4.76	0.065	0.04	0.065	0.075	13.30
28.5.76	0.80	0.075	0.150	0.150	0
31.5.76	1.25	0.200	0.625	0.650	3.80

Average % difference for the five tests = 5.44%

4.5.1 Climatological monitoring of the catchment was performed in order that the meteorological effects upon the water quality of the brook could be studied. This monitoring comprised the commissioning of a recording rainfall gauge at a site centrally positioned within the catchment and affording reasonable security for the instrument. The rainfall was recorded on a clockwork drum chart recorder, which rotated with a daily frequency. In conjunction with this data additional continuous rainfall records were obtained, from a gauge sited at a lower point within the catchment. This gauge was the property of the Yorkshire Water Authority and was sited within the Blackburn Meadows Sewage works.

The rainfall volumes were transposed from these chart records and stored on computer disk files for future use in relation to the water quality and quantity data analysis. Further data was obtained so that a comprehensive rainfall record for the whole catchment could be achieved. This data was recorded by the Water Authority using two total daily rainfall gauges, one sited at Wortley which is to the north of the catchment, the other at Thorpe Hesley which is centrally positioned to the east (see Fig. 3-1).

The increase in flow during storm conditions is not directly proportional to the total rainfall but to the total effective rainfall. This is the amount of rain which actually enters the river system as runoff. The amount of runoff is a function of the prevailing climatological conditions and the physical characteristics of the catchment. The effective rainfall can be calculated from storm hydrographs, as it represents the area under the hydrograph after base flow separation. If storm hydrographs are not available, as was the case for the period February 1975 to January 1976, another method of effective rainfall estimation has to be employed.

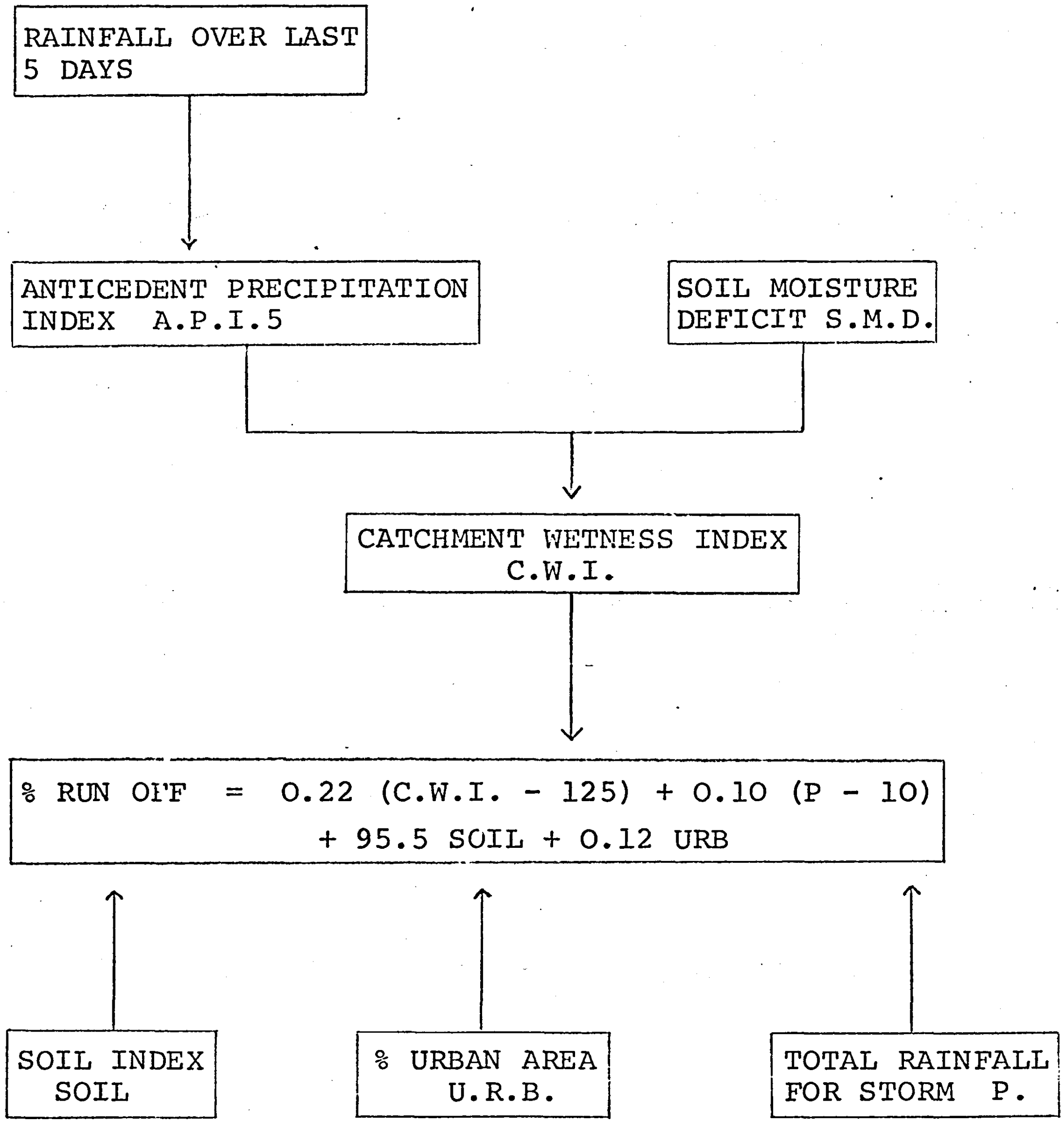
4.5.2 The flood studies report of 1975 contains a set of empirical equations based upon studies of various catchments of different types and sizes.[100] These equations enable the percentage total runoff to be calculated and hence the effective rainfall volume. The calculations are dependent upon the seven parameters outlined in Table T-4-4, see Fig.4-7.

Table T-4-4

i)	P	The quantity of rainfall for the storm studied, (mm).
ii)	Pd-n	The total rainfall for the past five days, that is where n = 1 to 5.
iii)	SOIL	The soil index of the catchment.
iv)	URB	The % urbanisation within the catchment.
v)	S.M.D.	The soil moisture deficit within the catchment.
vi)	A.P.I.$_5$	The Antecedent precipitation index.
vii)	C.W.I.	The Catchment wetness index.

The soil index (SOIL) for the catchment is taken as being a constant and relates to the capacity of the soils present to absorb the rainwater hence producing a lagging effect with respect to runoff. It is calculated from the equation:

Fig.4-7 THE ESTIMATION OF % RUN OFF



$$\text{SOIL} = \frac{0.15\ S1 + 0.3\ S2 + 0.4\ S3 + 0.45\ S4 + 0.5\ S5}{S1 + S2 + S3 + S4 + S5}$$

where S1 to S5 are values given to the five common types of soil. It is obviously unlikely that each soil type will be found in every catchment. The soil index (SOIL) for the Blackburn brook catchment was calculated from soil maps and soil type values present within the flood studies report,[100] the value was found to be 0.34.

The percentage urbanisation within the catchment was calculated from Ordnance Survey maps. It was assumed that impermeable areas such as pavements, roads and roofs provide 100% runoff. A figure of 20% urbanisation was estimated in this way, this value was the same as that subsequently calculated by the Yorkshire Water Authority.[102]

The Antecedent precipitation index (A.P.I.5) takes into account the rainfall conditions over the previous five days. This is an important factor as it relates to the extent of runoff already taking place prior to the start of the particular storm under study. This was calculated from the equation

$$\text{A.P.I.5} = 0.5^{\frac{1}{2}}(Pd\text{-}1 + 0.5Pd\text{-}2 + (0.5)^2 Pd\text{-}3 + (0.5)^3 Pd\text{-}4 + (0.5)^4 Pd\text{-}5)$$

where Pd-n was the total rainfall for the previous days from n = 1 to n = 5.

The Soil Moisture deficit (S.M.D.) was obtained from data published weekly by the meteorological office. The S.M.D. is a quantitative assessment of the demand for water, within the catchment's vegetation. It is calculated for the generalised catchment having 50% short rooted vegetation, 30% long rooted vegetation and 20% riparian land (where the permanent groundwater is so close to the surface that evaporation is always assumed to take place at the potential rate and no deficit is set up).

The Catchment wetness index was thus calculated from a knowledge of the A.P.I.5. and the S.M.D. by the equation:

$$\text{C.W.I.} = 125 + \text{A.P.I.5.} - \text{S.M.D.}$$

When all seven parameters were either calculated or determined they were fitted to the empirical equation:

$$\text{Vmm} = 0.22(\text{C.W.I.} - 125) + 0.10(\text{P} - 10) + 95.5\ \text{SOIL} + 0.12\ \text{URB}$$

where Vmm was the % runoff where P was expressed in millimetres. This was then converted into metres of effective rainfall, V, by

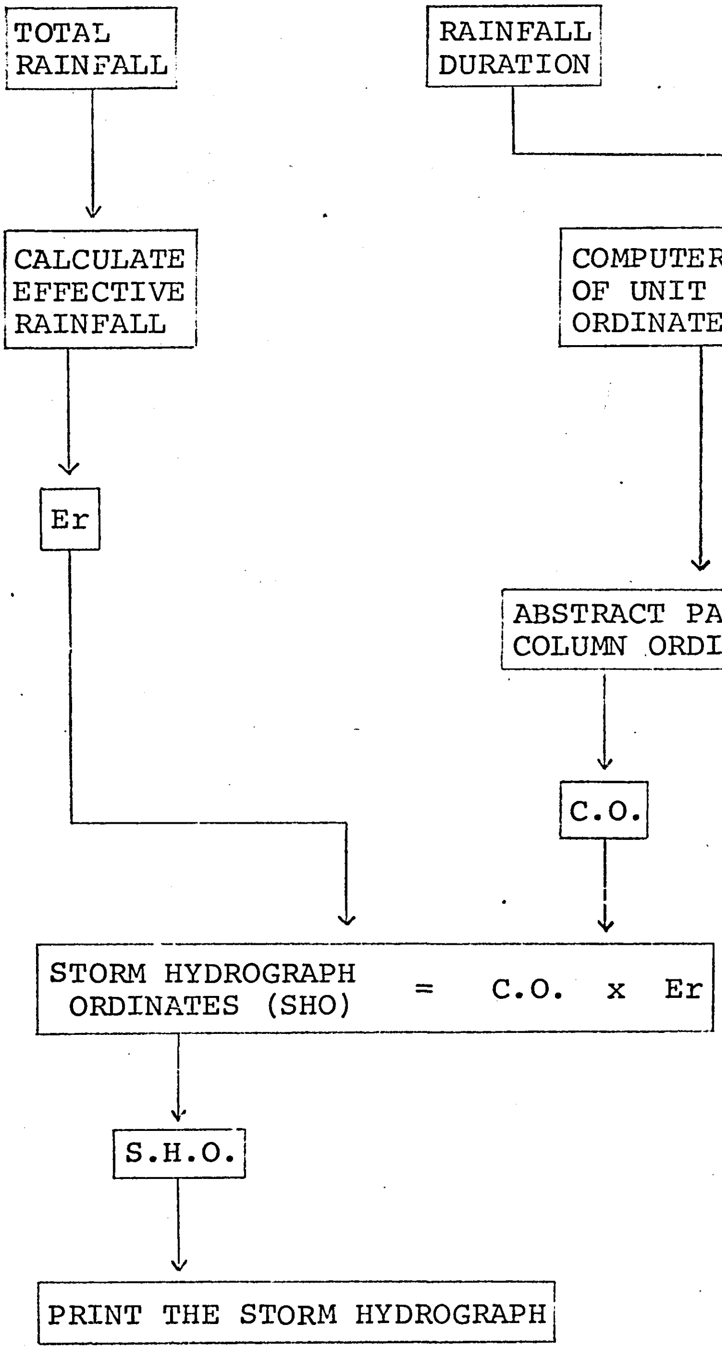
$$\text{Vm} = (\text{Vmm}/100) \times \text{P}$$

$$\underline{\text{V} = \text{Vm}/1000}$$

The equations necessary for the calculation of V, as described, were incorporated into a computer program Floest (see Appendix A), a schematic representation of which is shown in Fig.4-8.

Fig. 4-8 A SCHEMATIC DIAGRAM OF THE FLOW MODEL DEVELOPED FOR THE BLACKBURN BROOK CATCHMENT

FLOEST

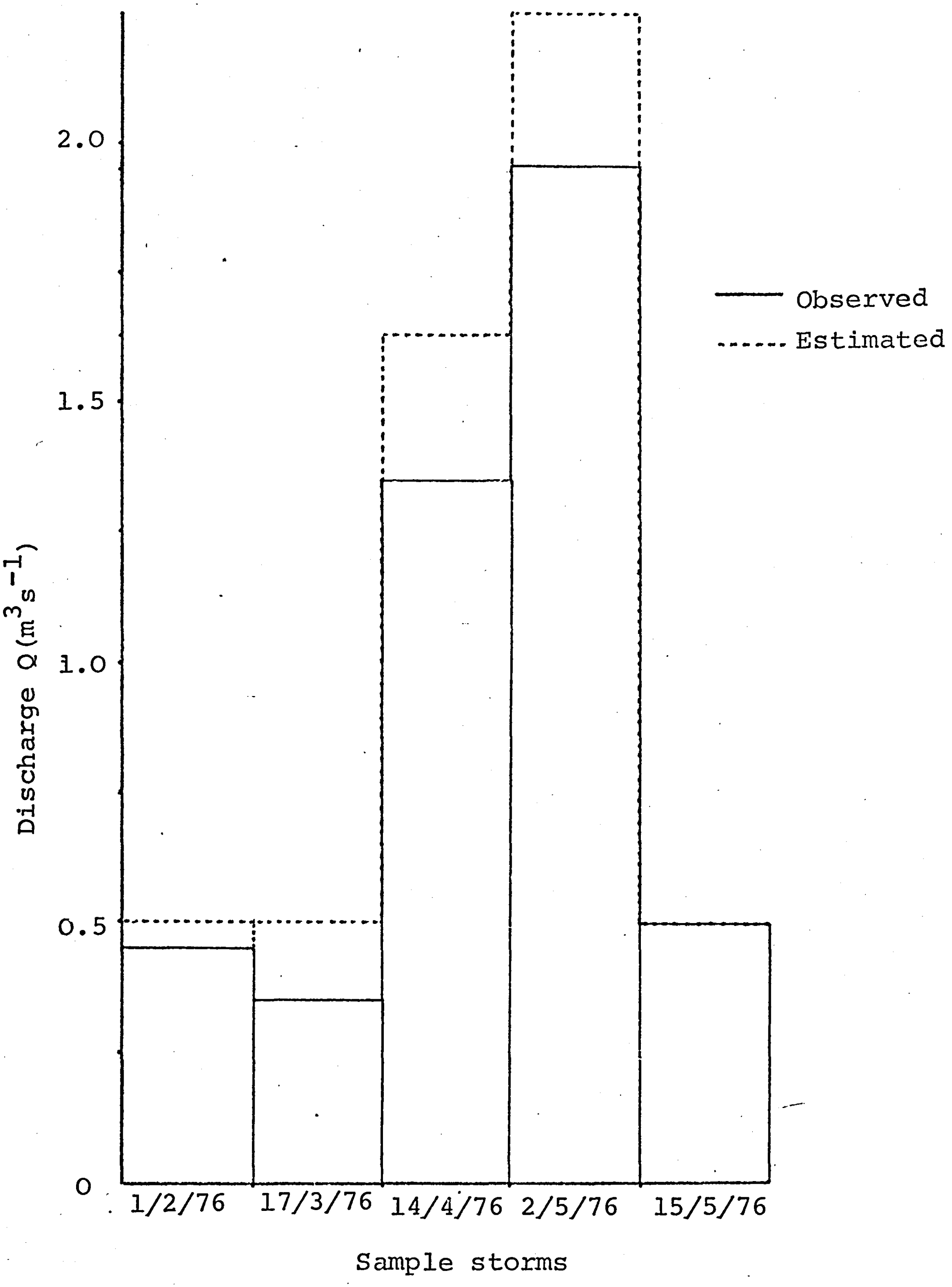


4.5.3 Floest utilised computer disk files of unit hydrograph ordinates. Unit hydrographs were produced for a range of rainfall intensities and durations, using S-hydrograph lagging techniques,[97] and held on disk. The program calculated the effective rainfall V for any storm, and subsequently selected the correct unit hydrograph for the specified storms intensity and duration from the disk files. The ordinates of the unit hydrograph were then multiplied by V, the result being added to the base flow. The estimated storm hydrograph ordinates were then printed as m^3s^{-1} of flow.

The validation of these flow estimates was performed using flow data obtained from the flow gauging station. It was discovered that over a sample range of flow conditions, as shown in Fig. 4-9 , the estimated and observed flows were within acceptable levels of agreement.

On the successful completion of Floest's validation, stream flows were estimated for the period February 1974 to January 1975 being subsequently stored along with the observed flow data.

Fig. 4- 9 The Validation of FLOEST against observed flow data for sample storms.



CHAPTER 5

Mathematical Modelling

5.1 Introduction

Mathematical models are small scale representations of large systems, expressed in mathematical terms; it is their ability to reduce the scale of the system, particularly the timescale, that makes them so valuable. Models provide the user with the ability to simulate the behaviour of the real system 'before the event'. The effects of variations within the system can be tested even though such changes need not have occurred. A model may consist of a set of equations, a computer program (or suite of programs), or a more visual representation, for example, a nomogram.[103]

5.2 Model Types

5.2.1 Deterministic models seek to describe the system in more or less real terms.[104] Given input data, the model generates a response or simulation that describes the behaviour of the system in space and/or time. An ecological model,[105] which describes the annual cycle of algal growth and productivity within a reservoir, is an example of such a model.

5.2.2 Stochastic models are used to transform inputs of random character into quantifiable expressions of measures of uncertainty, for instance, probability or reliability.[106] This type of model allows for a prediction of the likelihood of an event occurring at a future date. Hydrologists use such compartmental models to mirror detailed flow behaviour.[107] Such a model using time-series analysis can infer rainfaill runoff, directly from the observed data, the data being obtained by methods of statistical inference.

5.3 Statistical Models

Statistical techniques are of immense value to modellers, in that they allow the isolation of the most important aspects of a system, by reducing its complexity.[108]

A particularly useful method of achieving this end is by utilising regression analysis techniques.[7]

5.3.1 Linear regression models are a particular type of statistical model, based on the concept of regression analysis. They are used to described the dependence of one variable Y on one or more variables X,[110] and often to predict the value of Y from a knowledge of X. Figure 5-1 is a schematic representation of a linear regression model, $Y = \alpha + \beta x + \varepsilon$ where ε is the random error element. It shows the normal distribution of Y about the regression line $\alpha + \beta x$, the standard error of the estimate σ_e and the mean value of Y, μ, for the three particular values of X.

5.3.1.1 The least squares method of line fitting is a most useful and efficient technique, for the production of the required line,

$$Y = a + bX \qquad \text{..................} \qquad (5-1)$$

Fig. 5-1 Schematic representation of a linear regression model

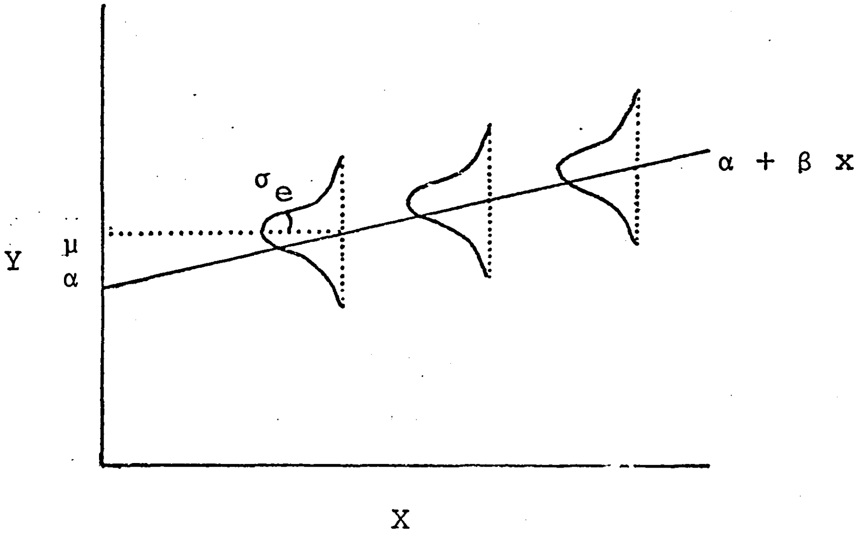
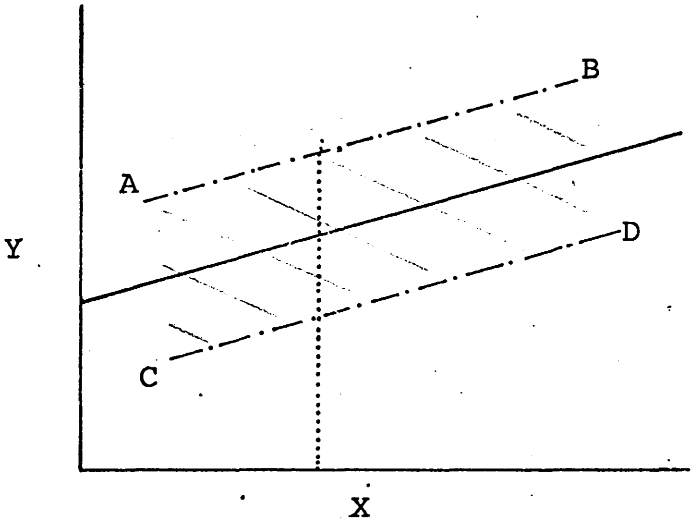


Fig. 5-2 Confidence zone about a regression line



Y is an estimate of μ, the true mean of all possible y_i values at a given point on the X scale and a, b are estimates of the parameters α, β (intercept and slope respectively).

The least squares line can be defined as being the two dimensional equivalent of the arithmetic mean.[110] The method requires the derivation of two simultaneous equations soluble for slope and intercept. It is required to find values of a and b for which $\Sigma\ (y_i - Y_i)^2$ or S is a minimum and therefore for which ds/da and ds/db are zero.

Hence $S = \Sigma\ (y_i - a - bX_i)^2$ or $\Sigma\ (y_i - a - bx_i)^2$ as $x \equiv X$.

$$\therefore\ S = \Sigma\ (y_i^2 - 2ay_i - 2bx_iy_i + a^2 + 2abx_i + b^2x_i^2)$$

Adding the squares for the sample of n pairs of values gives

$$S = \Sigma y_i^2 - 2a\Sigma y_i + 2ab\Sigma x_i - 2b\Sigma x_iy_i + b^2\Sigma x_i^2 + na^2 \quad \ldots\ldots (5\text{-}2)$$

Differentiating this with respect to a and equating to zero we obtain

$$dS/da = -2\Sigma y_i + 2b\Sigma x_i + 2na = 0$$

thus, $a = \Sigma y_i/n - b\Sigma x_i/n$

$$a = \bar{y}_i - b\bar{x}_i \quad \ldots\ldots\ldots\ldots\ldots\ldots (5\text{-}3)$$

Differentiating with respect to b and equating to zero gives,

$$dS/db = 2a\Sigma x_i - 2\Sigma x_iy_i + 2b\Sigma x_i^2 = 0$$

from which, after substituting for a in terms of equation (5-1) and putting $n\bar{x}_i$ for Σx_i where necessary,

$$b = (\Sigma x_i y_i - n\bar{x}_i y) / \Sigma x_i^2 - n\bar{x}_i^2$$

Thus the two unknown factors a and b can be calculated from the measured variables x_i and y_i.

The sample estimate of μ is Y which equals $\bar{Y} + bx$. Thus the predicted value of an individual $Y = Y_i = \bar{y}_i + bx_i$. The error within this prediction, that is $y_i - Y_i$ can be expressed as in equation 5-4, since $y_i = \alpha + \beta x_i + \varepsilon$

$$y_i - Y_i = (\alpha - \bar{y}_i) + (\beta - b)\ x - \varepsilon \quad \ldots\ldots\ldots\ldots (5\text{-}4)$$

The random element ε is an additional source of uncertainty to the error elements of the regression line itself. The error in the actual line can be expressed as

$$Y - \mu = (\alpha - \bar{y}_i) + (\beta - b)\ x$$

Thus the errors involved in the use of a regression model include a slope error, and consequently an intercept error and a random element error. This does not include any error within the independent variable x. As no instrument or manual measurement technique is perfect the assumption of the model equation being $y = \alpha + \beta x + \varepsilon$ is unrealistic. It would be more realistic to view the model as in equation 5-5,

$$y = \alpha + \beta X^1 + \varepsilon \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5\text{-}5)$$

where $X^1 = x + e$, e being the error in the measurement of x.

The number of independent differences, $\hat{Y}$, provided by the data after fitting the line is n - 2 and the division of $\Sigma\hat{Y}^2$ by the number of degrees of freedom gives an unbiased and most efficient estimator, S_e^2, of σ_e^2 (the variance from which confidence limits for the parameters can be found).

Thus when applied to the derivation of a linear relationship the method of least squares is particularly useful. It has many advantages including the ease of computation and its efficiency in obtaining the line which usually gives a better fit to the true line than those obtained by other methods.

5.3.1.2 Tests of significance and confidence limits, are an important aspect in the development of regression models. The production of a parameter estimate from the regression model poses some important questions. The first being, within what limits may the value of the parameter be expected to lie? The second being "Is it reasonable to suppose that the latter has some particular value?". The first question can be answered by stating 'confidence limits' which have a chosen probability of embracing the true value. The second question is answered by applying a 'test of significance'.[111] This examines whether the probability of the difference in the value of an estimator and the hypothetical value of its parameter being due to chance, is greater or less than some chosen figure, the significance level, P. If the chance of accidental occurrence is less than this, an observed difference is said to be significant.

An answer to the first question automatically answers the second if we place the same limits on what is to be regarded as the 'reasonable' or 'likely' operation of chance or to the vagaries of random sampling.

If calculations are performed to ascertain the confidence limits for various values of X and if these are plotted above and below the regression line one can thus represent the confidence zone of that regression. An example of such an exercise is shown in Figure 5-2. The confidence zone AB/CD represents the area within which, with due regard of the confidence limits, a value of μ_Y for any X will be likely to be found.

5.3.1.3 Multiple regression techniques are available where regression of Y on a single independent variable X has proven to be inadequate. Two or more Xs may be available to give additional information about Y by means of multiple regression on the Xs. The principle uses of multiple regression are:

i) the construction of an equation in the Xs that gives the best prediction of the values of Y ;

ii) when there are many Xs, to determine the subset which gives the best linear prediction equation;

iii) to discover which independent variables are closely related to Y and to possibly rate these in order of importance.

In practice it is usually found that iii) is used to determine ii) (i.e. the most important subset of independent variables), which then go to producing the most practical equation for the prediction of Y, as in i). The calculations involved in a multiple regression involving numerous independent variables are somewhat lengthy and it is thus difficult to avoid mistakes in computation. To remedy this, standard digital computer programs have been developed, providing an invaluable aid to modellers utilising statistical methods.

With only one independent variable the regression line can be plotted as in Figure 5-2, but if Y depends partly upon X, and partly upon X_2 for its value, 3-dimensional geometry is required, Figure 5-3.

A multiple regression plane[111] can be expressed by the equation $Y = \alpha + \beta_1 X_1 + \beta_2 X_2 \ldots\ldots \beta_j X_j + \varepsilon$ .... (5-6) where $\beta_1 - \beta_j$ are the partial regression coefficients for the j independent variables and ε representing the random error element within the equation. Given a sample of n values of the variables the prediction equation becomes

$$\hat{Y} = a + b_1 X_1 + b_2 X_2 \ldots\ldots b_j X_j \quad \ldots\ldots \quad (5\text{-}7)$$

The values of a, b_{1-j} being chosen so as to minimise $\Sigma(\hat{Y} - Y)^2$, the sum of squares of the n differences between the actual and predicted Y values. Gaussian theory shows that the resulting estimates of a, b and $\bar{Y}$ are unbiassed and have the smallest standard errors of any unbiassed estimates that are linear in the Y's.

In areas of research where controlled experiments are not practicable or in real field situations, multiple regression is extensively used to disentangle and measure the effects of different X-variables on some response Y. There are, however, important limitations on what can be learned from this technique in such studies. In a multiple linear regression model of two X variables such as

$$Y = \alpha + \beta_1 X_1 + \beta_2 X_2 + \varepsilon \quad \ldots\ldots\ldots\ldots \quad (5\text{-}8)$$

where the error element ε is assumed to be distributed independently of the X's with zero mean and variance σ^2, it is assumed that the X's remain fixed in repeated sampling.

In reality the sampling of the X values may lead to substantial errors, this being dependent upon, among other things, the source of data sampled. There is also the problem that it is not usually possible to say with certainty that there are no other X-variables related to Y in the population sampled. There may be variables which are thought unimportant, it may be impractical to measure or record them, or they may even be unknown. Consequently, instead of equation (5-8) the correct regression model is likely to be of the form

$$Y = \alpha + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \ldots\ldots \beta_k X_k + \varepsilon^1 \quad \ldots\ldots \quad (5\text{-}9)$$

where $X_3 \ldots\ldots X_k$ represent these additional variables, ε^1 being that part of Y which is distributed independently of X, and k being possibly quite large. For simplicity the additional terms are replaced by a single term $\beta_o X_o$, which represents the joint effect of all the terms omitted from the two variable model. Thus the correct model is

$$Y = \alpha + \beta_1 X_1 + \beta_2 X_2 + \beta_o X_o + \varepsilon^1 \quad \ldots\ldots\ldots\ldots\ldots \quad (5\text{-}10)$$

In a real situation it may not be necessary to take into account the $\beta_o X_o$ term shown in equation (5.10), provided the X-variables selected for the model are the most important with respect to the value of Y. This degree of importance can be ascertained by examining the standard partial regression coefficients of the variables available. 112

The variance of Y in the 'correct model', equation (5-9) is given by

$$\sigma_y^2 = \beta_1^2\sigma_1^2 + \beta_2^2\sigma_2^2 + \ldots\ldots\ldots \beta_k^2\sigma_k^2 + \sigma^2 \quad \ldots\ldots \quad (5\text{-}11)$$

where σ_1^2 denotes the variance of X_1, etc. The quantity $\beta_i^2\sigma_i^2/\sigma_y^2$ measures the fraction of the variance of Y attributable to its linear regression on X_i. This can be regarded as a measure of the relative importance of X_i in the regression. In a random sample from this population, providing the samples are large enough, the quantities $b_i^2\Sigma x_i^2/\Sigma y^2$ are sample estimates of these functions. The square roots of these quantities, $b_i \sqrt{(\Sigma x_i^2/\Sigma y^2)}$ is the standard partial regression coefficient. It is through ranking of these coefficients that the relative importance of the Xs (ignoring sign) may be ascertained.

In practice, correlations between the Xs make the procedure somewhat difficult. In many applications, X_1 and X_2 are positively correlated with each other and with Y, hence an already complex situation is made even more so, Fig. 5-3.

5.3.1.4 Partial and multiple correlation analysis can be of great help to the modeller in ascertaining the interrelationships which are present within the observed variables.

If there were three variables, there would be three sample correlations among them, ρ_{12}, ρ_{13}, ρ_{23}. A partial correlation coefficient, $\rho_{12.3}$, can also be obtained; this is the correlation between variables 1 and 2 when variable 3 is held constant.[112] Thus effectively removing it from the calculation.

Partial correlation does not involve the notion of independent and dependent variables; it is a measure of interdependence. On the other hand, the multiple correlation coefficient applies to the situation where, for example, one variable Y has been singled out for an examination of its joint relation with the other variables. The multiple correlation coefficient between Y and X_1, X_2 .... X_k is defined as the simple correlation coefficient between Y and its linear regression, $\beta_1 X_1 + \ldots\ldots + \beta_k X_k$ on $X_1 \ldots\ldots\ldots X_k$.

5.3.2 Curvilinear regression models are based on the fitting of suitable curves to the data, when standard linear regression analysis has given unsatisfactory results.[113]

Such models can be used to construct various types of non-linear curves, for example, exponential growth curves, asymptotic regression curves or as in Figure 5-4 polynomial regression curves, of the form

$$\hat{Y} = a + bX + cX^2$$

Fig. 5-3 A representation of a multiple regression plane formed from a regression containing two independent variables

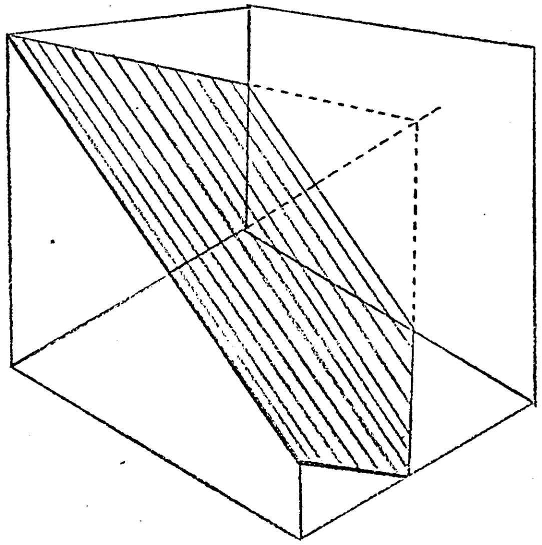
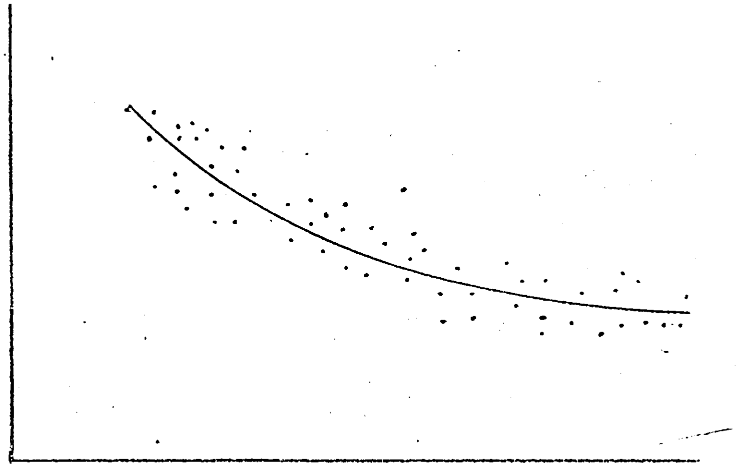


Fig. 5-4 An example of a Polynomial regression curve



5.4 Water Pollution Control Models

Goldman concluded that:

> 'It is more essential than ever that the population be alerted and that technology be harnessed for the prevention and treatment of pollution. Woefully this can and must be done if the affluent are not to choke on their own effluent.'

One of the more recent developments in the field of water pollution control is the water quality model.[115] Many such models have been developed both for estuarine as well as freshwater systems.[109] Although estuarine models have to contend with additional factors, for example, tides and stratification effects, their modelling is essentially similar to that of flowing freshwater systems.

5.4.1 Non-tidal river water quality models are rapidly becoming important in the management and control of river water systems. The prediction of the probable water quality in a river system ten or twenty years ahead, or the short-term forecasting of river water quality at an abstraction point, are examples of the utility of such models.

These models tend to be of two types, steady state and dynamic.

5.4.1.1 Steady state modelling would be used where the desired future levels of water quality were to be planned and where the quality of the effluents discharged to the river system were to be controlled at least cost.[117] Such a model, based on average concentrations of quality determinands and a general idea of their expected variations, would serve this purpose most satisfactorily.

A limitation of steady state modelling is that as the models are usually designed to operate on limited quantities of mean data, any predictions made must be viewed with this small data base in mind. The model of the river Trent[118] developed by Garland and Hart, is an example of a steady state model. It was developed using empirical relationships between mean and percentile values, relying upon annual mean data for its calculations.

5.4.1.2 Dynamic models have more extensive applications than do the steady state types within the field of river water pollution control.[119,120]

The utility of a model which can provide an indication of possible short-term water quality variations at, for example, an abstraction point, is obvious but such predictions have not been possible until recently. The successful development of the Bedford Ouse dynamic model[121] has now remedied this situation. That this model is dynamic is shown in its ability to forecast the quality of the water at a downstream site using observations of the quality at a point upstream. The model is at present restricted to forecasting dissolved oxygen concentration (DO mg dm^{-3}) and biochemical oxygen demand levels (BOD mg dm^{-3}), but it is anticipated that it will be further developed to incorporate other relevant water quality determinands.

5.5 The Use of Continuous Monitoring in Quality Modelling

Water quality models, in general, tend to suffer from the lack of a sound comprehensive data base.[115] For example, the Bedford Ouse dynamic model, although a great step forward in water quality modelling in this country, relied for its development upon data collected over a single summer period. It is suggested by Beck[119] that "to identify suitable dynamic water quality structures some heuristic feeling or physico-chemical understanding of the system is essential", and can best be achieved by the utilisation of a continuous monitoring programme. Thus it is desirable that a water quality model should possess the following properties.

i) It should be dynamic, being capable of accepting time dependent input functions and operating upon them to give output responses.

ii) It should be as simple as possible while still retaining the ability to adequately characterise all important variations within the system.

iii) It should provide a 'reasonable' approximation of the physico-chemical changes occurring in the river system and most important, it should be verified against data collected from the river over an extended period of time.

It is this final point which is to be emphasised with respect to the utility of continuous water quality monitors in the modelling of water quality systems.

5.5.1 The advantages of continuous water quality monitoring in model development are regarded as being substantial. Any model developed and tested using data collected continuously over a long period of time, will more accurately mirror the real system than one whose data base comprised of occasional discrete samples collected, for example, weekly or monthly. Any perturbations in water quality caused by either ergonomic or hydrological events would be recorded by the continuous programme but are unlikely to be detected by the discrete one. Thus the model developed using discrete data tends inherently to be a gross generalisation of the system and as such is often of only limited use. The model developed using continuous data, can provide a detailed and comprehensive view of the system with the ability to predict the effects of short term internal as well as external perturbations.

The other advantages of a continuous monitoring programme over that of a discrete one, include aspects of data precision, data handling and the computer compatibility of continuously monitored data.[122]

As models endeavour to mirror the real world they are severely limited by the fact that all the constraints which act on the system may not have been monitored. It is possible that other factors, which are either unknown or impractical to monitor, have influence upon the system generating indeterminate errors which reduce the reliability of any predictions made. It is thus accepted that all models will contain errors of some description[110]. A major advantage of automatic sampling and analysis techniques over manual methods, is the ease with which the precision of the analysis can be controlled. Precision is one of the major constraints upon the overall reliability of the data. If this can be guaranteed, by utilising regular automatic calibration techniques, one of the major contributors to the overall error factor of the model will have been removed.

The handling of the large amounts of data necessarily collected by a water quality monitoring programme has in the past been a major problem. It is not only a time consuming exercise but because of the human factor involved it can also generate undetected experimental errors. In recent years the advent of computerised storage and retrieval systems, has markedly improved the efficiency of such data handling.[122] Data generated by an automatic monitoring programme has the desirable capability of generally being computer compatible. Thus with very little manipulation the data can be either analysed immediately or stored for future analysis. Although it is possible to store and subsequently analyse discretely monitored data on the computer, the ease with which this can be performed, as will be appreciated, does not compare with that of automatically monitored data.[123]

Thus with a suitable designed continuous monitoring programme, it is possible to produce large amounts of precise data which can form the basis of a comprehensive computer designed water quality model for the system under study.

5.5.2 The disadvantages of continuously monitored data with respect to model development may be summarised as:

i) the rather large initial capital expense necessary to develop a monitoring programme of the required precision,

ii) the small number of relevant water quality determinands offered by commercially available monitoring systems.

This shortcoming obviously reduces the degree to which models developed using such systems, can fully simulate the real situation. Much research is being performed on this aspect of automatic monitoring systems and it can be expected that in the near future more determinands will be capable of being monitored continuously. An increase in the number of water quality determinands available for monitoring, would have the highly desirable effect of reducing the number of indeterminate errors within the system. Thus any models developed which utilise these additional determinands would have a greater precision and possibly an increased utility.

Discrete monitoring programmes have the capacity, in theory, to identify a larger proportion of the water quality determinands present. This advantage has to be considered alongside all the disadvantages of such a programme, with the possibility that an intelligent combination of the two systems would seem the best compromise.

5.6 Introduction to the Blackburn Brook model

It was decided after a thorough examination of the water system under study, its inputs and the data collection programmes to be used, that a statistical approach to the modelling of the brook would be the most effective.

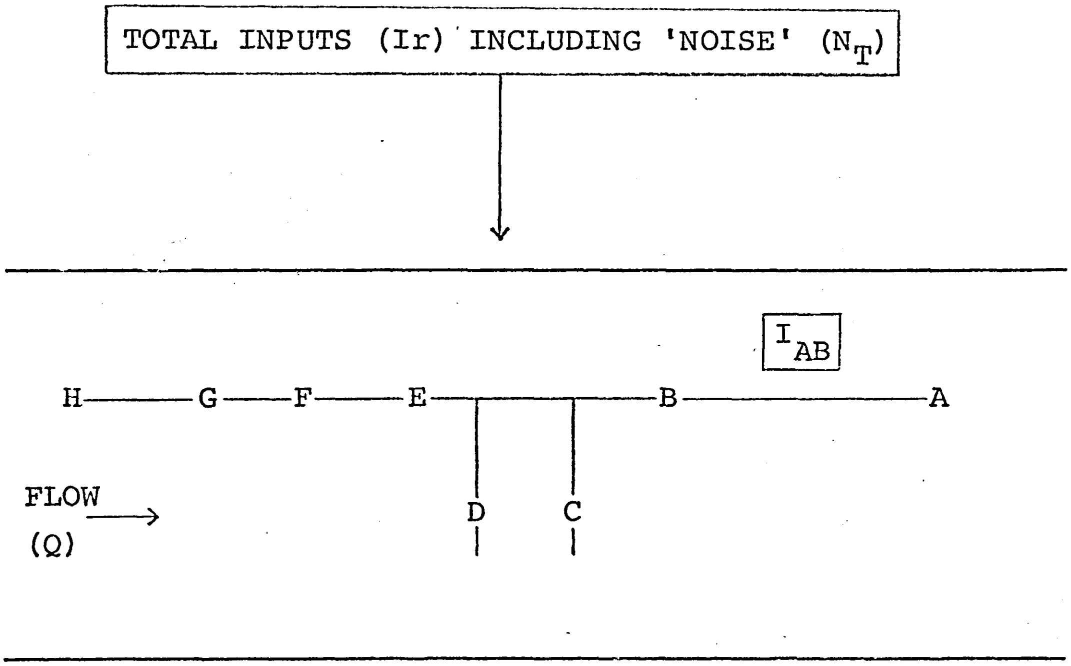
5.6.1 Problems associated with classical modelling techniques became apparent when the system was scrutinised. The usual method of modelling is to monitor both the inputs and the outputs, Fig. 5-5. By doing so one can determine the processes occurring within the particular system and develop the model accordingly. In this particular case this was not possible as by using only one continuous monitor only the output from the system could be monitored. Another factor, which effectively ruled out the possibility of modelling on classical lines, was that the inputs to the system were multiple and of a highly complex and diverse nature. Table T-5-1 outlines the five categories of inputs present. Some of these categories were interrelated, for example, SWO discharges and industrial effluent, this fact further complicated the already complex situation. Some of the inputs were capable of being determined or reasonably accurately estimated. Others, for example industrial effluents, were not.

The system, as represented schematically in Fig. 5-6, was also affected by external ergonomic events such as varying work practices, road and construction work and industrial holiday periods. All known ergonomic events, which had any relevance to the brook during the period of monitoring were recorded.

T-5-1 The Five Categories of input to the Blackburn Brook

(i)	Surface water runoff and Ground water	The quantity and quality of these inputs are a function of the catchment.
(ii)	Storm water overflow (SWO) discharge	See section 3.3
(iii)	Tributaries	The quality and quantity contribution of each has been assessed by discrete sampling and flow measurement.
(iv)	Motorway runoff	Drainage pipes lead directly from the motorway into the brook, which may contribute substantial pollution loading, e.g. increased conductivity due to 'salting' during cold weather. All motorway 'effluents' such as petrol, oil, lead and rubber will also be washed into the brook during storm periods.
(v)	Industrial effluents	The amount of effluent present within the system, is a function of the number of industrial complexes which utilise the brook's water. Its importance to the overall picture of the system is related to the consent levels imposed upon these industries and the degree to which these are observed.

Fig. 5-6 SCHEMATIC REPRESENTATION OF THE BLACKBURN BROOK SYSTEM



I_{AB} = TOTAL INPUTS INTO SUBSYSTEM A.B.

i_{AB} = TOTAL MEASURABLE INPUTS INTO A.B.

n_{AB} = TOTAL 'NOISE' WITHIN A.B.

$$\underline{I_{AB} \doteq i_{AB} + n_{AB}}$$

5.6.2 <u>The relevance of the discrete sampling programme</u> to the modelling of the brook may be expressed in a variety of ways. Apart from providing a knowledge of background pollution levels and major pollution sources, it facilitated the identification of inputs to the system which were not immediately obvious. For example, a high temperature input occurring within two of the discrete sampling sites was identified and subsequently its effect upon the system was quantitatively assessed.

5.6.3 <u>In conclusion</u> it was decided that by utilising multiple regression analysis techniques it would be possible to develop a meaningful water quality model of the Blackburn Brook. This development would be dependent upon the collection of data over a reasonably long period of time and covering every conceivable climatic, industrial and ergonomic condition possible.

CHAPTER 6.

Experimental

6.1 The continuous water quality monitoring programme

The five quality determinands which were monitored are outlined in table T-6-1.

6.1.1 The sensors contained within the monitoring station

are shown in table T-6-1. These were tested for their accuracy and precision by comparing their performance on a number of occasions, over a range of standards, with respect to other methods of analysis. Table T-6-2 outlines the tests performed and gives examples of the results obtained. On the basis of these results it was concluded that the monitors sensors were of sufficient reliability and accuracy for the proposed programme.

CONTINUOUSLY MONITORED DETERMINANDS

DETERMINANDS	UNITS	METHOD OF MONITORING	TIME INTERVAL
ELECTRICAL CONDUCTIVITY	μ S.cm^{-1}	CONDUCTIVITY CELL	¼ HOURLY
TEMPERATURE	^{o}C	PLATINUM RESISTANCE THERMOMETER	¼ HOURLY
SUSPENDED SOLIDS	F.T.U's (mg.dm^{-3})	TWIN GAP PHOTOELECTRIC SUSPENDED SOLIDS MONITOR	¼ HOURLY
pH		DUAL GLASS ELECTRODE	¼ HOURLY
DISSOLVED OXYGEN	% SAT	TEMPERATURE COMPENSATED DISSOLVED OXYGEN ELECTRODE (MACKERETH TYPE)	¼ HOURLY

T-6-2 Comparison of Sensor Performance against Standard Methods

Dissolved Oxygen mg dm^{-3}	Electrode Method	Winkler titration Method
	6.80	7.11
	8.40	8.82
	9.19	8.53
	9.21	9.14
	11.30	10.97
Electrical Conductivity μ S cm^{-1}	Partech instrument in WQMS	Portable laboratory meter
	262	255
	755	750
	1743	1750
Suspended Solids mg dm^{-3}	Dual beam SS monitor	Filtration and weighing
	10	9.5
	100	93
	250	237
	500	481
Temperature ^{o}C	Thermistor	Mercury in glass thermometer
	10	10
	15	15
	20	20
	25	25
pH	Electrode stds	Portable electrode
	2	2
	7	7
	10	10

Table T-6-3

Starting Date	Failure Date	Reasons/Remedies
11.02.75	18.02.75	New pump motor necessary. New conductivity meter fitted. New relays fitted.
27.02.75	14.03.75	Pump returned to manufacturer. Batteries malfunctioning.
12.05.75	29.05.75	Faulty battery charger.
11.06.75	15.07.75	Batteries malfunctioning.
29.07.75	7.08.75	Batteries malfunctioning. End sensor unit piston sticking. Broken impeller blades in pump.
22.08.75	30.09.75	New battery charger fitted.
30.09.75	6.10.75	Impeller blades replaced. Batteries malfunctioning.
14.10.75	17.10.75	Station shut down at weekend to prevent damage from a fall in water level due to raised penstocks.
20.10.75	27.11.75	Weekend shutdowns ceased. Float switch fitted. New mono-pump installed.
2.12.75	17.12.75	Flood of 'alarm sample' in caravan. Solenoid valve on alarm bottle stuck open due to high solids content. Batteries failed, charger stuck in boost mode.
4.03.76	29.04.76	Batteries malfunctioning.
3.05.76	15.07.76	Batteries malfunctioning.
23.07.76	24.09.76	Tape 11 removed, later found to be unusable.
29.09.76	22.10.76	Completion of programme.

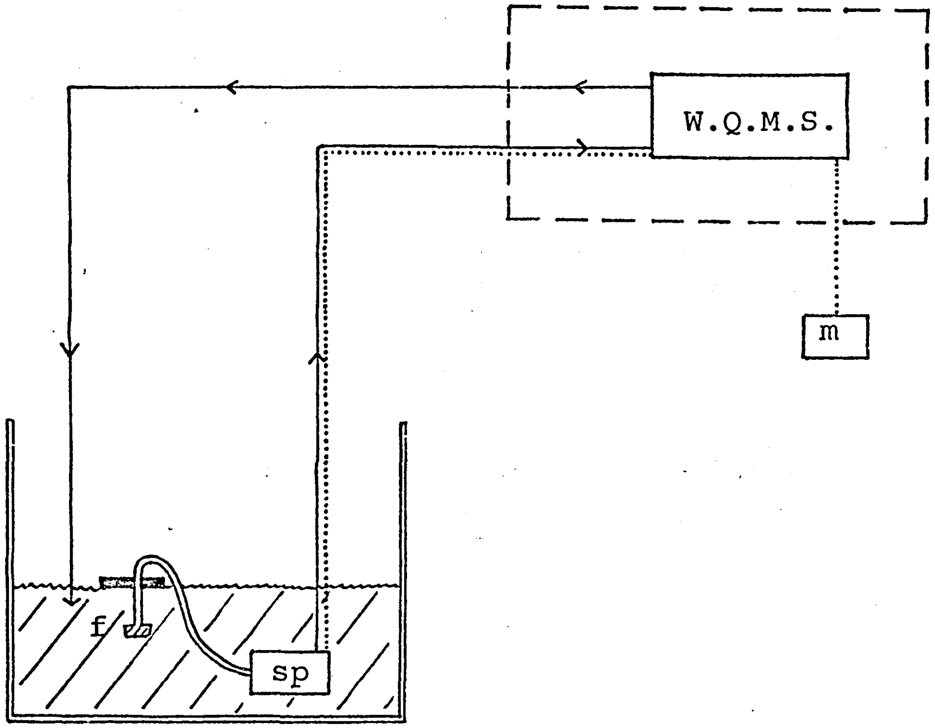
6.1.2 The sampling system required modification part of the way through the programme. This was due in part to the poor performance of the submersible pump, resulting from a change in the work practices within the steelworks.

During a period of short time working Lees found it necessary to raise the penstock sluice gates over the weekend as a precaution against possible flooding. This practice had the effect of reducing the level of the brook from around 2m to approximately 0.1m. The submersible pump was sited at a constant depth hence the lowering of the water level had the effect of isolating it above the water line. This obviously had grave consequences not only with respect to the pump and its impeller blades but also with the sensors and, possibly more importantly, the continuous data record.

Table T-6-3. outlines a log of the monitoring programme which shows the dates the station was not functioning and a brief summary of the reasons.

6.1.2.1 The initial modification to the pumping system, which was made in order to alleviate the problems caused by the depth variations within the brook, are shown in Fig. 6-1. The intake on the pump was extended by means of a section of flexible tubing, a strainer being fitted to the open end. This was then held at a suitable depth by using a polystyrene float. This system had limited success but was hampered by the water draining completely out of the pump during periods of low water so causing the pump to lose its prime. This problem along with the inherent faults of the submersible pump, as outlined in table T-6-3,

Fig. 6-1 Initial monitoring system



W.Q.M.S.	Water Quality Monitoring Station
sp	Submersible pump
f	Float with foot valve and strainer
m	Electric mains power supply
	Polythene hydraulic pipework
	Power cables

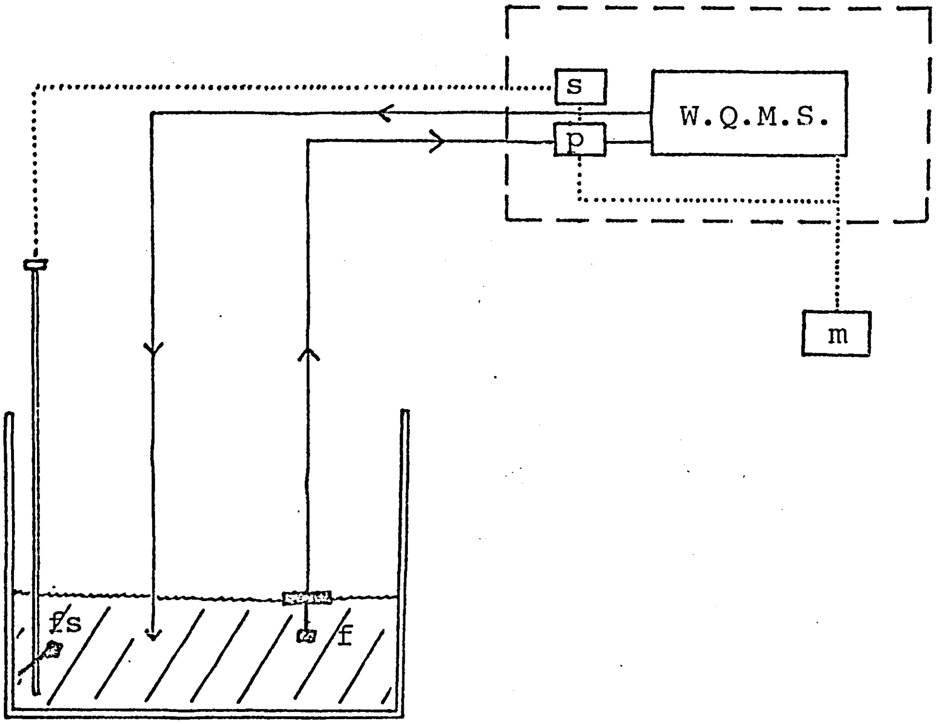
prompted the development of the second system.

6.1.2.2 The second modification of the sampling system, Fig. 6-2, entailed fitting a completely different type of pump and mounting it within the caravan. This pump had a stainless steel impeller and this afforded some protection against the great variations in pH, which seemed to be a major factor in previous impeller failures.

Another slight modification was the design of a 'water lock' around the pump, which resulted in passage of water in such a way that when the pump was deactivated it did not lose its prime. To also aid in the solution of this problem, the strainer was replaced by a foot-valve and strainer mechanism of the same gauge, effectively a one-way valve preventing any loss of prime within the system. A further safeguard was built into the system in the form of a float switch. This deactivated the pump during periods of low water by means of a submerged float and solenoid switch.

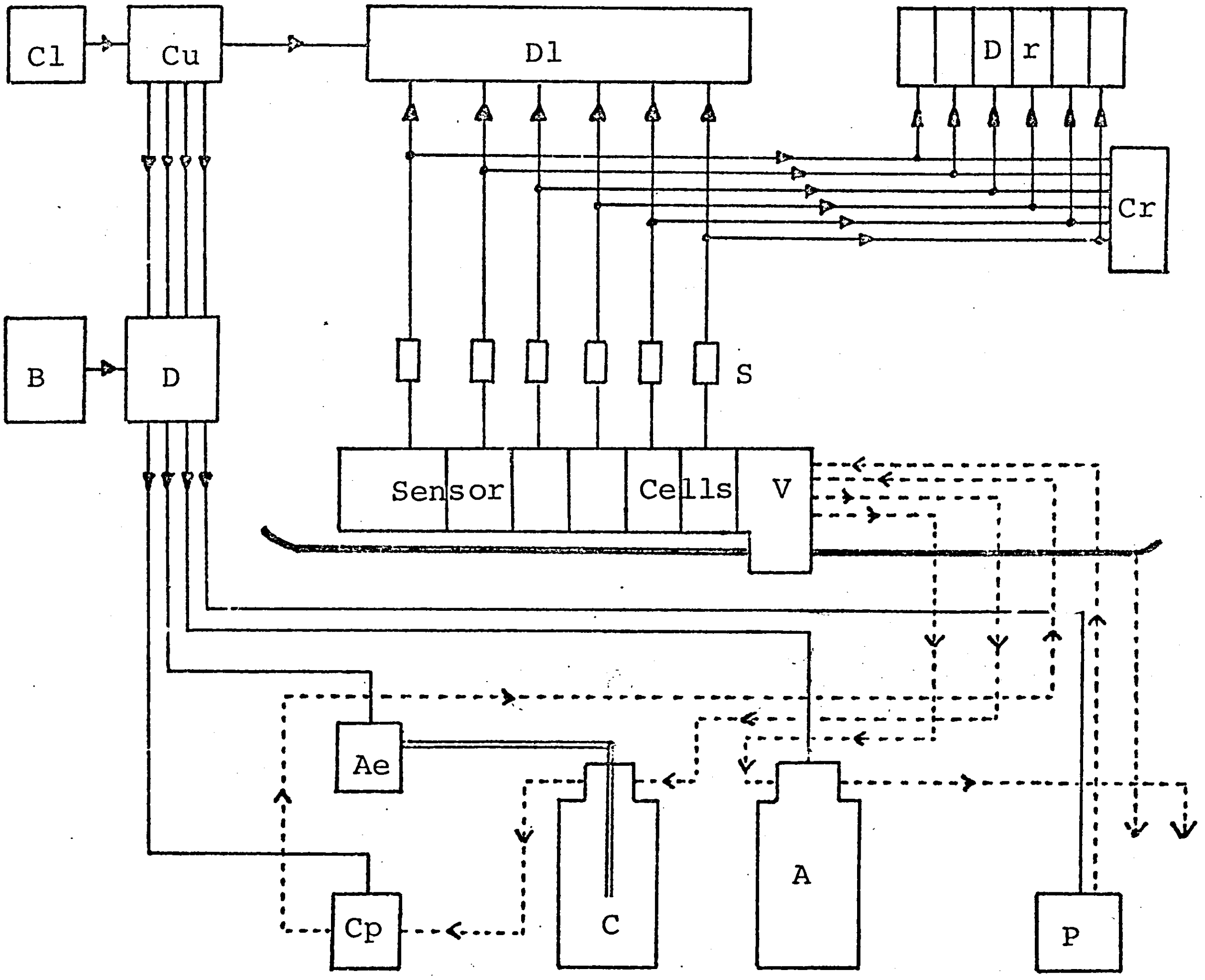
6.1.2.3 The mode of operation of the monitor is outlined in Fig. 6-3. The water was pumped from the inlet to the monitor through black polythene tubing, ostensibly to minimise algal growth, although in this case the Brook was too grossly polluted to support any such life. The inlet pipe was approximately 25m long and the head, from inlet to sensor blocks, was about 4.5m.

Fig. 6-2 Final monitoring system



W.Q.M.S.	Water Quality Monitoring Station
s	Solenoid switch
p	Land mounted mono pump
fs	Float switch
f	Float with foot valve and strainer
m	Electric mains power supply
	Polythene hydraulic pipework
	Power cables

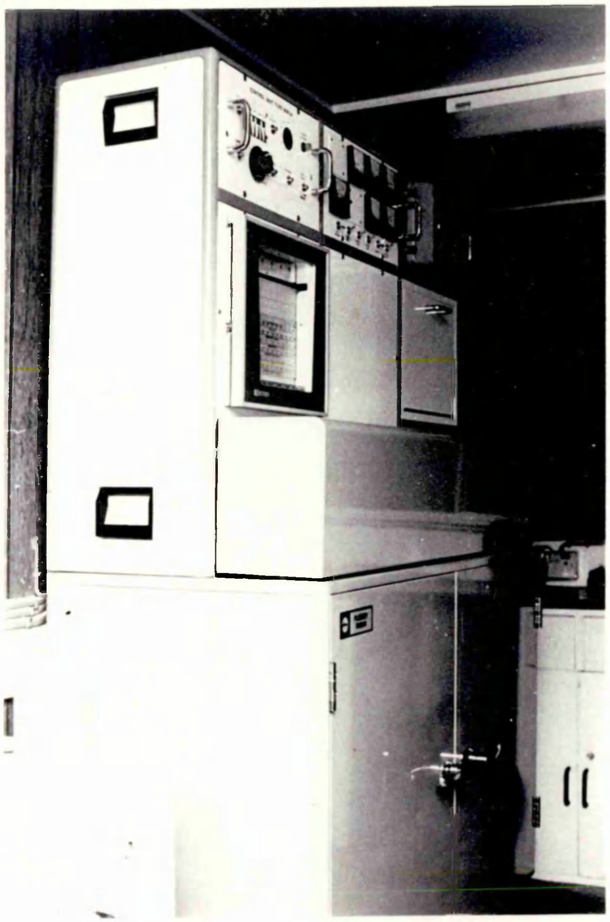
Fig. 6-3 Water Quality Monitoring Station (Schematic diagram)

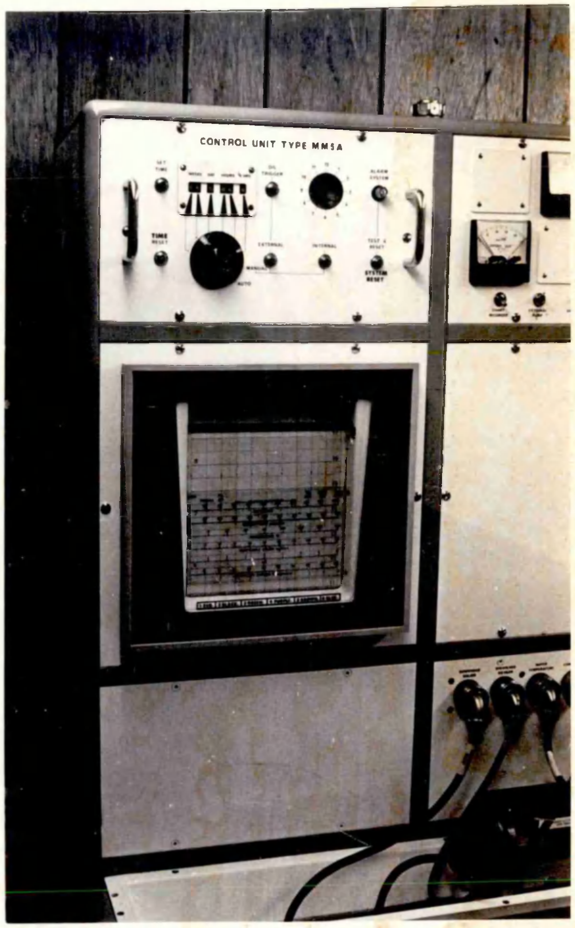


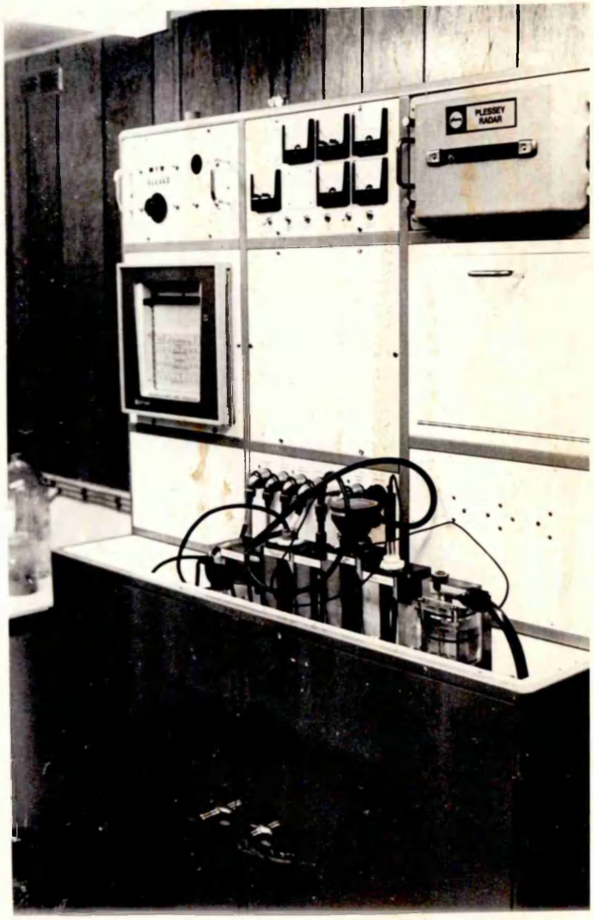
KEY			
A	Alarm sample bottle	Cl	Clock
Ae	Aerator	D	Distribution Unit
B	Batteries	Dr	Direct reading meters
C	Calibration fluid bottle	Dl	Data logger
Cu	Control unit	P	Pump
Cr	Chart recorder	S	Sensor units
Cp	Calibration pump	V	Valve

The monitor, Fig. 6-4, had the capability of being operated manually or on an automatic cycle. In this particular case it was operated on a 15 minute automatic cycle controlled by an independent battery operated clock incorporating a microswitch. On commencement of an automatic cycle, water was pumped around the sensor blocks for approximately three minutes. After three minutes the meters showed that the adaptor circuits had been activated, hence recording the data readings. The data was recorded on chart paper by means of a dot recorder and ¼" magnetic tape as well as being shown on the direct readout meters. After a total time of 4 minutes the pump and station were deactivated until the microswitch operated the next ¼ hourly cycle. In theory the magnetic tape had a storage capacity of 55,200 data points or thirteen weeks of continuous data, assuming no breakdowns. The tape was advanced each time the monitor was deactivated, so as to indicate a break in the data record.

6.1.2.4 Sensor calibration cycles were included in the monitors operation, occurring at 24 hour intervals from 1200h. This internal cycle operated instead of the normal external one, delivering cleaning fluid (Decon 90 solution) into the system, from a container fitted within the monitor. This operation is quoted by the manufacturers[124] as being a calibration cycle. It was found, however, that any calibration fluid rapidly became contaminated and was thus rendered useless. The calibration of the sensors was thus performed manually. It proved convenient to do this along




CONTROL UNIT TYPE MM5A


PLESSEY RADAR

with the weekly sensor and sensor block cleaning. Table T-6-4 outlines some typical results of these calibrations, and shows that weekly calibration of the sensors was adequate for maintaining acceptable sensor accuracy.

As can be seen from T.6-4 the suspended solids sensor proved to be the most unreliable. This was probably due to its particular sensitivity to the high levels of organic pollution found within the Brook. Organic pollution, which in this case was mainly sewage based proved to be the worst possible type of contaminant for this particular sensor system. Not only was it highly coloured but the microorganisms present within it seemed to find the suspended solids sensor block an ideal niche in which to develop. This resulted in a 'slime type' fouling of the sensor's optical surfaces. Although, as previously mentioned, the monitor had a cleaning cycle operating every 24 hrs, and a more intensive manual cleaning every week, it still proved necessary to clean the optical surfaces of the monitor on every visit. The station was visited on most days during the duration of the programme thus indicating the extent of the maintenance problem.

Sensor fouling was also a problem with the dissolved oxygen electrode. Although this was not as serious as with the S.S. sensor, it was thought advisable to regularly clean it in addition to the routine weekly cleaning programme.

The high pollution loading of the water also led to fouling of the sensor blocks. These blocks proved difficult to clean as the network of channels linking each block was highly convoluted and of narrow gauge. In order

T-6-4 Examples of Weekly Calibrations

	E.C.		D.O.		T	S.S.			pH	
	μ Scm^{-1}		% Sat		^oC	mg dm^{-3}				
Standards	1000	2000	0	100	20	10	50	100	2	10
	950	1900	0	98	20	13	57	110	2	10
	1000	1850	1	96	20	15	60	112	2	10
	1100	2050	1	101	20	12	55	106	1	9
	1000	2000	0	96	20	13	56	110	2	11
	950	1850	2	101	20	11	53	108	2	11

that these blocks be kept clean it became necessary to soak the blocks for a considerable time in an acid/detergent mixture which results in a small degree of lost data over the monitored period.

6.1.2.5 Monitor performance during the monitoring period was unfortunately often interrupted. The various malfunctions, which are outlined in table T-6-3 occurred mainly before the second monitoring system was instigated. A lot of the faults were 'teething troubles' which were not unexpected although the problems associated with the submersible pump were.

The new system was not totally responsible for the subsequent increase in monitor reliability, as shortly after its implementation Arthur Lee's commenced normal working so that the problems associated with the massive depth variations were removed.

There were 20,536 quarter hourly analyses performed during the monitoring period of twenty months, yielding 102,680 items of water quality information.

6.1.3 Initial monitoring results were obtained prior to any magnetic tape translations, from the chart recordings. It was discovered from these that very interesting quality variations were periodically taking place within the Brook. Examples of some of these variations are shown in Figures 6-5 and 6-6.

Figure 6-5 shows the effect upon the dissolved oxygen concentration of a very large increase in suspended solids loading. It also shows doubling of the conductivity

Fig. 6-5 Example of the Monitored data (Suspended Solids event)

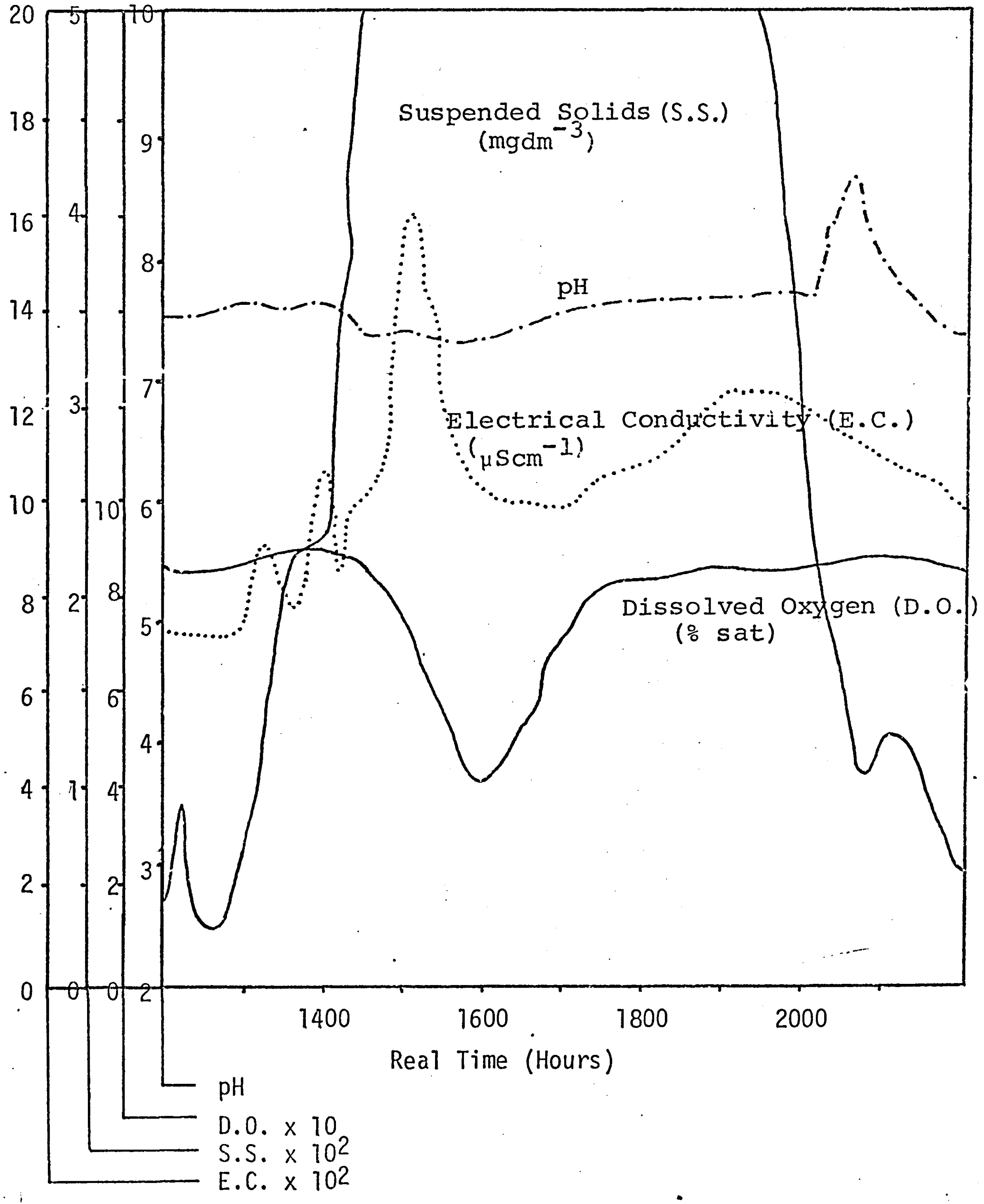
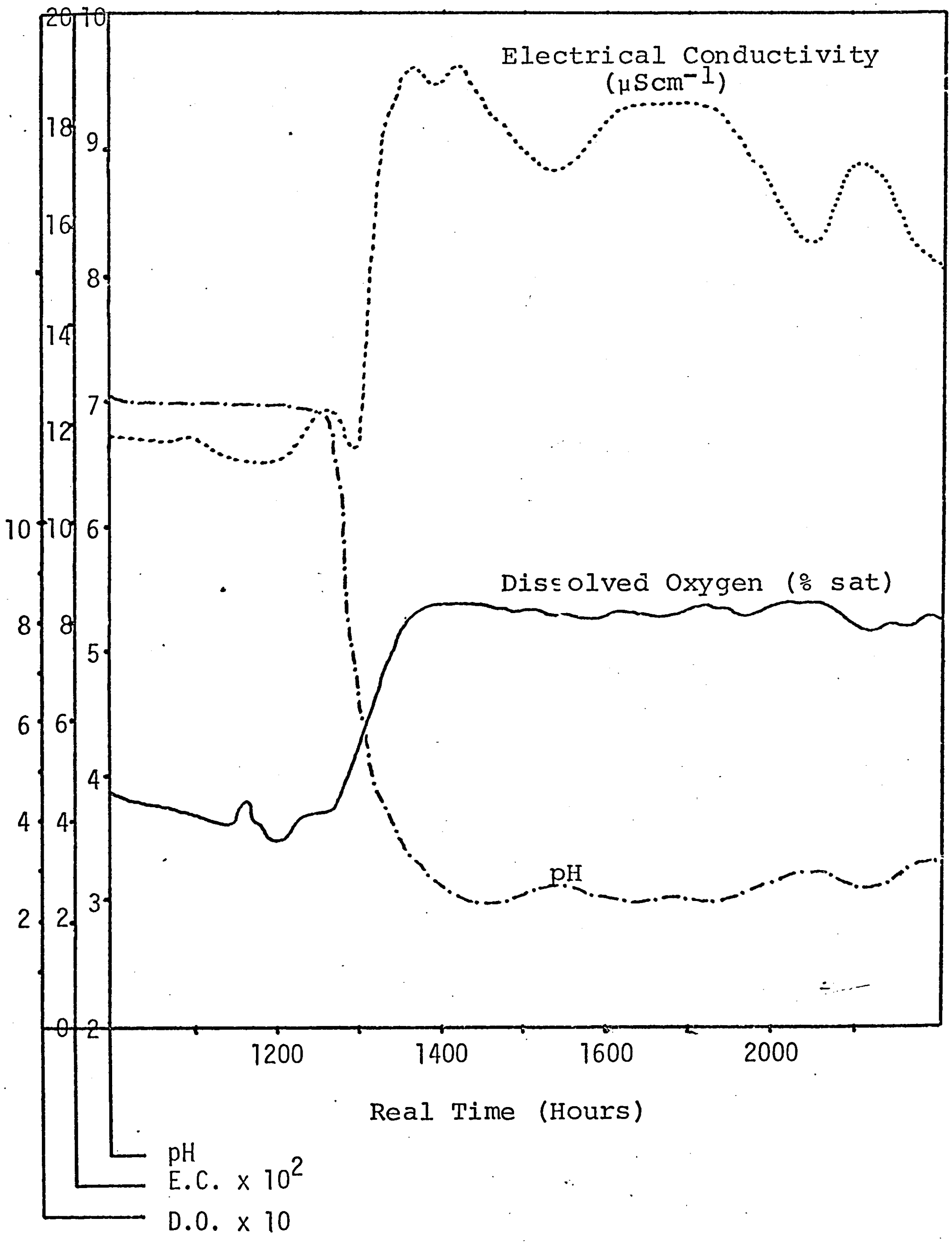


Fig. 6-6 Example of the monitored data (pH event)



value with no change in pH. Conclusions drawn from this particular early chart indicated the possibility of sewage contamination via discharging stormwater overflows. The fall in dissolved oxygen from around 90% to 40% saturation with no appreciable change in temperature suggests that a large amount of organic matter was exerting a strong oxygen demand. This along with the vast increase in suspended solids was very strong evidence of sewage contamination. This chart along with others which were similar and the visual evidence which was present, prompted an intensive search for the discharging overflows. The results of this search are shown on the map, Fig. 3-1. The increase in conductivity was also thought likely to be linked to the discharging overflows or possibly to other inputs to the system, for instance, motorway runoff, particularly after 'salting' has taken place. On the day the data was recorded (6.3.75) there was a short heavy storm within the catchment, lasting approximately one hour and taking place around mid-day. It was the first rain the catchment had experienced for some days. Thus not only could the large amount of suspended matter have originated from a first flush of the S.W.O's, but it is possible that the sudden increase in stream flow also contributed to the situation by stirring up benthal deposits.

It is seen from Fig. 6-6 that E.C. seems to respond directly with D.O., whereas in Fig. 6-5 the response was indirect. It is possible that this direct correlation was in fact due to a secondary factor, that is pH, since neither S.S. or T. altered appreciably over this period. The pH value altered by four units from a value of approximately 7, within one hour, with the DO concentration responding immediately. This rapid fall suggests that an acid discharge of considerable magnitude had occurred. The curve shape seems to indicate that either the acid 'plug' had remained intact on its journey downstream from its source, or more probably that it had been discharged very close to the intake of the monitor. If this were so, the rapid rise in DO observed would not be unexpected, as it is likely that any acid waste discharge would be highly oxygenated.

Considering both figures 6-5 and 6-6 it would seem that the effect of changes in EC, upon the level of DO were not as marked as changes in SS or pH were.

6.2 The Discrete Monitoring Programme

Portable analysis equipment was used whenever possible so as to obtain in-situ results of the monitored determinands. Table T-6-5 outlines the determinands monitored and the equipment used for the analyses.

The monitoring was originally performed every Monday at approximately the same time each week. This was changed to Tuesday not only for reasons of convenience but also because it was discovered that this was the day which was regarded as being the one of maximum industrial output.

6.2.1 The monitored determinands as outlined in Table 6-5 included some which were additional to the five monitored continuously. These were performed so that not only could the discrete data be used as a comparison with the continuous but also to supply a more comprehensive account of the pollution present at different sites.

T-6-5 DISCRETELY MONITORED DETERMINANDS

DETERMINAND	UNITS	METHOD OF MONITORING	TIME INTERVAL
ELECTRICAL CONDUCTIVITY	$\mu.S.cm^{-1}$	CONDUCTIVITY CELL	WEEKLY
TEMPERATURE	°C	MERCURY THERMOMETER	WEEKLY
SUSPENDED SOLIDS	F.T.U. ($mg.dm^{-3}$)	TURBIDITY METER	WEEKLY
pH		GLASS ELECTRODE	WEEKLY
DISSOLVED OXYGEN	% SAT.	MACKERETH GALVANIC ELECTRODE	WEEKLY
B.O.D.	$mg.dm^{-3}$	DILUTION METHOD RESPIROMETER METHOD	WEEKLY WEEKLY
C.O.D.	$mg.dm^{-3}$	DICHROMATE REDUCTION METHOD	MONTHLY
FREE AMMONIA	$mg.dm^{-3}$	AMMONIA ELECTRODE (BUFFERED AT pH 11)	MONTHLY

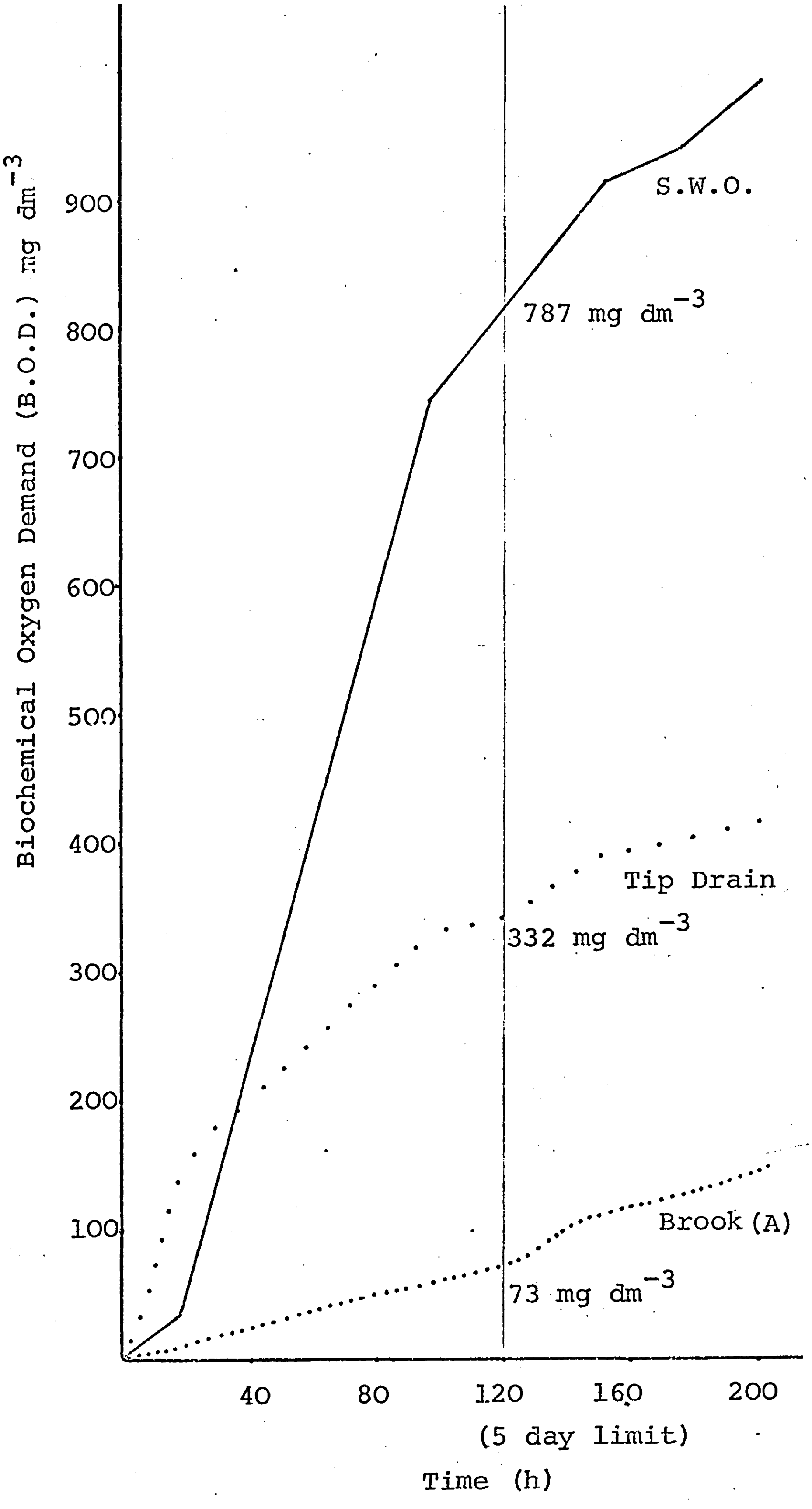
VARIOUS OTHER DETERMINANDS e.g. HEAVY METALS
INTERMITTENTLY

6.2.1.1 Biochemical oxygen demand (B.O.D.) analyses were performed by two different methods.

a) Respirometry; this involved the use of the E/BOD Respirometer system (Oceanography International Corporation, USA). Unfortunately this system could only accommodate three samples per analysis and thus it was somewhat limited in its utility to the discrete sampling programme. It did however prove useful in the determination of BOD's for special discrete samples from, for example, storm water overflows, various drains which provided inputs to the Brook and 'alarm' samples collected by the W.Q.M.S.

An advantage of using this instrument, was that the respirometer provided a continuous readout of oxygen consumed hence facilitating the construction of BOD curves. Examples of some BOD curves obtained are outlined in Fig. 6-7. In, for example, primary effluent studies, this facility could be of use in studying both the carbonaceous and nitrification stages of the BOD reaction. In polluted waters such as were analysed, these stages are not clearly defined, due to the mixing of various components at different stages of the BOD reaction. The 5-day BOD's were obtained for three samples as shown in Fig. 6-7. The Brook sample was taken at Station A; the sample of tip drainage water, with a high hydrogen sulphide content, was taken from above Station B and the SWO sample originated from a continuously discharging overflow again from above Station B. It can be seen from these typical results that organic pollution was entering the Brook and having detrimental effects upon the water quality of Station A.

Fig. 6-7 5-day B.O.D.'s of three discrete samples



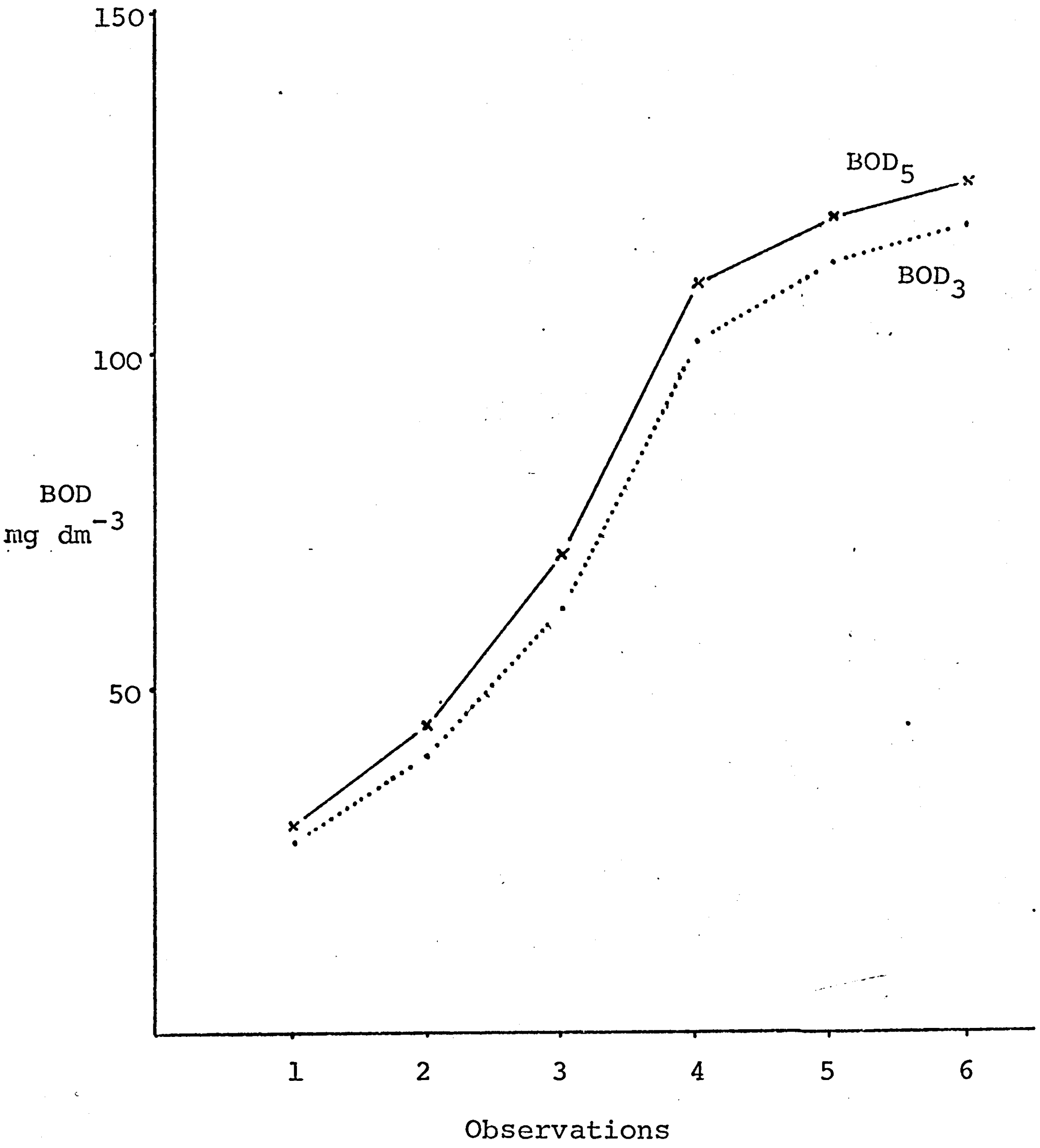
b) The dilution method was performed using a dissolved oxygen electrode, rather than the Winkler titration method. Initially both methods were used and compared but as Table T-6-3 shows, the difference in accuracy was minimal. It was decided that the electrode method would be the best one to use routinely, because of its speed, convenience and its slightly better precision.

The five days required for a BOD analysis is highly inconvenient when sampling is being performed on a regular weekly basis. No matter when the samples are obtained within one working week, their analysis cannot be completed until the next. As the BOD levels were chiefly required only as comparisons rather than absolute and accurate values, it was decided to alter the incubation procedure in an attempt to overcome the disadvantages of the five day test. This was achieved by increasing the temperature to 31°C while reducing the time period to three days. The temperature of 31°C being calculated from theory[125].

The performance of this 'reduced time' method was checked against the normal method, the results being outlined in Fig. 6-8. As the results of this check were acceptable it was decided to incorporate this new method into the discrete monitoring programme. Thus the BOD's of samples taken on Tuesdays could be completed by Friday of the same week.

Table T-6-6 outlines a typical set of results from the discrete programme, showing how the BOD along with the other determinand concentrations alter throughout the length of the Brook.

Fig. 6-8 Performance of BOD_3 with BOD_5



T-6-6 Typical Discrete Sampling Results

Station	EC $mScm^{-1}$	T ^oC	SS $mgdm^{-3}$	pH	DO %sat	BOD $mgdm^{-3}$	COD $mgdm^{-3}$	NH_3 $mgdm^{-3}$	Cl^- $mgdm^{-3}$
A	1.8	6.4	400	5.3	45	53	760	4.4	134
B	1.5	4.5	30	6.2	48	26	360	7.5	195
C →	0.85	4.4	4	5.8	78	8		1.1	125
D →	0.7	4.2	3	6.1	85	3		0.9	72
E	3.0	14.8	180	5.9	51	10	170	7.5	250
F	1.8	5.8	120	6.2	50	34		6.5	132
G	1.0	6.3	9	5.4	83	12		1.4	73
H	0.9	7.5	15	5.3	81	8		0.9	70

6.2.1.2 Chemical oxygen demand (COD) analyses were performed using the standard dichromate reflux method[67]. Table T-6-6 outlines the variations in COD which were observed and the typical values obtained from a sampling operation. As was expected the highest COD levels occurred, along with high BOD levels, at the sites of greatest sewage pollution.

6.2.1.3 Determinands monitored intermittently included ammonia, chloride, and some specific metal ions.

i) Ammonia, this was monitored by means of a gas sensing ion-selective electrode[126]. As outlined in T-6-7 the samples containing the greatest proportion of ammonia were those most affected by sewage discharges. Thus ammonia concentration levels were used as an indicator of the state of the organic pollutants as well as indicating possible high BOD results, this aided the determination of the correct degree of dilution necessary for standard BOD analyses.

ii) Chloride, this was monitored by a solid state ion-selective electrode[127]. Chloride concentrations were monitored since a proportion of the conductivity in the Brook, especially in the winter months, was expected to arise from the salting of the nearby roads and motorway. The results of the analyses performed, T-6-6 , seem to confirm that this original assumption was at least in part correct.

iii) The metal ions which were occasionally monitored included iron, calcium and magnesium. The analyses were performed using analytical atomic spectroscopic techniques[128]. Suitable agents were added to reduce interferences, for example, lanthanum chloride was added in the analysis of both calcium and magnesium to reduce phosphate interference.

The results of the iron analysis showed that the majority was to be found in the suspended solids in the ferric oxidation state.

A more detailed analysis of the trace heavy metals within the Brook, for example copper, nickel and lead, may be useful in 'fingerprinting' pollutants and subsequently determining their source.

6.2.1.4 Discrete biological monitoring was performed in an attempt to ascertain the biological quality of the Brook. Microscopic examination of the water indicated that little life existed within the Brook downstream of Chapeltown. The only organisms found were parasitic worms of the Phylum *Nematoda* and activated sludge protozoans, for example, *Vorticella*.

Microbiological examination of the water was carried out using the Presumptive and Differential Coliform tests[129]. The presumptive test is quantitative for the total number of Coliform organisms present. The test indicates the presence of faecal bacteria of the type *E. Coli* and *A. aerogenes*. While these micro-organisms themselves may not be harmful to life they indicate that pathogenic micro-organisms may also be present.

The test is based upon the fact that coliform organisms will ferment lactose in the test fluid (MacConkey's broth), with the subsequent production of gas. The differential coliform test is to ascertain whether the coliform bacteria detected in the presumptive test are typical coliforms *(E.Coli)* or atypical coliforms (*Aerobacter aerogenes* and Wilsons Irregular type II and IV). The results for one typical examination are outlined in section 6.2.1.4.B, these were calculated using McCrady's probability tables.

The confirmed coliform count of 66,000 per 100cm^3 of sample indicated an extremely high degree of recent sewage contamination within the Brook. Such a high level would be classified as a grave health risk for any one who came in contact with the water.

The drinking water standard presently in use is 1 coliform per 100cm^3. In the United States the standard for ordinary river water is 2000 faecal coliforms per 100cm^3 or 4000 total coliforms per 100cm^3.

These examples serve to illustrate the extent of the sewage pollution problem within the Brook.

6.3 Impulse Salting Experiment

On initial analysis of the continuously monitored data, distinct types of data curve were noted, Figs. 6-5, 6-6. It was thought that the different curve shapes may have been indicative of different types of input, for example, conservative or non-conservative species entering the system continuously or as occasional impulses. An impulse salting experiment was thus designed to examine this theory, with a view to producing data curves from inputs of known concentration and distance. These synthetic data curves would then be capable of being used as standards, with reference to the continuously monitored data. Impulse

6.2.1.4.B. Typical Results from a McConkeys Experiment

The sample under analysis was obtained from the continuous monitoring station at A Lees, 24/4/75 a.m.

Sterile saline was used as dilution fluid.

(i) 5 tubes of $10cm^3$ sample and $10cm^3$ double strength McConkeys Fluid

(ii) 5 tubes of $1cm^3$ sample and $5cm^3$ single strength McConkeys Fluid

(iii) 5 tubes of $0.1cm^3$ sample and $5 cm^3$ single strength McConkeys Fluid

(a) The Presumptive Coliform Test

Tubes incubated for 24 hours at 37°C.

Dilution	Number of +ve results, i.e. gas production	
$\frac{1}{600}$	(i)	+ + + + +
	(ii)	+ + + 0 0
	(iii)	0 0 0 0 0
$\frac{1}{6,000}$	(i)	0 0 0 0 0
	(ii)	0 0 0 0 0
	(iii)	0 0 0 0 0

These results indicate a probably number of 48,000 coliform bacteria $100cm^{-3}$, using McCradey's probability tables.

The -ve tubes, from above, were incubated for another 24 hours

$\frac{1}{600}$	(i)	+ + + + +
	(ii)	+ + + 0 0
	(iii)	+ 0 0 0 0
$\frac{1}{6,000}$	(i)	+ 0 0 0 0
	(ii)	0 0 0 0 0
	(iii)	0 0 0 0 0

$\frac{1}{60,000}$	(i)	0 0 0 0 0
	(ii)	0 0 0 0 0
	(iii)	0 0 0 0 0

These results indicate the total probable number of 66,000 coliform bacteria 100cm^{-3}.

(b) <u>The Differential Coliform Test</u>

Subcultures of all +ve samples after 24 hours were made and incubated at 44°C for a further 24 hours.

$\frac{1}{600}$	(i)	+ + + + +
	(ii)	+ + + 0 0
	(iii)	0 0 0 0 0

These results indicate that the coliforms detected in the presumptive test were all <u>typical coliforms</u> (E. Coli).

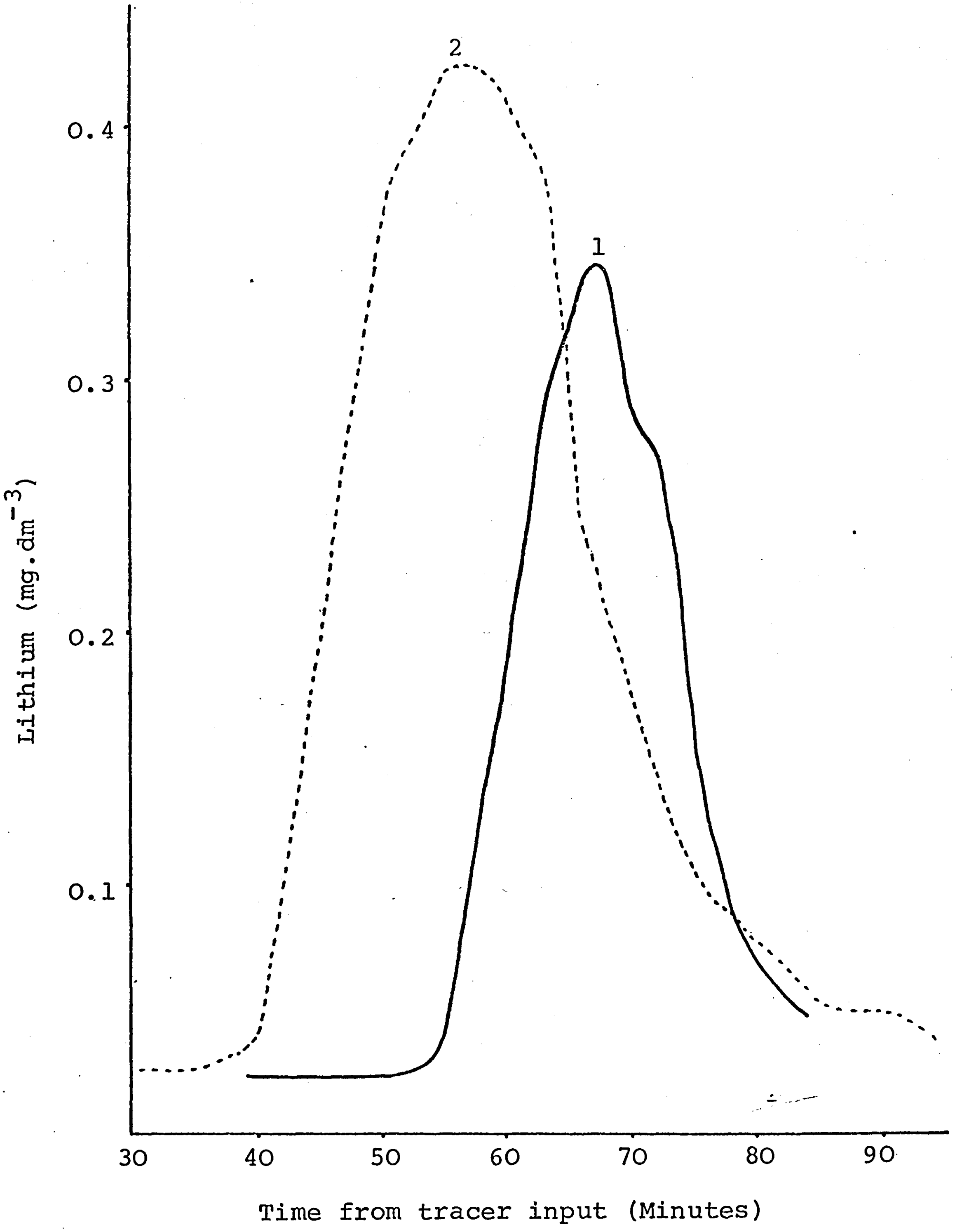
salting is widely used for the measurement of streamflows, thus it was decided to use one of the most common tracer techniques, that is, the integration or 'gulp' method. By utilising this method with a prior knowledge of the flow and concentration of tracer added, it was hoped that valuable information concerning how the water system reacted to pollutant loading would be ascertained.

An initial experiment using sodium chloride solution as the tracer was undertaken, the electrical conductivity of the water being used as the tracer determinand. It was concluded after repeated attempts using this method, that the amount of sodium chloride necessary to produce an adequate peaking of the chosen determinand was prohibitive. Thus various alternative procedures were suggested including dyes and radioactive tracers[130].

It was thought impractical and unnecessary, in this study, to use any such alternative procedures. Thus it was decided to use an essentially conservative chemical tracer, lithium chloride. Lithium was chosen, even though it was known to present adsorption problems, because of its minimal background concentration and because low levels can be easily detected using analytical atomic emission spectrometry.

A known amount of the tracer was applied instantaneously to the brook at a known distance upstream of the monitoring station. The flow of the brook was measured and thus after a suitable time period, the water pumped into the monitoring station was sampled at regular intervals.

Fig. 6-9 Lithium Dispersion Curves (Recorded at W.Q.M.S.)



This experiment was performed on three occasions using differing concentrations of tracer and distances upstream, unfortunately one experiment proved unsuccessful due to the inability to sample within the main body of the Brook, the other two are outlined in Fig. 6-9.

In the first experiment, (18.10.76) marked 1 on Fig. 6-9, 750g of Lithium Chloride was made up to $2dm^3$ of solution with deionised water, this represented 244g of Lithium. This was added instantaneously to the Brook at Station B, 1600m upstream of the WQMS. The flow of the Brook at this point was determined using a velocity gauging technique and found to be $0.38m^3s^{-1}$.

Samples were taken by the WQMS by manual use of the mono-pump. Additional manual samples were taken at a point approximately midway between the input site and the WQMS. On analysis of the samples collected, using analytical atomic emission spectrometry, it became apparent that the manually collected samples contained little or no lithium. It was concluded that this was due to the poor positioning of the sampling point. As has been reported by Belcher[131], in many rivers mixing of tracers throughout the depth may be quite rapid, but lateral mixing may only occur after many kilometres of travel. The samples obtained from the WQMS were analysed and curve 1 was the result. Analysis of the total area under the curve showed that it represented only $4.5mg.min.dm^{-3}$ of lithium. One explanation for this low tracer retrieval could be due to the phenomenon of adsorption of the lithium onto sediments and suspended matter. Impulse salting experiments, using chemical traces such as lithium, have in the past been shown to be prone to such interferences.

The second experiment was performed on 13 February 1976 under the higher flow conditions of 0.53m^3s^{-1}. The lithium (325g) was added again in solution at the same input site, sampled and analysed in the same way as before. The dispersion curve obtained, marked as 2, is shown in Fig. 6-9.

Although more tracer was added and the flow was greater there was still a very strong resemblance between the two curves. It is usual that with increasing distance a more normal distribution would be observed. As the curves both appeared skewed it was surmised that 1600m was still, as far as the hydraulic properties of the Brook was concerned, relatively close to the sampling point. The 'plug' of tracer had not, in either case, dispersed a great deal although only a fraction of the lithium added, was recovered. These facts would seem to indicate that the very large determinand perturbations observed at the WQMS, e.g. Fig. 6-6, must have been due to massive inputs of pollutants.

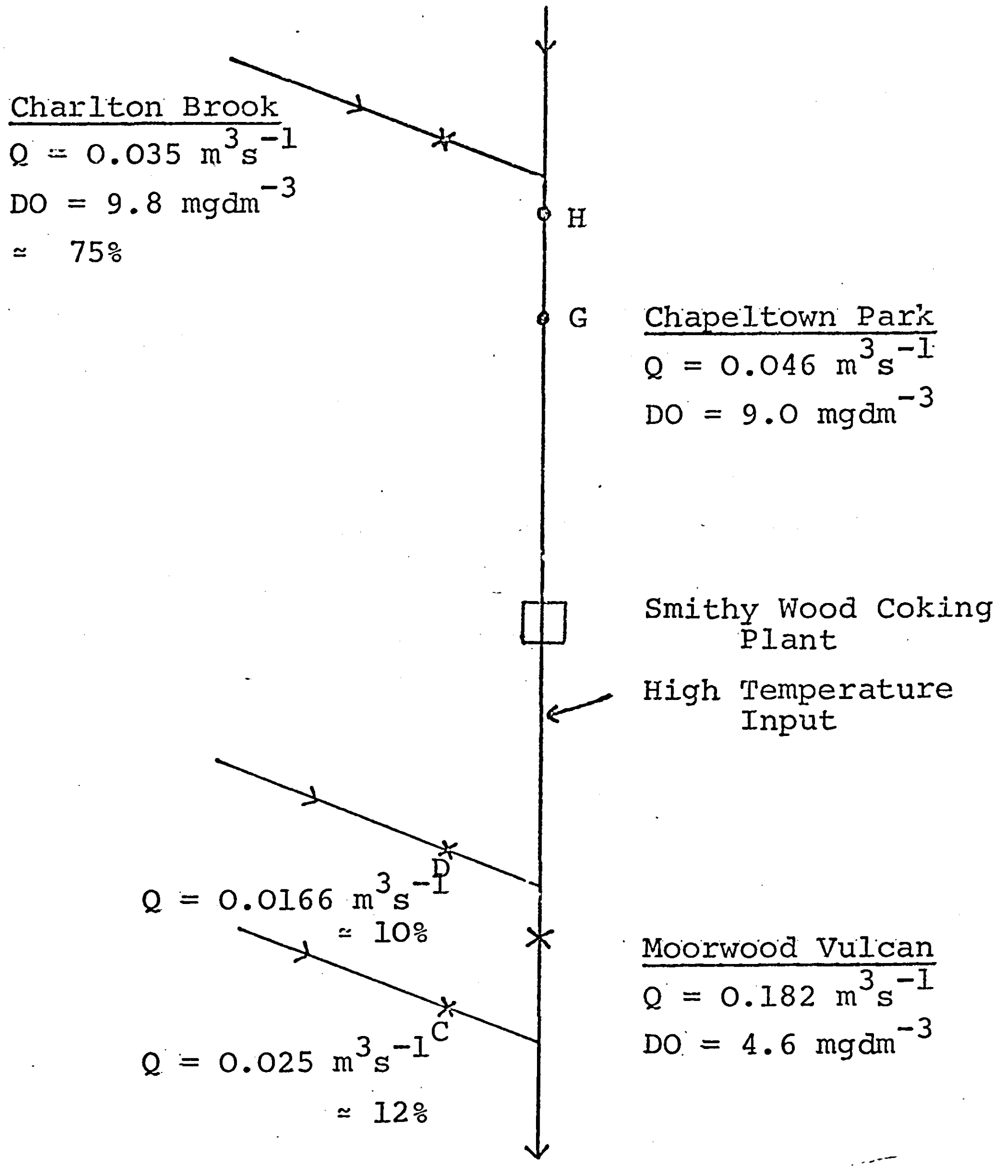
6.4 Survey of the main tributaries of the Brook

This was performed in an attempt to estimate the contribution of the tributaries to the overall flow and quality of the Brook.

Figure 6-10 outlines the results obtained from one typical survey.

The three main tributaries contributed approximately 35% to the flow in the Brook, the major contribution coming

Fig. 6-10 Survey of the Brook's main tributaries



from Charlton Brook which contributed around 75% of the flow at G. The most important feature of Fig. 6-10 was the contribution by the area below G of around 60% of the flow at Moorwood Vulcan. The variation in DO indicated that some of the inputs, in this reach were rather poor in quality.

One of these inputs, the high temperature input from Smithy Wood coking plant, was analysed for its particular contribution to the Brook. This was performed by utilising the temperature balance of the area around the input. This was done because the input was partially submerged and no other convenient method of flow gauging was possible. The position of the high temperature input can be seen from Fig. 6-10 along with points 1, 2 and 3. At each of these points the temperature was recorded. The results of this analysis being:

1. = 22.5°C
2. = 30.4°C
3. = 23.5°C

The temperature balance relies upon the fact that heat energy carried by a stream in unit time = MCT:

where T = temperature;
C = specific heat;
M = mass of water;
If Q = flow;
ρ = density of water;
then $MCT = Q\rho CT$

we can consider $\rho \approx$ constant

$C \approx$ constant

$$\therefore \quad Q_1\rho_1C_1T_1 + Q_2\rho_2C_2T_2 = Q_3\rho_3C_3T_3$$

$$Q_1T_1 + Q_2T_2 = Q_3T_3$$

and since $Q_1 = Q_3 - Q_2$

$$\therefore \quad Q_2 = Q_3 \frac{(T_3 - T_1)}{(T_2 - T_1)}$$

$$\therefore \quad \frac{Q_2}{Q_3} = \frac{T_3 - T_1}{T_2 - T_1} \equiv \text{ratio of input to stream flow}$$

then $\frac{Q_2}{Q_3} \times 100$ = % contribution to the stream flow by the input.

In this particular case the results were

$$\frac{Q_2}{Q_3} = \frac{23.5 - 22.5}{30.4 - 22.5} = \frac{.1}{7.9} = \underline{\underline{0.13}}\ m^3s^{-1}$$

Thus the high temperature input was contributing, at the time of analysis, 13% of the stream flow at that point. It can thus be seen that it would only take a few such inputs to the brook, along with the known SWO inputs, to account for the 68% total contribution within this reach. The lowering of the DO concentration is quite probably due to the action of the SWO's, the effluent from one being known to be particularly bad within this section of the Brook.

CHAPTER 7

Data Analysis and Model Development

7.1 Introduction

The continuously monitored data was recorded in a ten bit binary code on ¼" magnetic tape. Simultaneous recording was also made on an autographic chart recorder which was used to check calibration runs, as were the visual display meters, and as an indication of quality trends early on in the monitoring programme. The data record held on the magnetic tapes was that which was primarily used in the data analysis and subsequent model development.

7.2 Data Handling and Initial Analysis

The magnetic tape data was converted by the Plessey Company to a coded paper tape form. It was necessary to develop a computer program to decode the tapes and to transpose the data onto punched cards for subsequent disk file storage. This circuitous method of data transposition had to be performed because of the inability of the IBM 370 computer, on which the data analysis was to be performed, to accept punched paper tape input. Thus the punched cards were produced from the paper tape via the less advanced IBM 1130 machine.

A typical example of a computer printout of the stored data is shown in Fig. 7-1. The program not only stored the data, but also referenced it in a specially designed code with respect to time of the day, day of the

Fig. 7-1 Computer printout of stored data

A,B,C,D = The quarter hours

E,F,G = The week,the day and the hour

1 = Electrical conductivity $\mu S cm^{-1}$.
2 = Temperature °C.
3 = Suspended solils $mg\ dm^{-3}$.
4 = pH
5 = Dissolved oxygen % sat.

```
              A                      B                     C                     D             E  F  G
   1  2   3  4   5

   45513923059 62   45714019160 67   46114013260 64   46913912460 63   68 3 17
   473140 7560 67   477139 5960 68   484139 4260 69   488139 3859 69   68 3 18
   488139 3859 68   488140 4260 69   488140 5160 69   494140 4360 69   68 3 19
   500139 4061 69   506139 4161 69   510139 4262 68   512138 3962 69   68 3 20
   516138 3462 69   518137 3462 69   521137 3162 69   527137 2962 69   68 3 21
   531137 3162 68   531136 3162 68   531136 3962 67   531136 3762 67   68 3 22
   533135 3663 67   541135 3663 66   555135 3863 66   565135 3863 67   68 3 23
   570134 3463 66   576134 3563 66   576134 4063 65   574133 4663 64   68 3  0
   572131 4663 64   572131 4664 63   578131 4167 63   584130 4666 62   68 3  1
   586129 5364 61   586128 5864 60   586128 6364 59   590126 6264 58   68 3  2
   598126 6764 56   604125 6864 56   611125 7064 55   623125 6964 54   68 3  3
   629124 7064 54   639125 7164 53   641125 6664 53   647125 7064 53   68 3  4
   652125 6464 52   656125 6364 51   660125 5864 51   666125 5764 51   68 3  5
   658125 5464 51   654125 4564 52   649126 4664 52   647126 4264 52   68 3  6
   643126 4264 52   641126 3864 52   637126 4064 52   639126 3764 51   68 3  7
   647126 3464 52   651126 3164 52   658125 2664 52   664125 2664 53   68 3  8
   670126 2964 52   672126 3265 53   680126 3465 52   684126 3465 52   68 4  9
   694127 3066 53   715128 1966 55   735129 1766 56   748129 1165 58   68 4 10
   764129  965 59   770131  765 60   766131  765 60   760132  865 60   68 4 11
      0  0  0 0  0  725133  665 60   723133  665 61   735133  665 63   68 4 12
   744133  465 64   750132  365 65   762136  365 66   762135  465 66   68 4 13
   754132  366 66   750133  266 66   744133  266 67   746134  266 67   68 4 14
   758135  466 67   785136 1765 67   834137 1064 67   918137  264 68   68 4 15
   993136  163 67  1053137  361 64  1106138  859 61  1137141 1057 58   68 4 16
  1151141  956 57  1161142  955 56  1163142 1255 55  1163142 1555 54   68 4 17
```

week and the number of weeks from the commencement of monitoring.

Coincident with the data being stored on disk, experiments were performed to ascertain the best way of analysing it. It was already known from the visual chart record and the discrete monitoring programme that various interrelationships existed within the determinands. It was decided that a thorough study of these interrelationships would possible yield the greatest amount of information and that this could best be achieved by utilising multiple regression analysis.

The initial results of the analyses proved reasonably satisfactory but it was thought that the maximum amount of information was not being abstracted. The data at this stage was being analysed as it was produced, prior to any addition of flow information. It was thus decided that an overall new approach to data handling and analysis was required. This was initially performed by incorporating both monitored and estimated stream flows into the data files and hence into the analyses. The time of year was used to isolate discrete data sets and these were analysed with flow being included as a sixth determinand. It was decided that if the flow data was removed from direct involvement in the regression analyses, while still retaining its influence, then the interrelationships within the quality determinands could be more readily observed. This was achieved by the production of flow regime subfiles, a regime being a range of flows which fall between two pre-determined limits. The subfiles were chosen, as shown by Fig. 7-2, to

Fig. 7 - 2 Production and Layout of the Subfiles

	Flow regimes (m^3s^{-1})	1 (0.06 - 0.08)	2 (0.08 - 0.1)	3 (0.1 - 0.2)	4 (0.2 - 0.4)	5 (0.4 - 1.0)
Day	Time of Day (h)					
Sunday	a (0800-1800)	Sun a 1	Sun a 2			
	b (1800-2300)	Sun b 1	Sun b 2	etc		
	c (2300-0800)	Sun c 1	Sun c 2			
Monday	a	Mon a 1				
	b	Mon b 1				
	c etc	Mon c 1	etc			
Tuesday	a					
	b					
	c	etc				
Wednesday	a					
	b					
	c					
Thursday	a					
	b					
	c					
Friday	a					
	b					
	c					

(0800 - 1800h)	Working Day
(1800 - 2300h)	Evening Period
(2300 - 0800h)	Night-time

identify all possible quality variations with respect to time and flow.

Although the flow within the Brook was monitored continuously, only hourly flow values were recorded due to practical considerations with regard to the reading of the gauge charts. It was thus thought that a better understanding of the system could be achieved if the large amount of quality data was also expressed in terms of hourly variations. Mean hourly data was therefore produced, which although smoothing out short term perturbations, was able to incorporate them in the averaged value. This would not have been possible if discrete hourly data had been used.

The program used to produce the subfiles also added the DO concentration in mg dm^{-3}, calculated from the percentage saturation figure and the temperature. The data record was later altered again to include the mass flows of DO and SS, both being expressed in mg s^{-1}.

The data was analysed in a variety of ways, the intention throughout being to ascertain as much information as possible as to how and why the determinands varied.

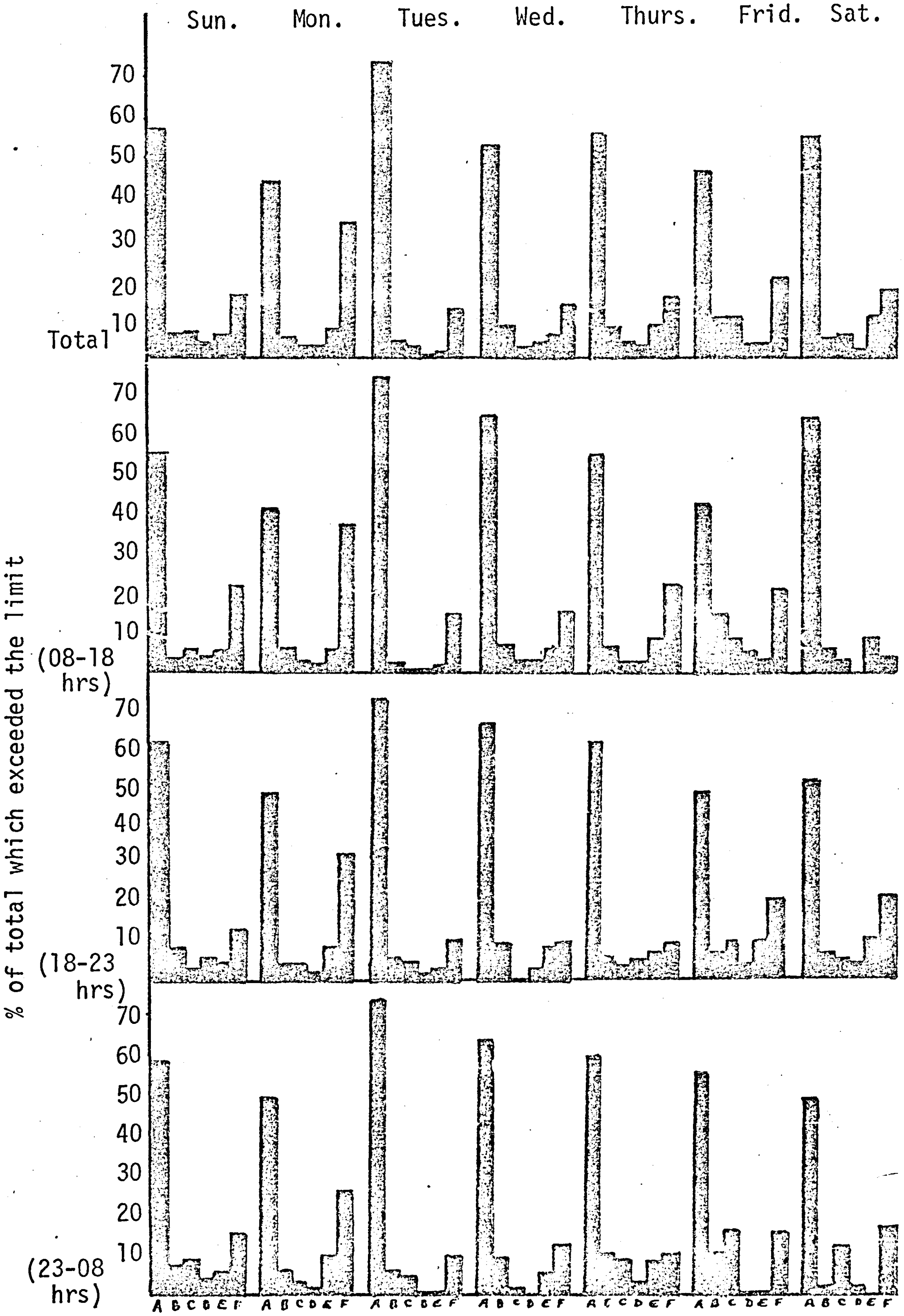
7.2.1 Quality regimes were produced to identify possible temporal trends within the data which may have had some bearing upon the model development.

A series of quality limits were written into a program which if exceeded prompted that row of data to be subsequently stored and referenced. These quality limits imposed were chosen so as to indicate when the Brook was experiencing particularly heavy pollution. All the subfiles were subjected to this analysis with a view to producing a comprehensive account of the variations. It was hoped that the results would indicate trends within the system and possibly give some added information on determinand interrelationships.

The results of these analyses are shown in Figs. 7-3, 7-4, 7-5 and 7-6. The charts show the variation of the number of data records, expressed as a percentage of the total analysed, which fall within six specified quality regimes, with respect to day of the week and period of the day. Flow regimes are not included in this analysis. It was assumed that, considering the extent of the sample population, and the fact that the data was taken from the whole of the monitored period, there would be very little probability of the flow being correlated to the days of the week.

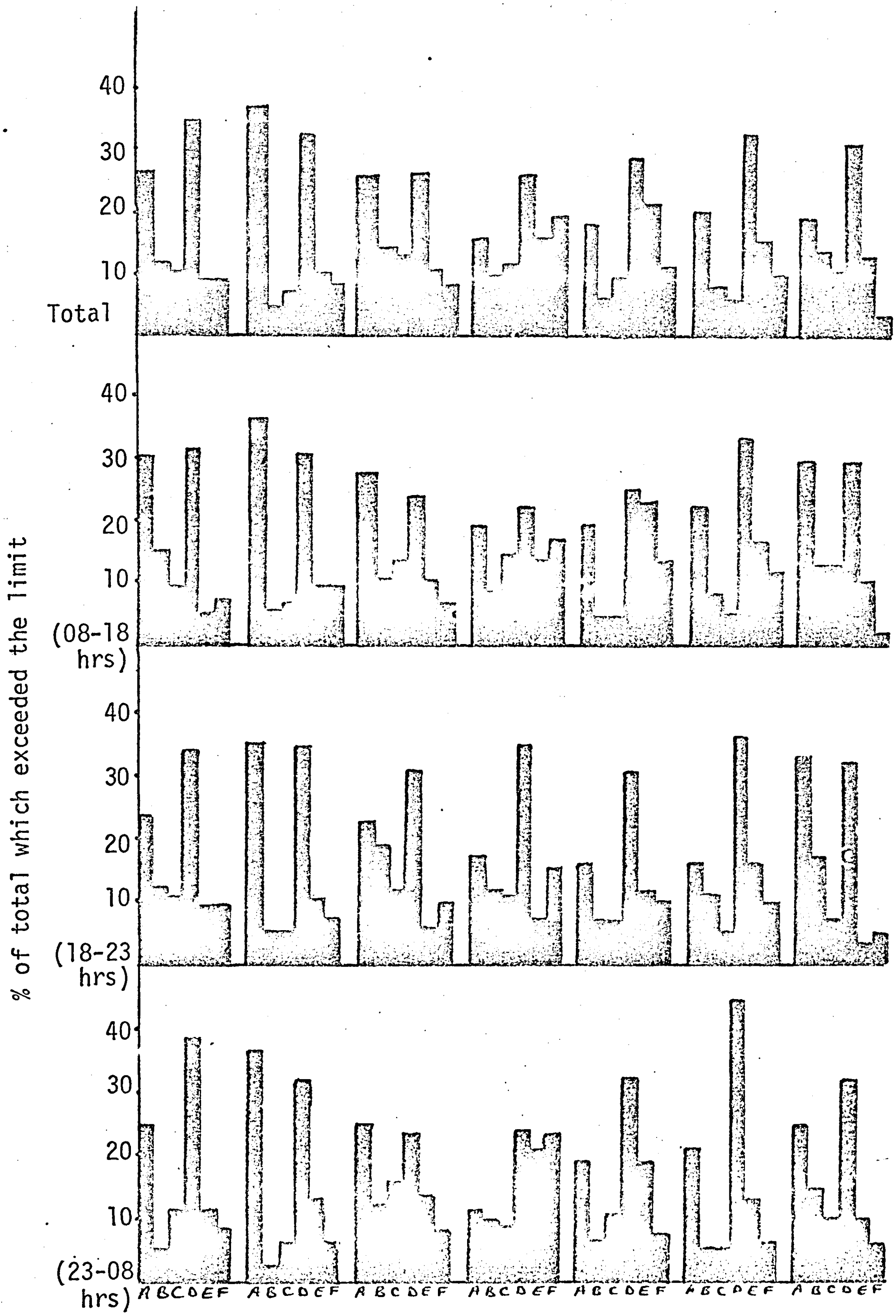
Figure 7-3 shows that the SS concentrations within the Brook tend to be either high or low, this situation tending to be biased towards the lower concentration limits. This is applicable on every day except Monday when a greater percentage of the data was found in the higher concentration regime. It was assumed that this probably resulted from the increased SS carriage within the sewers on this traditional washing day. As could be expected from a knowledge of the works practices within the catchment, a higher percentage of values within the high SS regime were discovered during the working day (0800-1800h).

Fig. 7-3 Quality Regimes (Suspended Solids)



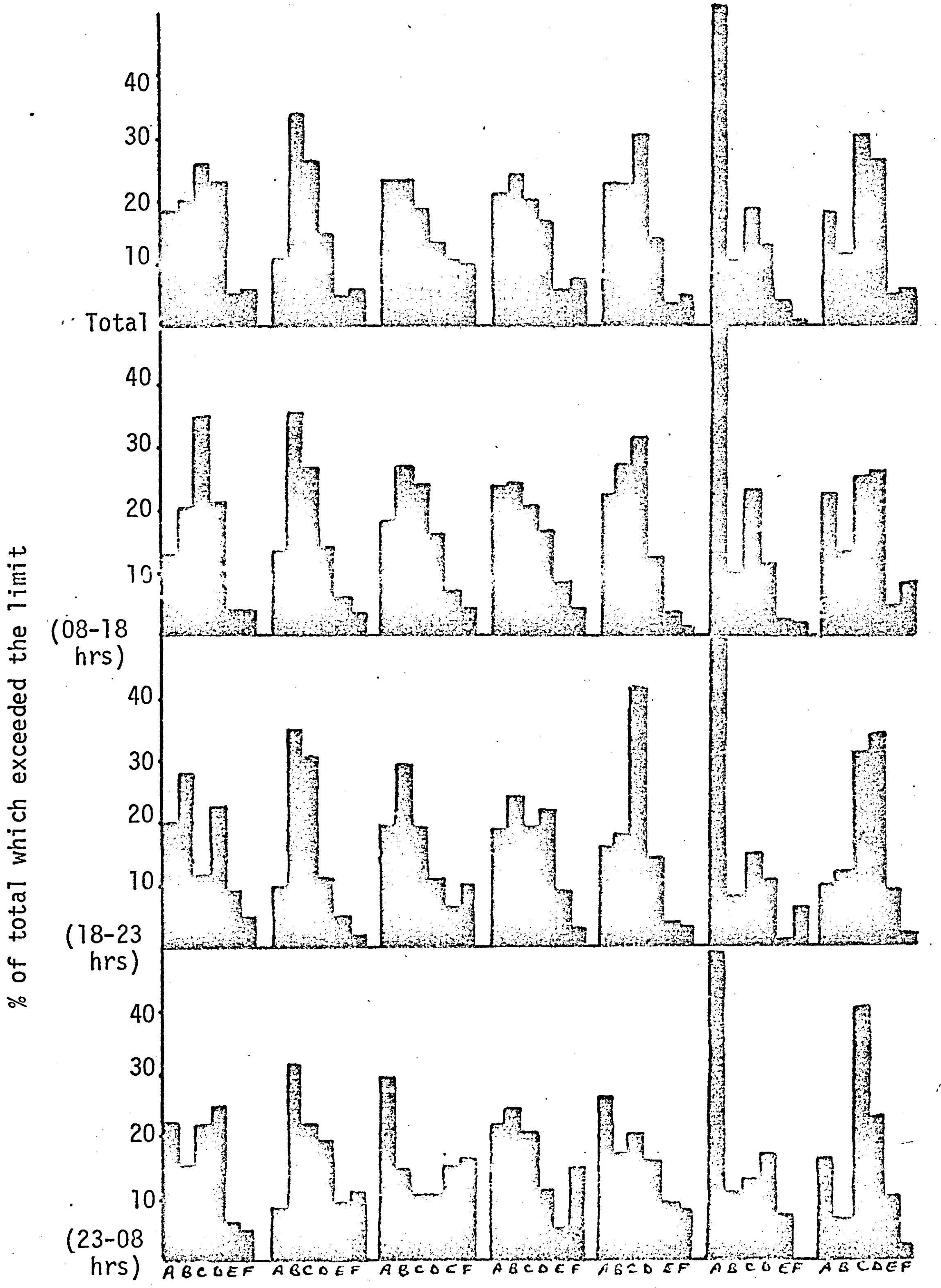
A = 0 - 50 mg dm^{-3}
B = 50 - 75 mg dm^{-3}
C = 75 - 100mg dm^{-3}
D = 100 - 125mg dm^{-3}
E = 125 - 150mg dm^{-3}
F = 175 - 200mg dm^{-3}

Fig. 7-4 Quality regimes (Dissolved Oxygen)



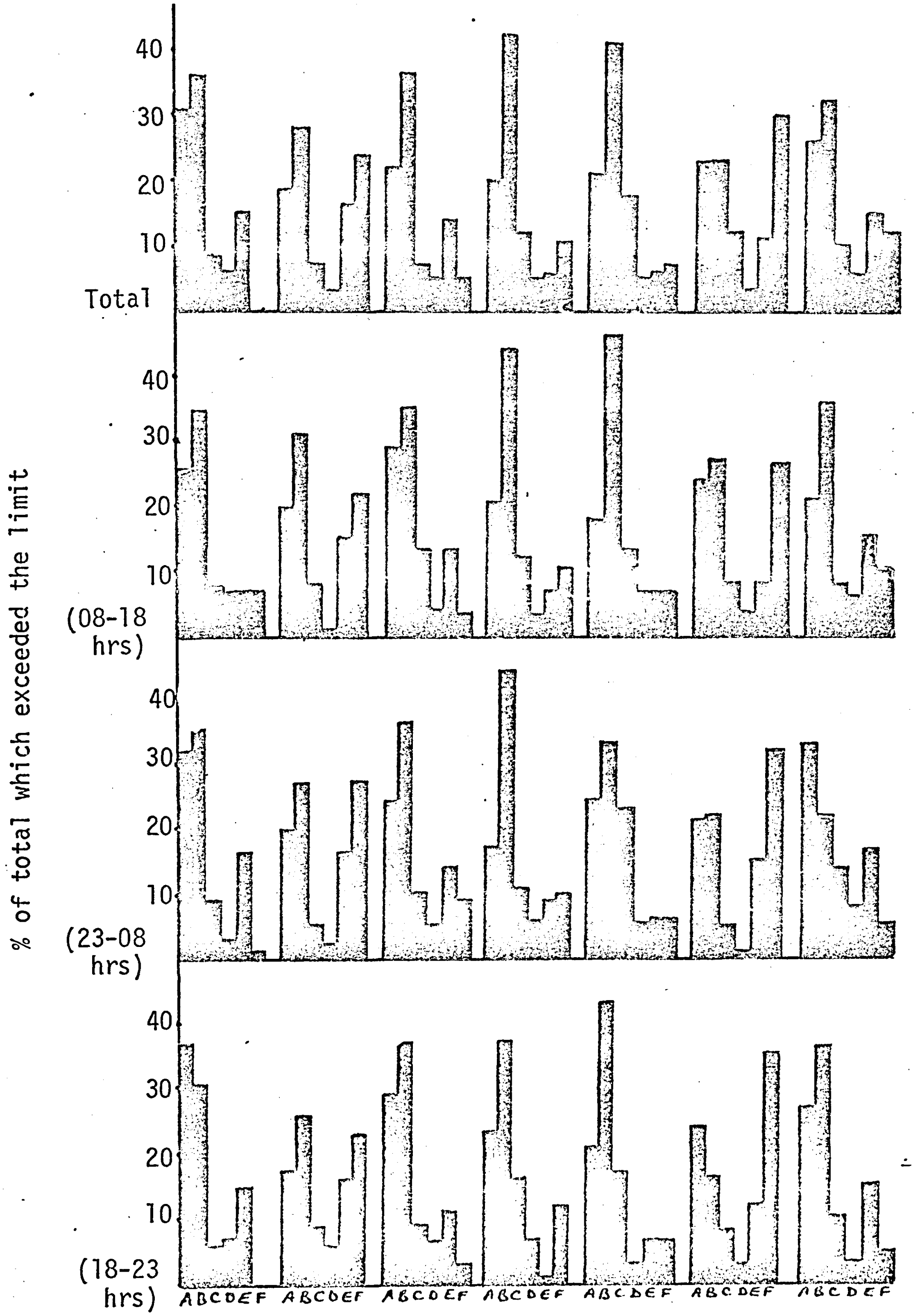
A = 80 - 70 (% sat)
B = 70 - 60 (% sat)
C = 60 - 50 (% sat)
D = 50 - 40 (% sat)
E = 40 - 30 (% sat)
F = 30 - 20 (% sat)

Fig. 7-5 Quality regimes (Electrical Conductivity)



A = 500-75o (μ S cm^{-1})
B = 750-1000(μ S cm^{-1})
C =1000-1250(μ S cm^{-1})
D =1250-1500(μ S cm^{-1})
E =1500-1750(μ S cm^{-1})
F =1750-2000(μ S cm^{-1})

Fig. 7-6 Quality regimes (pH)



A = 8 - 7 (pH)
B = 7 - 6 (pH)
C = 6 - 5 (pH)
D = 5 - 4 (pH)
E = 4 - 3 (pH)
F = 3 - 2 (pH)

Figure 7-4 as with SS shows two dominant DO quality regimes, (80-70%) and (50-40%). This correlates well with the SS situation, the high SS periods being when the DO falls below 50% saturation. The poor quality of the Brook can be clearly observed from this figure, with in most cases more than half of the DO observations being in the regimes below 50% saturation. On the whole there is little change with respect to time of day although in some cases a slight diurnal variation is observed, e.g. Wednesday where there was a change from approximately 45% of the data being above 50% saturation during the day to less than 30% being above it at night. This seems to indicate that even though there has proven to be little or no photosynthetic activity, there seem to be other temporal events which influence the level of dissolved oxygen within the Brook. These events could possibly be either hydrologic or ergonomic in nature, or a combination of both.

Figure 7-5 outlines the quality regimes of electrical conductivity. In general the distribution of the regimes throughout the day was not particularly variable. The Tuesday histogram for the working day (0800-1800h) is however significantly different to the night-time (2300-0800h). In the latter there is a departure from the normal distribution to produce the opposite i.e. high or low extremes. On analysis with respect to the day of the week it appears that from Tuesday to Friday the pattern of observations is very similar. These days show a typically high predominance of low EC levels with a gradual tailing off towards the upper limits. This is unlike Monday which tends to show a more normal distribution.

In conclusion, although there were no striking variations in the distribution of the conductivity regimes observed during the day, there do appear to be definite changes with respect to days of the week.

Figure 7-6 outlines the distribution of the pH quality regimes throughout the day and the week. The variations which occur with respect to time of day do not seem to be prominent enough to be of importance, unlike the variations through the week. Even though one could reasonably expect a lowering of the buffering capacity of the water due to the reduction in industrial activity at night, with a subsequent reversal to a 'natural' low pH level maintained by minewater infiltration, this does not appear to occur. This could possibly be in part explained by considering the operation of the storm water overflows. The fact that most industrial effluent is discharged to sewer during the day does not eliminate the possibility of infiltration of effluent into the Brook at night. This lagging effect of the sewers along with the possibility of unusual works practices with regard to effluent disposal, may account for the relatively constant level of pH with respect to time of day.

With the exception of Monday and Friday the distribution of the observations tends to be very similar, with the majority of them being between pH 8 and pH 6. Monday and Friday are seen to be completely different, in that there is an increase in the number of observations below pH 4 with a subsequent reduction in those above pH 5. Throughout the whole of the week, with the exception of Sunday, there is an alarmingly high percentage of observations below pH 3. The average percentage for the days Tuesday, Wednesday, Thursday and Saturday being 7.5. It is unlikely that these high acidic conditions are the result of random inputs or minewater infiltration since if they were, it is probable that they would have been detected, especially at Station H, by the discrete monitoring programme (see section 3.4.2), which in fact failed to discover any such conditions. The high proportion of acidic conditions throughout most of the week, with the excessive amounts on Monday and Friday, could possibly indicate a more systematic discharge of pollution. The extent of these discharges must have been massive when one considers the pH levels observed, their duration and the inate buffering capacity one could reasonably expect to be present within such a polluted stream. They could possibly reflect delivery or discharge practices at premises very close to the station.

7.2.2 Mass flow analysis

This was performed by the mean values of the mass flows for both SS and DO being calculated from each subfile, see Fig. 7-2. The intention of this analysis was to discover any trends within the variation of the actual quantities of SS and DO within the Brook.

A preliminary examination of the variation in mass flow of the two determinands throughout the day revealed that no obvious trends were present. It was thus decided to total the mass flows for each day and examine their variation through the week.

Fig. 7-7 Mean mass flow of SS with days of the week

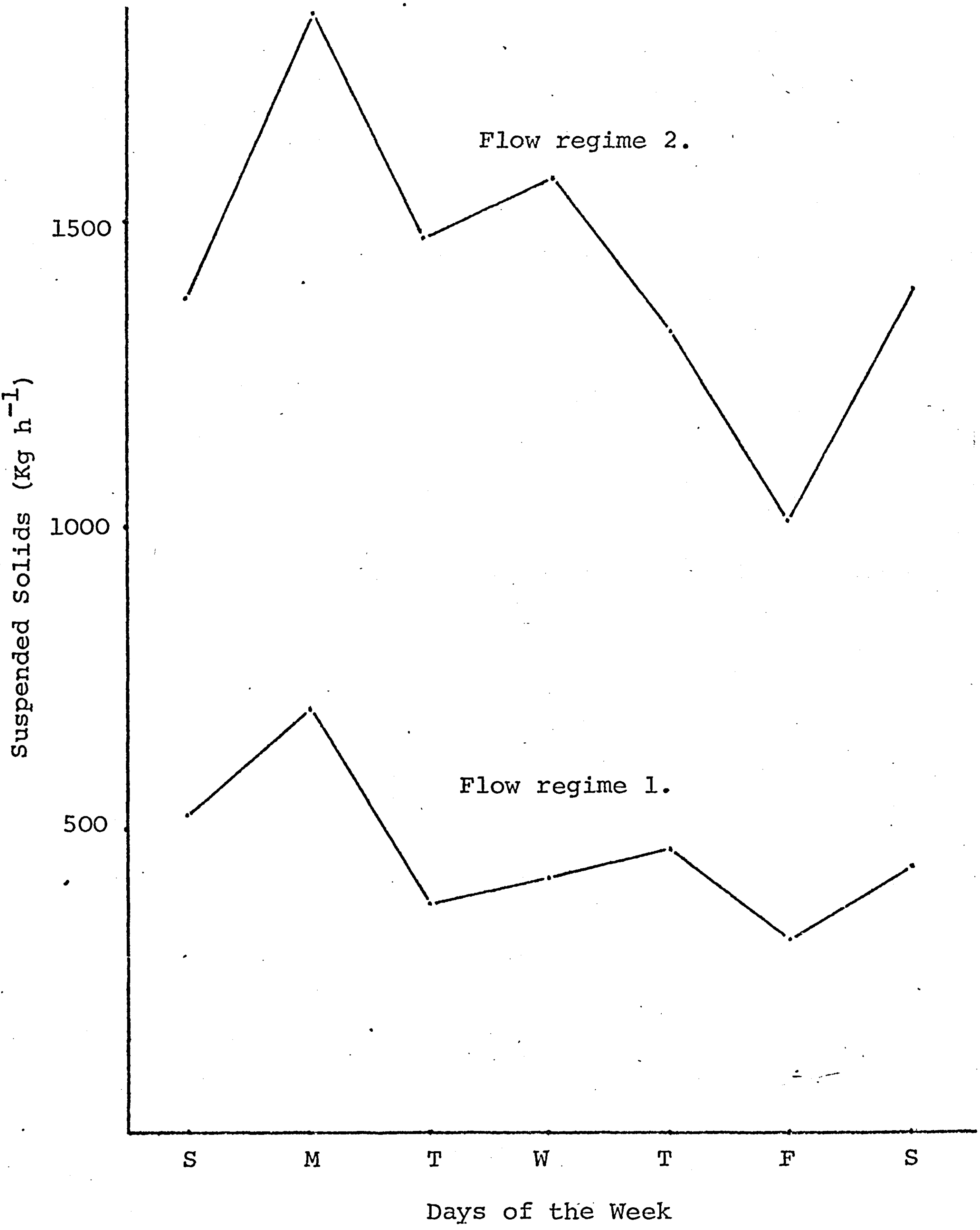


Figure 7-7 outlines the variations in SS observed within the first two flow regimes. The observation of greatest SS loading on Monday agrees with the results of the quality regime analysis, Fig. 7-3. The low mass flow values for Friday could possibly be explained by the pH conditions of the water on this day. As indicated in Fig. 7-6 Monday and Friday were days on which the Brook, at the sampling position, was on average of a highly acidic nature for considerable periods of time. It is possible that the acidic nature of the water contributed in some way to the variations observed in SS, e.g. it is known (section 6.2.1.3.) that the majority of the iron within the Brook was present within the suspended solids, in the oxidized iron III state presumably as aggregates of colloidal basic iron III oxides. In acidic conditions these would tend to go into solution e.g. as iron III chloride complexes so reducing the concentration of suspended matter. The SS level would be further reduced if the ferric aggregates were acting as nucleating agents with respect to colloidal material, the dissolution of the iron hence encouraging the breakdown of the suspended conglomerates.

The SS carried by the Brook originated from many sources and hence was of a highly complex and diverse nature. Although it would be difficult to accurately predict the occurrence of particular types of suspended matter, in such a dynamic system, it may be useful to consider the possibility of the SS load carried on Monday being of a different type to that carried on Friday. This theory could be possibly reinforced by the knowledge, that on Mondays the sewers would be expected to be carrying increased domestic loading,

Fig. 7-8 Mean Mass Flow of DO with days of the week

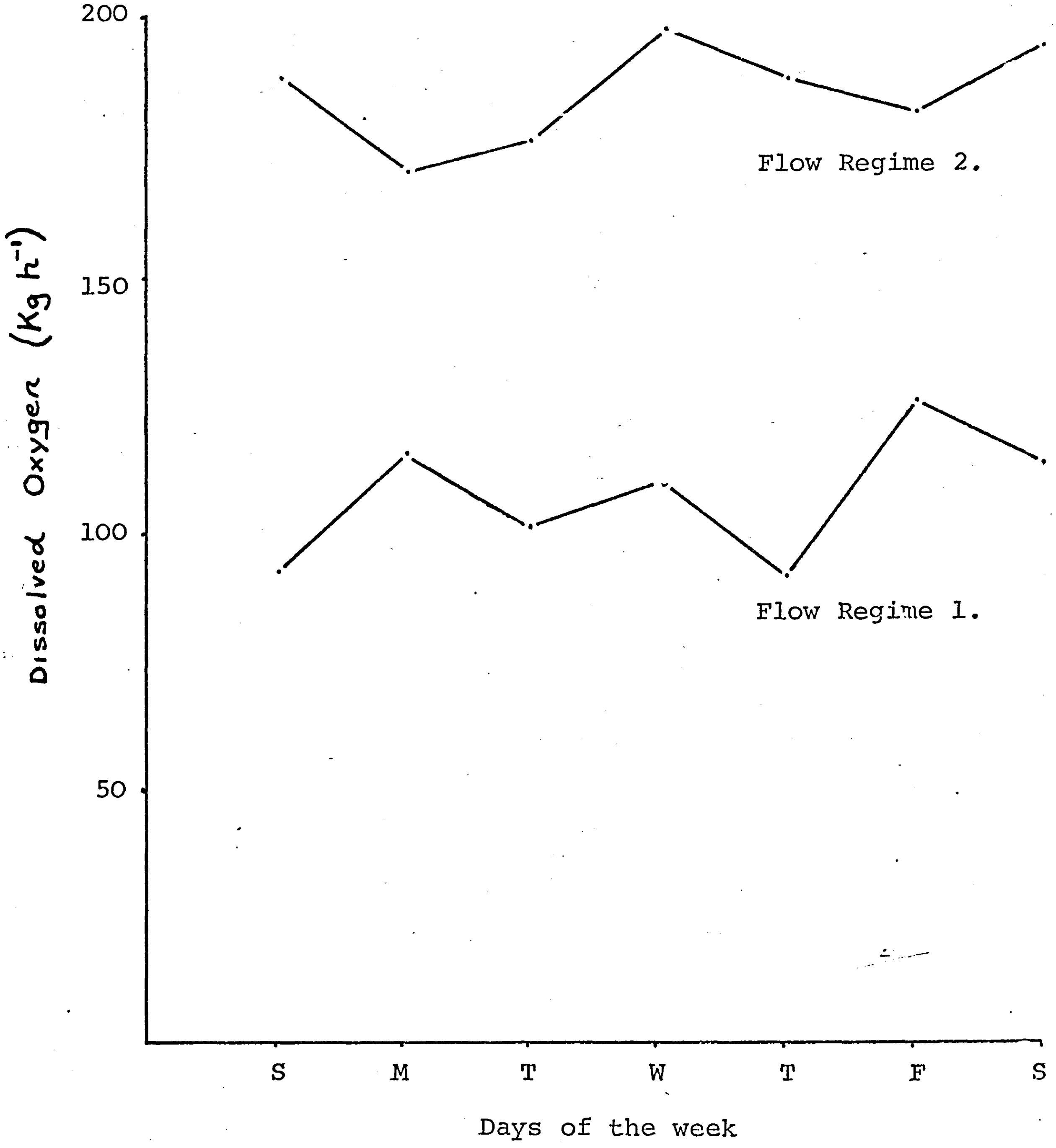
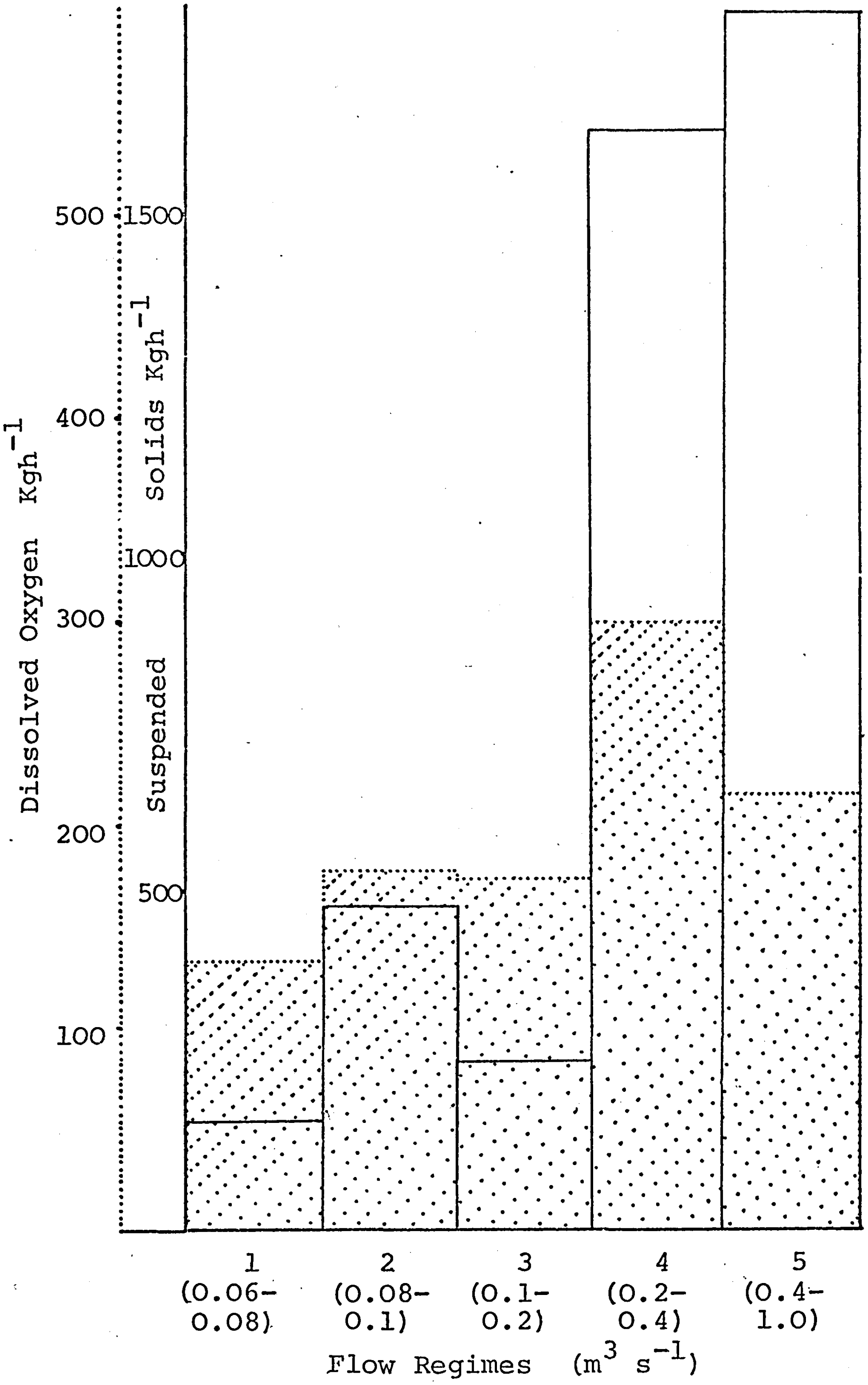


Fig. 7-9 Mean mass flows of Suspended Solids and Dissolved Oxygen



as it is the traditional wash day.

Dissolved oxygen did not show such trends in its relationship to the day of the week, as shown in Fig. 7-8. This further emphasises the fact that although closely related to SS, its presence within the Brook was also controlled by many other factors.

The mass flow values of the subfiles in each flow regime were then totalled and averaged, as shown in Fig. 7-9. This showed that with the exception of flow regime 3 an increase in stream flow resulted in an increase in the mass of suspended matter present within the Brook. It would be dangerous to draw too many conclusions from the apparent fall in SS mass flow in regime 3, as the delineation of the regimes was performed somewhat arbitrarily. Although regime 3 does seem somewhat of an anomaly there does appear to be some overall difference between SS mass flow conditions below regime 4 and those above it. As would be expected the majority of observations made were within the lower flow regimes, the first three accounting for some 94% of the total. This fact may have some bearing upon Fig. 7-9 in that it is probable that in regimes 4 and 5 the data was derived from the extreme conditons experienced during heavy storm periods, for example the first flush of suspended matter from SWO's.

The great variation in mean mass flows of suspended matter shown between regimes 3 and 4 may thus serve to re-emphasise the complex nature of the system under study. Throughout the whole system there are many different types of effluent which pollute the Brook. As previously indicated it is thought likely that the major contributor to the water pollution within the Brook is the inadequate sewerage system, but even within this there is complexity. There are some SWO's which as already mentioned discharge continuously, there are others which in fact operate correctly and only discharge under storm conditions and finally there is a whole series of overflows which operate somewhere in between these two extremes. Thus under such conditions to expect there to be a simple relationship between flow rate and suspended solid concentration may be somewhat naive.

The presence of so many diverse effluent inputs could logically lead to the suggestion that there could be different types of suspended matter present. If this were true it is possible that each type would have its own properties with respect to the variation in stream flow. One such property of great importance is the susceptibility of a suspended particle to deposition or scour. Such action is not only dependent upon the particle size but also upon the velocity of the water. Shields [133] has defined a critical scouring velocity in terms of the physical characteristics of the particle concerned and various coefficients. Shields formulae is outline in equation (7-1)

$$V_c = \frac{\sqrt{8\ Bg\ (s-1)d}}{f} \qquad \ldots\ldots\ldots\ldots\ (7\text{-}1)$$

where V_c is the mean channel velocity (m s^{-1}) at which scour commences; B is a constant; g is the gravity constant f is the Weisbach-Darcy friction factor; s is the specific gravity of the particle and d its diameter.

The determination of the scouring velocity V_c enables the type of suspended matter present within the watercourse to be ascertained. Thus if the stream velocity is below V_c then it is likely that the SS present has been derived from recent inputs to the system, whereas with velocities above V_c the SS could not only be derived from such inputs but also from the effects of scour upon the benthos of the stream. In the particular case of the Blackburn Brook, the discrete sampling programme identified numerous sites of suspended matter deposition, particularly immediately downstream of surcharging SWO's. Such sites would be ideal sources of vast amounts of organic suspended matter should V_c be exceeded.

Tests have shown that for freshly settled organic matter V_c 0.18 m s^{-1} (134) this was for granular organic matter with diameters up to 1mm. The coefficient B takes into account the amount of compaction which has occurred within the organic deposit. If the stream velocity falls below V_c over extended periods, then organic settleable solids will deposit. During deposition the particles tend to coalese to form larger aggregates; hence the sizes to be scoured increase with the resultant increase in the velocity required to induce scour.

Within the flow regimes apertaining to this particular study, regime 5 and probably regime 4 would have V_c values in excess of 0.18m s^{-1}. As previously explained in section 4.4, the flow gauging had to be performed some little distance upstream of the sampling position. Therefore the V_c value calculated below only relates to the water velocity at the gauging point, although it does indicate the typical magnitude of water velocity within the Brook.

Total cross sectional area
of weir = 5 x h (m) where h = depth (m).

From theory (see section 4.4.1)
at $h = 0.09m$, $Q = 0.2$ (m^3s^{-1})
where Q = discharge

$\therefore\ 5 \times 0.09 \times V = 0.2$ where V = velocity ($m\ s^{-1}$)

$\therefore\ \underline{V = 0.44\ m^3s^{-1}}$

Thus in flow regime 4 (0.2 - 0.4 m^3s^{-1}) the velocity of the water at the gauging site was much greater than V_c. It is therefore suggested that the large increase in SS within regimes 4 and 5 is possibly due, not only to the increased flow from already surcharging SWO's and the operation of ones previously not discharging, but also to the stream velocity exceeding the mean scouring velocity, V_c, and hence lifting material, mainly organic in nature, from the bed of the Brook as well as from areas of previous deposition.

The variation in mean dissolved oxygen mass flow with respect to flow regime, is also outlined in Fig. 7-9. This shows a variation with increased flow, although once again it must be remembered that the flow regimes are somewhat arbitrary and so at best only general trends can be deduced from them. The most interesting aspect of Fig. 7-9, with regard to DO, is the depression of the mass flow during periods of very high streamflow. This indicates that there is not one simple explanation for DO variation such as increased flow leading to increased turbulence hence more DO. Although this simplistic argument may in part be valid, the physical and chemical condition of the actual water has also to be taken into consideration.

Therefore the DO depression within regime 5 was probably a direct result of the large increase in the organic loading of the Brook, and the low dissolved oxygen concentration of the sewage based effluent.

7.3 Statistical Analysis

Initial multiple regression analysis was performed on all the early data, with each of the determinands, excluding temperature, in turn being taken as the dependent variable. These analyses indicated relationships which were present as well as indicating that although pH and EC were important determinands the quality of the Brook could best be described by the dissolved oxygen concentration, a universally accepted overall quality indicator and the suspended solids concentration, a determinand of great importance in this particular Brook. This fact is also born out by the results of the discrete monitoring programme.

It was thought that SS and DO were more amenable to modelling than were the other two variables due to their close relationship with hydrological variations and other quality parameters. It was also thought that a model based upon these two determinands would prove more useful, as they can be regarded as being good examples of two distinct types of determinand i.e. primary and secondary. Suspended solids is regarded as a primary determinand since its concentration depends largely upon the quantity of suspended matter introduced into the Brook. Dissolved oxygen on the other hand may be regarded as a secondary determinand as its concentration is dependent upon a multitude of other factors, e.g. temperature and oxygen demand. Thus it was decided to restrict the modelling, at least initially, to the two dependent variables, dissolved oxygen and suspended solids.

The first consideration was to quantify the interrelationships which were known to be present, while also determining the most important controls on the two dependent variables analysed. This was performed by the production and analysis of partial correlation coefficients.

7.3.3.1 Partial correlation coefficients were calculated for all four independent variables per dependent variable for each flow regime. These coefficients provided a means of ranking the independent variables in order of importance with relation to the dependent variable in question. This was most important as an inherent simplicity is one of the most important characteristics of any useful model. Hence the need to ascertain the lowest number of independent variables necessary to produce an acceptable prediction of the dependent variable.

The partial coefficients were examined to ascertain if the various interrelationships between the variables were affected by the flow regime, the day of the week or the time of day. Although no trends were observed with respect to the day of the week or the time of day there were distinct variations observed through the five flow regimes. In order that the partial coefficients could be better compared with respect to the flow regimes, mean partials were produced for every independent variable under every flow regime. This was performed by imposing 90% confidence limits upon the partial coefficients of each independent variable. For example, the effect of electrical conductivity on the dependent variable, dissolved oxygen under flow regime 1, was expressed by twenty one individual partial correlation coefficients, all needing to be analysed.

After imposing the 90% confidence limits the mean value was determined as was the standard deviation. In an attempt to utilise the standard deviation, it was decided to subtract it from the mean value in every case. Thus mean coefficients were produced which compensated for the standard deviation within the population.

These compensated partial correlation coefficients (CPC) were then analysed to deduce which independent variables were the most important with regard to dependent variable prediction.

In an attempt to display the significance of the various coefficients to the dependent variable, 'half-moon' diagrams were constructed. These relate the value of the coefficients irrespective of sign, to the angle from the horizontal. The 180^o arc was divided up and related to the maximum coefficient value of 1.0. Thus every CPC was multiplied by 180^o to obtain its relative angle from the horizontal. The size of this angle, α as shown in Fig. 7-9, is therefore an indication of the significance of that particular independent variable to the dependent variable. That is, the greater the size of angle α the more significant is the independent variable.

Table T-7-1 and T-7-2 outline the mean partials, the standard deviations and compensated partials calculated. They also show the angle each CPC represents in relation to the 'half-moon' diagrams. Half-moon diagrams were constructed

Table T-7-1

Dependent variable	Flow Regime		Independent variables			
			EC	T	SS	pH
DO	1	$\bar{p}$	-0.248	-0.321	-0.277	-0.216
		s	0.095	0.162	0.111	0.085
		P	-0.153	-0.159	-0.166	-0.131
		A	152	151	150	158
DO	2	$\bar{p}$	-0.274	-0.398	-0.333	-0.293
		s	0.111	0.153	0.132	0.147
		P	-0.162	-0.245	-0.201	-0.146
		A	151	136	144	154
DO	3	$\bar{p}$	-0.307	-0.451	-0.448	-0.490
		s	0.137	0.197	0.220	0.147
		P	-0.170	-0.254	-0.228	-0.343
		A	149	134	139	118
DO	4	$\bar{p}$	-0.695	-0.846	-0.701	-0.512
		s	0.062	0.171	0.272	0.111
		P	-0.633	-0.775	-0.429	-0.401
		A	66	41	103	108
DO	5	$\bar{p}$	-0.438	-0.336	-0.285	-0.458
		s	0.269	0.276	0.191	0.170
		P	-0.169	-0.060	-0.094	-0.388
		A	150	169	163	128

$\bar{p}$ = mean partial correlation coefficient.

s = standard deviation

P = $\bar{p} - s$ i.e. compensated partial correlation coefficient

A = angle from horizontal in degrees.

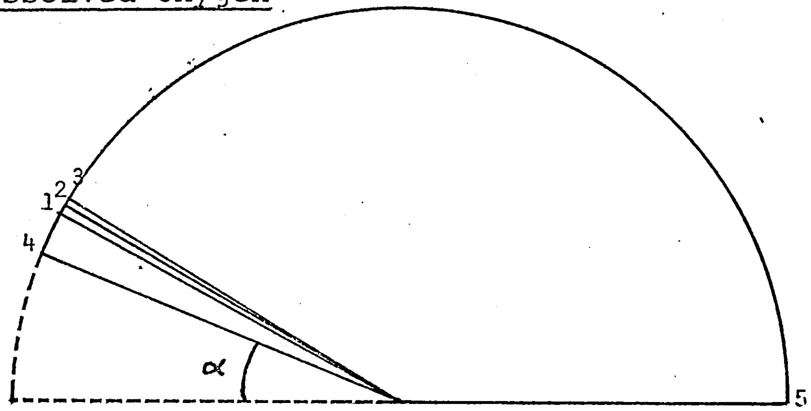
Table T-7-2

Dependent variable	Flow regime	Independent variables				
			EC	T	pH	DO
SS	1	$\bar{p}$	-0.291	-0.237	+0.236	-0.266
		s	0.110	0.126	0.101	0.112
		P	-0.181	-0.111	+0.135	-0.154
		A	147	160	156	152
SS	2	$\bar{p}$	-0.310	+0.424	+0.407	-0.333
		s	0.194	0.200	0.179	0.132
		P	-0.116	+0.224	+0.228	-0.201
		A	159	139	139	144
SS	3	$\bar{p}$	-0.272	-0.360	+0.244	-0.448
		s	0.171	0.192	0.147	0.220
		P	-0.101	-0.168	+0.097	-0.228
		A	162	150	162	139
SS	4	$\bar{p}$	+0.306	+0.635	+0.402	-0.701
		s	0.247	0.417	0.111	0.272
		P	+0.059	+0.218	+0.291	-0.429
		A	169	141	128	103
SS	5	$\bar{p}$	+0.329	-0.443	+0.454	+0.285
		s	0.184	0.381	0.370	0.191
		P	+0.145	-0.062	+0.084	+0.094
		A	154	169	165	163

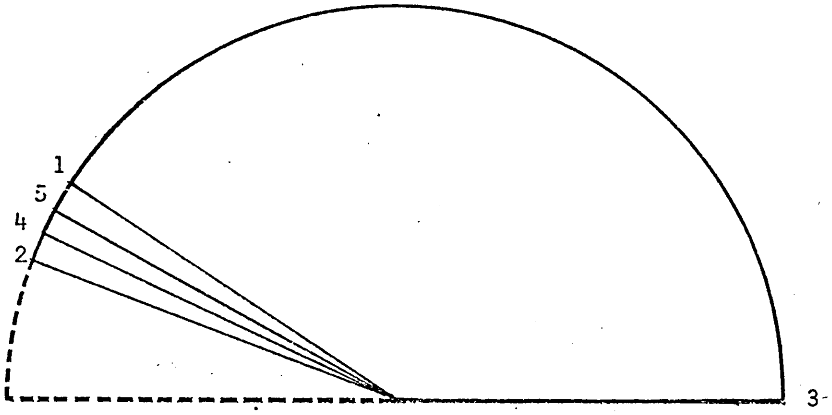
Fig. 7-10 Compensated Partial Correlation Coefficients

Flow Regime 1 (0.06 - 0.08)

Dissolved Oxygen



Suspended Solids



1 - Electrical Conductivity

2 - Temperature

3 - Suspended Solids

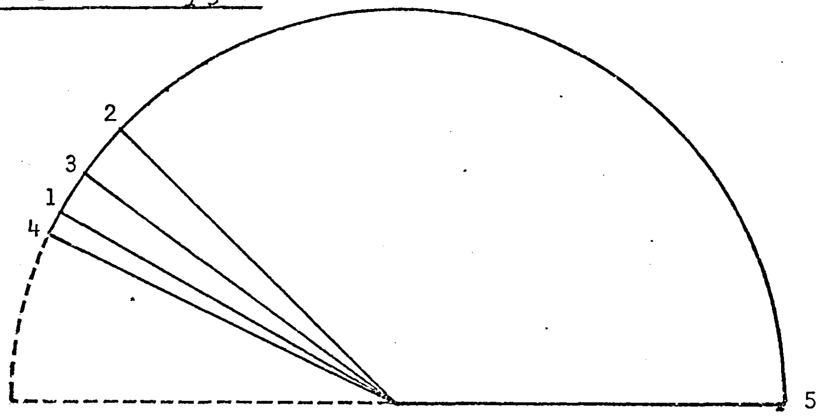
4 - pH

5 - Dissolved Oxygen

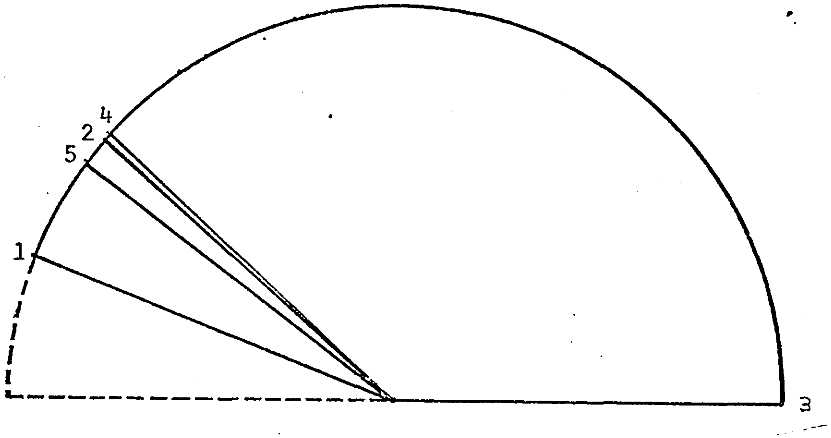
Fig. 7-11

Flow Regime 2 (0.08 - 0.10)

Dissolved Oxygen



Suspended Solids

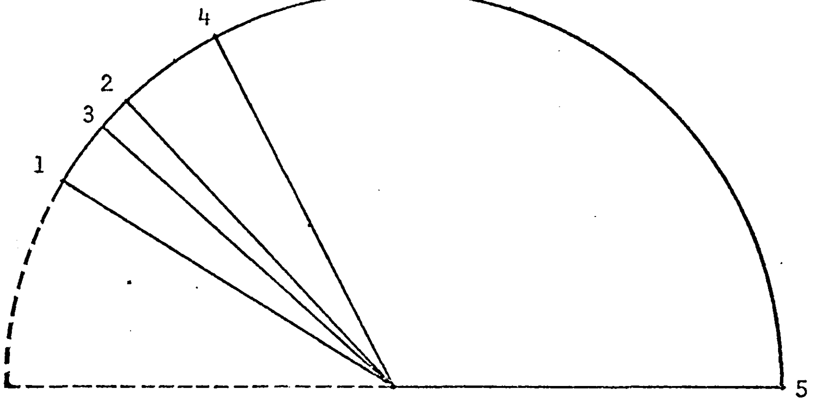


1 - Electrical Conductivity
2 - Temperature
3 - Suspended Solids
4 - pH
5 - Dissolved Oxygen

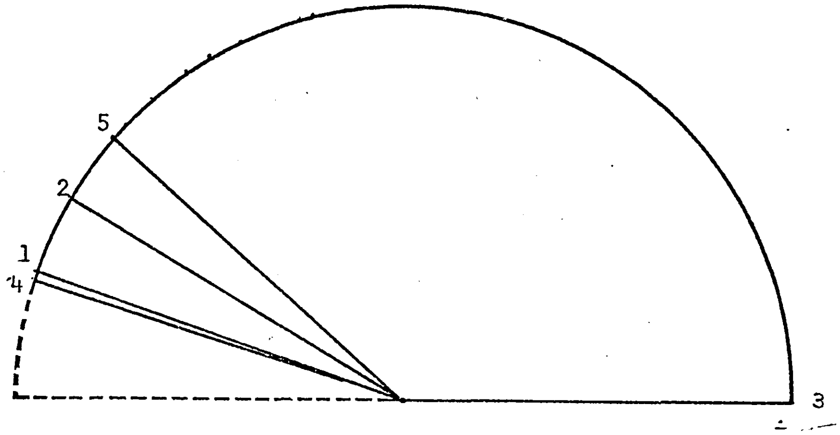
Fig. 7-12

Flow Regime 3 (0.10 - 0.20)

Dissolved Oxygen



Suspended Solids

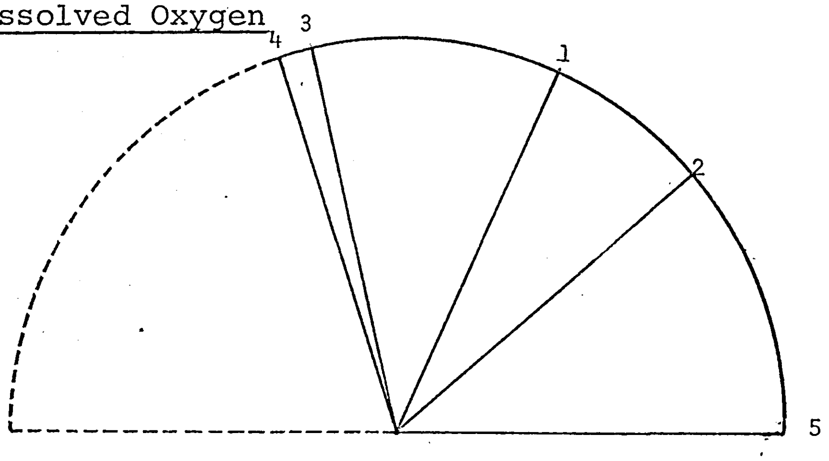


1 - Electrical Conductivity
2 - Temperature
3 - Suspended Solids
4 - pH
5 - Dissolved Oxygen

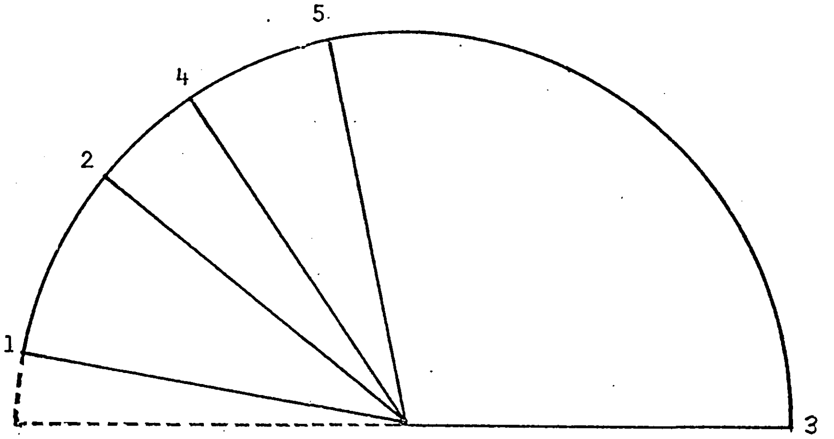
Fig. 7-13

Flow Regime 4 (0.20 - 0.40)

Dissolved Oxygen



Suspended Solids

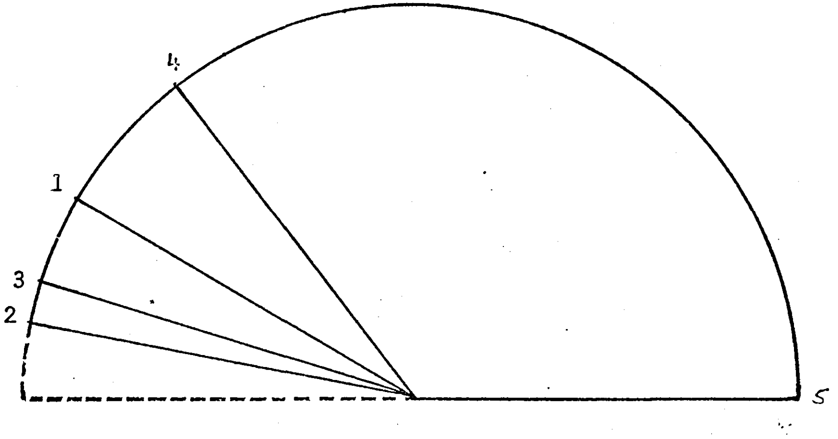


1 - Electrical Conductivity
2 - Temperature
3 - Suspended Solids
4 - pH
5 - Dissolved Oxygen

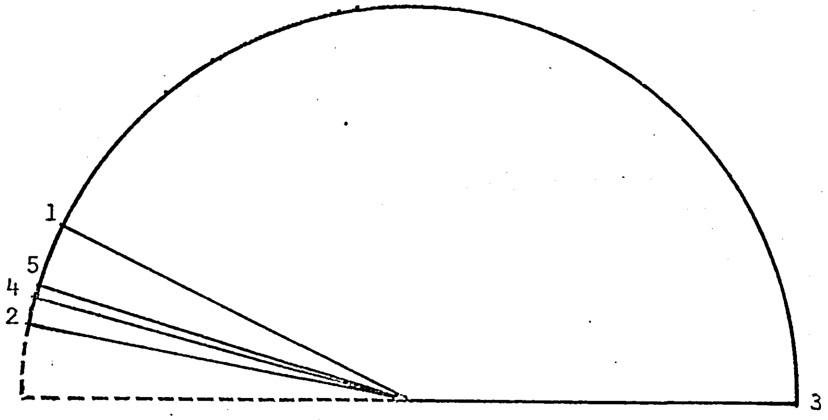
Fig. 7-14

Flow Regime 5 (0.4 - 1.0)

Dissolved Oxygen



Suspended Solids



1 - Electrical Conductivity
2 - Temperature
3 - Suspended Solids
4 - pH
5 - Dissolved Oxygen

for each of the two dependent variables DO and SS, for each flow regime, as shown in Figs. 7-10, 7-11, 7-12, 7-13 and 7-14. It was possible to see from these diagrams the extent of the relationship existing between the dependent and independent variables. It was also apparent from the diagrams that in most cases, the compensated partial correlation coefficients were rather small. There was only one instance of a CPC exceeding the value of 0.7, that was the temperature effect on dissolved oxygen in flow regime 4. In fact the average of the largest CPC for each flow regime was only 0.363 for DO and 0.242 for SS.

There are a number of explanations for these disappointing coefficient values, but possibly the most important relates to the fact that in reality the individual determinands do not operate within such a complex system as the Blackburn Brook, in isolation. This means that the actual values of the partial correlation coefficients are possibly therefore not as important, as their ranking with respect to the dependent variable. It can be clearly seen from the 'half-moon' diagrams, that this ranking of importance of the individual independent variables varies with flow regime.

Dissolved oxygen as dependent variable showed some interesting variations within the independent variable rankings. Under the low flow conditions of regimes 1 and 2 the most important determinands were seen to be suspended solids and temperature. Although these two determinands were shown to be the most important, the gap between the highest and lowest with respect to their partial correlation coefficients was very small. This gap however was shown to increase with increasing flow regime.

Suspended solids is shown in all cases to be a most important determinand, although with increased flow it does appear to lose, at least partially, its controlling powers. This once again emphasises the complex nature of the system studied. It is undoubtedly true that an increased flow generally results in an increased SS loading, as outlined in Fig. 7-9, but it also appears that after the SS concentration has reached a high level, a further increase is not necessarily concurrent with a proportional decrease in dissolved oxygen concentration. This is born out again by Fig. 7-9, where SS mass flow levels are shown to rise markedly in flow regime 4, whereas DO levels rose proportionally more slowly. This could be one of the reasons why SS was seen to be less dominant in DO control under these higher flow conditions. Another reason may be the fact that DO is a much more complex determinand than SS. The DO determinand is the concentration of a gas within a liquid, a liquid which in this case contained numerous diverse and possibly toxic chemicals. The concentration of oxygen in the water is controlled by many factors, physical, chemical and biological. These include the presence or absence of photosynthetic flora and/or oxygen demanding micro-organisms. Another aspect is that oxygen is less soluble in highly conductive water, which polluted water may be. Water of high ionic strength would also tend to give low readings on a dissolved oxygen electrode since the electrode measures activity. The amount of turbulence within the watercourse also has a marked effect upon DO concentration although the presence of surface active chemicals from, for example, synthetic detergents, could act as aeration inhibitors. Along with these points are many others which include such important factors as water temperature, depth and the presence or absence of sludge banks which may be stationary point sources of high BOD and possibly anaerobic activity.

Thus it can be seen that the level of oxygen dissolved in a stream can be affected by any one or combinations of a multitude of factors. Whereas suspended solids concentrations have been shown to be mainly affected by stream flow and as such are somewhat simpler to study.

Suspended solids as the dependent variable also showed some interesting relationships. Under low flow conditions EC and DO were shown to be the most important independent variables, although in flow regime 2, T and pH had the highest coefficient values. This would seem to indicate the possibility that under the conditions of low flow, the nature and quantity of the suspended solids had a great influence upon the overall water quality of the Brook, as noted in section 7.3.2.

The closeness of the coefficient values is an interesting feature of this analysis. This closeness, among all four independent variables, can be better understood when examined in the context of the system studied. It is known, for example, that there have been frequent discharges of oxygenated acid waste into the Brook (see section 6.1.3.). Such events would not only have the effect of reducing the pH and increasing the conductivity, but also possibly reducing the population of oxygen demanding bacteria and/or lowering the suspended solids concentration by taking some suspended matter into solution. It can thus be appreciated that even when considering only five quality determinands the interrelationships are so complex that only the development of a generalised model could ever be considered feasible.

With increased flow, as shown in regimes 3, 4 and 5 this variation in the most important variables continues, although it is seen that the DO partial correlation coefficient is now consistently one of the largest calculated. This is as one would expect if, as suggested, the vast proportion of the suspended matter is sewage based, entering via SWO's brought into operation as a result of increased sewer loading. An interesting point shown by the results of this analysis, Table T-7-2, is the change in EC coefficient sign under high flow conditions. This may suggest that under such conditions industrial effluent constitutes an increased proportion of the Brook's input and is positively linked to the increased suspended solids loading. This could be possibly due to the inputs originating from the same source, that is, the surcharging SWO's. It is also possible that under conditions of high flow, highway effluent and in particular motorway effluent could be washed, via the drains, directly into the Brook. Such effluent may contain dissolved inorganics, for instance road salt, which would readily increase the conductivity. A situation could then possibly arise where the SS concentration increased due to the discharging SWO's with the EC increasing because of the highway effluent input. If such a situation did occur then it would be possible for two important quality determinands to be positively correlated in the analyses, while not being directly linked in reality.

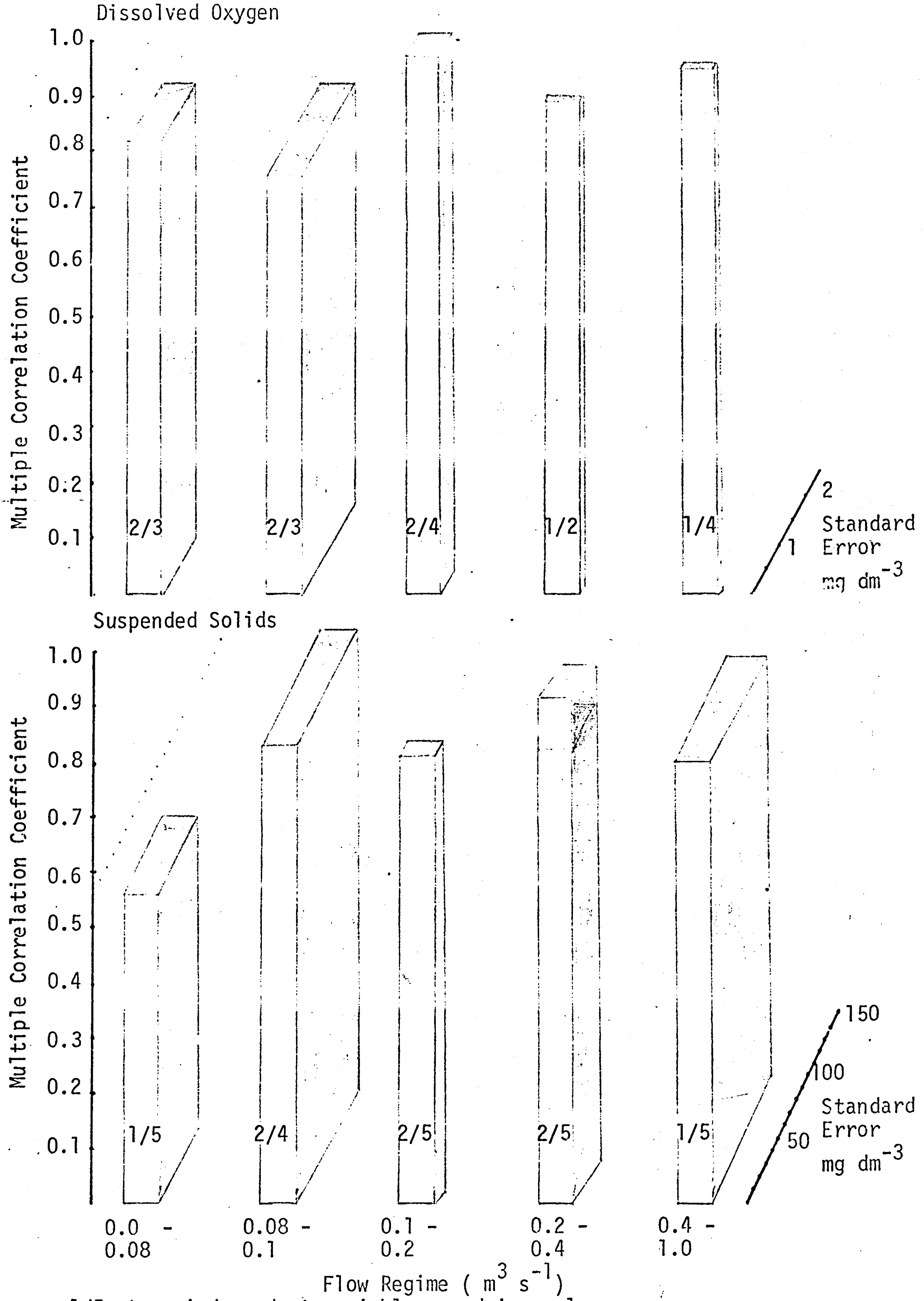
7.3.4 Multiple Regression Analysis

The partial correlation coefficients were used to identify the most useful independent variables for inclusion within the multiple regression analyses. These analyses were performed upon the data subfiles with compensated mean multiple correlations obtained for individual flow regimes. The compensated mean values were obtained by placing a 90% confidence zone around the normal distribution of their means, with the standard deviation of the coefficients being subtracted.

The coefficients obtained are outlined in Fig. 7-15. This represents the mean multiple correlation coefficients and standard errors of both DO and SS. The taller and thinner the column, the more meaningful the correlations are. The figure indicates that, even though the partial correlation coefficients were low, when the best two independent variables were analysed by multiple regression techniques, reasonably high multiple correlation coefficients were obtained, with in most cases acceptable standard errors. This multiple technique shows its practical value in statistical modelling, by giving the modeller the ability to observe the behaviour of independent variables, within the complex matrix of the Brook. The fact that this technique produced high correlation coefficients and also some quite high standard errors emphasises the point that in the modelling of environmental systems and in particular when attempting to optimise the variables necessary for prediction, only a generalised model can realistically be developed.

As can be seen from the diagram, Fig. 7-15, very high correlation coefficients were obtained for DO as dependent variable with a decreasing standard error from low to high flow. In the case of SS as dependent variable the coefficients were not quite so high with one or two of the flow regimes showing rather large standard errors. This is possibly due to the fact, as previously explained with regard to suspended solids, that its influence upon the Brook is so great and diverse that to select one or two variables which accurately predict its value is in practice impossible. All that can be done is to ascertain the general trend of interrelationships present and build on these. This is what was achieved, although even this approximation can be ruined by an unforeseen random input. Such a random input could drastically alter the situation within the Brook so that it behaved contrary to the way it had been modelled. The probability of such an event invalidating the model, can be reduced by the utilisation of large amounts of data in the model building. This once again shows an advantage of continuous monitoring over discrete methods of data collection.

Fig. 7-15 Mean Multiple Correlation Coefficients (90% Confidence Limits)



1/5 etc = independent variables used in analyses.

1 = EC, 2 = T, 3 = SS, 4 = pH, 5 = DO.

7.4 Model construction

With the statistical analysis of the stored continuously monitored data completed, it was possible to begin the construction of the water quality model. As the initial data analysis had been based adequately on linear regression, it was decided to construct the model on the linear relationships obtained from the multiple regression analysis. These analyses not only provided correlation coefficients but also the regression coefficients and intercepts necessary for such an exercise.

In order that the model should have the maximum possible utility and because it would rely upon many pre-stored coefficients it was necessary to develop the model as a digital computer program. In designing the program emphasis was placed upon simplicity of operation thus facilitating possible future use by persons not necessarily well acquainted with computer programming techniques. Therefore it was written in a conversational manner, to be operated from a computer terminal.

The computer program (Appendix C) is shown in schematic form in Fig. 7-16. It has the following capabilities:

(1) the estimation of dependent variable concentrations, for both DO and SS, from values of two specified independent variables under known flow conditions;

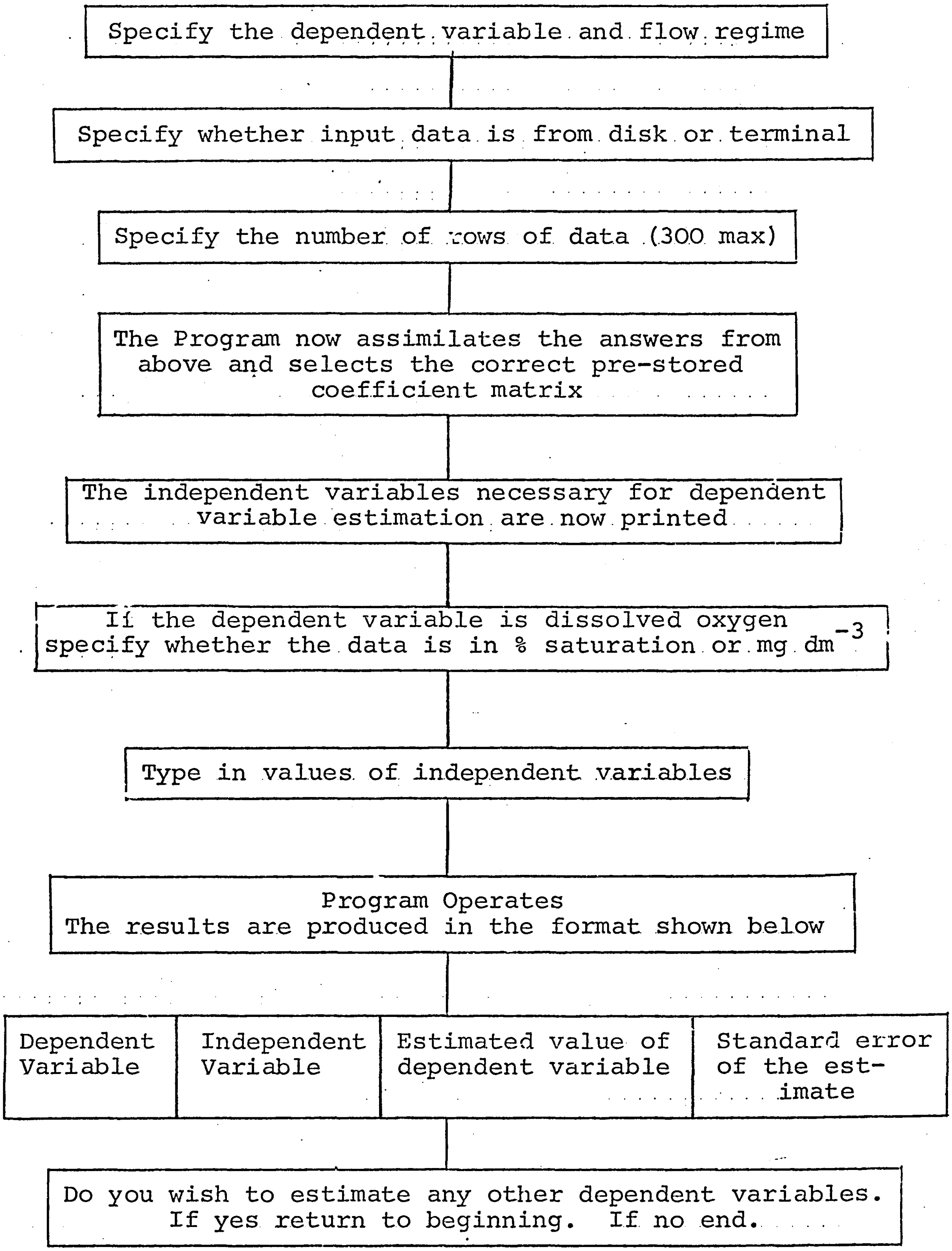
(2) the ability to handle reasonably large amount of continuously monitored data as well as smaller quantities of discretely monitored data;

(3) the ability of accepting either % saturation or mg dm^{-3} values of dissolved oxygen as input;

(4) the ability to accept data from either terminal or pre-stored disk files;

(5) the ability to be run from a terminal, in a conversational mode, for increased speed and convenience.

Fig. 7-16 Schematic representation of the model (WQMDL)



7.5 Model Validation

This was performed in an attempt to quantify the accuracy of the model under different flow conditions. Data from two sources was used for this validation. The first tests used data abstracted from files holding the monitored quality levels prior to any 'handling', that is, before any sorting of the files for model development (see Fig. 7-3) had taken place. It could thus be reasonably argued that this data was separate from that used to calculate the various coefficients and was hence valid for testing purposes. The files used for validation purposes were chosen because they contained the largest amount of data appertaining to the particular flow regimes. This was a particularly important consideration with respect to the higher flow regimes, in which less quality data was available. The results of these first tests are shown in Figs. 7-17 to 7-21.

The second set of tests were performed on data abstracted from chart recordings for the period August to September 1976. Disk stored information for this period, was not available for model development, due to problems in data transposition from magnetic tape II. It was thus assumed that the chart data would provide a completely independent check upon the accuracy of the model. The results of the tests are shown in Figs. 7-22 to 7-25.

The mean standard errors of the estimates of the tests are outlined in tables T-7-3 and T-7-4. These show a variation in the mean standard error as a percentage of the range, of 13.5 to 7 for dissolved oxygen and 19 to 7.5 for suspended solids. To obtain a more quantitative

Fig. 7-17 Dissolved Oxygen

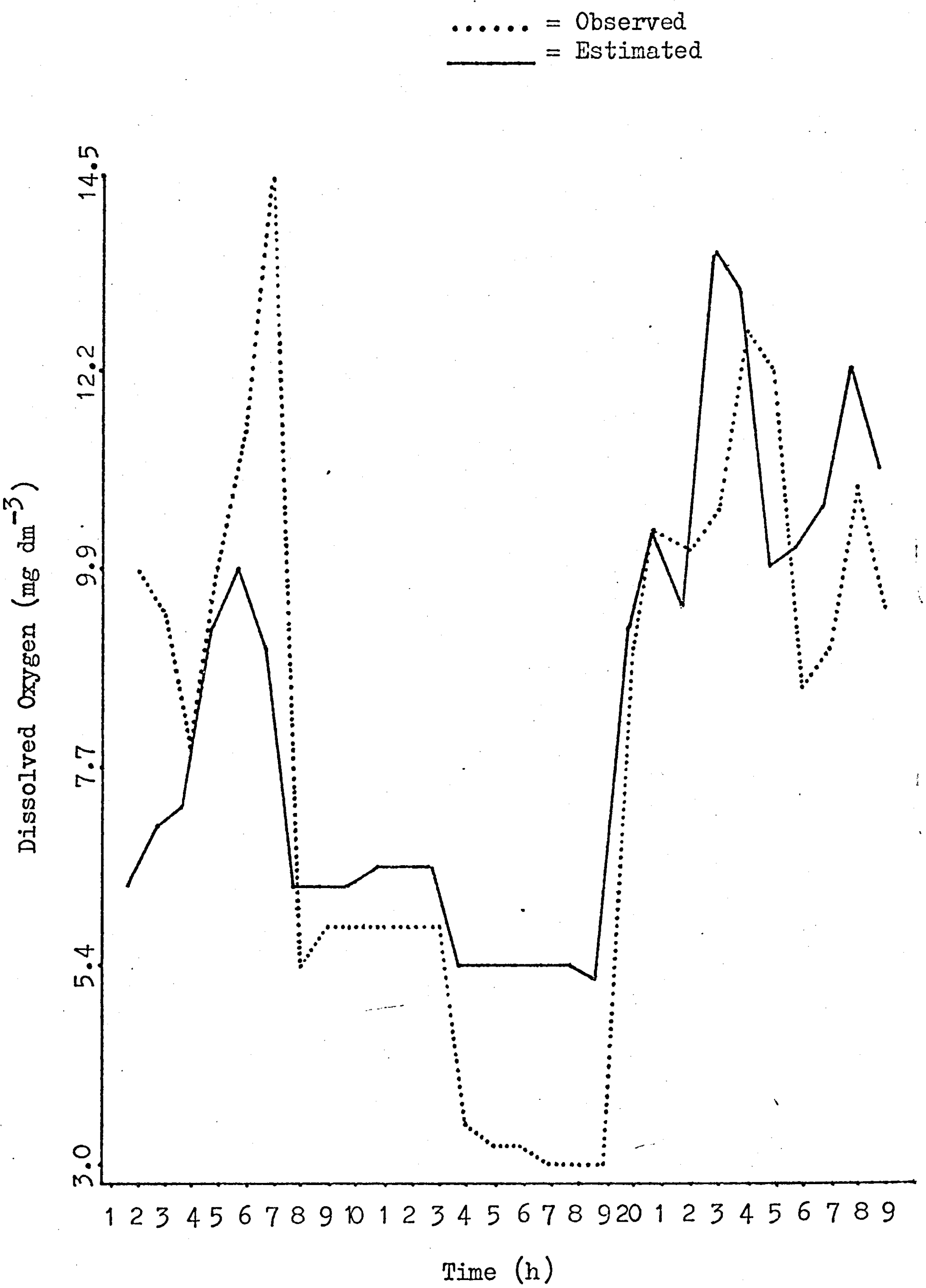


Fig. 7-18 Dissolved Oxygen

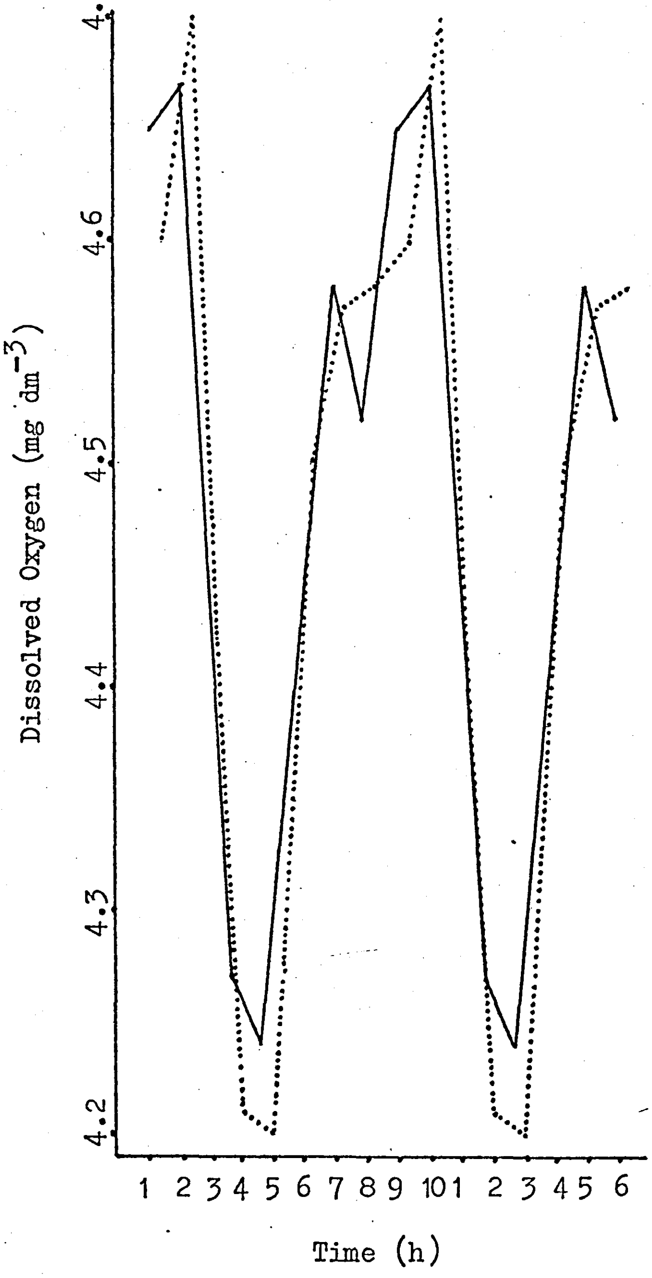


Fig. 7-19 Dissolved Oxygen

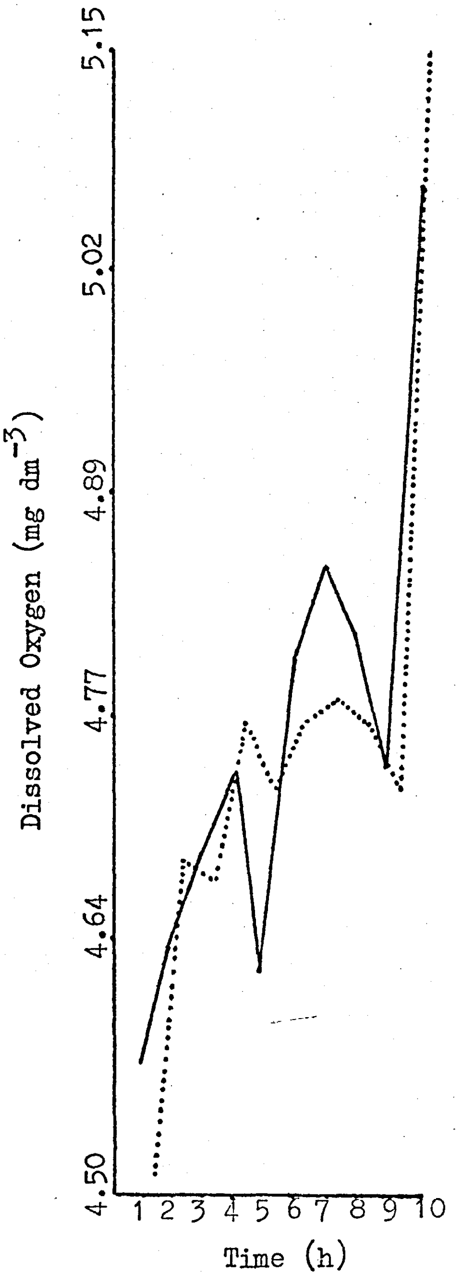


Fig. 7-20 Suspended Solids

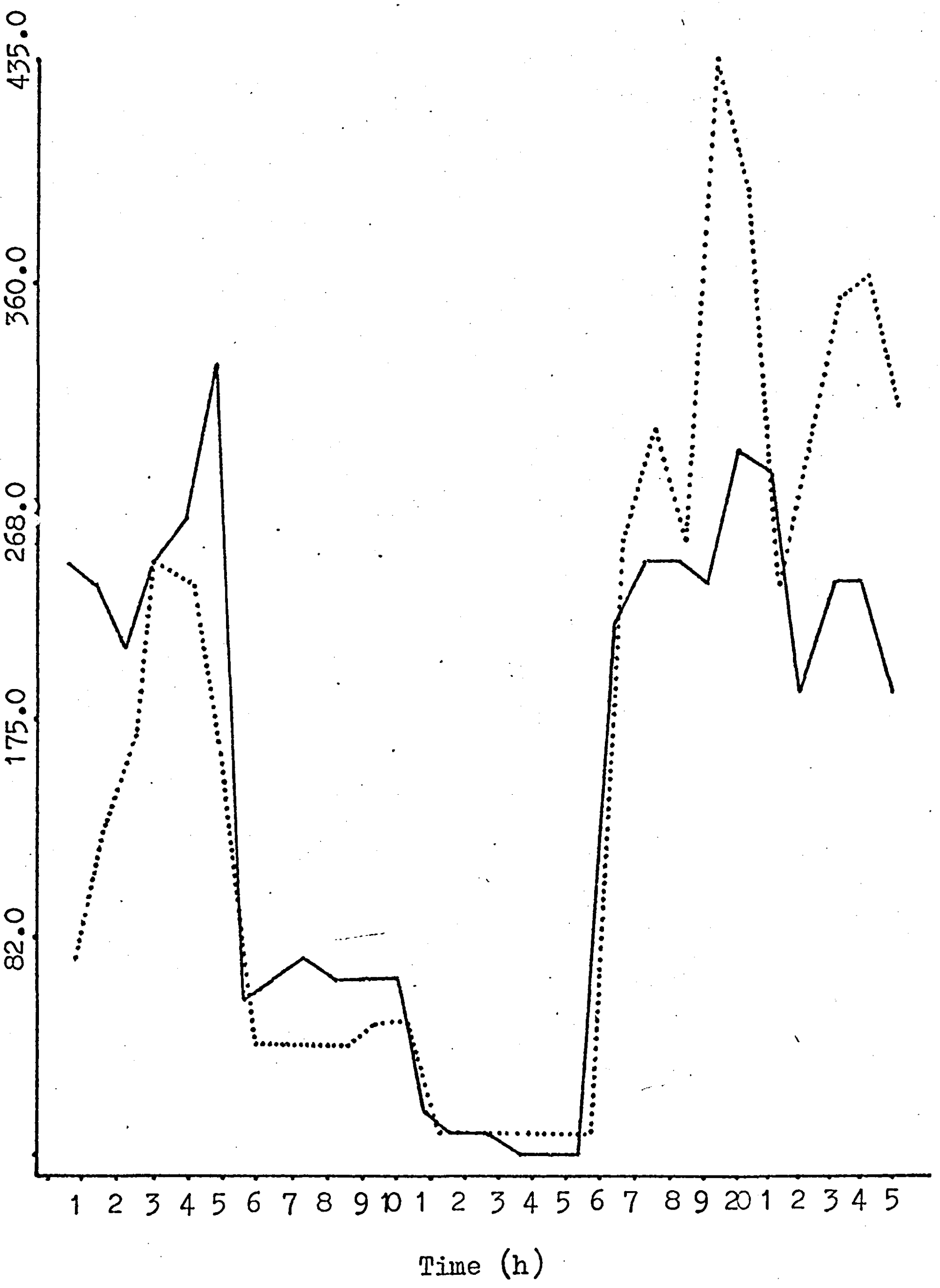


Fig. 7-21 Suspended Solids

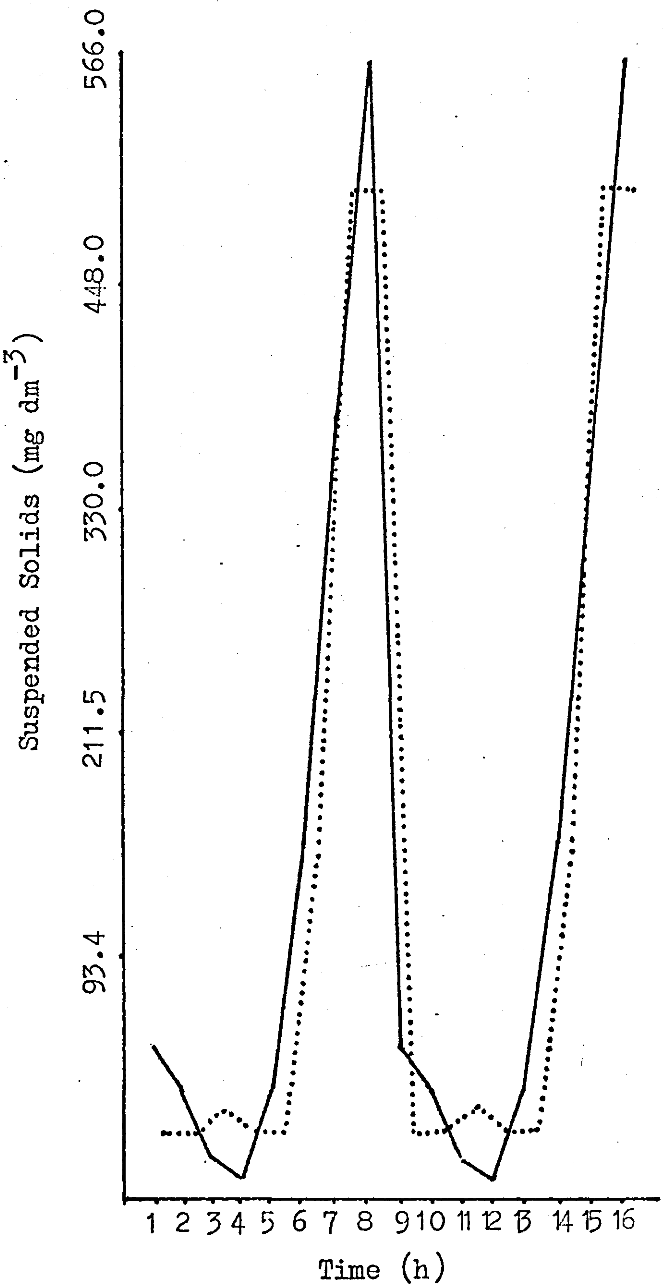


Fig. 7-22 Dissolved Oxygen

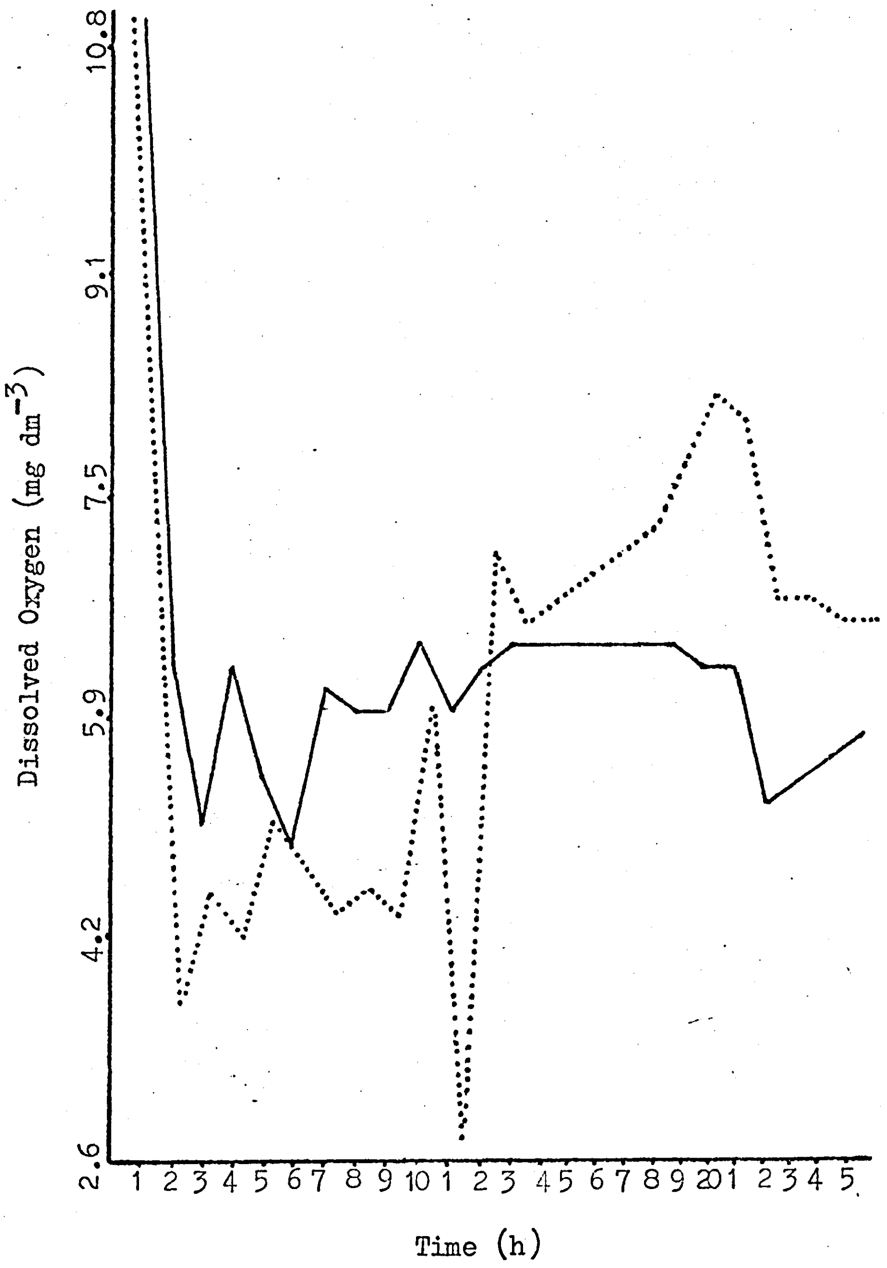


Fig. 7-23 Dissolved Oxygen

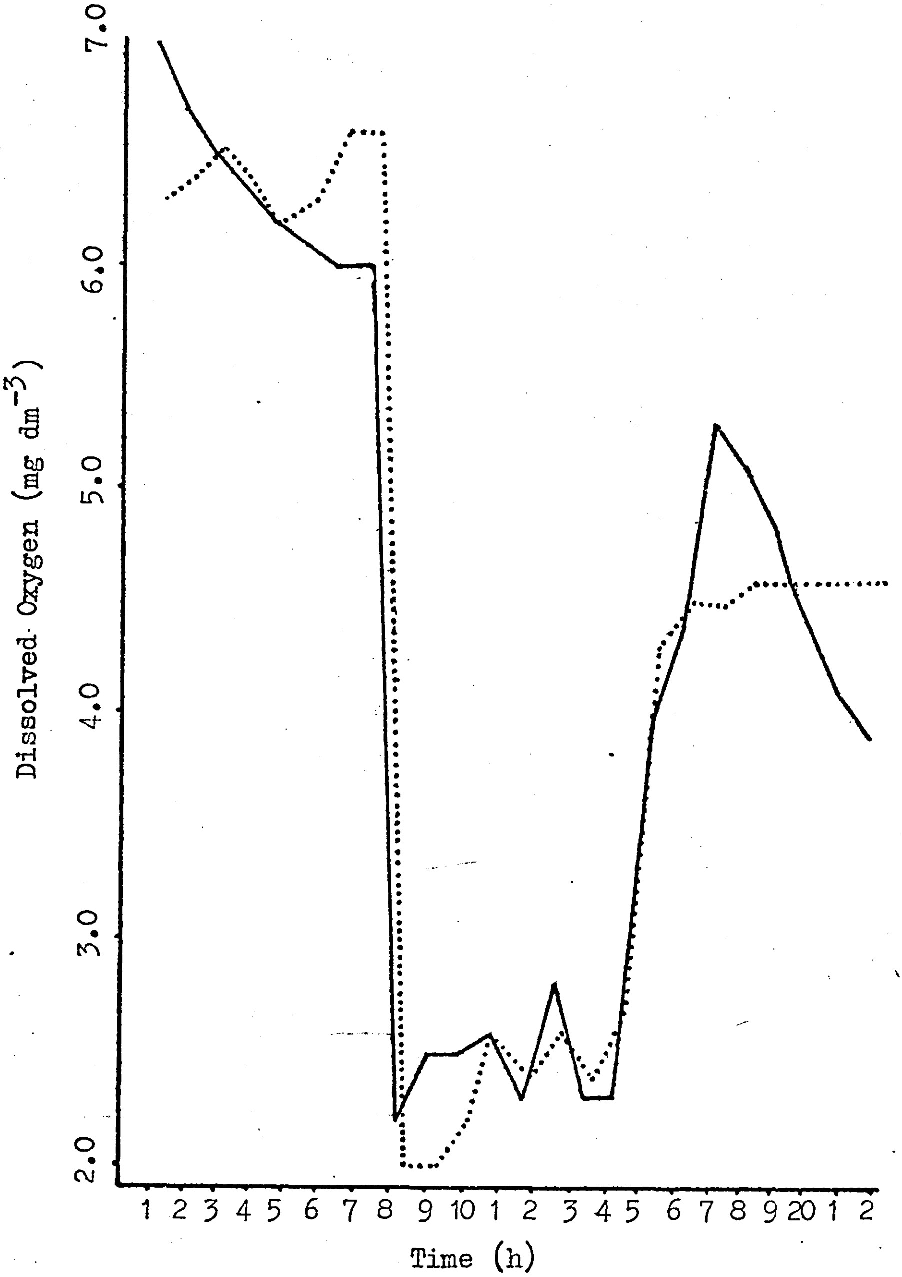


Fig. 7-24 Suspended Solids

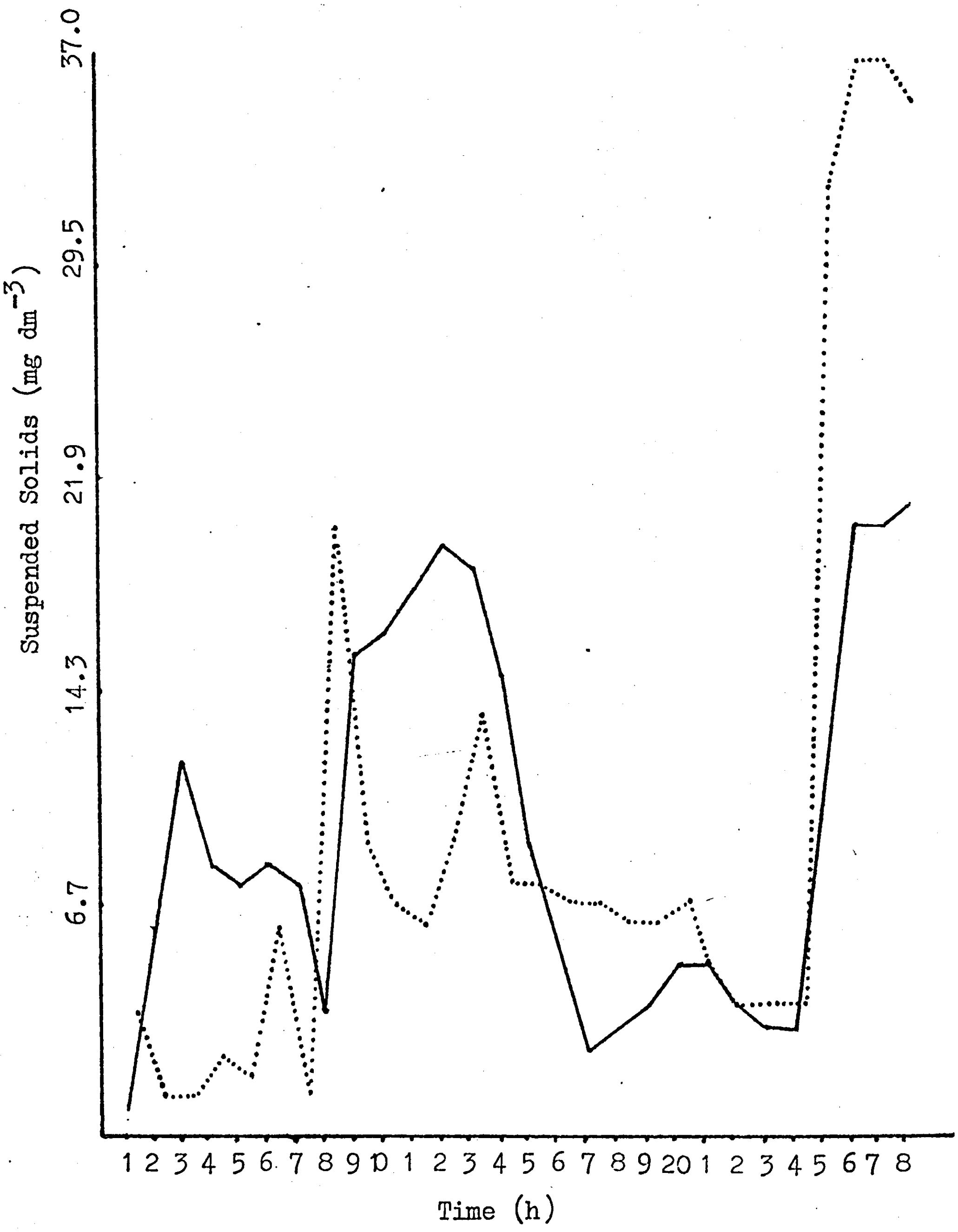


Fig. 7-25 Suspended Solids

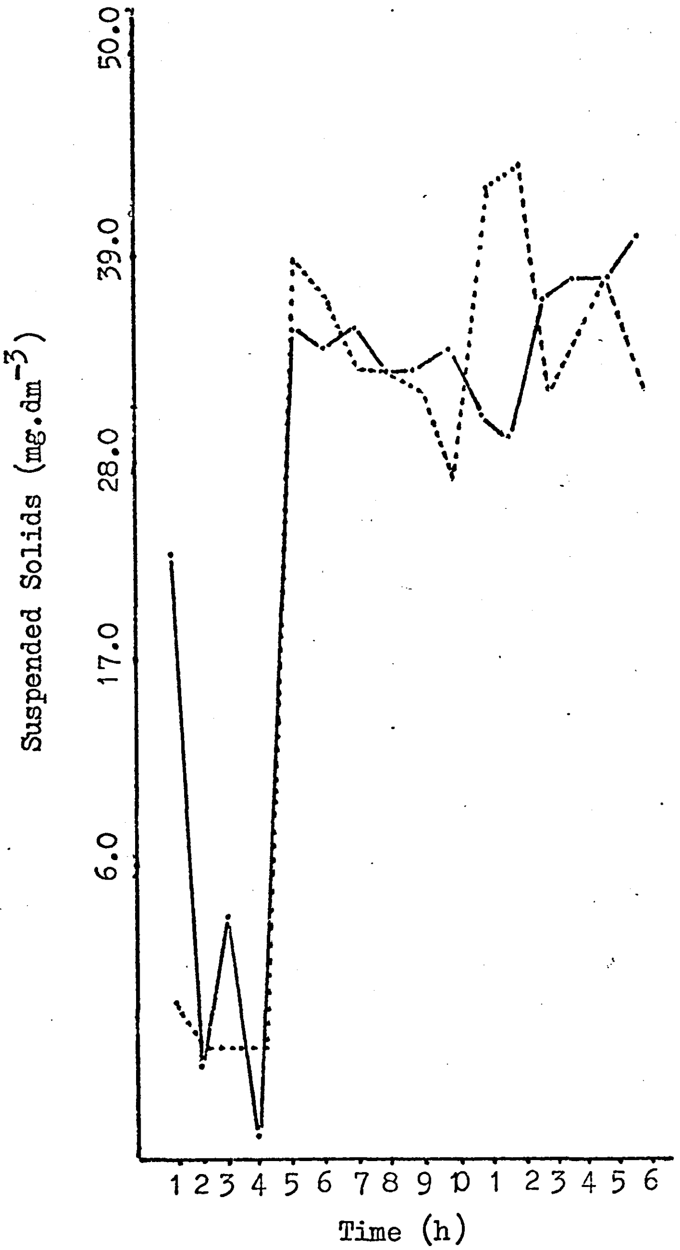


Table T-7-3 A Summary of the Validation of the DO estimates

Data	Flow Regime	Range (mg dm^{-3})	Mean error of estimate (mg dm^{-3})	Mean error as % of range
Raw Data				
March '75	2	11.4	1.52	13%
October '75	4	0.6	0.05	8%
September '75	5	0.6	0.07	12%
Tape II Data				
August '76	1	8.2	1.11	13.5%
September '76	3	4.5	0.32	7%

Table T-7-4 A Summary of the Validation of the SS estimates

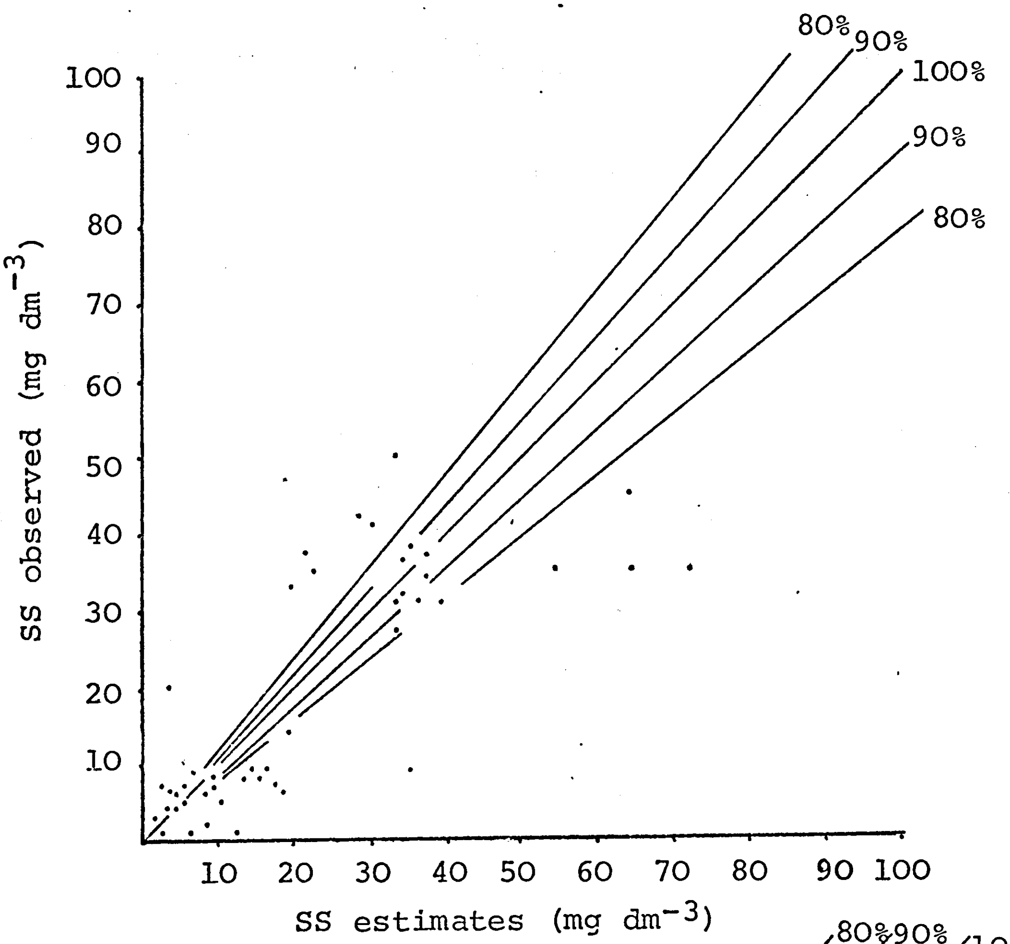
Data	Flow Regime	Range (mg dm^{-3})	Mean error of estimate (mg dm^{-3})	Mean error as % of range
Raw Data				
March '75	2	453	57	13%
September '75	5	566	42	7.5%
Tape II Data				
August '76	1	37	6.9	19%
September '76	3	50	6.5	13%

assessment and visual representation of the accuracy of the model, graphs were plotted of observed versus estimated readings, Figs. 7-26 and 7-27. These scatter diagrams show the individual results estimated by the model in relation to the monitored values and indicate the amount of deviation about the 100% accuracy line. Confidence lines were drawn to show 90 and 80 per cent limits with respect to the observed readings.

As is seen in Fig. 7-26 the model only produced estimates within the 80% limits for 42% of the suspended solids validation data, within the 0-100 mg dm^{-3} range, this was increased to 61% for the range 0-600mg dm^{-3}. If examined in isolation these results indicate a rather poor model, but if the validation graphs Figs. 7-20, 21, 24 and 25 are taken into account it can then be seen that in most instances the variations in SS are predicted most accurately. The ability to accurately predict the trends within a dynamic quality determinand, while not necessarily predicting very accurate individual values, would seem to indicate that some extraneous factor, which has not been modelled, is influencing in a positive manner, the determinand in question.

Examination of Fig. 7-27 may help to explain the apparent poor performance of the model with respect to suspended solids. This figure outlines the observed dissolved oxygen levels in relation to the estimated ones. It shows that 56% of the data used for model validation was within the 90% confidence limits while 76% was within the 80% limits. These results indicate a most useful model which, as also shown by Table T-7-3, can produce estimates with a

Fig. 7-26 Scatter diagrams of observed and estimated Suspended Solids values



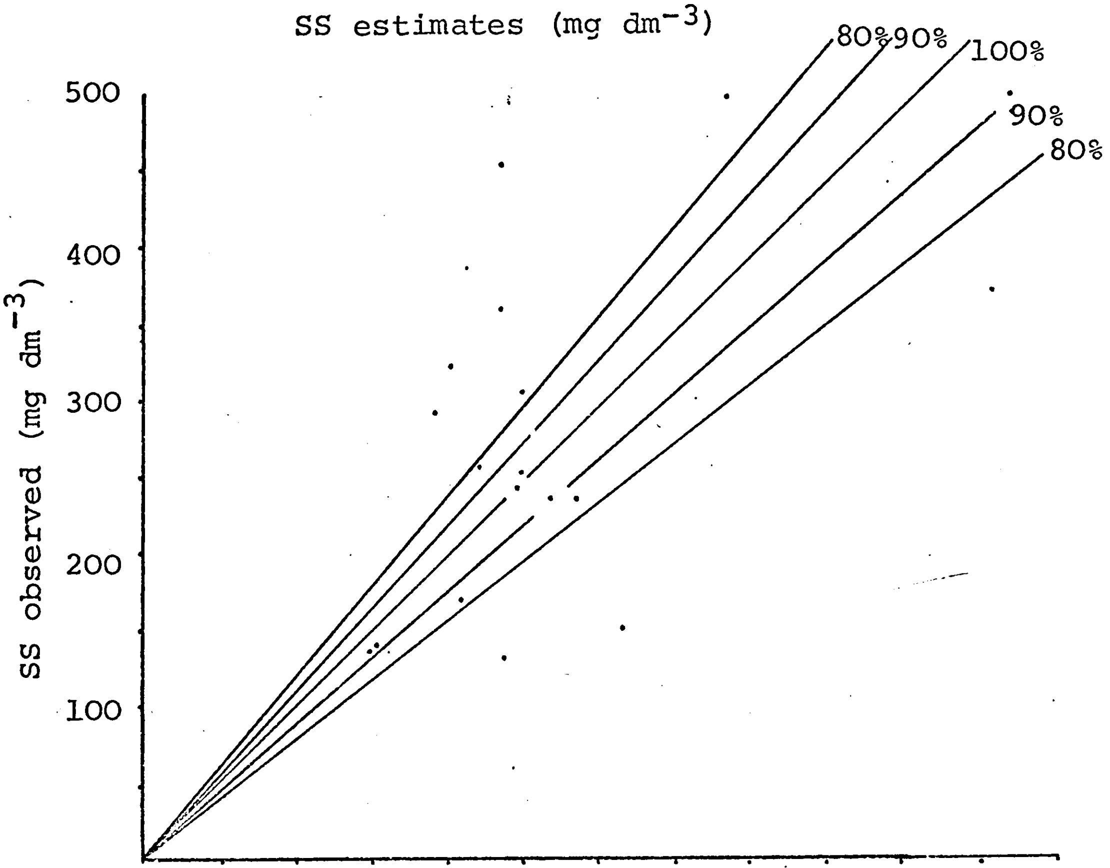
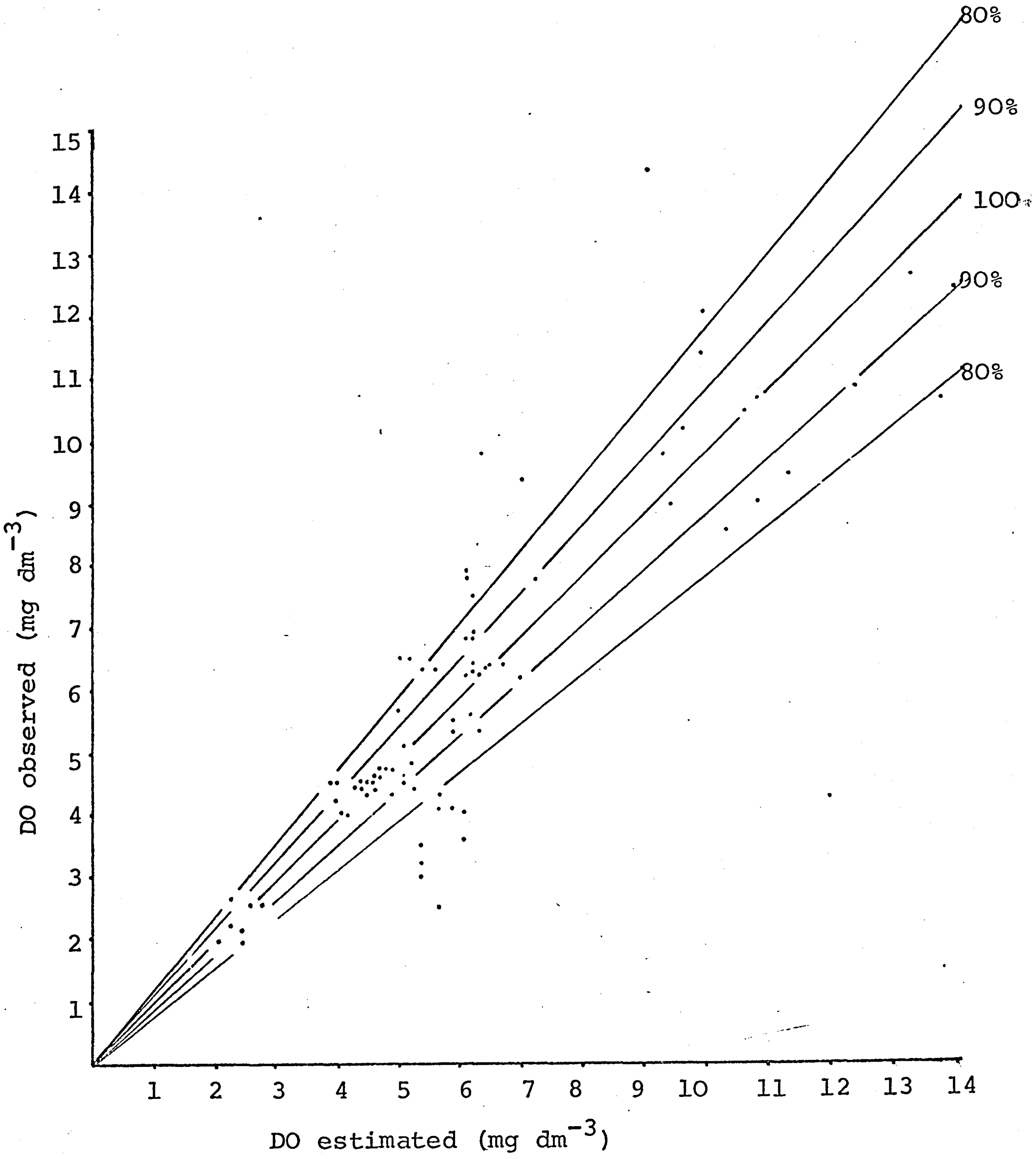


Fig. 7-27 Scatter diagram of observed and estimated Dissolved Oxygen values



high degree of accuracy. A comparison of the performance of the model in estimating DO and SS levels underlines the fact that the SS determinand is under much less control from other quality determinands than is DO. The DO level is shown to be very much a secondary determinand, under internal control from its fellow determinands and hence easier to model using continuous monitoring, while SS seems to be a primary determinand, whose level is more dependent upon external factors than internal ones.

In conclusion the results of the various tests shown that a statistical model, based on continuously monitored data, can, within acceptable limits, estimate water quality determinands, particularly dissolved oxygen and to a lesser extent suspended solids, of a grossly polluted water system . The design of the model was purposely simple while the system modelled was extremely complex, hence the degree of accuracy obtained was considered highly encouraging.

Conclusions

8.1 The Monitoring Programme

This has shown that a commercially available water quality monitoring station, with a limited number of adaptations, can be successfully operated within the hostile environment of a grossly polluted system. The adaptations which proved necessary, included changes in the hydraulic system and cleansing cycle as outlined in section 6.1 . The problems experienced in the routine cleaning and general maintenance of the sensor blocks of the WQMS has led to the construction of a new system. This is a continuous flow through chamber made from perspex, which was suitably designed for an adequate sample flow rate. This new system has been incorporated into the current research project in which the WQMS is being used.

The successful operation of the continuous monitoring programme has proved that, although the determinands monitored were limited to those available in the commercial monitor used, they can be adequately used to describe the system studied. The discrete monitoring programme was used to indicate some of the pollution sources, as well as describing the system in terms of particular determinands e.g. B.O.D., which were not monitored continuously. This assisted in the explanation of the observed water quality variations within the continuously monitored data, in some cases indicating where additional analyses e.g. micro-biological, could be of particular use.

A stream flow monitoring programme was also successfully performed. This relied upon the construction and operation of a flow gauging station recording water depths continuously. Subsequent analyses proved the essential nature of the water quantity data, with validation of the method used, by testing against a standard velocity gauging technique, proving its reliability. It was necessary to develop a method for determining stream flow levels for the period, early in the monitoring programme, prior to flow gauge installation. This method was based upon unit hydrograph theory and has been shown to provide adequate estimates of stream flows, from a knowledge of the precipitation within the catchment. The method was developed as a computer programme and validated against the standard velocity gauging technique.

8.2 The Monitored Data

The continuously monitored data was stored on magnetic tape within the data logger of the WQMS, the stored data being subsequently transposed onto punched paper tape by the instrument manufacturer. The paper tapes were then translated, with the data being stored on card and computer disk files, by the use of a computer programme developed especially for this purpose. The programme proved capable of effectively handling all the monitored data and should be a useful aid in any future monitoring, which utilizes the WQMS.

The large volumes of continuously recorded data, both of water quality and water quantity, were thoroughly analysed using a variety of statistical techniques. These analyses elucidated and quantified many of the complex interrelationships which were present within the monitored determinands. They were also successful in outlining the way in which future data handling and model development was to proceed. They also indicated the presence of primary and secondary water quality determinands, see section 7.2, as well as showing the overriding importance of stream flow to the overall water quality level.

8.3 Model development

The various water quality determinand interrelationships, which were elucidated by the data analysis, were used to develop a statistical water quality model, with a predictive capability for dissolved oxygen and suspended solids. The model was designed in the form of a computer programme which was capable of being utilized by people with limited computer experience. The model relies upon the various determinand interrelationships, as quantified by multiple correlation and regression coefficients, for its estimations of the two determinands which were modelled. It was found that these two particular determinands, DO and SS, were capable of describing the water quality of the Blackburn Brook quite effectively, hence their choice as dependent variables, see section 7.4. It was also discovered that reproducible and reliable estimates of the two dependent variables could be made by utilizing only two of the possible independent variables available. This was considered most useful, as the less complex the input data requirements of the model are, the greater is its utility.

The model was validated for the two particular dependent variables, using data monitored over a range of stream flow conditions, as outlined in section 7.5. The validation exercise showed that the model developed for the Blackburn Brook fulfilled its role as a water quality determinand estimator to a highly encouraging extent. Its successful validation showed that even with a limited number of monitored independent variables, useful estimates of important water quality parameters can be made.

8.4 Suggestions for future work

There are a number of ways in which this particular project could be modified so as to provide future research areas. If for example two sites on the Brook were continuously monitored it would facilitate the development of a more traditional compartmental model. This could be achieved by modifying the WQMS so that it abstracted water from two inlets alternately, the data from each being suitably referenced for future analysis. It would be possible, for example, for such a system to be set up above and below a surcharging storm water overflow. In this way it would be possible to quantify the effect of the overflow with respect to the overall river water quality. A similar system could be operated over a longer reach, for example above and below sites of industrial abstraction and effluent input.

Within the Blackburn Brook system possible future continuous monitoring and modelling could be performed to ascertain whether or not the new relief trunk sewer, shortly to come into operation, succeeds in its aim of removing the problem of domestic effluent pollution within the catchment. If it is shown that it does then the monitoring programme would be useful as a study of industrial pollution within a water system effectively devoid of domestic contamination. Such a programme could also be used as a means of determining the cost effectiveness of the new sewerage system within the catchment. The ability of the modelling programme to perform this task would then substantially increase its utility with respect to other similar polluted catchments. A model of the Brook, after completion of the new sewer would possibly not be as dominated by the suspended solids and dissolved oxygen determinands as the present model is. Thus if this was the case, it may be possible to consider other water quality determinands within the confines of the new model. Various ion selective electrodes are now available, which may be capable of being incorporated into a future monitoring programme. Any increase in the knowledge of how the contents of the Brook, as an example of a grossly polluted water system, interact; would be of immense use in determining the most efficient and least expensive method of pollution control.

The new combined trunk sewer has been designed as a relief rather than a replacement sewerage system. The new system will also incorporate a larger catchment than the present system. A comparison between the model described in this thesis, obtained using data collected prior to the installation of the new sewer, and a model developed from data after the initiation of the new system, would provide a valuable means of examining the decisions taken by the Water Authority on the new sewer. It may also be possible for such an exercise to be performed in other catchments, where the quantified impact of a new sewerage scheme, in terms of improved stream or river water quality, would be of value.

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-APPENDIX A FLJEST-

```
/LOAD FORTG1
      DIMENSION R1(1),R2(2),R3(1),R4(1),R5(1),S(1),
     1P(1),NUDAT(1),D(1),BASE(1),IHR(300),FLOW(300),IWK(1),
     2ID(1),IH(1),U1(30),U2(30),U3(30),U4(30),U5(30),U6(30),
     3U6(1),U7(30),U8(30)
      READ(9,10) R1(1),R2(1),R3(1),R4(1),R5(1),S(1),P(1),NUDAT(1),
     4D(1),BASE(1),IWK(1),ID(1),IH(1)
   10 FORMAT(5(F4.1,1X),I2,1X,F4.1,1X,I3,1X,I1,1X,F4.2,1X,I2,1X,
     5I1,1X,I2)
      N=NUDAT(1)
      API5=0.707*(R1(1)+(R2(1)*0.5)+(0.25*R3(1))+(0.125*R4(1))
     6+(0.0625*R5(1)))
      CWI=125+API5-S(1)
      VMM=(0.22*(CWI-125))+(0.1*(P(1)-10.0))+34.87
      VM=(VMM/100)*P(1)
      V=VM/1000
      DO 300 J=1,N
      READ(5,30) IHR(J),U1(J),U2(J),U3(J),U4(J),U5(J),U6(J)
     7,U7(J),U8(J)
   30 FORMAT(I2,1X,F6.3,1X,F6.3,1X,F6.3,1X,F6.3,1X,F6.3,1X,F6.3,1X,
     8F6.3,1X,F6.3)
      IF(ID(1).EQ.1) GO TO 101
      IF(ID(1).EQ.2) GO TO 102
      IF(ID(1).EQ.3) GO TO 103
      IF(ID(1).EQ.4) GO TO 104
      IF(ID(1).EQ.5) GO TO 105
      IF(ID(1).EQ.6) GO TO 106
      IF(ID(1).EQ.7) GO TO 107
      IF(ID(1).EQ.8) GO TO 109
  101 CONTINUE
      FLOW(J)=(U1(J)*V)+BASE(1)
      GO TO 200
  102 CONTINUE
      FLOW(J)=(U2(J)*V)+BASE(1)
      GO TO 200
  103 CONTINUE
      FLOW(J)=(U3(J)*V)+BASE(1)
      GO TO 200
  104 CONTINUE
      FLOW(J)=(U4(J)*V)+BASE(1)
      GO TO 200
  105 CONTINUE
      FLOW(J)=(U5(J)*V)+BASE(1)
      GO TO 200
  106 CONTINUE
      FLOW(J)=(U6(J)*V)+BASE(1)
      GO TO 200
  107 CONTINUE
      FLOW(J)=(U7(J)*V)+BASE(1)
      GO TO 200
  108 CONTINUE
      FLOW(J)=(U8(J)*V)+BASE(1)
      GO TO 200
  200 WRITE(10,250) IHR(J),FLOW(J),IWK(1),ID(1),IH(1)
  250 FORMAT(I2,1X,F6.3,1X,I2,I1,I2)
  300 CONTINUE
      CALL EXIT
      END
/DATA
```

```
/LOAD WATFIV
      dimension iarr(8),arr(8),jarr(6,4),marr(6,4),karr(6,4)
      ind=0
      iar=0
      ira=0
      loop=0
      ihr=9
      iqhr=0
      iweek=30
      iday=2
      n=0
      ibrek=0
  I0  continue
      call hegty (iarr,ind)
      ind=I
  20  continue
      if(loop.eq.2) go to 90
      do 30 i=I,8
  30  arr(i)=iarr(i)
      if(brr(I).gt.50.0.and.arr(I).lt.200.0) go to I0
      if(arr(I).gt.I000.0) iday=iday+I
      if(arr(I).gt.I000.0) ihr=9
      if(iday-8) 60,50,50
  50  iday=I
      iweek=iweek+I
  60  continue
      if(loop.eq.3) go to 70
      if(arr(I).lt.I000.0) go to 320
      if(iweek.eq.200) go to 330
  70  continue
      loop=2
      go to 20
  90  continue
      n=n+I
      if(n.eq.5) ihr=ihr+I
      if (n.eq.5) n=I
      if(ihr-24) I30,I20,I20
 I20  ihr=0
 I30  jarr(2,n)=iarr(2)x2000.0/I023.0
      jarr(3,n)=((iarr(3)x40.0/I023.0)-5.0)xI0.0+0.5
      jarr(4,n)=iarr(4)x500.0/I023.0
      jarr(5,n)=((iarr(6)x8.0/I023.0)+2.0)xI0.0+0.5
      jarr(6,n)=iarr(7)x200.0/I023.0
      if(jarr(2,I).ge.2000.and.ihr.eq.9) iday=iday+I
      if(jarr(2,n).le.I00) go to I40
      go to I60
 I40  continue
      do I50 j=2,6
 I50  jarr(j,n)=2
 I60  if(arr(I).le.950.0.and.arr(I).ge.750.0) go to 200
      if(n.ne.I.and.arr(I).gt.I000.0) go to I70
      go to 240
```

```
I70   if(iday.eq.I) iweek=iweek+I
      if(iday.eq.1) iday=8
      do I80 j=2,6
I80   karr(j,n)=jarr(j,n)
      do I90 j=2,6
I90   jarr(j,n)=I
      ibrek=I
      iday=iday-I
      go to 250
200   continue
      do 2I0 j=2,6
2I0   jarr(j,n)=0
      if(n.eq.I) go to 259
      do 230 j=2,6
230   jarr(j,n)=I
      ihr=II
      ibrek=2
      go to 250
259   ihr=I2
240   continue
      loop=3
      if(n.ne.4) go to I0
250   write(5,260)(jarr(j,I),j=2,6),(jarr(j,2),j=2,6),
     I(jarr(j,3),j=2,6),(jarr(j,4),j=2,6),iweek,iday,ihr
      write(2,25I)(jarr(j,I),j=2,6),(jarr(j,2),j=2,6),
     2(jarr(j,3),j=2,6),(jarr(j,4),j=2,6),iweek,iday,ihr
260   format(Ih ,4(i4,i3,i3,i2,i3,Ix)Ix,iI,Ix,i2,Ix,i2)
25I   format(4(i4,i3,i3,i2,i3,Ix)Ix,iI,Ix,i2,Ix,i2)
      if(ibrek-I) 3I0,270,290
270   continue
      do 280 j=2,6
280   jarr(j,I)=karr(j,n)
      ihr=9
      n=I
      ibrek=0
      iday=iday+I
      if(iday.eq.8) iweek=iweek+I
      if(iday.eq.8) iday=I
      go to 240
290   continue
      do 300 j=2,6
300   jarr(j,I)=marr(j,n)
      n=I
      ibrek=0
      ihr=I2
      go to 240
3I0   n=0
      ihr=ihr+I
      go to I0
320   continue
      loop=I
      go to I0
330   write(2,340)
340   format(Ih0,'END OF TAPE')
      CALL EXIT
      END
```

```
/FILE DISK=(1,CIWVREMT),VOL=MUSIC2,DISP=(SHR,KEEP)
/LOAD WATFIV
      DIMENSION JV1(1),JV2(1),JV3(1),JV4(1),JV5(1),AV1(300),
     1AV2(300),AV4(300),AV5(300),IDV(1),AT(300),NUDAT(1),
     2IS(300),AO(300),IFP(1),AP(300),EDV(300),ASE(1),E(1),IC(300),
     3B0(1),B1(1),B2(1),AREG(25,5),AS(300),AC(300),IANS(1),MK(1)
     4,ADO(300),IO(300),FMT(5),IDATA(1)
      READ(1,10)(AREG(I,1),AREG(I,2),AREG(I,3),AREG(I,4),AREG(I,5),
     4I=1,10)
   10 FORMAT(F3.2,F9.4,F9.4,F9.4,F7.2)
      IANS(1)=0
      WRITE(6,15)
   15 FORMAT('WHEN REQUESTED TYPE IN THE NUMBER TO INDICATE THE'/
     1'DEPENDENT VARIABLE, 1=ELECTRICAL CONDUCTIVITY(S.CM-1*10-6)'/
     2'                    2=TEMPERATURE(DEG.C)'/
     3'                    3=SUSPENDED SOLIDS(MG.DM-3)'/
     4'                    4=PH'/
     5'                    5=DISSOLVED OXYGEN(MG.DM-3 OR %SAT.)')
   19 CONTINUE
      WRITE(6,20)
   20 FORMAT('SPECIFY THE DEPENDENT VARIABLE')
      READ(9,30) IDV(1)
   30 FORMAT(I1)
      IF(IANS(1).EQ.1) GO TO 41
      WRITE(6,40)
   40 FORMAT('SPECIFY THE FLOW REGIME BY INDICATING A NUMBER 1 TO 5'/
     1'                    1=0.06 - 0.03 M3S-1'/
     2'                    2=0.03 - 0.10     "  '/
     3'                    3=0.10 - 0.20     "  '/
     4'                    4=0.20 - 0.40     "'/
     6'                    5=0.40 +          "')
   41 CONTINUE
      WRITE(6,42)
   42 FORMAT('SPECIFY THE FLOW REGIME')
      READ(9,50) IFP(1)
   50 FORMAT(I1)
      WRITE(6,51)
   51 FORMAT('SPECIFY WHETHER THE DATA IS TO BE INPUTTED FROM'/
     1'DISK OR TERMINAL,(0=DISK,1=TERMINAL)')
      READ(9,511) IDATA(1)
  511 FORMAT(I1)
      IF(IDATA(1).EQ.0) GO TO 53
      IN=9
      GO TO 54
   53 IN=5
   54 CONTINUE
      WRITE(6,60)
   60 FORMAT('SPECIFY THE NUMBER OF ROWS OF DATA,300 MAX.'/
     1'HTU')
      READ(9,70) NUDAT(1)
   70 FORMAT(I3)
      N=NUDAT(1)
      IF(IDV(1).EQ.3.AND.IFP(1).EQ.1) GO TO 301
```

```
      IF(IDV(1).EQ.3.AND.IFP(1).EQ.2) GO TO 302
      IF(IDV(1).EQ.3.AND.IFP(1).EQ.3) GO TO 303
      IF(IDV(1).EQ.3.AND.IFP(1).EQ.4) GO TO 304
      IF(IDV(1).EQ.3.AND.IFP(1).EQ.5) GO TO 305
      IF(IDV(1).EQ.5.AND.IFP(1).EQ.1) GO TO 501
      IF(IDV(1).EQ.5.AND.IFP(1).EQ.2) GO TO 502
      IF(IDV(1).EQ.5.AND.IFP(1).EQ.3) GO TO 503
      IF(IDV(1).EQ.5.AND.IFP(1).EQ.4) GO TO 504
      IF(IDV(1).EQ.5.AND.IFP(1).EQ.5) GO TO 505
 301  B0(1)=AREG(6,1)
      B1(1)=AREG(6,2)
      B2(1)=AREG(6,3)
      E(1)=AREG(6,5)
      CALL SPEC16 (IC,AO,N,JV1,JV2,JV3,JV4,JV5,AV1,AV2,AT,IO,FMT,IN,
     1M)
      GO TO 600
 302  B0(1)=AREG(7,1)
      B1(1)=AREG(7,2)
      B2(1)=AREG(7,3)
      E(1)=AREG(7,5)
      CALL SPEC24 (AT,AP,N,JV1,JV2,JV3,JV4,JV5,AV1,AV2,FMT,IN,M)
      GO TO 600
 303  B0(1)=AREG(3,1)
      B1(1)=AREG(3,2)
      B2(1)=AREG(3,3)
      E(1)=AREG(3,5)
      WRITE(6,361)
 361  FORMAT('IF THE DISSOLVED OXYGEN DATA IS TO BE EXPRESSED'/
     1'IN MG.DM-3,TYPE A 0,IF IN %SAT. TYPE A 1')
      READ(9,362) MK(1)
 362  FORMAT(I1)
      IF(MK(1).EQ.1) GO TO 363
      GO TO 364
 363  WRITE(6,365)
 365  FORMAT('SPECIFY THE FORMAT OF THE INDEPENDENT VARIABLES'/
     1'TEMPERATURE AND DISSOLVED OXYGEN')
      READ(9,366)(FMT(K),K=1,5)
 366  FORMAT(5A4)
      WRITE(6,99)
  99  FORMAT('SPECIFY THE VALUES')
      READ(IN,FMT)(AT(J),IO(J),J=1,N)
      CALL DOTEMP(N,AT,AO,IO)
      GO TO 731
 364  CONTINUE
      WRITE(6,36)
  36  FORMAT('SPECIFY THE FORMAT OF THE INDEPENDENT VARIABLES'/
     1'TEMPERATURE AND DISSOLVED OXYGEN')
      READ(IN,FMT)(AT(J),AO(J),J=1,N)
 731  CONTINUE
      DO 733 J=1,N
      AV1(J)=AT(J)
      AV2(J)=AO(J)
 733  CONTINUE
      JV1(1)=0
```

```
      JV2(1)=2
      JV3(1)=0
      JV4(1)=0
      JV5(1)=5
      GO TO 600
304   B0(1)=AREG(9,1)
      B1(1)=AREG(9,2)
      B2(1)=AREG(9,3)
      E(1)=AREG(9,5)
      CALL SPEC24 (AT,AP,N,JV1,JV2,JV3,JV4,JV5,AV1,AV2,FMT,IN,M)
      GO TO 600
305   B0(1)=AREG(10,1)
      B1(1)=AREG(10,2)
      B2(1)=AREG(10,3)
      E(1)=AREG(10,5)
      CALL SPEC16 (IC,AO,N,JV1,JV2,JV3,JV4,JV5,AV1,AV2,AT,IO,FMT,IN,
     1M)
      GO TO 600
501   B0(1)=AREG(1,1)
      B1(1)=AREG(1,2)
      B2(1)=AREG(1,3)
      E(1)=AREG(1,5)
      CALL SPEC23 (AT,IS,N,JV1,JV2,JV3,JV4,JV5,AV1,AV2,FMT,IN,M)
      GO TO 600
502   B0(1)=AREG(2,1)
      B1(1)=AREG(2,2)
      B2(1)=AREG(2,3)
      E(1)=AREG(2,5)
      CALL SPEC23 (AT,IS,N,JV1,JV2,JV3,JV4,JV5,AV1,AV2,FMT,IN,M)
      GO TO 600
503   B0(1)=AREG(3,1)
      B1(1)=AREG(3,2)
      B2(1)=AREG(3,3)
      E(1)=AREG(3,5)
      CALL SPEC24 (AT,AP,N,JV1,JV2,JV3,JV4,JV5,AV1,AV2,FMT,IN,M)
      GO TO 600
504   B0(1)=AREG(4,1)
      B1(1)=AREG(4,2)
      B2(1)=AREG(4,3)
      E(1)=AREG(4,5)
      WRITE(6,36)
 36   FORMAT('SPECIFY THE FORMAT FOR THE INDEPENDENT VARIABLES'/
     1'ELECTRICAL CONDUCTIVITY AND TEMPERATURE')
      READ(9,73)(FMT(K),K=1,5)
73    FORMAT(5A4)
      WRITE(6,74)
74    FORMAT('SPECIFY THE VALUES')
      READ(IN,FMT) (IC(J),AT(J),J=1,N)
      DO 33 J=1,N
      AV1(J)=IC(J)
      AV2(J)=AT(J)
 33   CONTINUE
      JV1(1)=1
```

```
      JV2(1)=2
      JV3(1)=0
      JV4(1)=0
      JV5(1)=0
      GO TO 600
 505  B0(1)=AREG(5,1)
      B1(1)=AREG(5,2)
      B2(1)=AREG(5,3)
      E(1)=AREG(5,5)
      WRITE(6,93)
  93  FORMAT('SPECIFY THE FORMAT OF THE INDEPENDENT VARIABLES'/
     1'ELECTRICAL CONDUCTIVITY,TEMPERATURE AND PH')
      READ (9,94) (FMT(K),K=1,5)
  94  FORMAT (5A4)
      WRITE(6,944)
 944  FORMAT('SPECIFY THE VALUES')
      READ(IN,FMT)(IC(J),AT(J),AP(J),J=1,N)
      DO 95 J=1,N
      AV1(J)=IC(J)
      AV2(J)=AP(J)
  95  CONTINUE
      JV1(1)=1
      JV2(1)=0
      JV3(1)=0
      JV4(1)=4
      JV5(1)=0
      GO TO 600
 600  CONTINUE
      WRITE(6,601)
 601  FORMAT('DEPENDENT VAR. INDEPENDENT VARS. EST.OF.DEP.VAR. ERROR'
      WRITE(6,602) IDV(1),JV1(1),JV2(1),JV3(1),JV4(1),JV5(1),E(1)
 602  FORMAT(7X,I1,10X,I1,2X,I1,2X,I1,2X,I1,2X,I1,13X
     6,F6.2)
      DO 700 J=1,N
      EDV(J)=B0(1)+(B1(1)*AV1(J))+(B2(1)*AV2(J))
 700  CONTINUE
      IF(IDV(1).NE.5) GO TO 710
      CALL DOMTOP (AT,EDV,N,ADO)
 710  CONTINUE
      WRITE(6,690)(EDV(J),ADO(J),J=1,N)
 690  FORMAT(34X,F7.2,2X,F5.1)
      WRITE(6,701)
 701  FORMAT('DO YOU WISH TO ESTIMATE ANY OTHER DEPENDENT VARIABLES'
     1'TYPE 1 FOR YES,0 FOR NO')
      READ(9,702) IANS(1)
 702  FORMAT(I1)
      IF(IANS(1).EQ.1) GO TO 19
      CALL EXIT
      END
      SUBROUTINE DOMTOP
```

```
      DIMENSION AF(300),EDV(300),AC(300),AT(300),AD(300),AE(300),
     2ADO(300),AS(300)
      DO 3000 J=1,N
      AF(J)=EDV(J)
      AC(J)=14.652-(AT(J)*0.41022)
      AD(J)=(AT(J)**2)*0.007991
      AE(J)=(AT(J)**3)*0.000077774
      AS(J)=AC(J)+AD(J)-AE(J)
      ADO(J)=100*(AF(J)/AS(J))
 3000 CONTINUE
      RETURN
      END
      SUBROUTINE SPEC23 (AT,IS,N,JV1,JV2,JV3,JV4,JV5,AV1,AV2,FMT,IN,
     1M)
      DIMENSION AT(300),IS(300),AV1(300),AV2(300),JV1(1),FMT(22)
     1JV2(1),JV3(1),JV4(1),JV5(1)
      WRITE(6,33)
  33  FORMAT('SPECIFY THE FORMAT OF THE INDEPENDENT VARIABLES'/
     1'TEMPERATURE AND SUSPENDED SOLIDS')
      READ(9,34)(FMT(K),K=1,5)
 34   FORMAT(5A4)
      WRITE(6,344)
 344  FORMAT('SPECIFY THE VALUES')
      READ(IN,FMT)(AT(J),IS(J),J=1,N)
      DO 31 J=1,N
      AV1(J)=AT(J)
      AV2(J)=IS(J)
  31  CONTINUE
      JV1(1)=0
      JV2(1)=2
      JV3(1)=3
      JV4(1)=0
      JV5(1)=0
      RETURN
      END
      SUBROUTINE SPEC24 (AT,AP,N,JV1,JV2,JV3,JV4,JV5,AV1,AV2,FMT,IN,
     1M)
      DIMENSION AT(300),AP(300),AV1(300),AV2(300),FMT(22)
     1,JV1(1),JV2(1),JV3(1),JV4(1),JV5(1)
      WRITE(6,336)
 336  FORMAT('SPECIFY THE FORMAT OF THE INDEPENDENT VARIABLES'/
     1'TEMPERATURE AND PH')
      READ(9,337)(FMT(K),K=1,5)
 337  FORMAT(5A4)
      WRITE(6,338)
 338  FORMAT('SPECIFY THE VALUES')
      READ(IN,FMT)(AT(J),AP(J),J=1,N)
      DO 377 J=1,N
      AV1(J)=AT(J)
      AV2(J)=AP(J)
 377  CONTINUE
```

```
       JV2(1)=2
       JV3(1)=0
       JV4(1)=4
       JV5(1)=0
       RETURN
       END
       SUBROUTINE SPEC16 (IC,AO,N,JV1,JV2,JV3,JV4,JV5,AV1,AV2,AT,IO,FM
      1IN,M)
       DIMENSION IC(300),AO(300),AV1(300),AV2(300),FMT(22)
      1,JV1(1),JV2(1),JV3(1),JV4(1),JV5(1),AT(300),IO(300),MK(1)
       WRITE(6,511)
  511  FORMAT('IF THE DISSOLVED OXYGEN IS TO BE EXPRESSED IN'/
      1'MG.DM-3,TYPE  0,IF IN % SAT. TYPE 1')
       READ(9,512) MK(1)
  512  FORMAT(I1)
       IF(MK(1).EQ.1) GO TO 150
       GO TO 160
  150  WRITE(6,151)
  151  FORMAT('SPECIFY THE FORMAT OF THE INDEPENDENT VARIABLES'/
      1'ELECTRICAL CONDUCTIVITY,TEMPERATURE AND DISSOLVED OXYGEN')
       READ(9,152)(FMT(K),K=1,5)
 152  FORMAT(5A4)
       WRITE(6,155)
  155  FORMAT('SPECIFY THE VALUES')
       READ(IN,FMT)(IC(J),AT(J),IO(J),J=1,N)
       CALL DOTEMP(AT,IO,N,AO)
       AV1(J)=IC(J)
       AV2(J)=AT(J)
       AV3(J)=IO(J)
       GO TO 153
  160  CONTINUE
       WRITE(6,51)
   51  FORMAT('SPECIFY THE FORMAT OF THE INDEPENDENT VARIABLES'/
      1'ELECTRICAL CONDUCTIVITY AND DISSOLVED OXYGEN')
       READ(9,52)(FMT(K),K=1,5)
   52  FORMAT(5A4)
       WRITE(6,552)
   552 FORMAT('SPECIFY THE VALUES')
       READ(IN,FMT) (IC(J),AO(J),J=1,N)
  153  CONTINUE
       DO 522 J=1,N
       AV1(J)=IC(J)
       AV2(J)=AO(J)
  522  CONTINUE
       JV1(1)=1
       JV2(1)=0
       JV3(1)=0
       JV4(1)=0
       JV5(1)=5
       RETURN
       END
       SUBROUTINE DOTEMP(AT,IO,N,AO)
       DIMENSION ADO(300),IO(300),AB(300),AT(300),AC(300),
      1AD(300),AE(300),AO(300)
```

```
      ADD(J)=ID(J)
      AB(J)=ADD(J)/100
      AC(J)=14.652-(AT(J)*0.41022)
      AD(J)=(AT(J)**2)*0.007991
      AE(J)=(AT(J)**3)*0.00077774
      AO(J)=AB(J)*(AC(J)+AD(J)-AE(J))
  900 CONTINUE
      RETURN
      END
/DATA
```