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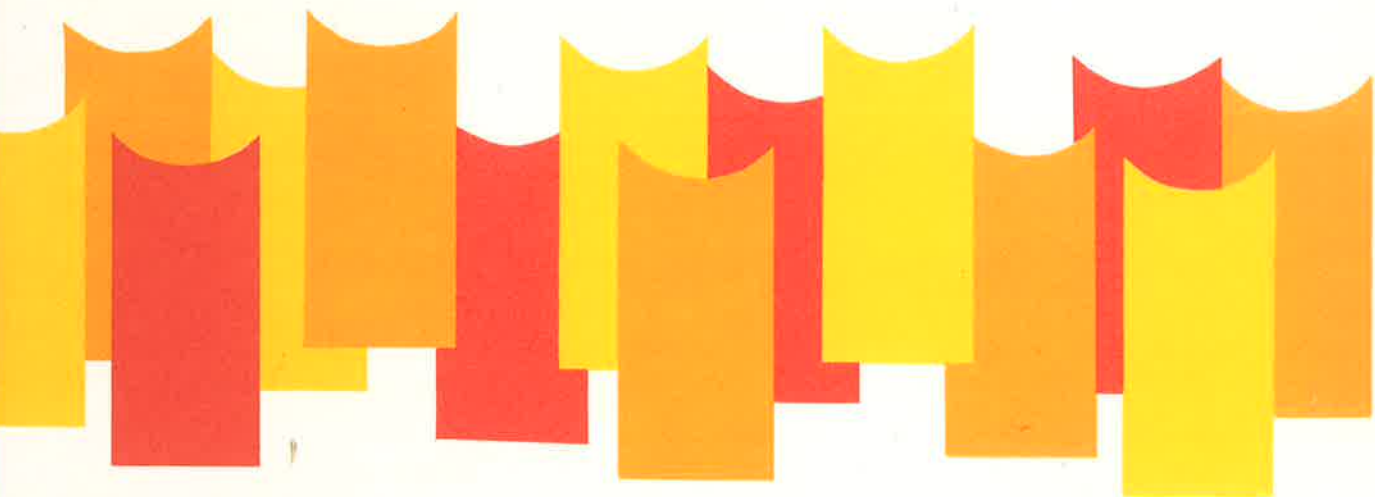

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Contents

Foreword

This Seminar was held in the new Student Union Building, University of Waikato, on 25–26 November 1980. It was arranged by the Hamilton Science Centre, Ministry of Works and Development, under the sponsorship of the National Water and Soil Conservation Organisation (NWASCO). It is the second in the series of annual Seminars organised by the Centre, the first in 1979 being on the topic of *Physical Aspects of Coastal Zone Problems.*

The function of these Seminars is to provide a forum for discussion of a topic of research related to water quality on which the Centre is engaged, thus including a number of speakers from other organisations.

The topic for this Seminar, *Aquatic Oxygen,* was selected because a substantial amount of unreported work on this important topic had been carried out over the country in the preceding few years. The opportunity was taken to bring together many of the workers in this field and hopefully assess the state-of-the-art and consider desirable directions for future research, with particular regard to the development of useful tools for water quality management.

The Seminar was attended by 89 individuals from: Government departments (29), regional water boards (20), industries (13), local authorities (7), universities (7), research institutes (7), private consultants (4), and NWASCO (2). Administrative arrangements were ably planned and co-ordinated by Messrs T. S. Hughes and P. J. Ryan, with excellent assistance from Mesdames C. Mackenzie and C. Savage.

G. B. McBRIDE
Seminar Organiser.

SESSION I SIGNIFICANCE OF OXYGEN IN NATURAL WATERS

Dissolved oxygen requirements for fish

D. SCOTT

Zoology Department, University of Otago, Dunedin

Dissolved oxygen criteria for freshwater fish are considered in relation to sublethal responses. Guidelines are developed using the criteria, and the expected interaction of environmental variables. Standards appropriate to New Zealand are then developed, and it is concluded that an existing standard of 5 mg/ℓ is rather low for moderate protection.

Introduction

Aquatic environments in New Zealand, as elsewhere, are normally characterised by dissolved oxygen well distributed through the water column, and to a lesser extent the substratum below the column. As a first level requirement it can therefore be said that dissolved oxygen is necessary as a vital part of the metabolism of what we regard as normal or typical aquatic environments.

The significance of oxygen is most readily seen in relation to the biological communities. Without oxygen in the water, very large sections of these communities are absent, and the communities that function in the absence of oxygen (anaerobic) produce metabolites (e.g., sulphides, amines, mercaptans) that are generally considered objectionable.

The level of oxygen required to provide acceptable conditions cannot be separated from the intended uses and as a general statement it can be said that the requirements for oxygen *per se* in relation to recreation, aesthetics, water supply, agriculture and industry are neither high nor specific. If these uses do appear to have a requirement, it is typically because of a correlation between oxygen and the distribution of organisms.

Oxygen requirements thus tend to resolve into the levels necessary to exclude undesirable communities (anaerobic) or to permit the existence of desired species.

Maintenance of desired species

Fish are of economic and recreational significance, and their oxygen requirements have been studied in some detail. At the same time dissolved oxygen standards have often been fixed with fish in mind. This concentration on one group of organisms has tended to obscure the fact that fish are part of a community, certain elements of which may be at least as sensitive as fish, if not more so. An example is provided by Nebeker (1972) who showed that in a laboratory situation, reduction of the oxygen concentration to 6 mg/ℓ prevented completion of the life cycle in terms of hatching by a factor of 70–85% in three species of mayflies. This example is particularly significant in New Zealand where mayflies form a major component in the food supply of stream fish.

However the tendency has been to assume that if the fish are protected the other communities are also. This viewpoint is accepted here for convenience, but particularly sensitive invertebrates should be borne in mind (Davis 1975).

1 Species differences

The sporting and economic significance of salmonids has resulted in a concentration of research on this group. By a fortunate coincidence, however, their oxygen requirements are relatively high (Doudoroff & Shumway 1970; Warren *et al.* 1973; Davis 1975), so that standards set to protect this group tend to protect all fish. Of the groups in New Zealand other than salmonids, the non-salmonid exotics tend to have lower oxygen requirements, while the New Zealand natives are virtually unknown in this respect. Some, such as the eels and swamp dwellers, may have lower requirements, but the species inhabiting colder, fast streams may be similar to salmonids (Benzie 1968).

2 Development of criteria

Useful recent summaries of the effects of reduction in the level of dissolved oxygen are provided by Warren *et al.* (1973), and Davis (1975). The first major point to emerge is that various responses are apparent in different species at different levels of reduction, and the degree of risk or adversity increases with the degree of hypoxia. It is therefore incorrect to consider particular levels as providing a clear division between a normal healthy population and one adversely affected. The one exception is the 'no effect' level and this can be considered first.

Doudoroff & Shumway (1970, p. 265) consider this level to be represented by the existing natural regime, i.e., no depression on a seasonal basis below the estimated natural minimum level for the same season. This is of doubtful value from a general point of view since the natural regime could involve a greater or lesser degree of pollution. However the context suggests minimal pollution, so that the criterion suggests no significant adverse effect with no reduction of high natural levels. This view is based on, but not directly related to, a large amount of experimental data. Warren *et al.* (1973) working with largemouth bass and coho salmon come to substantially similar conclusions. Davis (1975) surveys the literature for the level at which sublethal responses first become apparent (i.e., the incipient sublethal threshold). The responses involved were behavioural and physiological, and the groups considered are freshwater species, marine non-anadromous, anadromous, and eggs and larvae. He considers criteria in terms of both content (concentration) and availability (pressure) and proposes a negligible effect level 1 S.D. above the mean incipient response level for the group (Table 1). As an example of the data used by Davis, for freshwater salmonids, the number of observations was 19, the mean incipient response level was 90.35 mm Hg and 1 S.D. was 28.84. Thus the minimum no effect level is 119.2 mm Hg, and Davis considers that as the data are normally distributed the 1 S.D. should protect more sensitive individuals in the population.

Table 1. No effect level of dissolved oxygen (from Davis 1975)

Group	Press. O_2 mm Hg	mg O_2/ℓ	% sat. at 15 °C
Freshwater mixed (no salmonids)	95	5.50	60
Freshwater salmonid	120	7.75	76
Marine	140	8.75	100
Salmonid larvae and eggs	155	9.75	98

The criteria developed by Davis have impressed the writer as being the most soundly based available, and due weight will be given to his opinion.

When levels at which adverse responses are apparent are considered a wide range for both species and response curve is evident, and the situation can best be illustrated by examples. Only some of the types of response studied are given here.

GROWTH

Doudoroff & Shumway (1970, p. 136) describe experiments in which young coho salmon were fed abundantly at 18 °C and O_2 concentration of 9 mg/ℓ. Reductions of O_2 concentration to levels of 5, 4, and 3 mg/ℓ showed corresponding reductions of growth based on net weight of 8, 17, and 42%. Graphical presentation for the relation between growth and oxygen levels for largemouth bass and coho salmon are given by Warren *et al.* (1973) in Fig. 1 and 2.

SWIMMING ABILITY

Fish swim in several modes but two readily recognisable are maximum speed and maximum sustained speed. Both are important in different contexts, but information on the relation of oxygen levels to performance is available only for the latter. Experimental evidence on this is given in Table 2.

Table 2 Hypoxia and swimming performance

Species	T °C	Size	O_2 mg/ℓ	O_2 % sat.	Swimming	Author
Rainbow trout	14.1	12.5 cm	5.13	50	Reduction in M.S.S. by 43%	Jones 1971
Rainbow trout	22.4	11.8 cm	4.33	50	Reduction in M.S.S. by 30%	Jones 1971
Atlantic salmon	15	87–135 g	4.5	44	M.S.S. of 55 cm/sec not maintained below this level	Kutty and Saunders 1973
Largemouth bass	25	Juvenile	5–6	60–71	M.S.S. reduced below this level	Dahlberg *et al.* 1968
Largemouth bass	25	Juvenile	3	36	10% reduction of M.S.S. as compared with 100% saturation value	
Coho salmon	20	Juvenile	5–6	55–66	Reduction of M.S.S. of 10% compared with 100% saturation	Dahlberg *et al.* 1968
			3	33	Reduction of M.S.S. of 30% compared with 100% saturation	
			2.5	27.5	Reduction of M.S.S. of 40% compared with 100% saturation	

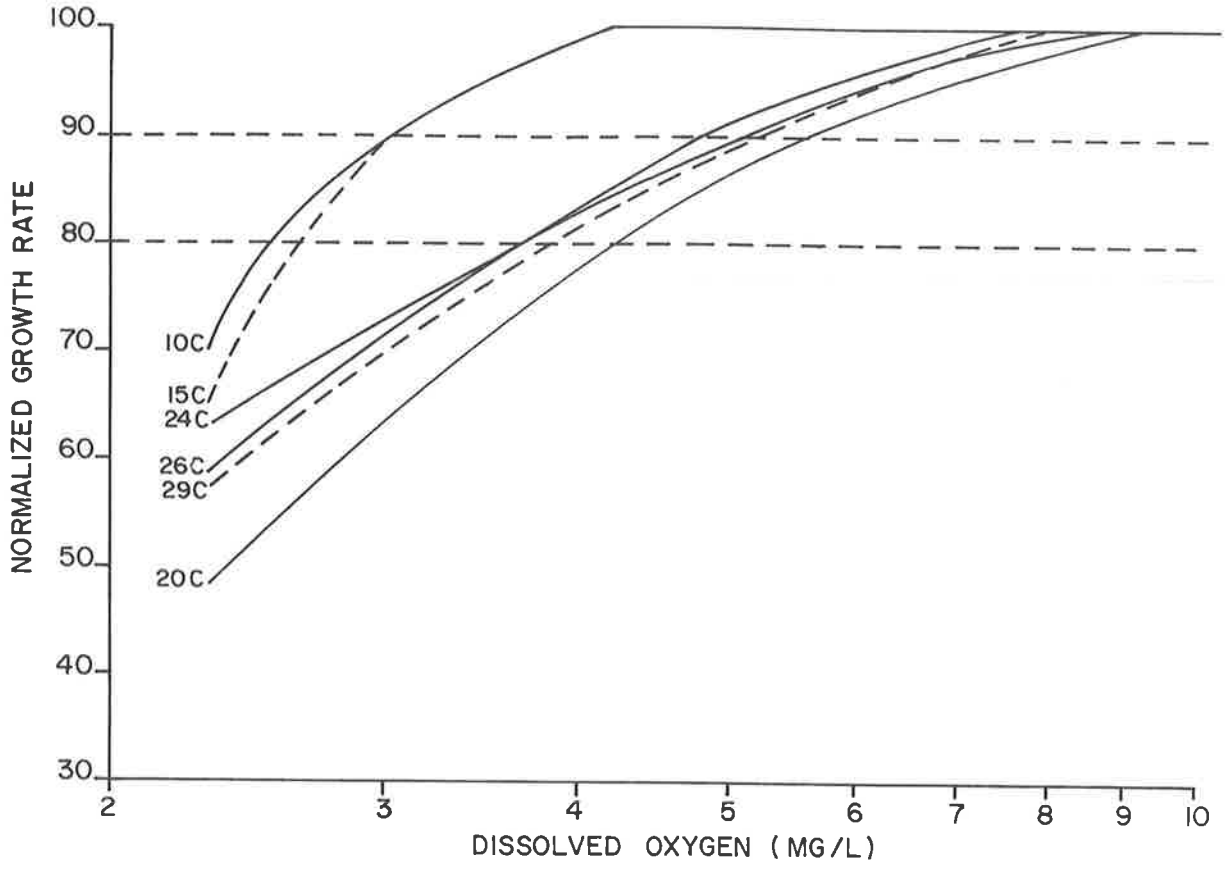

Fig. 1 Relationships between dissolved oxygen concentration and the normalized growth rate of juvenile largemouth bass reared in aquaria and fed to repletion on live food at temperatures ranging from 10 to 29 °C. Growth rates were normalized on the basis that maximum growth occurred at air saturation levels of oxygen. (From Warren *et al.* 1973).

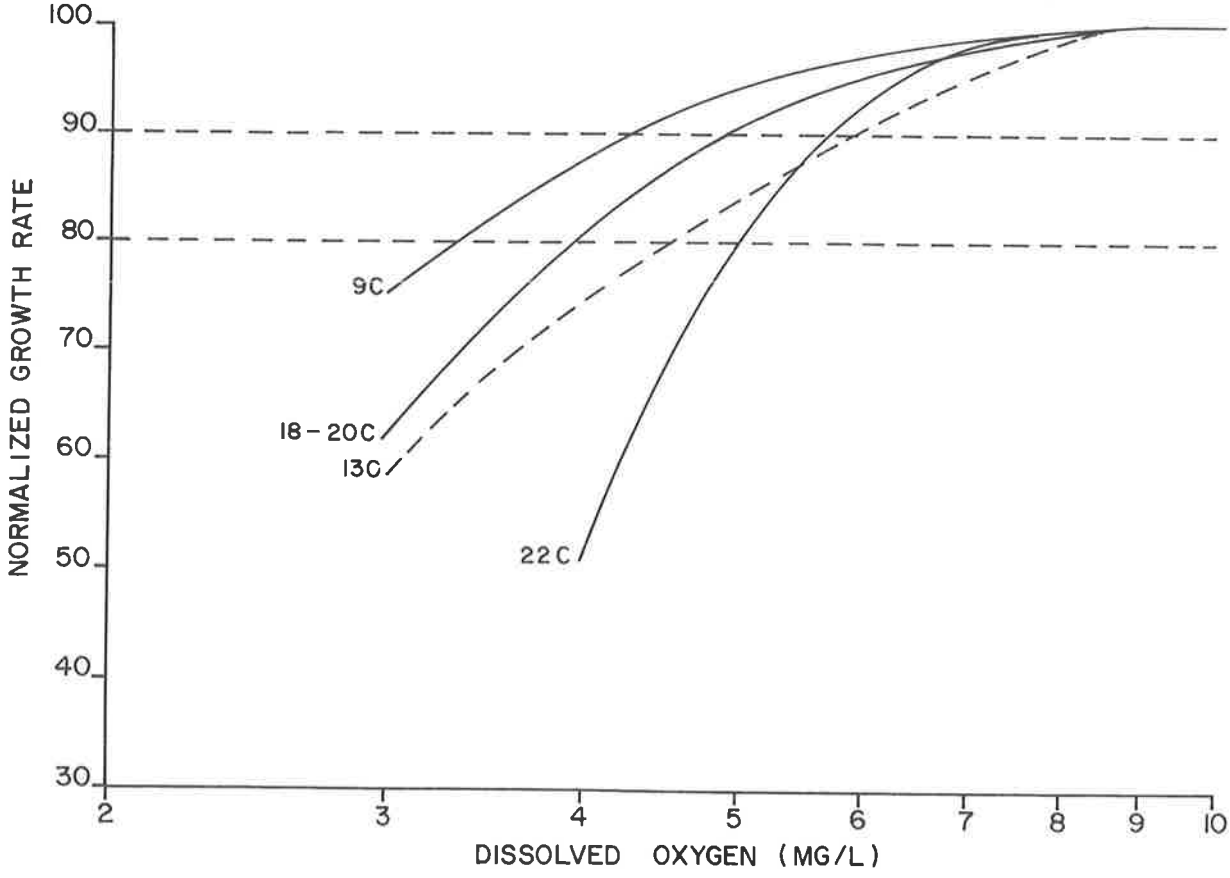

Fig. 2 Relationships between dissolved oxygen concentration and the normalized growth rate of juvenile coho salmon reared in aquaria and fed unrestricted rations of live food at temperatures ranging from 9 to 22 °C. Growth rates were normalized on the basis of determined or estimated growth rates at air saturation levels of oxygen. The 18–20 °C curve is based on many more experiments than the other curves and is considered to be more reliable (from Warren *et al.* 1973).

EMBRYONIC DEVELOPMENT

The results of studies in this area are well summarised by Doudoroff & Shumway (1970).

1. No clear evidence exists showing a general increase in egg mortality (or failure to hatch) over a range of oxygen concentrations down to 2–3 mg/ℓ in various species of salmonids in laboratory experiments.
2. Reduction in oxygen concentration during incubation resulted in a reduction in weight of the newly hatched larvae. For three salmonid species, mean weights at hatching at O_2 levels of 2.5–3.0 mg/ℓ were ¼ to ½ of the controls of air saturation.
3. Increases of the velocity of water movement around the embryos tend to reduce the effects of hypoxia because of an increased rate of delivery of oxygen to the egg surface.
4. High mortality of salmonid embryos in stream gravel when the intra-gravel oxygen was relatively high(4–8 mg/ℓ) does not indicate that these oxygen levels were associated with the mortality.
5. Embryos of non-salmonid species show a range of minimum oxygen concentration required for normal development from 2–5 mg/ℓ.

Still lower levels of dissolved oxygen raise the possibility of defining lethal levels. A major problem here is the time period over which the test is made, and while tests over 24 hours or 7 days give useful information in developing guidelines they do not necessarily indicate a true tolerance threshold (incipient lethal level). The last index can be defined as the level at which 50% of the test animals appear capable of surviving indefinitely. A variety of factors can influence the estimates obtained and the practical significance of most of the tests reported is dubious. Doudoroff & Shumway (1970) tabulate tests on 95 species, but discard many of these as being of little value. The most useful type of test was when a constant level of O_2 was maintained, and for 29 species in this type of test, the lethal levels are well below 3 mg/ℓ. For 8 species of salmonids lethal levels ranged above 2.2 mg/ℓ, and the authors concede that the salmonids are among the fish most sensitive to O_2 deficiency.

There is considerable variation in resistance with various factors including exposure time, size, age, temperature, season, and these factors need to be considered in applying the results of research to management.

A further phenomenon discussed by Doudoroff & Shumway (1970) is that of acclimation to low oxygen concentrations.

3. Development of guidelines

This requires the basic criteria derived experimentally, and also the environmental variables and likely interactions. Socio-economic criteria are then applied to reach a level that is acceptable.

TEMPERATURE

Temperature variation is particularly significant here since an increase in temperature reduces the solubility of oxygen and the partial pressure of oxygen, and at the same time normally increases the metabolic demand of the fish. Thus when the fish requires a greater rate of supply of dissolved oxygen, the amount in the water decreases markedly. One practical conclusion from this is that it is more useful to set levels in terms of saturation, since this helps to compensate for temperature variation. This point is emphasised by Davis (1975) and illustrated in recommendations below.

ACTIVITY LEVEL

Setting of minimal oxygen levels too low may result in reduced possibilities for vital activities. Brett (1970) determined the oxygen requirements for young sockeye salmon at 20°C for important activities (Table 3.)

Table 3 Oxygen requirements for young sockeye salmon at 20°C (from Brett 1970).

Activity	O_2 cost of energy expenditure as mg O_2/kg wt of fish/hour	% active metabolic rate
Agression	180	22.9
Feeding—maintenance ration	300	37.3
Feeding—maximum ration	450	55.4
Migrating up river	625	75.0

Since the active metabolic rate is already limited by oxygen levels at temperatures above 15°C (Brett 1964), significant reduction in saturation level would severely limit energy expenditure for important activities.

INTERACTION WITH POLLUTANTS

Reduced oxygen levels are typically associated with products of organic pollution, and in a complex situation a variety of toxic substances may be present. In general, toxins and low oxygen show positive interaction on mortality, e.g. increased toxicity of kraft pulp with effluent (Alderdice & Brett 1957) increased toxicity of high pH (Townsend & Cheyne 1944) increased toxicity of ammonia, salts of zinc, lead and copper, and a mixture of monohydric phenols (Lloyd 1961). The possible mechanism is an increased rate of uptake of the toxin at the gills due to accelerated gill ventilation due to hypoxia.

The practical conclusion is that if organic toxins are regularly associated with reduced oxygen, then any movement of minimum levels should be upward.

RECOMMENDATIONS

Three sets of recommendations are discussed here as representing the most recent level of informed opinion.

1. Doudoroff and Shumway (1970)

These authors recognise the need for differing levels of protection in different situations. What is distinctive about their approach is that they relate

these levels to the existing seasonal minima. The choices they suggest are summarised as follows:

Level	Protection
A	Maximum protection, unimpaired productivity.
B_1	High level of protection for major spawning grounds of salmonids.
B	High level of protection but some risk of damage.
C	Moderate protection, some reduction in production expected.
D	Low level of protection for unimportant fisheries. Permits persistence of tolerant species. Elimination of salmonids likely.

These levels are reproduced graphically in Fig. 3 from the authors. As an illustration of the application, the writer has estimated a summer minimum in Otago and Southland as follows: typical undersaturation during darkness is 90%, a maximum night temperature of 18 °C, giving a minimum of 8.5 mg/ℓ. In small shallow streams the degree of undersaturation could be 80%, and this would give a minimum of 7.6 mg/ℓ. Interpolation on the graph gives figures as follows:

	Curve B	Curve C
90% saturation	7.4	6.0
80% saturation	6.8	5.6

Thus even at 80% saturation and the lowest level that could reasonably be expected for salmonids the minimum is nearer 6 than 5 mg/ℓ.

2. Warren, Doudoroff, and Shumway (1973)

These authors lay much stress on production of coho salmon and largemouth bass. Their recommended levels of oxygen for these species are given in Table 4. It is worth noting that these authors recommend the use of the guidelines given by Doudoroff & Shumway (1970) where general protection of freshwater fisheries on a nationwide basis is required.

3. Davis (1975)

This author emphasises the importance of the oxygen pressure required to drive the gas across fish gills, as well as the amount available. He therefore expresses his levels as % saturation and takes into account the effect of temperature on metabolic rate and gas solubility. He allows three levels of protection as follows:

Level	Specifications
A	One standard deviation above the mean incipient oxygen response level for the group. There is little depression of oxygen from saturation, and a high degree of protection is assured for important fish stocks.
B	Based on the group mean, this level is where the average member of the community starts to exhibit distress. Some degree of risk to part of the community if the oxygen minimum is prolonged beyond a few hours.
C	One standard deviation below the group mean. A large proportion of the community affected by low oxygen. Deleterious effects may be severe if the minima are prolonged beyond a very few hours. To be applied only if fish populations are dispensable.

Table 5 summarises the above recommendations.

Davis further adds that application of his criteria on a nationwide basis is questionable. A more satisfactory approach is to take regional variation into account.

4. Standards

The fixing of standards in New Zealand has been accompanied by much comment. The application of the previous classification was not accepted as satisfactory by fisheries authorities, and at the hearing in Invercargill before the Town and Country Planning Appeal Board in 1974, the Southland Acclimatisation Society and the Ministry of Agriculture and Fisheries presented evidence on oxygen levels. The finding at that hearing was that 6 mg/ℓ rather than 5 mg/ℓ was a more appropriate level for salmonid fisheries. Since then, the useful paper of Davis (1975) has come to hand suggesting further upward revision of levels for fisheries, and Church *et al.* (1979) have briefly reviewed requirements for fish in New Zealand rivers.

If the guidelines are considered in relation to a minimum level of dissolved oxygen of 5 mg/ℓ, it can be said that while this level would certainly prevent visual or olfactory offence, it could not be regarded as giving much protection to freshwater fisheries. In the warmer parts of New Zealand, the night temperature could rise above 18 °C, and the saturation in

Table 4 Recommended levels of oxygen

Level	Coho salmon	Largemouth bass
A. No reduction of production from maximum	No reduction from near saturation at any temperature	>15 °C, no reduction from saturation <15 °C, minimum of 4.2 mg/ℓ
B. 10% reduction in production	At 22 °C or over, 5.5–6 mg/ℓ	<15 °C, 3 mg/ℓ
	<22 °C, 5 mg/ℓ	>20 °C, 5 mg/ℓ
C. 20% reduction in production	At 22 °C or over, 5 mg/ℓ	<15 °C, 2.5 mg/ℓ
	<22 °C, 4 mg/ℓ	>20 °C, 4 mg/ℓ

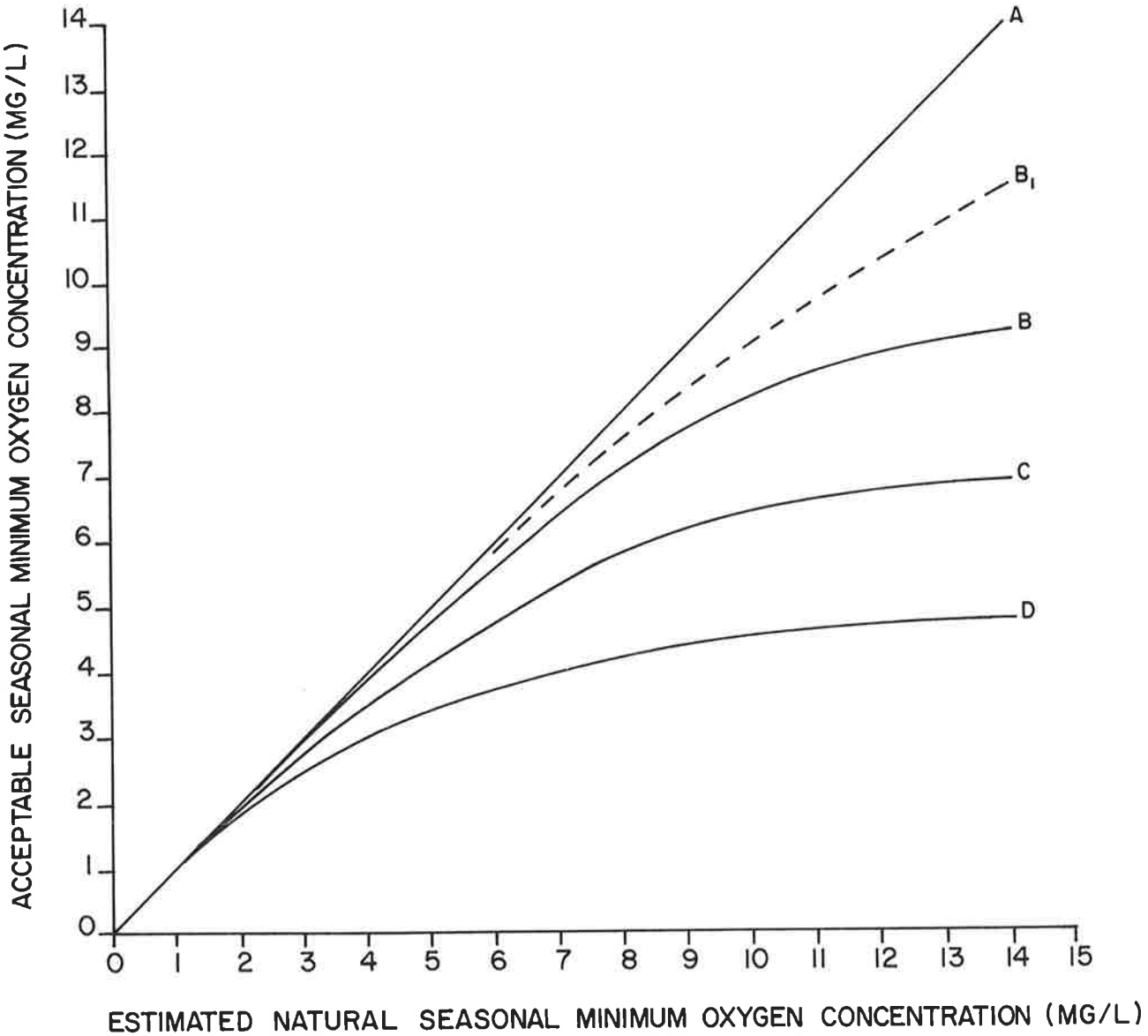

Fig. 3 Proposed dissolved oxygen criteria for protection of freshwater fisheries: Curves relating "acceptable" seasonal dissolved oxygen minima, or minimum levels that are deemed appropriate to different, specified levels of protection of fisheries, to estimated natural seasonal minima. Curves or lines designated A, B1, B, C, and D correspond to levels of protection described in the text (from Warren *et al.* 1973).

very weedy rivers could reach 80 % or less depending on conditions. This would tend to give a lower seasonal minimum. The fact remains that from Doudoroff and Shumway's guidelines a level nearer 6 mg/ℓ is indicated for moderate protection of freshwater fisheries.

The criteria of Davis would also prevent offence, but his ecological groupings are more specific. Freshwater salmonids would be receiving dubious protection at 5 mg/ℓ (49 % saturation at 15 °C). Marine fish at 5 mg/ℓ (63 % saturation at 15 °C) would also not be well looked after.

Oxygen requirements in spawning areas are higher for two reasons. The parent fish in these areas are of crucial importance and reproductive behaviour should not be limited by oxygen deficiency. A high level in the water column is also required to ensure an adequate but lower level in the intra gravel water, so that the incubating eggs and hatching larvae are not damaged. At a B level of protection at 15 °C, about 80% saturation is required.

An example of New Zealand standards developed by a Regional Water Board is provided by Otago in their proposals for a water management plan (O.R.W.B., 1980). Briefly, a concept of zoning is related to water quality types as follows:

Water type	O_2 level
1	Substantially greater than 85% saturation
2	Greater than 85% saturation
3	Substantially greater than 70% saturation
4	Greater than 70% saturation

These levels are higher than those in the 1967 Water and Soil Conservation Act and if distributed in accordance with the proposed land zoning they would imply a high level of protection for uses where oxygen is involved, and also a substantial protection of present quality.

Table 5 Oxygen criteria for ecological groups of fish with three levels of protection. The percentage saturation values are expressed for a temperature range and are derived from pressure and concentration values. At the lower temperatures the percentage saturation value used the pressure values essential for maintaining the necessary gradient between water and blood for proper gas exchange. Higher percentage saturation values are necessary at higher temperatures to provide sufficient oxygen content to meet the requirements of respiration as defined by the mg O_2/ℓ values. Saturation values are defined as the minima at each level of protection. (From Davis 1975)

Group	Protection level	Press O_2	ml O_2/litre	mg O_2/litre	%Sat. at C for criteria					
					0	5	10	15	20	25
Freshwater mixed fish population including salmonids	A	110	5.08	7.25	69	70	70	71	79	87
	B	85	3.68	5.25	54	54	54	54	57	63
	C	60	2.28	3.25	38	38	38	38	39	39
Freshwater mixed fish populations with no salmonids	A	95	3.85	5.50	60	60	60	60	60	66
	B	75	2.80	4.00	47	47	47	47	47	48
	C	55	1.75	2.50	35	35	35	35	35	36
Freshwater salmonid population (including steelhead)	A	120	5.43	7.75	76	76	76	76	85	93
	B	90	4.20	6.00	57	57	57	59	65	72
	C	60	2.98	4.25	38	38	38	42	46	51
Salmonid larvae and mature eggs of salmonids	A	155	6.83	9.75	98	98	98	98	100	100
	B	120	5.60	8.00	76	76	76	79	87	95
	C	85	4.55	6.50	54	54	57	64	71	78
Marine nonanadromous species	A	140	6.13	8.75	88	88	95	100	100	100
	B	110	4.73	6.75	69	69	74	82	90	98
	C	80	3.15	4.50	50	51	51	55	60	65
Anadromous marine species including salmonids*	A	160	6.30	9.00	100	100	100	100	100	100
	B	125	4.55	6.50	79	79	79	79	87	94
	C	90	2.80	4.00	57	57	57	57	57	58

*Percentage saturation calculations based on salinity of 28‰

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DISCUSSION FOR SESSION I

Dissolved Oxygen Requirements For Fish

Presented by: D. SCOTT

M. S. CARRIE : Taking into account the limited duration of low oxygen in streams both as regards distance and time, is it necessary to impose a rigid standard over the whole of the stream? The fish are mobile and can avoid temporary or localised low concentrations.

SCOTT : The use of mixing zones does meet your point to some extent. However many river fish are territorial and they tend to remain in one limited area for moderate periods of time. They would not necessarily respond to adverse conditions by moving out of, and then back into a section. So, mixing zones apart, I would suggest that it is better to apply standards over reasonable distances.

F. MICHAELIS : Trout are not abundant in the warmer waters of Auckland, North Auckland, and the Bay of Plenty. In these northern waters, what indicator species should be used—other native or introduced fish, or invertebrates such as mayflies?

SCOTT : You could choose some other species, but it might be difficult to find one that was convenient and widespread.

It might be easier to make allowance for altered regional factors through management plans.

C. D. STEVENSON : How would indicator organisms other than trout be used in determining suitable DO levels in normal streams?

A study of indicator oxygen requirements seems likely to be a major research project with perhaps minor benefit.

SCOTT : This is similar to the question from Francis Michaelis. Some people would argue that the New Zealand native species have been badly neglected, so perhaps there is justification for research.

M. E. U. TAYLOR : Your paper makes the assumption that waters should be managed almost exclusively for trout populations which are "valuable".

Might it not be advantageous to manage waters in such a way that they would support a much wider range of fish, in, for example, more enriched conditions than suit trout? The wider range of fish might turn out to be more valuable.

SCOTT : In fact, fisheries administrators in many areas manage waters for a fair range of species. In many waters in the South Island one river will support perch, eels, whitebait, and trout. In the Waitaki three salmonid species as well as eels and whitebait are fished for; lowering standards would tend to decrease the most valued component without increasing the range of species.

D. G. SMITH : It is very desirable to develop various levels of protection for fish but I suggest that they are only valid in the absence of other environmental stresses, e.g., toxic species. Comment please?

SCOTT : If there are other adverse factors present there is often positive interaction. For example temperature and oxygen stress, or oxygen and a heavy metal. This would have to be borne in mind and management plans could accommodate this point by setting higher standards for the interacting parameters. This is where management plans are more flexible than national standards.

K. CURRIE : In view of the variety of factors influencing the development of DO criteria (species involved, natural conditions etc), would you be in favour of replacing nationally established criteria with national guidelines from which Regional Water Boards can develop regional criteria?

SCOTT : As I understand the present views on the new Water and Soil legislation, national classification would not be obligatory, and Regional Water Boards would be able to develop their own management plans with their own standards. So there need not be a conflict.

I think you are touching on a more difficult issue, because if there is a set of national standards in the legislation it will be argued that this may make it more difficult for Regional Water Boards to maintain their management plan, unless this latter has statutory recognition. Guidelines would be associated with the new legislation but would apply to only certain parameters.

SESSION II MEASUREMENT OF DISSOLVED OXYGEN AND OXYGEN DEMAND

Measurement of dissolved oxygen

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The underlying principles of dissolved oxygen (DO) measurement are described, along with the relative effects of temperature, barometric pressure, altitude and salinity. The error in standard saturation DO–temperature tables is described, and a compilation of values based upon a recent critical review of data is given. The two major techniques for measuring DO (Winkler titration and membrane electrode systems) are described along with the kinds of error arising from each technique. For the Winkler method iodine volatilisation is probably the major source of error, but diminishes in importance at lower levels of DO. For electrode systems sample aeration and electrolyte blank response are the major causes of error, and a procedure aimed at minimising this for membrane systems is given.

Introduction

The importance of dissolved oxygen (DO) to aquatic organisms in natural waters is undisputed, and most guidelines for preserving natural water quality include a DO standard. Such standards are based upon the minimum concentration that will sustain a healthy fish population, and in most cases this is 5 or 6 mg/ℓ (Water and Soil Conservation Act 1967; US-EPA 1976). In order to monitor such classified waters the DO measuring technique must be capable of achieving accuracy within at least ± 0.5 mg/ℓ and, in situations where the impact of a pollutant is studied by following the change in DO, it may be necessary to attain a measured precision of ± 0.2 mg/ℓ or better. Other kinds of study may require an even greater precision (i.e., smaller uncertainty in measured DO values) and the choice of technique for measuring DO may depend upon the permissible tolerances. Most methods are capable of at least ± 0.05 mg/ℓ reproducibility in laboratory conditions, but, special care should be taken when taking measurements under more trying conditions, or when comparing results obtained from different methods (Wilcock *et al.* 1980).

Basic Principles

1 Henry's Law

Oxygen in contact with water will tend to an equilibrium position in which the concentration of DO is directly proportional to the partial pressure of oxygen, at a given temperature. This is Henry's Law and may be expressed.

$$P_{O_2} = K_H C_S \quad (1)$$

where P_{O_2} is the partial pressure of oxygen and is usually taken as being 0.2094 (P–v), in which P is the atmospheric or barometric pressure and v is the saturation vapour pressure of water at the given temperature. The Henry's Law constant, k_H, is a function of temperature, and C_S is the equilibrium or saturation solubility of oxygen in water for these conditions. The saturation DO values at a reference pressure of 101.325 kPa* are given at different temperatures in laboratory handbooks, such as Standard Methods (A.P.H.A. 1976). However the Standard Methods list, as well as many others commonly in use, is based upon old measurements and may be in error by up to 0.14 mg/ℓ in the range 10–20 °C, and worse at higher temperatures (Wilhelm *et al.* 1977). A compilation of saturation DO values, based upon a recent critical review of gas solubilities in water (Wilhelm *et al.* 1977) is appended here.

The variation of C_S with atmospheric pressure, under conditions of water vapour saturation (as for instance occurs during the moist-air calibration procedure for membrane sensors) may be calculated from

$$C_S(P) = \frac{C_S^\circ (P\text{-}v)}{101.325\text{-}v} \quad (2)$$

or less precisely

$$C_S(P) = \frac{C_S^\circ P}{101.325} \quad (3)$$

*101.325 kPa = 1.01325 bar = 1 atmosphere = 760 mm Hg.

where $C_s(P)$ = the DO solubility in mg/ℓ at pressure P kPa, and C_s° = the DO solubility in mg/ℓ at 101.325 kPa at the given temperature.

Variations in atmospheric pressure affect moist-air calibrations, but the magnitude of this effect is normally quite small (max. error of up to ± 0.15 mg/ℓ DO).

2 Altitude and Other Effects

Atmospheric pressure diminishes with increasing altitude, so that the saturation DO at 15 °C drops by roughly 1 mg/ℓ per 1000 m.

Dissolved ionic species exert a "salting out" effect on DO, causing C_s to be reduced. The size of this effect is dependent upon the nature of the dissolved species, their concentrations and the temperature. Weiss (1970) and Carpenter (1966) have derived an empirical relationship for the dependence of DO on salinity and temperature. Relationships for dissolved salts other than those found in sea water are available in the literature, but it is more usual in these cases to determine empirically the individual saturation DO's by a proven method.

The relative magnitudes of these effects, expressed as percentage changes in DO for unit change in each of the variables, are shown in Table 1. It is clear that temperature and barometric pressure have the most significant effect on C_s in fresh waters.

Table 1. Percentage change in C_s with unit change in:—temperature, atmospheric pressure, altitude, and salinity, at different temperatures.

	$\%(\frac{\Delta C_s}{C_s})/\Delta X$		
X	5 °C	10 °C	20 °C
temperature (°C)	-2.82	-2.75	-2.65
pressure (kPa)	1.02	0.98	0.98
altitude (m)	-0.012	-0.012	-0.012
salinity (‰)	-0.74	-0.71	-0.67

Methods for Measuring Dissolved Oxygen

The many techniques for measuring aquatic DO fall into two broad groups: those based upon chemical reactions of oxygen, and physical methods. By far the most commonly used techniques are the Winkler method and its modifications (A.P.H.A. 1976) which is a titrimetric method belonging to the first group, and the membrane electrode techniques, which are physical methods based upon the original concepts of the Clark oxygen electrode (Clark *et al.* 1953) and the Mackereth electrode (Mackereth 1964). Only these methods will be discussed here. Detailed descriptions that may be found in standard texts, or laboratory manuals will not be given.

1 The Winkler Method

This test is based upon the reaction of DO with manganous ions, the product of which reacts with iodide under acidic conditions to give iodine. The iodine produced is directly proportional to the DO, and is estimated by thiosulphate titrimetry.

CHEMICAL REACTIONS

While the exact nature of the manganese species formed in this test is not known, a likely scheme is as follows:

Step 1. Reaction of manganous ions with oxygen

$$4Mn^{2+} + 8OH^- + O_2 = 4MnO(OH) + 2H_2O$$

Step 2. Acidification to give manganic ions

$$MnO(OH) + 3H^+ = Mn^{3+} + 2H_2O$$

Step 3. Production of iodine

$$2Mn^{3+} + 2I^- = 2Mn^{2+} + I_2$$

Step 4. Titration of iodine with thiosulphate

$$I_2 + 2\,S_2O_3^{2-} = S_4O_6^{2-} + 2I^-$$

INTERFERENCES AND SOURCES OF ERROR

Oxidising and reducing agents may interfere with the method by causing either liberation or reduction of iodine. Such substances are: ferrous and ferric salts, chromate, nitrite, residual chlorine, sulphite, sulphides, and readily oxidisable organic matter. Nitrite is probably the most commonly encountered of this group, and is eliminated by reaction with azide, usually included with alkaline-iodide reagent of most recommended versions of the Winkler method (A.P.H.A. 1976), according to the reaction:

$$N_3^- + NO_2^- + 2H^+ = N_2 + N_2O + H_2O$$

This is the Alsterberg or azide modification.

Carpenter (1965) in his review of the Winkler method cited the major sources or error as:

(a) air oxidation of iodide,
(b) volatilisation of iodine,
(c) oxygen contributed by reagents,
(d) chemical contamination of the reagents, and
(e) errors associated with the titration end-point.

He concluded that conditions could be arranged so that all but (c) are negligible, and an overall precision of ± 0.1 percent (i.e., ± 0.01 mg/ℓ at a DO of 10 mg/ℓ) attainable. Both Carpenter (1965) and Montgomery *et al.* (1964) conclude that the major source of error in most procedures is iodine loss by volatilisation during the titrimetric manipulations, and accordingly recommend either titrating the thiosulphate directly into the DO bottle (instead of decanting a measured volume into a titration flask), or increasing the concentration of iodide in the alkaline-iodide azide reagent. This latter measure pushes the equilibrium

$$I_2 + I^- \rightleftharpoons I_3^-$$

further to the right, and is the basis for some authors (Montgomery *et al.* 1964; S.C.A. 1980) recommending the Pomeroy-Kirschman modification (Pomeroy & Kirschman 1945) of the Winkler method, which increases the triiodide/iodine ratio by a factor of six. However, the small benefit gained is offset by the awkwardness of handling much more viscous reagents than usual, especially when performing analyses outdoors. Furthermore, the loss of iodide by volatilisation is appreciably less for lower DO samples because of the relatively greater amount of unreacted iodide. The usual azide modification is

capable of a precision of ± 0.04 mg/ℓ for natural waters.

OTHER MODIFICATIONS

Special modifications of the Winkler method are available for solutions having appreciable concentrations of suspended solids, organic materials, ferrous or ferric ions (A.P.H.A. 1976). Many of these interferences can be overcome by using the membrane electrode technique instead.

PROCEDURE FOR THE WINKLER METHOD

Analyses conducted outdoors should be titrated as soon as possible, or taken to the *acidification* stage, prior to transport to the laboratory for titration with thiosulphate.

Water samples being transported for later analysis should be stored without air bubbles or headspace (unless very large samples are collected) at, or slightly below, the temperature of the water being sampled. Thermal expansion may cause the container to shatter, while a headspace volume of 0.4 ml/ℓ of water will give a DO error of about 0.1 mg/ℓ (Wilcock *et al.* 1980). Samples may be preserved from microbial activity by the addition of mercuric chloride (40 mg/ℓ), but analysis should be performed a soon as is practicable. Any sample transferences should be by siphoning, to avoid aeration errors.

If results are to be expressed as percentages of saturation it will be necessary to know the ambient temperature and barometric pressure (and possibly the altitude) at the time of sampling, in order to calculate C_s (equation 2).

CALCULATION OF RESULTS

The DO concentration may be calculated from the reaction scheme stoichiometry (see **Chemical Reactions** above), so that

$$DO = 8000\ FxM/W \quad mg/\ell \qquad (4)$$

where x = volume in ml of M molar sodium thiosulphate titre, W = volume in ml of water sample titrated, and F = dilution factor for addition of reagents.

$F = \frac{V_s}{V_s - V_r}$ in which V_s is the DO sample bottle volume (ml) and V_r is the total volume (ml) of reagents added.

2 Membrane Electrodes

Electrode systems are often the most convenient way of measuring DO, especially in continuous monitoring situations or outdoors. This is because the need to carry strong chemicals to the site of each analysis can be avoided, and because individual determinations are generally easier and quicker than Winkler titrations. Electrode systems in capable hands can achieve comparable precision to the Winkler method.

PRINCIPLE OF OPERATION

Membrane electrodes are of two kinds: galvanic (potentiometric) and polarographic (amperometric). Both types are composed of two solid metal electrodes in contact with a volume of electrolyte separated from the sample solution by a gas-permeable membrane made of either teflon or polythene. The electrode materials for the more common polarographic cell are typically gold for the cathode and silver for the anode, with the electrolyte being a solution of potassium chloride.

Polarographic cell reactions are:—

cathode reaction $O_2 + 2H_2O + 4e^- = 4OH^-$

anode reaction $Ag + Cl^- = AgCl + e^-$

total cell reaction $O_2 + 2H_20 + 4Ag + 4Cl^- = 4OH + 4AgCl$

The galvanic cells usually have a lead anode with potassium hydroxide solution as electrolyte, and an overall cell reaction of

$$2Pb + 2OH^- + O_2 = 2PbOOH^-$$

The galvanic principle involves measurement of the potential across the electrodes, while the polarographic systems have an external polarising voltage applied to the electrodes, with the resulting current being measured. In both cases the electrical output signal is proportional to the concentration of oxygen diffusing into the electrolyte, and this is in turn controlled by the partial pressure of oxygen in equilibrium with the test water, in accordance with Henry's Law (equation 1).

Galvanic sensors usually consume less DO than polarographic probes and therefore require less stirring to maintain equilibrium between the electrolyte and sample water.

INTERFERENCES AND SOURCES OF ERROR

Wastewaters having a high oil or grease content may form a coating on the membrane, giving unreliable results.

A correction for the salting out effect must be made for DO measurements in estuarine waters, or in waters having a high ionic strength. This can be done either by application of an empirical formula (Weiss 1970; Carpenter 1966) or by measuring C_s by an established technique (e.g., the Winkler method) at the temperatures of interest.

Certain electro-oxidisible gases, notably H_2S, can severely affect the performance of the DO electrode. Carbon dioxide may interfere with the operation of some galvanic sensors.

The effects of temperature and barometric pressure on C_s, as noted previously, should be born in mind. Those meters having automatic temperature compensation should be checked regularly to ensure that the thermistors are giving reliable results.

By far the commonest error is sample aeration, usually caused by over-vigorous stirring, or insufficient time allowed to decrease the electrolyte blank response to a negligible level, when determining low DO values.

PROCEDURE FOR MEASURING DO BY METER

Preliminary checks

Before using a membrane electrode-meter system the following checks should be made:—

The DO meter thermometer mode should be calibrated against a standardised laboratory thermometer, over the range 0–30 °C.

The time taken to reach thermal equilibrium should be estimated by first placing the DO sensor in ice-water and then in water at 20 °C, and noting the time it takes to give a stable reading of temperature. The procedure should be reversed and the average

time used to estimate thermal response in the most adverse conditions.

The instrument's response to low DO levels should be gauged by placing the sensor in a saturated solution of sodium sulphite and noting the time it takes to reach equilibrium.

The instrument should from time to time be compared with a known method, such as the Winkler method, for a range of DO values.

DO meter systems are typically capable of ± 0.1 mg/ℓ precision.

Calibration

The usual methods described in most manuals are water vapour-saturated air calibration, air-saturated water calibration, and comparison with a known standard. In each case the measured C_s value should be corrected for atmospheric pressure, altitude etc., as already described.

Measurement of DO

Electrodes require a minimum stirring rate to ensure that cathodic oxygen consumption does not exceed the rate of diffusion across the membrane and thereby give "low" answers. Care should be taken to minimise agitation of the sample or contact with air, in order to avoid aeration (positive error). Galvanic sensors may be preferred in some situations where minimal stirring is required. Results are usually expressed as parts per million (p.p.m. = g/m^3) or % saturation concentration. For dissolved oxygen g/m^3 ÷ 32 = millimoles O_2/ℓ.

Conclusions

This paper has endeavoured to clarify the principles of operation of the two most popular DO analytical techniques, and explain some of the rationale for the modifications of the Winkler method in particular. It is hoped that this may assist those active in DO measurement, either in getting maximum value for their efforts or in being made aware of the limitations of these techniques.

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Appendix: Saturation solubilities of dissolved oxygen in water

Temperature (°C)	Saturation Dissolved Oxygen (mg/ℓ)	
	Wilhelm *et al.* 1977	APHA 1976
0	14.57	14.6
1	14.17	14.2
2	13.79	13.8
3	13.43	13.5
4	13.08	13.1
5	12.76	12.8
6	12.43	12.5
7	12.12	12.2
8	11.83	11.9
9	11.55	11.6
10	11.29	11.3
11	11.02	11.1
12	10.77	10.8
13	10.54	10.6
14	10.30	10.4
15	10.09	10.2
16	9.86	10.0
17	9.66	9.7
18	9.46	9.5
19	9.27	9.4
20	9.09	9.2
21	8.91	9.0
22	8.73	8.8
23	8.58	8.7
24	8.41	8.5
25	8.26	8.4
26	8.10	8.2
27	7.95	8.1
28	7.81	7.9
29	7.68	7.8
30	7.55	7.6
31	7.42	7.5
32	7.29	7.4
33	7.17	7.3
34	7.06	7.2
35	6.95	7.1
36	6.83	7.0
37	6.72	6.9
38	6.61	6.8
39	6.51	6.7
40	6.41	6.6
45	5.94	6.1
50	5.50	5.6

Standard BOD and other oxygen demand tests

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The standard BOD test is discussed in terms of its conceptual and practical shortcomings. Although there are a large number of problems involved with its use as a water treatment plant control parameter, it is concluded that the test provides a critical parameter for the measurement of waste assimilation in natural receiving waters. Alternative tests, although generally quicker and more precise to operate, are often difficult to interpret in terms of final receiving water oxygen demand. These tests may be usefully employed in conjunction with long term respirometric tests thus providing substrate depletion and BOD progression data for a better understanding of receiving water processes.

Introduction

In considering the topic of biochemical oxygen demand (BOD), it is essential to distinguish between the concept of BOD and the BOD test itself. In essence BOD is a measure of the amount of oxygen utilised by aquatic heterotrophic micro-organisms engaged in breaking down waste nutritive material in a water sample. It is used to assess the potential for deoxygenation of that water sample (and hence of the water body from which the sample was taken) by these micro-organisms. It is also used to monitor the performance of a waste treatment plant.

Optimal use of a water body is not possible if the dissolved oxygen falls below the level required to maintain an ecological balance. BOD, as a bioassay for organic compounds, is a reasonable and logical concept which provides a basic approach to assessing the strength of oxygen demanding material in wastes and the potential for oxygen removal from waters receiving those wastes. It does however have some shortcomings. This paper discusses the basis and shortcomings of the BOD test, and reports on usefulness of alternative measures of oxygen demand.

The BOD test

The BOD test employs the metabolism of micro-organisms, being those organisms that will break down waste nutritive material in a sample, to produce a depletion of oxygen in a bottle test under a limited number of defined conditions—(APHA 1976).

Samples are contained in 200–300 ml bottles and incubated at 20 °C ± 1 °C in the dark (to suppress photosynthesis of algae) for 5 days. The samples are not stirred and nitrification is generally not inhibited, though it can be (Montgomery & Borne 1966).

A BOD test is considered valid and accepted if:

1. the DO depletion in dilution water is less than 0.2 mg/ℓ;
2. the test solutions seeded show oxygen depletion greater than 2.0 mg/ℓ;
3. a residual DO of more than 1 mg/ℓ remains in the sample at the end of the test.

Several dilutions of the sample may be required in order to meet these criteria. A number of dilutions are suggested in Standard Methods — "0.1–1.0% for strong trade wastes, 1–5% for raw and settled sewage, 5–25% for oxidised effluents, and 25–100% for polluted river waters".

Dilution water is prepared which contains phosphate, nitrogen (as ammonium chloride), magnesium, calcium and ferric ions. This solution should be kept long enough at 20 °C to become saturated with oxygen or be aerated using compressed air.

The initial DO of the samples and dilution water are determined, the samples are incubated and the final DO readings made. The BOD_5 result is then simply calculated.

If a sample is sterile or very low in biomass of micro-organisms and also contains a large organic content, seeding may be necessary. The standard seed material is settled domestic wastewater that has been stored at 20 °C for 24–36 hours. Generally a 1% innoculation of seed is used and appropriate control samples are incubated.

There are a number of mechanical problems associated with the BOD test.

1. Obtaining a representative sample can be difficult when very large dilutions are involved.
2. It is very difficult to achieve the correct DO depletion in a bottle when dealing with concentrated wastes. The large number of dilutions performed in duplicate, results in very time consuming set-up and analysis.

3. One does not know what dilutions are suitable for samples with a large range of possible BOD_5.
4. A large amount of glassware is required for preparation, aeration, and incubation. This all requires cleaning.
5. The 5-day period is difficult to accommodate in a working week.
6. Large numbers of samples take up a large amount of incubator space.

Interpretation of BOD test results

In considering the BOD test results one must look at the microbiological processes that occur in the sample bottle. The substrate concentration is rather low in the BOD bottle because the aim of the technique is to make the carbon source, not the dissolved oxygen supply, or any other nutrient source, the limiting factor, and most importantly the microbial population is a heterogeneous or natural one. If one plots data generated by sampling at various times a system innoculated with a relatively small number of micro-organisms in relation to the carbon supply, the familiar curve of microbial growth and substrate depletion is developed (Fig. 1).

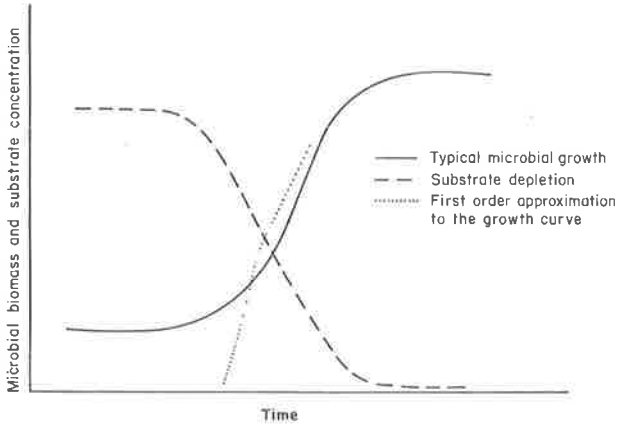

Fig. 1 Microbial growth curves.

A curve of this form is generally observed, irrespective of the means used to assess the microbial growth. The general shape of the BOD progression is similar to that of the microbial growth curve. The point of inflection of the microbial growth curve separates the first order increasing rate portion (logarithmic growth) and the decreasing rate portion which may approximate first-order decreasing kinetics (dashed line).

The initial lag period may vary greatly in its duration if either a metabolic acclimation or an adaption (population selection) is required prior to substrate utilisation. This lag phase may be an important period if natural receiving water populations are used rather than some previously adapted culture. If the substrates are complex and so require extracellular enzymatic degradation prior to metabolism by the cells, this may further increase the lag period.

The curve, in general, need not follow this simple sigmoidal form but may have one or more plateaux. These may represent sequential degradation of substrates or may mark the beginning of mechanisms other than carbonaceous oxygen-removal by the bacteria.

In cultures of sewage origin a large number of protozoa may be present which exist on bacteria as food. In using a sewage inoculum for the dilution BOD a number of protozoa may be introduced and these may exert a significant oxygen demand towards the end of the microbial growth period as their numbers increase (Bhatla & Gaudy 1965). The role of protozoa in natural aquatic systems which are not otherwise heavily polluted could be expected to be low and a natural inoculum would not show this protozoal oxygen demand.

The autotrophic metabolism of the nitrifying bacteria may also appear as a secondary rise in oxygen uptake. This oxygen utilisation is brought about by the oxidation of ammonia to nitrite (*Nitrosomas* spp.) and then nitrate (*Nitrobacter* spp.). Each milligram of ammonia (expressed as ammonia–N) results in the removal of more than 4 milligrams of oxygen. In wastes containing large amounts of ammonia or nitrogenous organic matter (e.g., protein) this may significantly increase the BOD. Normally this exertion is not a factor during the standard 5-day BOD incubation period since it normally does not occur until after this time (Gaudy 1972). Usually the number of nitrifying bacteria in a sample is low, their growth is relatively slow, and their proliferation depends on adequate supplies of both reduced inorganic nitrogen compounds and inorganic carbon.

In general, the oxygen demand of the nitrifying bacteria is not large compared to carbonaceous oxygen demand in New Zealand streams, but significant nitrification may occur with highly proteinaceous or secondary treated waste.

Shortcomings of the BOD test

1 Treatment plant operation

(a) Not able to be standardised — the 'accuracy' of the test cannot be defined because there is no 'true' value which may be independently obtained. No primary standard has ever been available for the BOD_5 test.

(b) Five days is too long—for the efficient running of a wastewater treatment plant 5 days is too long to wait for a control parameter.

(c) Lack of precision in reproducibility may be affected by: the basic procedural methods of different operators; the types of micro-organisms present vary with each new test; lack of stirring especially if particulate material is present.

2 Receiving water oxygen balance analysis

(a) Does not give the BOD progression easily—a very large number of BOD bottles are required to perform a staged BOD progression, where bottles are opened at intervals during the 5-day incubation.

(b) May not have the required similarity of substrate and bacterial concentrations—both these parameters determine where the BOD_5 test starts on Fig. 1. The characteristics of the organic substrates in the waste determine how much breakdown can occur in the 5-day period. The concen-

tration of the substrate is well accepted as the rate-determining parameter, providing sufficient micro-organisms are present (Monod 1949; Gaudy 1972). This means that if the BOD progression is supposed to approach that of the receiving water body, it must at least contain a similar concentration of dissolved substrate.

(c) Not stirred and so does not match turbulence—the natural water body generally has far more turbulence than a BOD bottle. An unstirred BOD bottle can produce concentration gradients, and settling out of organisms generally resulting in a reduced BOD.

(d) Algal interference—the presence of algae and macrophytes in a natural water body may substantially increase oxygen concentrations with photosynthesis by day, while adding to the oxygen demand during the night. Both algae and macrophytes have been shown to excrete large amounts of reduced carbon during photosynthesis (Allen 1971 a & b; Nalewajho 1977) and so increase the naturally occurring substrates present. When enclosed in a BOD bottle (in the dark) the algae cause an apparent BOD because of their endogenous metabolism, and die-off may occur within 1 to 2 days with subsequent cell lysis and release of organic material (Fallon & Brock 1979).

(e) Does not model nutrient imbalances—a natural receiving water may have nutrient imbalances which will affect the metabolism of the micro-organism, and so the resultant natural BOD exertion. The standard test eliminates nutrient deficiencies and may add a slight additional oxygen demand with NH_4 as the nitrogen source. If nitrate (NO_3^-) is used as the nitrogen source a significant decrease in the apparent BOD ($\sim$ 80% of the NH_4 value) has been shown to result when the micro-organisms are grown on simple sugars (Lewis & Busch 1965). This BOD difference would not be apparent if other forms of reduced nitrogen were available for growth and NO_3 reduction was not required.

(f) Wrong temperature—the BOD test requires incubation at 20 °C which may or may not be the *in situ* temperature. For every 10 °C increase in temperature the rate of oxygen demand generally doubles but is affected by the type of organism present and the season of sampling (Wright 1971).

(g) Benthic and bottle effects—the presence of benthic micro-organisms in a natural receiving water may greatly increase the rate of the BOD exertion. These organisms are absent from any BOD bottle. Bottle effects are somewhat variable effects which may result from organisms growing on the walls of the bottle and these may interfere with low BOD estimations.

Alternatives to the BOD test

A number of alternatives to the standard BOD test have been suggested and most of these are for Waste Treatment Plant operations. The published procedures are generally based on rapid BOD techniques or chemical methods based on a number of principles:

1. Arbitrary selection of a shorter time with incubation at 20 °C or higher.
2. Correlation of BOD with chemical oxygen demand (COD), total organic carbon (TOC), total oxygen demand (TOD) (i.e., complete pyrolysis to CO_2) (see Sherrard *et al.* 1979; Aziz & Tebbutt 1980).
3. Use of a massive inoculum of mixed or pure culture.
4. Use of the concept of the plateau value.
5. Use of manometric techniques.

A general review of these methods has been published by Le Blanc (1974) and some are considered by Heddle in his paper to this Seminar.

The COD test

Chemical oxygen demand (COD) provides an alternative to BOD in that it involves virtually complete chemical oxidation of the organic compounds present. Most types of organic matter are oxidised by a boiling mixture of potassium dichromate and sulphuric acid, with the excess dichromate being titrated with ferrous ammonium sulphate. The amount of oxidisable organic matter, measured as oxygen equivalent, is proportional to the potassium dichromate consumed.

The advantages of the COD test over the BOD test are that it has greater accuracy and precision as a test, and it may be completed in about 2 hours. It fails, however, to include a number of compounds which are available for oxidation by micro-organisms. These compounds include acetic acid, straight chain aliphatics, aromatic hydrocarbons, pyridine, and ammonia. The COD test includes in its oxidation a large number of high molecular weight complex organic molecules which show a very slow BOD decay, e.g., cellulose.

Interferences with the COD test are caused by the presence of Cl^- (corrected by inclusion of mercurous sulphate) and any reduced compounds, e.g., Fe^{2+}, aldehydes.

For a given effluent a reasonable relationship between BOD_5 and COD may be established. However, in no cases can the correlation be applied directly to another waste even though the waste may be of the same type (see BOD_5 and COD values for different wastes in Table 1). Any change in the fraction of the organic matter which is biodegradable will affect the correlation to the BOD_5 result. This is especially so for a multi-component waste which may have different organic substances with different bio-oxidation kinetics, e.g., milk. Toxic substances become important here because they may inhibit the BOD of a sample with a high COD. Indeed toxic substances form a unique case because their effect may vary greatly within a BOD test because of different dilutions involved. BOD_5 and COD are helpful for receiving water samples, because comparison gives some idea of stability of the substrate.

Total organic carbon analysis

Total carbon analysers (TOC) have become available, if at some considerable cost, in recent times. A comparison between BOD, COD, and TOC has recently been published by Aziz & Tebbutt

Table 1. Comparative strength of effluents*.

Type of Waste	Main Pollutants	BOD_5	COD
Abattoir	Suspended solids, protein	2600	4150
Beet sugar	Suspended solids, carbohydrate	850	1150
Board mill	Suspended solids, carbohydrate	430	1400
Brewery (bottle washing)	Carbohydrate, protein	550	
Cannery (meat)	Suspended solids, fat, protein	8000	17940
Chemical plant	Suspended solids, extremes of acidity or alkalinity, organic chemicals	500	980
Coal carbonisation:			
Coke ovens	Phenols, cyanide	780	1670
Gas Works	Thiocyanate, thiosulphate	6500	16400
Smokeless fuel	Ammonia	20000	
Distillery	Suspended solids, carbohydrate, protein	7000	10000
Dairy	Carbohydrate, fat, protein	600	
Domestic sewage	Suspended solids, oil-grease, carbohydrate, protein	350	300
Grain-washing	Suspended solids, carbohydrate	1500	1800
Kier	Suspended solids, carbohydrate, lignin	1600	3600
Laundry	Suspended solids, carbohydrate, soap	1600	2700
Maltings	Suspended solids, carbohydrates	1240	1480
Pulp mill	Suspended solids, carbohydrate, lignin, sulfate	25000	76000
Fermentation industry:			
Fermentation segment		4560	4120
Chemical-synthesis segment		960	1580
Formulation, packaging segment		145	217
Petroleum refinery	Phenols, hydrocarbons, sulphur compounds	850	1500
Resin manufacture	Phenol, formaldehyde, urea	7400	12900
Starch reduction of flour	Suspended solids, carbohydrate, protein	12000	17150
Tannery	Suspended solids, proteins, sulfide	2300	5100

*Adapted from J. W. Abson & K. H. Todhunter, pp. 318–319 in N. Blakebrough (ed.), "Biochemical and Biological Engineering Science," Vol. 1, Academic Press, London, 1967.

(1980) and although they find good correlation between BOD and COD for domestic waste effluents, only very poor correlations are found between these parameters and TOC. Problems with the TOC analysis may arise because of the small sample size (20 $\mu\ell$) not producing a representative sample in a heterogenous waste. The TOC analysis also includes substances which would not otherwise be readily oxidised, e.g., lignin, humic acids.

Both COD and TOC tests have their greatest potential in looking at specific samples, with comparison of both unfiltered and filtered values. They are especially useful in following the substrate in a BOD progression but the results may not be readily interpreted when mixed substrates are involved.

Conclusion

BOD_5 is of limited usefulness for water treatment plant operation, leading some to call for its abandonment, e.g., Sherrard *et al.* (1979). However, for all its shortcomings it is a highly valuable parameter for use in assessment of the aquatic oxygen balance, (Velz 1970). Indeed Velz (1979) took issue with the views of Sherrard *et al.* who implied that BOD was of no use for receiving water studies. Some of the shortcomings of the BOD test in terms of both the mechanics of the test and its lack of similarity to the processes occurring in aquatic environments, can be overcome by use of respirometers, particularly in obtaining the BOD progressions. However, it is still of considerable value in aquatic oxygen demand studies.

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Respirometric oxygen demand tests for waste waters

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The design principles of respirometers are reviewed, and the strengths and weaknesses of various designs are outlined. The design of a novel type of manometric recording respirometer based on solid state pressure transducers and other electronic components is described. The use of respirometry as a research tool in the field of waste water analysis is outlined as are attempts to adapt respirometric methods to measure BOD_5.

Some of the shortcomings of the BOD_5 test are discussed and another, potentially better, bioassay method for the assessment of the amount of oxygen needed to degrade an organic waste is presented together with supporting data. This test has the following advantages, stoichiometric repeatability, there is no need to dilute the sample, and results may be to hand within 24 hours of sampling.

Introduction

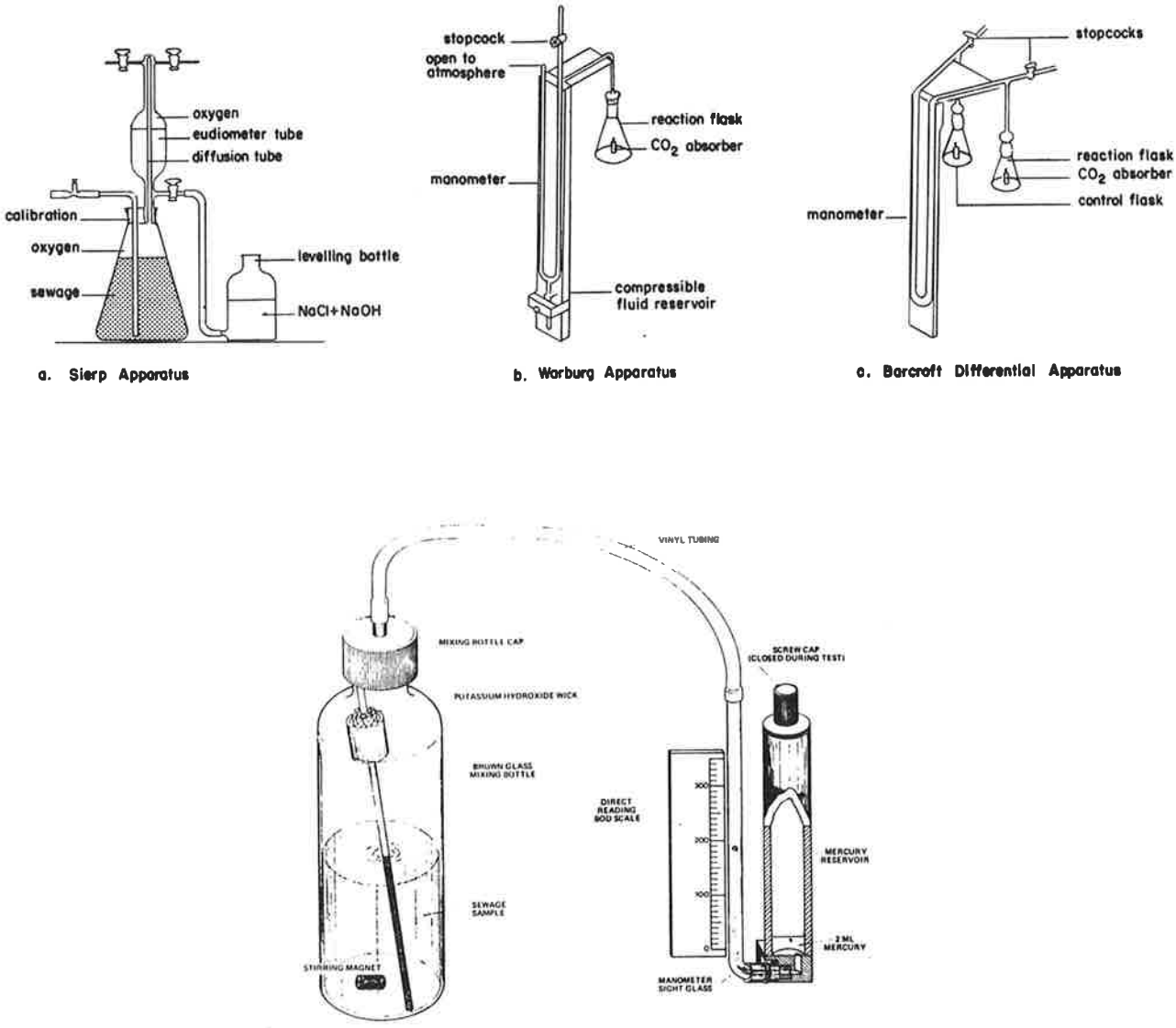
Respirometry has long been a useful tool for workers in the field of water pollution research. Accordingly, over the years a wide variety of respirometric devices have been produced. Reviews of respirometers have been published by Jenkins (1960), Montgomery (1967) and Steinecke (1976), and anyone who seeks a detailed review of the development of respirometers is recommended to read these. This paper sets out the basic design principles of respirometers, with examples of the basic types, and describes some of the applications of respirometers to waste water evaluation. Research carried out at MIRINZ on a bioassay method for water pollution assessment, using a recording respirometer, is described. This could form a useful addition to the range of tests currently available.

Principles of respirometers

With the exception of the through-flow type of respirometer described by Clarke *et al.* (1978), whose main application would appear to lie in the field of process control, all respirometers operate on the same basic principle. A volume of respiring culture is agitated in a closed vessel and oxygen is transferred into the culture medium from the headspace gas. Carbon dioxide evolved by the respiring organisms is absorbed in an alkali medium. The oxygen utilized is measured either as a function of reduced pressure at constant volume and temperature, or reduced volume at constant pressure and temperature. Examples of the first (constant volume) principle are the Warburg, the Barcroft differential, and the Hach respirometers. Examples of the second (constant pressure) principle are rarer; the Sierp apparatus and its derivatives are the best examples. These four types are shown in Fig. 1. One of the principal advantages of respirometric methods of measuring O_2 uptake over the use of dilution bottles is the ease with which the progression of O_2 uptake may be monitored. A desire to allow this progression to be monitored overnight and at weekends probably led to the development of a way of recording O_2 uptake automatically. The constant volume principle appears in automated form as the "Pollumat" (Veits 1977), as a device described by Arthur *et al.* (1979), and as the MIRINZ compensated device (Heddle & Tavener 1979; Tavener 1979). The constant pressure principle has been automated by Simpson & Nellist (1970) and Coutois *et al.* (1971). Both these devices rely on sensing a small drop in internal pressure and restoring it by metering in O_2 from a reservoir with a pump. Oxygen uptake is monitored as a function of pump displacement. The devices described by Arthur *et al.* 1979 and Simpson & Nellist 1970 are shown in Fig. 2.

The most widely used recording respirometer utilises a combination of both these principles. The electrolytic recording respirometer (Clark 1960) operates by sensing small reductions in internal pressure in the respirometer flask, and restoring this pressure drop by allowing an electric current to electrolyse a reservoir of acidified water. The O_2 produced at the anode restores the drop in pressure, while the hydrogen produced at the cathode is vented to the atmosphere. An example of this type is shown in Fig. 3. Oxygen uptake is a function of the coulombs of electricity consumed.

Respirometers tend to be fragile, complex, and expensive; recording respirometers especially so. In addition, unless some system of internal compensation is incorporated into the design, respirometers are prey to errors induced by variations in ambient



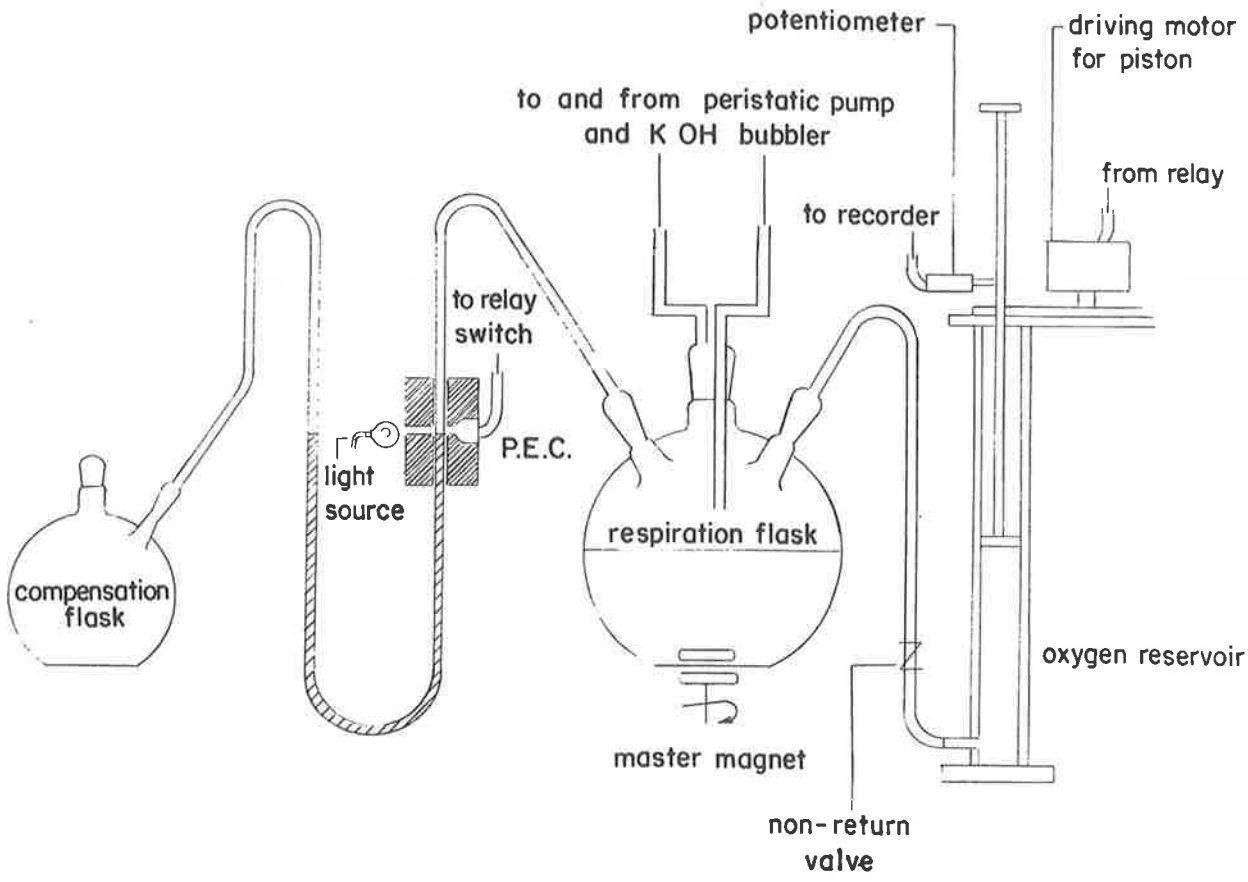
a. Sierp Apparatus

b. Warburg Apparatus

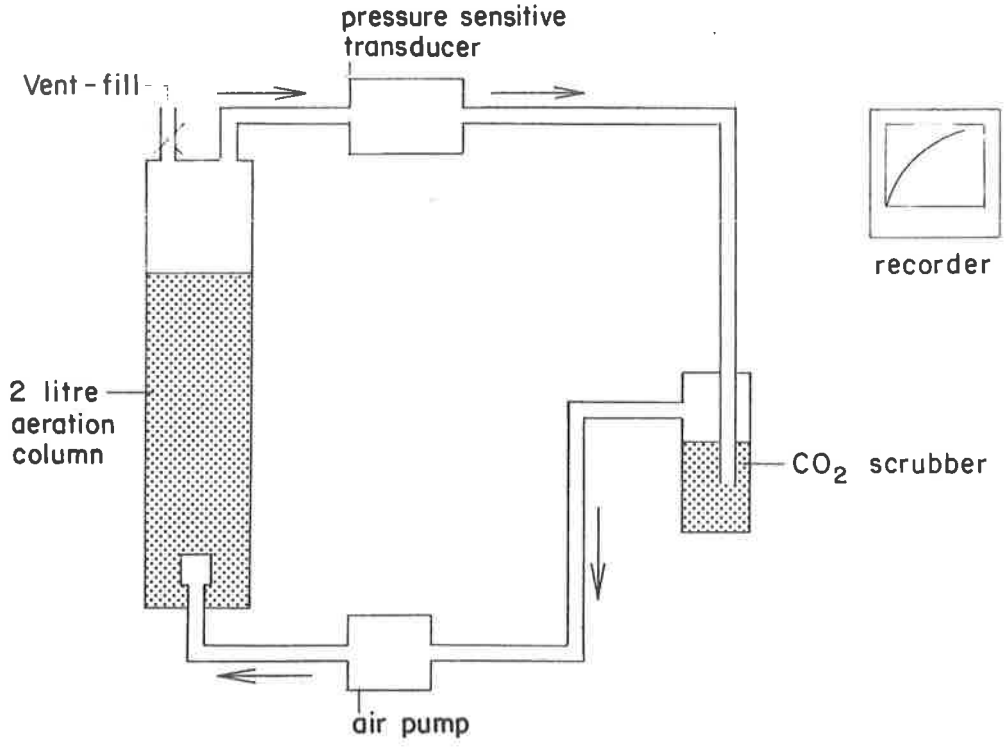
c. Barcroft Differential Apparatus

d. Hach direct reading apparatus, one unit of 5 in complete system.

Fig. 1 Types of non-recording respirometer.



(a) Constant pressure device (Simpson & Nellist 1970).



(b) Constant volume device (Arthur *et al.* 1979).

Fig. 2 Recording respirometers.

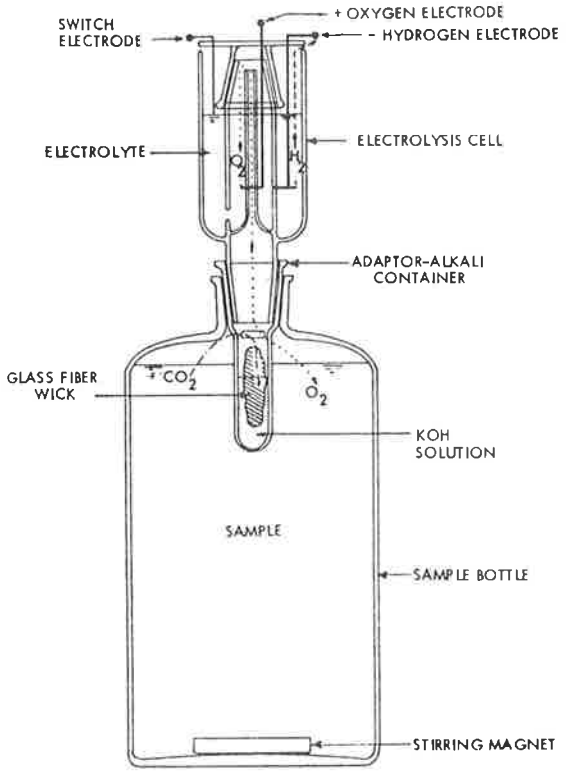


Fig. 3 Recording respirometer: Electrolytic device.

temperature and pressure. Among manually read respirometers, the Hach Corporation's device was designed to overcome both these areas of difficulty, but the mercury manometer is a crude measuring device. The object of the MIRINZ work was to produce a compensated recording respirometer which was robust, simple, moderately priced, and with high discriminatory ability.

The MIRINZ recording respirometer uses solid state pressure transducers to measure the reduction in pressure in a compensation flask containing distilled water, and in a series of test flasks containing respiring culture. All flasks have containers for soda lime chips which absorb the carbon dioxide produced. In the case of a single-channel system (Fig. 4), the pressures measured by the two transducers are compared in a differential amplifier, and the output is logged on a suitable recorder. The system may be expanded to multichannel operation, though to do this the output of the compensation sensor needs to be boosted by the addition of a zero gain amplifier. Once this is done the output of the compensation sensor may be continuously compared with the outputs of a number of test transducers. The compensated outputs may then be recorded, either continuously or at intervals, as required. The device built at MIRINZ has provision for up to 12 channels to run simultaneously. The compensation flask and the flasks of test culture are stirred, using a multiplace magnetic stirrer designed and built for the purpose in the MIRINZ workshop. The electronic components were assembled onto printed circuit boards and incorporated into modules to fit a standard 'vero' case by the staff of the MIRINZ instrumentation section. The designs of the stirrer and of the electronic components are such as to allow assembly by a competently staffed light machine shop and electronic workshop respectively. The compensated outputs from the pressure transducer modules are recorded on a Honeywell Brown multipoint recorder with a timer to allow the interval between scans to be varied.

The reaction flasks are standard 1 litre, wide-mouthed, chemical reagent bottles, taking ground-glass stoppers. The flasks are connected to the electronic components by replacing the ground-glass stoppers with 'Quickfit' tubing adapters, which are connected to the nozzles of the sensors by carefully measured lengths of Tygon tubing.

The relationship between pressure drop and oxygen uptake is calculated as mg/ℓ by using an equation derived by Caldwell & Langelier (1948).

To ensure adequate oxygen transfer capability, a series of tests were undertaken using sodium sulphite catalysed with cobalt chloride. A stirrer speed of 360 rpm, using 50 mm stirrer magnets, was selected as affording the best compromise between high oxygen transfer and integrity of the magnetic coupling.

The electronic sensing and recording equipment was tested for stability of baseline, linearity of response, and the efficiency of its compensation system. All were found to be highly satisfactory. With regard to the effectiveness of the compensation system, the basic calibration of the instrument allows oxygen uptake values to be measured to full-scale values between 40 and 3200 mg/ℓ. This may be extended downwards by increasing the gain of the electronic sensing system by a factor of ten, so the minimum full-scale value that can be recorded is 4 mg/ℓ. (In this way O_2 uptake over narrow bands of partial pressure may be studied.) At this sensitivity a peak to trough variation of 2.5% of full scale was seen. This was ascribed to residual uncompensated temperature effects, since the test was carried out in a room whose temperature control was not better than ±0.5 °C. The peak to trough variation could be considerably reduced by the use of a precisely controlled water bath.

This brief description will serve to show that the MIRINZ device is simple to construct from moderately priced, readily obtained components. Experience has shown it to be simple to operate, and its glass components are robust enough to withstand routine laboratory use. In addition to these characteristics, the MIRINZ device gives enough sensitivity and freedom from extraneous signals to allow it to be used as a high precision research tool whose output may be monitored continuously or at specified intervals, as required. The MIRINZ device has been fully described elsewhere (Heddle & Tavener 1979; Tavener 1979; Heddle & Tavener 1981).

Uses of respirometry

Historically, respirometry has been used for two purposes; as a tool for research into microbial physiology, and for bioassay work into water and effluent quality. There is considerable overlap between the two areas.

The first report of the use of respirometry in water pollution monitoring was by Adeny (1890), reported by Jenkins (1960), but Adeny's method did not allow

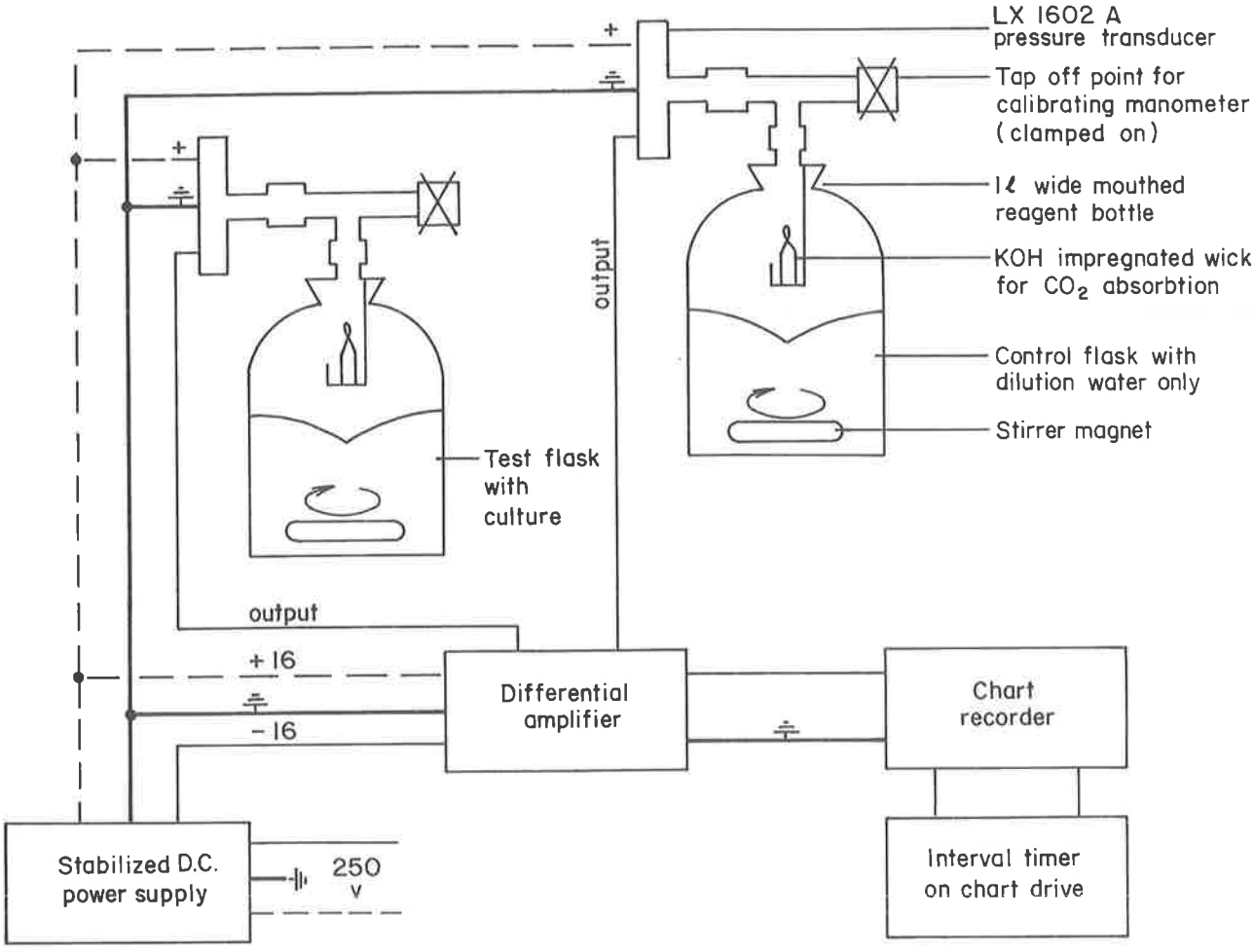


Fig. 4 The MIRINZ Recording respirometer — Schematic diagram of a single channel.

for adequate oxygen transfer ability, and the dilution bottle method, which was developed into the APHA BOD_5 standard method, was favoured over it.

However, a respirometric BOD_5 method involving the use of the Warburg principle was included as a tentative method in the 11th edition of APHA Standard Methods, but was dropped in the next edition on the grounds that the two methods produced different results. This should not really surprise anyone, as the two test methods are radically different. The principal differences are the relative concentrations of substrate employed, where a factor of 5 or 10 may be involved, and the fact that the respirometric test involves vigorous agitation.

In the field of basic waste treatment research, respirometry offers a wide range of opportunities. In many respects the rate of oxygen uptake by a waste when introduced into an aerobic treatment plant is just as, if not more, important than the total oxygen uptake. Similarly, nutrient imbalances can exert a critical effect on the workings of an aerobic treatment process. These can be assessed respirometrically, as can the effects of pH and toxins. All of these could be masked by the requirement to add buffer and nutrients to the dilution water and the high degree of dilution needed in the BOD_5 test (Alaerts 1977). The oxygen demand of organic sediments may also be measured respirometrically.

Bioassay Tests for Oxygen Demand

The most commonly used and quoted bioassay test of oxygen demand in waste waters and receiving waters is the APHA BOD_5 test. This is subject to a number of conceptual and practical shortcomings, the principal of which are as follows. The BOD_5 test does not measure a parameter that is definable in terms of anything other than the BOD_5 test itself. The reason for selecting the 5-day term is unclear; some suggest that it represented the longest river run in dry weather in the U.K. at the time (the 1890s); others, that the period was chosen to minimize intrinsic errors. Neither involves any inherent biochemical or microbiological reason. The term of the test raises problems with available working days, besides which the answers when obtained tend to be of historical interest only. Because the test does not run to completion, the rate of oxygen uptake is still significant at the end of the test 5-day period. Consequently, small variations in incubation temperature and period can introduce significant errors into the results (Heddle & Russell, to be published). Young & Baumann (1972) (Fig. 5) demonstrated that measured BOD_5 per mg of substrate for a defined medium drops with increasing in-bottle substrate concentration. This they ascribed to the setting up of localized diffusion gradients

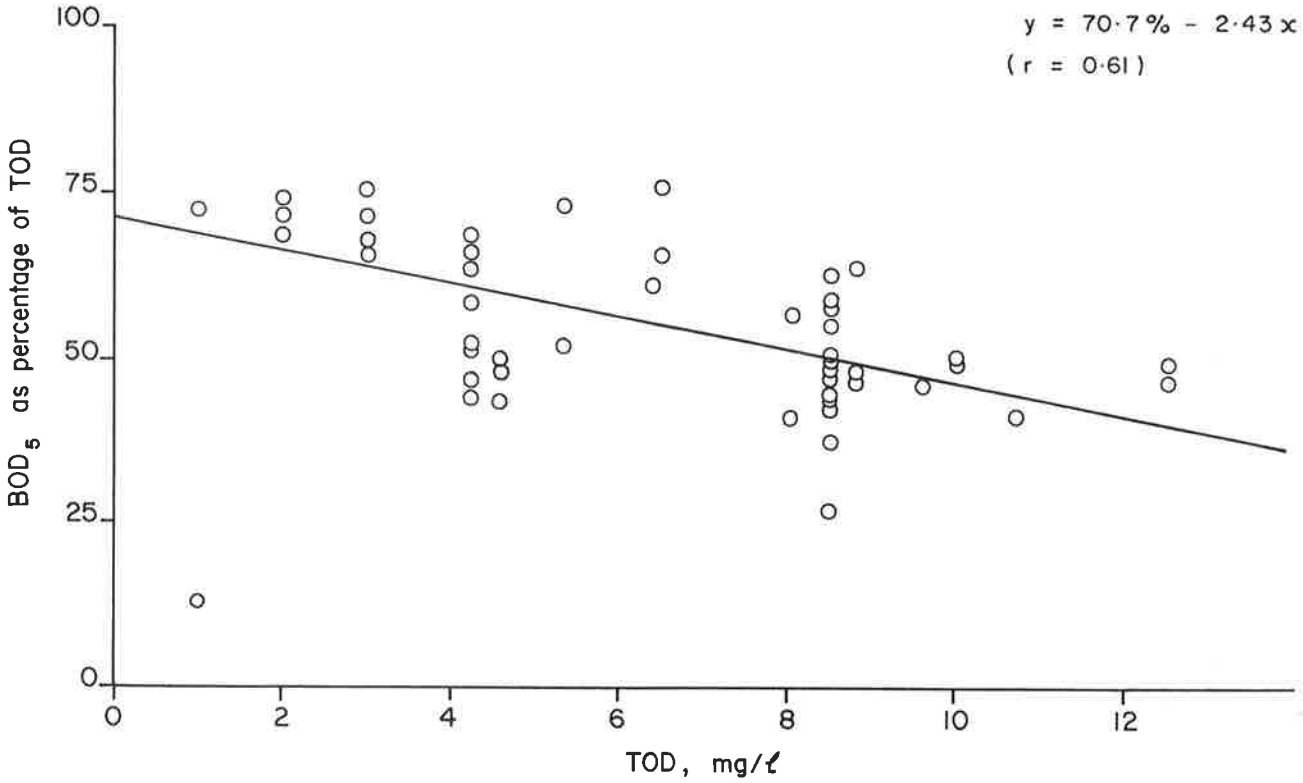


Fig. 5 Analysis of dilution BOD data indicates an inconsistent relationship between BOD_5 and TOD.

around the individual microbial floc particles. Finally, the precision achievable in interlaboratory study is not good (APHA 1976).

These shortcomings were deemed to be sufficiently serious by the American Society for Testing & Materials (ASTM) to recommend that the BOD_5 test be dropped without replacement (Stack 1973). An auto-recording respirometer could be used for measuring BOD_5, but in our opinion it would be a wasteful misapplication of technology—like using a laser rangefinder to answer the question, "How long is a piece of string?". Besides which, Young & Baumann (1972), using an electrolytic respirometer, showed that the 5-day BOD value measured using dilution bottles was reached in 3 days with the respirometer. This was probably due to the enhancement of nitrification in the latter, since the addition of a nitrification inhibitor restored a more or less 1:1 correlation between the 5-day value by the two methods.

That the BOD_5 test has not been "dropped without replacement" reflects, in our opinion, more on the inherent usefulness of any measure of biological oxygen uptake in water, on the lack of a suitable alternative, and on the accumulated inertia of nearly 100 years of use, rather than on any intrinsic merits of the test.

There is a better bioassay test available. Work in the MIRINZ pollution research laboratory (Heddle & Tavener 1981) and elsewhere has established its stoichiometric significance and it is reproducible in a way the BOD_5 test never could be. In addition, this test will give results within, at the worst, 24 hours of sampling, and potentially within 3–4 hours. This test estimates the total amount of oxygen needed to convert the organic matter present to carbon dioxide, water, mineral salts and refractory residuals in the presence of a nitrification inhibitor. This parameter is most accurately described as "the Total Carbonaceous Biochemical Oxygen Demand"—T_cBOD. The definition of T_cBOD and its relationship with other parameters are set out in Fig. 6. It is approximately the same as the 20-day BOD, measured with nitrification inhibited, but with the conceptual difference that it is defined not in terms of an arbitrary time limit, but by the cessation of observable oxygen uptake. It may be measured in this fashion, by incubating to completion, but this will be time-consuming even at 37 °C. Alternatively, it may be estimated as the sum of the following:

(1) **The Plateau BOD**—the amount of oxygen required to convert a given amount of a given substrate to CO_2, water, refractory residuals and new cells. This parameter was first noted by Busch (1958) and has since been shown to be a stoichiometric constant for a given substrate (Schroeder 1968) and independent of temperature (Flegal & Schroeder 1976) and the size of the inoculum of acclimated microorganisms added (Vernimmen *et al.* 1967; Péters *et al.* 1975).

(2) **The Carbonaceous BOD of the cells produced** This may be derived from the dry weight of cells produced (itself a stoichiometric constant for a given amount of a given substrate; see Pipes *et al.* 1963) by means of two conversion factors thus:

(a) COD of cell mass ≅ 1.41 x dry weight of cells (Gaudy *et al.* 1964)
(b) BOD of cell mass ≅ 0.75 x COD of cells (Stack 1973) ∴ BOD of cells ≅ 1.06 x dry weight of cells.

The BOD of the cells may also be derived from the ΔCOD figure (Gaudy & Gaudy 1972) (Fig. 6) thus:

$$\Delta COD = \text{Plateau BOD} + \text{COD of cells}$$
$$\therefore \text{BOD of cells} = 0.75\,(\Delta COD - \text{Plateau BOD})$$

This method of estimating T_cBOD was proposed by Stack (1973) (under the title: "Stabilization Oxygen Demand") and by Flegal & Schroeder (1976) (under the title: "Total" or "ultimate" BOD). Unfortunately, neither Gaudy *et al.* (1964) nor Stack (1973) gave evidence of validation of the conversion factors cited above, and neither Stack (1973) nor Flegal & Schroeder (1976) gave evidence to support the stoichiometric relationship between T_cBOD and substrate concentration, or for the precision and accuracy obtainable by the methods they proposed.

At the MIRINZ pollution laboratory we undertook a proving programme to provide the needed evidence. Progression of BOD to the plateau was monitored using the recording respirometer described above. The use of a large volume respirometer allows the use of large samples without dilution. This will allow the confidence of working with a representative sample and will ensure that toxicity and pH effects will not be masked by dilution and buffering. Similarly, nutrient imbalances will not be masked by the addition of nutrients (Alaerts 1977; Verstraete *et al.* 1974).

Five substrates were examined, two pure substrates (glucose, and serum albumin) to assess stoichiometric relationships, and to assess precision and accuracy attainable with both methods of estimating cell BOD, and three real effluents to see if precision and accuracy deteriorated and whether there were any operational problems with real wastes.

The results are shown in Tables 1–3 and Fig. 7. The stoichiometric relationships shown with pure substrates are of a high order of significance. Both methods of estimating cell BOD are satisfactory, with the proviso that in the case of real wastes with high ratios of viable micro-organisms to soluble substrate, the method using TSS to measure cell mass can be inaccurate if the plateau is over-run by a significant margin and the cells are allowed to waste themselves to a significant degree by autolysis. This work was undertaken at 20 °C with a small seed; it should be possible to reduce the incubation period to 2–3 hours by the use of elevated temperatures and mass culture methods. This possibility is currently being explored.

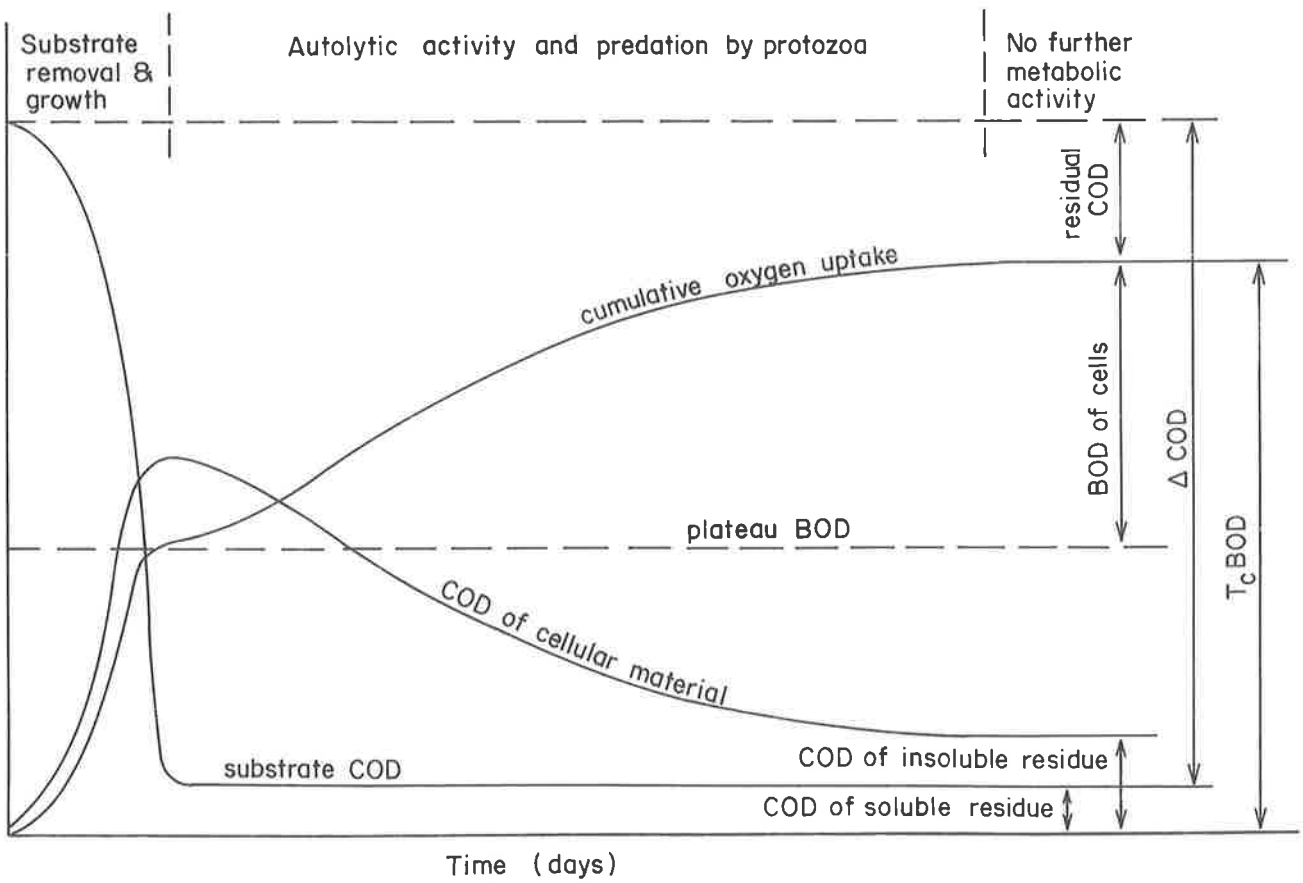


Fig. 6 Events during biological degradation of a waste.

Table 1 Stoichiometric relationships between T_cBOD and substrate concentrations

(a) with glucose

Glucose conc. mg/ℓ	Plateau BOD mg/ℓ	New cells produced mg/ℓ	Final filtered COD mg/ℓ	ΔCOD mg/ℓ	BOD of cells from TSS of cells mg/ℓ	BOD of cells from ΔCOD mg/ℓ	T_cBOD from TSS of cells mg/ℓ	T_cBOD from ΔCOD mg/ℓ
100	42	42	2	104	46.5	46.5	85.5	86.5
200	84	75	12	199	87	96	159	171
300	127	127	14	304	135	133	262	260
400	167	167	75	349	177	134	345	304
500	210	207	9	521	219	233	429	443
600	251	244	37	598	259	261	510	512

(b) with serum albumin

albumin conc.								
100	70	46	16	128	49	43.5	119	114
200	148	88	20	268	93	90	241	238
300	215	126	32	400	134	139	349	354
400	288	188	37	539	199	188	487	476
500	358	212	49	671	225	234	582	592
600	428	256	45	820	271	294	699	722

Table 2 Precision and accuracy data for T_cBOD rapid methods with pure substrates

Substrate	Plateau	BOD of cells by TSS method	BOD of cells by ΔCOD method	T_cBOD by TSS method	T_cBOD by ΔCOD method	T_cBOD by direct bio-oxidation
glucose 500 mg/ℓ	205 ± 5*	223 ± 11*	226 ± 6*	428 ± 15*	431 ± 4*	430 ± 18#
serum albumin 500 mg/ℓ	375 ± 13*	256 ± 14*	251 ± 6*	631 ± 15*	628 ± 5*	637 ± 22#

* standard deviation on 12 replicates
\# standard deviations on 4 replicates

Table 3 Precision and accuracy data for T_cBOD methods on effluent.

Run No.	Substrate	Feed Total mg/ℓ	COD Soluble+ mg/ℓ	Plateau BOD mg/ℓ	BOD of cells by (TSS)+ mg/ℓ	BOD of cells by (ΔCOD) mg/ℓ	T_CBOD by TSS method mg/ℓ	T_cBOD by COD method mg/ℓ	T_cBOD by direct bio-oxidation mg/ℓ
1	settled sewage	318	196	67 ± 2.6*	121 ± 10*	147 ± 2*	188 ± 9*	213 ± 2*	
2	settled sewage	155	69	13.6 ± 0.9*	59 ± 5*	88 ± 5*	73 ± 6*	102 ± 5*	
3	settled sewage	270	121	38 ± 2.3*	-	119 ± 4*	-	157 ± 2*	152 ± 6#
4	DAF effluent	1285	798	434 ± 13*	577 ± 8*	562 ± 16*	991 ± 18*	996 ± 9*	995 ± 75#
5	DAF effluent	912	605	306 ± 10*	392 ± 12*	394 ± 8*	702 ± 6*	700 ± 6*	
6	DAF effluent	580	308	110 ± 8*	268 ± 18*	290 ± 6*	378 ± 26*	400 ± 3*	
7	Sedn. tank effl.	2700	1260	654 ± 26*	1357 ± 9*	1385 ± 25*	2012 ± 61*	2074 ± 50*	
8	Sedn. tank effl.	2700	1260	662 ± 13*	1124 ± 223*	1387 ± 20*	1783 ± 237*	2047 ± 20*	
9	Sedn. tank effl.	735	428	200 ± 10*	307 ± 46*	357 ± 14*	510 ± 50*	557 ± 9*	553 ± 17#

\+ filtered through a Whatman GF/C filter paper
* standard deviation of 6 replicates
\# standard deviation of 4 replicates

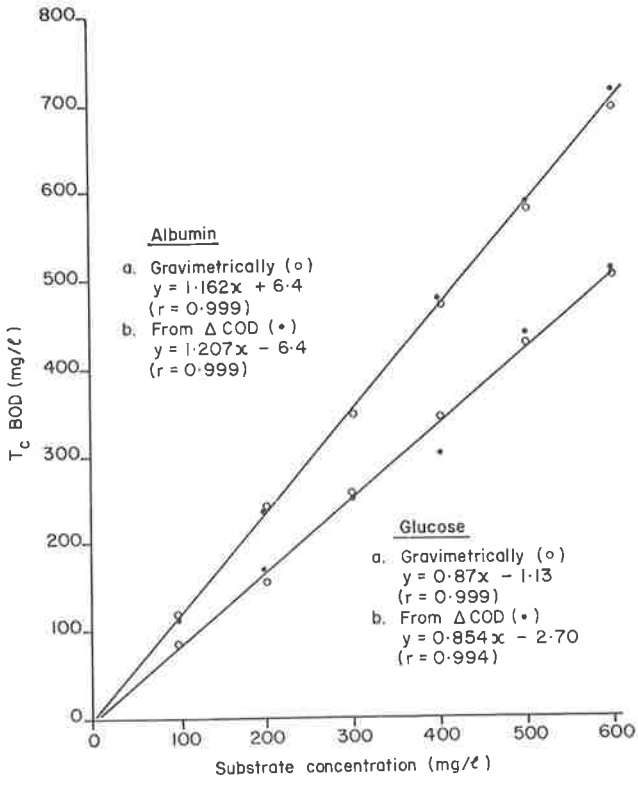


Fig. 7 Stoichiometric relationships between T_cBOD (y) and concentrations of glucose and serum albumin substrates (x).

Conclusions

Respirometry is not really suitable for measuring BOD_5 as defined in the APHA test, since the dilution bottle test is definable only in terms of itself, and altering any aspect of the procedure will fundamentally alter the results obtained.

The BOD_5 test has a number of conceptual and practical shortcomings which render it unsuitable for many of the purposes for which it is currently used. This unsuitability has led to calls for its abandonment.

That the BOD_5 test has not been abandoned shows the need for a bioassay method to measure oxygen uptake by wastes.

A better bioassay method is available and described in this paper. The use of a recording respirometer is almost obligatory. This test is stoichiometrically definable, and rapid, in a way the BOD_5 test cannot be. It will use undiluted samples, and this will allow the effects of nutrient imbalances, toxins, and rate data to be routinely monitored while performing the test.

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Electrolytic respirometric oxygen demand tests for receiving waters

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Modifications to an electrolytic respirometer are described which allow precise measurements of BOD progressions for low substrate concentration (BOD_5< 50 mg/ℓ) and therefore are suitable for use on natural waters receiving organic enrichment. Samples may be incubated at any desired temperature or dissolved oxygen concentration with automatic hourly monitoring of the BOD progression; subsamples may be withdrawn at any time without interference to the measurement. At present, cost of production and fragility limit this instrument to a research tool but with future modifications it is hoped to produce a more versatile instrument at a reasonable price.

Introduction

The biochemical oxygen demand (BOD) test is one of the most important tests used in the analysis of the oxygen balance of streams receiving wastewater discharges. The basic test (APHA 1976) produces a single result (the BOD_5) after a 5-day incubation period. In application to the stream situation the progression of this BOD between day 0 and day 5 of the test is of interest, as the rate of utilisation of organic material present dictates the rate at which oxygen must be supplied in the natural system. Many New Zealand streams exhibit their maximum DO sag with 1 day's travel time.

The term BOD is used in this paper in a broad sense to refer not only to the common analytical measurement traditionally conducted by the standard dilution method but also to the respirometric measurement of oxygen uptake by micro-organisms in aqueous suspension.

The "electrolysis" method was first introduced by Clark in 1960 as an instrument especially suitable for the examination of BOD progression in receiving waters. The electrolysis BOD measurement system basically consists of a reaction vessel, electrolysis cell and a direct current power supply. In principle, the test technique involves the continuous and automatic maintenance of the oxygen pressure within an enclosed vessel by supplying the sample with oxygen produced from the electrolysis of water in a weak electrolyte solution.

A number of electrolyte cell systems have been reported in the literature and some have been developed as commercial units. Liebman and Offhaus (1966) have described the Sapromat A6, a patented electrolytic respirometer which is available from J. M. Voith GmbH (West Germany) and incorporates a sulphuric acid - copper sulphate electrolyte inside a cell which is sealed from fluctuations in atmospheric pressure. A similar apparatus has been designed and reported by Bridie (1969).

The electrolysis cell of Clark (1960) as developed by Young & Bauman (1972 a & b) has been marketed by the USA Oceanography International Corporation (OIC). This is the machine purchased for our laboratory and the rest of this paper deals with this apparatus and modifications that we have made to it.

Description of the electrolysis BOD measuring system

The electrolysis system consists of three major parts. A reaction vessel which contains the sample and has provision for agitation to mix the sample and suspend the biological growth. An adaptor unit or similar container which holds potassium hydroxide or another basic solution to absorb metabolically produced carbon dioxide from the atmosphere above the sample. The critical part of the system is the electrolysis cell which contains a weak electrolyte such as sulphuric acid, sodium sulphate or sodium hydroxide. The electrolysis cell may double as a manometer to detect pressure changes or as an oxygen generator to maintain a constant partial pressure in the atmosphere within the sample container. The electrolysis BOD measuring system then is actually a large volume respirometer which provides semicontinuous and automatic registering and adjustment of the pressure change that is brought about within the reaction vessel because of oxygen consumption by micro-organisms.

The operation of the standard OIC electrolysis system is shown schematically in Fig. 1 and is described as follows: As oxygen is utilised by the micro-organisms in the waste sample, metabolically produced carbon dioxide (CO_2) is absorbed in a potassium hydroxide (KOH) solution, and a slight

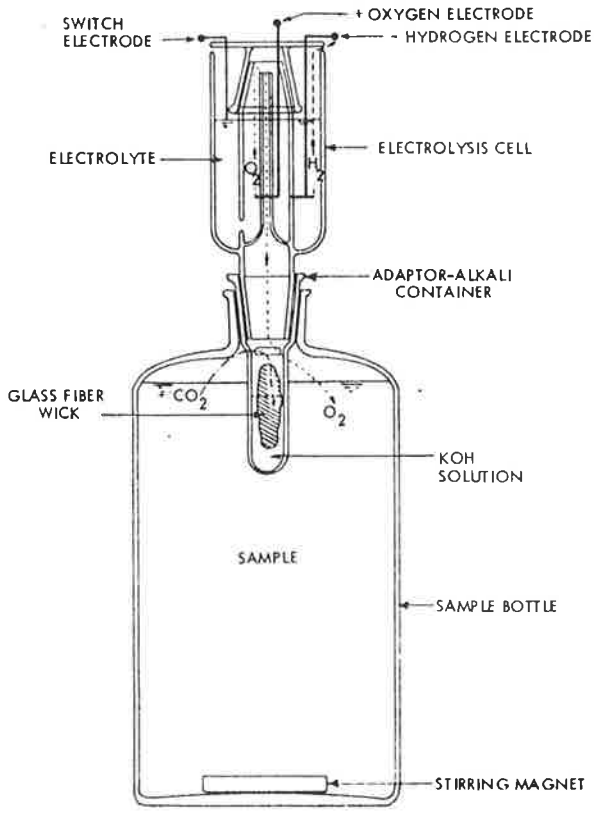

Fig. 1 Schematic diagram showing the basic operation of the electrolysis system for measuring BOD.

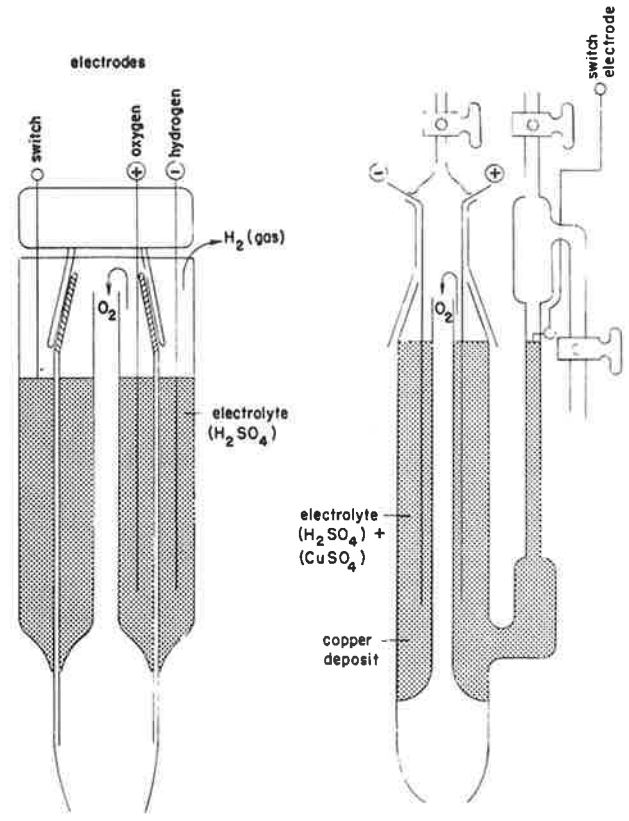

Fig. 2 Cross section view of
(a) Standard electrolytic manometer
(b) Modified electrolytic manometer.

vacuum is created in the reaction vessel. As this vacuum increases, the electrolyte level in the outer chamber of the electrolysis cell drops, breaking contact with the switch electrode. This action activates a direct current power supply causing a controlled direct current to flow through the electrolyte so that oxygen is produced within the electrolysis cell at the positive, or oxygen, electrode. This oxygen increases the sample oxygen supply until the original gas pressure inside the reaction vessel is re-established. When electrolyte contact is again made at the switch electrode, the power supply is inactivated until a slight pressure decrease due to oxygen use is again registered. Hydrogen produced at the negative electrode is vented to the atmosphere.

The EBOD units are designed to incubate the sample bottles, but not the manometric electrolysis cells, in a constant temperature air bath.

For the measurement of the BOD progression samples with a BOD_5 of less than 50 mg/ℓ these electrolysis units lack sufficient precision. Fluctuations in external air temperature affect the volume of air inside the manometer, and changes in atmospheric pressure also cause volume changes within the experimental flask. Both these perturbations result in either addition of excess oxygen or inhibition of oxygen supply to the experimental flask. Under some conditions, calculated corrections can be made to the BOD progression curve, but one cannot be assured of always obtaining the correct curve.

To circumvent these problems we redesigned the electrolysis cell as shown in Fig. 2. Both electrodes are now included in the single chamber and the electrolyte is now a sulphuric acid/copper sulphate mixture. Solid copper is now deposited at the cathode which is now enclosed: previously gaseous hydrogen was vented to the atmosphere requiring the cathode to be open. The manometric trigger has been positioned in a fine bore tube to increase trigger sensitivity. This modified electrolysis cell is totally submersed in a water bath which allows precise temperature control for kinetic studies.

These modifications to the electrolysis cell enable the electrolysis unit to produce precise and reproducible results for kinetics of oxygen demand for samples with small BOD_5. An example set of results is shown in Fig. 3 for BOD progression of a pure culture of bacteria growing on a single substrate (initial glucose 10 mg/ℓ).

The electrolysis BOD measuring system provides a number of advantages over the standard methods BOD test in the measurement of BOD exertion:

1 Little or no dilution of high BOD samples is required. The exact concentration of the waste in the receiving water may be used.
2 Larger and more representative samples may be analysed.
3 Tests can be run for days or weeks without attention.
4 Samples may be taken at any time for analysis, without interference with BOD measurement.
5 The BOD exerted may be read at any time during the incubation and suitable equipment can record the BOD at preset intervals.
6 The electrolysis cell may be used to titrate oxygen into any suitable volume of sample to either

increase or decrease the oxygen demand, e.g., a 5 ℓ or 50 ml sample volume.

7 The partial pressure of oxygen may be maintained at any desired preset level, either above or below the normal partial pressure of oxygen.

8. The electrolysis unit has sample bottles which allow recirculation of enclosed air rather than stirring. This allows measurement of oxygen demand with certain types of sediment present.

9 Electrolysis cells may be fitted to any convenient vessel to allow, with multiple ports, simultaneous measurements with other instruments (e.g., pH, redox potential, specific electrodes).

A number of disadvantages also occur with use of an electrolytic respirometer:

1 The electrolysis cells are fragile and expensive to replace.

2 Samples must be exactly equilibrated to the incubation temperature.

3 Automatic BOD progression monitoring equipment is an additional cost.

4 Equipment is bulky to house.

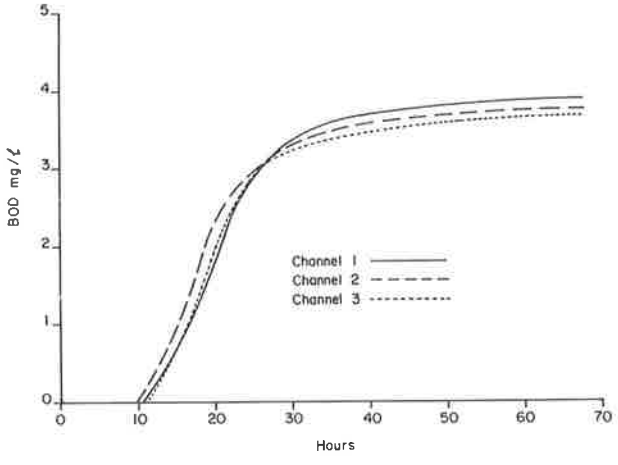

Fig. 3 Replicate BOD progression measurements for a pure bacterial culture growing on glucose (10 mg/ℓ initial concentration).

Operational considerations

In experimental studies on pure cultures and natural stream systems, a number of factors must be considered for routine procedures:

1 Temperature adjustment of samples.

2 Algal growth.

3 Inhibition of nitrification.

4 Addition of nutrients and buffers.

5 Removal of CO_2.

1 Temperature adjustment of samples

The initial temperature equilibration of the sample is critical to establish the oxygen saturation for that temperature. If the initial temperature is too high or too low then the initial rate of oxygen uptake for the sample will be erroneous, being high or low respectively.

The temperature of incubation is also an important consideration for kinetics of micro-organism growth. The standard BOD test is performed at 20 °C, however, natural waters are often greatly different from this temperature. The Q_{10} for respiration and growth of micro-organisms is about 2 (i.e., rate doubles for each 10 °C increase in temperature, e.g., Gillespie & Spencer 1980; Wright 1975). For accurate assessment of stream dynamics it is better to perform oxygen demand measurements at the in-stream temperatures.

2 Algal growth

In general it is necessary to prevent algal photosynthetic interference by performing experiments in the dark. In certain cases, however, when algal populations are very large, their removal may be necessary prior to BOD estimation. This removes the algal endogenous respiration which would otherwise be extremely high and interfere with the BOD exertion. Interferences from algae may also be caused by excretion of metabolites (Wright 1975) and by cell death (Fallon & Brock 1979).

3 Inhibition of nitrification

A chemical nitrification inhibitor (e.g., 2-chloro-6-(trichloromethyl) pyridine (TCMP) (Hack Chemical Co.)) or allyl thiourea may be added to samples in which inhibition of nitrification is desired. This would not normally be used with average stream water samples but would be used as an additional sample for high strength wastes, proteinaceous waste or waters with high ammonia concentrations. These nitrification inhibition chemicals have been shown to have no observable effect on the carbonaceous BOD of domestic wastewaters (e.g., Montgomery & Borne 1966; Young & Bauman 1976b). We have not performed any investigations with the sole purpose of investigating inhibition of nitrification, however we have measured some BOD progression curves (Fig. 4).

4 Addition of nutrients and buffers

With industrial or synthetic wastes containing relatively pure compounds, such as carbohydrates or proteins, additional nutrient materials may be needed for microbial growth, and a buffer may be needed to

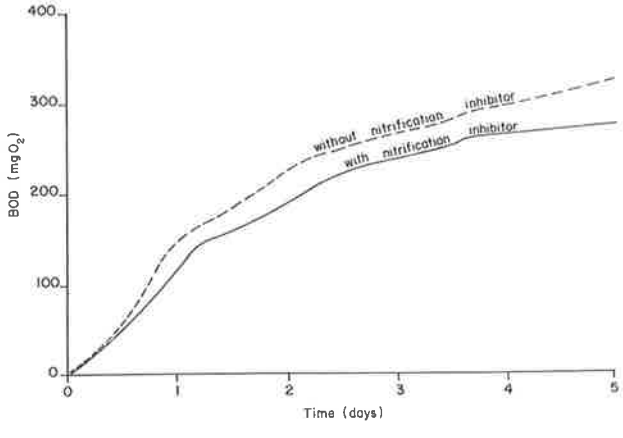

Fig. 4 BOD progression for AFCO effluent (50% dilution) with and without nitrification inhibitor (Hach Chemical Co.).

prevent pH changes which can adversely affect the metabolism of micro-organisms. These problems would usually not occur for natural stream water. However, those draining a eutrophic lake or reservoir may experience some nutrient deficiencies during summer algal blooms.

5 Removal of CO_2

Many workers generally accept that the complete removal of metabolically produced carbon dioxide is necessary in manometric systems. Young & Bauman (1976 a & b) suggest that a KOH absorption trap should be used at all times with the EBOD vessels.

For many years, however, it has been known that many bacteria, yeasts and protozoa require CO_2 (Wimpenny 1969). More recent work has shown that the absence of CO_2 prolongs lag phase and results in decreased rate of removal of COD. The lag period was shown to be inversely proportional to microbial inoculum size (i.e., the more bacteria the less CO_2 necessary for active growth—Gaffney (1965)). This long lag period has also been shown to occur with sewage inoculum if the CO_2 is sufficiently well scrubbed (Tebbutt & Berkun 1974). We have found that with pure bacterial cultures and low substrate concentrations (< 100 mg/ℓ glucose) the vigorous removal of CO_2 results in a greatly increased lag period (from 3 hours with CO_2 to 20 hours without CO_2). There is also some experimental evidence that organisms which are scrubbed of CO_2 show decreased metabolic efficiency (i.e., greater respiration of oxygen per unit of biomass formed).

Small amounts of HCO_3^- may be added to samples to provide some free CO_2. Alternatively 'CO_2 buffers' are available using an aqueous solution of diethanolamine. These are not entirely satisfactory, however, owing to the need for careful pre-equilibration to the desired CO_2 tension and some tendancy for oxygen absorption by the 'buffer' (Krebs 1951).

Monitoring of EBOD and data handling

At present we have a printer which is capable of recording the oxygen consumed in each of 6 channels at either ¼ or 1 hour intervals. This data is then manually transferred to a PDP 11/34 minicomputer for data presentation. This presentation is shown diagrammatically in Fig. 5 which shows the cumulative oxygen demand for Waikato River water with the addition of whole milk together with the rate of oxygen consumption plot as mg/ℓ hr. We hope, in the near future, to be able to provide an automatic analogue interface with the minicomputer to directly measure the oxygen input of each sample. This would allow a larger number of samples to be run simultaneously.

Comparison with Standard Methods BOD test

We do not have a large amount of experimental data in this area, however we have generally found the 5 day EBOD shows a 20% increase over the conventional BOD_5 test. This figure may be greater if samples contain a large amount of particulate material, and Young & Bauman (1976b) suggest an EBOD 3-day test should be compared to the conventional BOD_5 test.

Other uses

We have used the EBOD units for internal toxicity testing work. Here a control flask is used with a known amount of seed organism and glucose/glutamate added. A similar flask is innoculated which contains the water to be tested. By comparison of the lag time and the final oxygen demand some measure of toxicity can be made. This test may also be extended to include a flask to test for nutrient inbalances by addition of suitable nutrients (e.g., NO_3^-, HPO_4^{2-}).

These units have potential for oxygen demand studies with aquatic invertebrates and fish life which may otherwise be sensitive to depleted oxygen levels.

Possible modifications

We are also interested in building an electrolysis cell which is controlled by a dissolved oxygen probe. This unit would offer advantages for working with CO_2 in the system and with sediments where denitrification may be occurring, as the unit would be less

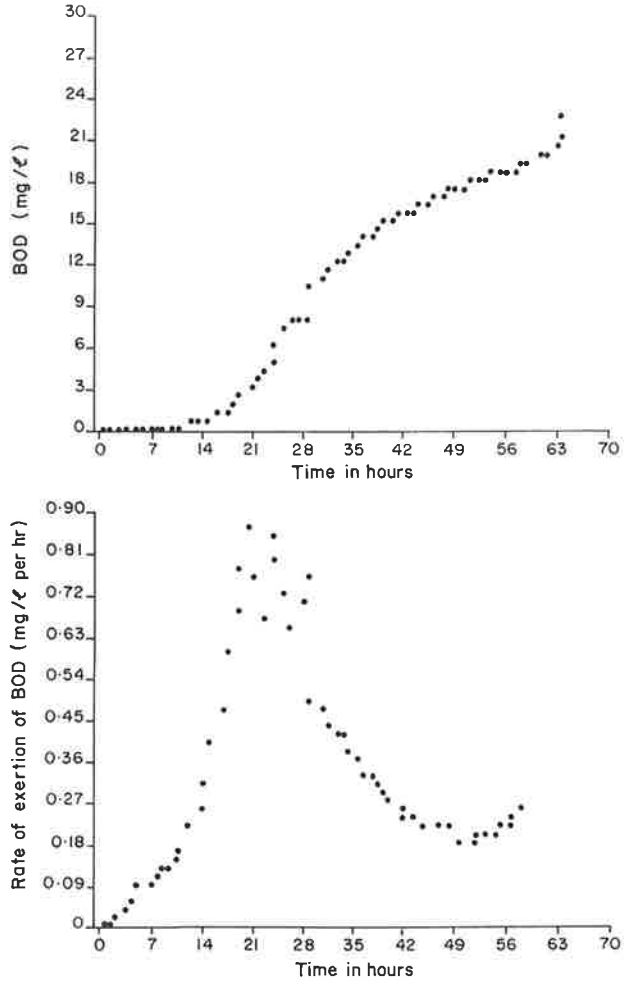

Fig. 5 Waikato River water (Cobham Bridge) BOD progression with addition of whole milk (0.25 ml/ℓ initial concentration).

sensitive to atmospheric pressure changes. Continuous flow reactor vessels could also be used with this type of apparatus.

Summary

At a cost of about $4,200 for each three channel electrolytic respirometer we have some reservations in recommending their use as a routine instrument for receiving water analysis. The basic off-the-shelf EBOD unit is well suited to high strength wastes for which it is easy to operate and use. To use the principle of electrolytic respirometers for low strength waters (such as river water) we have had to make substantial modifications to the manometers of these units. Based on this experience it would appear that with such a manometer and the use of modern electronics a very versatile and much more compact electrolytic device could be produced for a fraction of this cost. We expect that such a unit would be very valuable in showing the kinetics of oxygen uptake in polluted waters. Our present research is directed toward that end.

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DISCUSSION FOR SESSION II

Measurement of Dissolved Oxygen
Presented by: R. J. WILCOCK

G. B. McBRIDE : Is it widely recognised that tables of saturation DO vs temperature in many standard works are in fact in error?

WILCOCK : Yes, the tables of saturated DO values at different temperatures, given in many handbooks such as Standard Methods 14th Edition, are in fact based upon work by Whipple & Whipple (1911). The saturation DO values appended to this paper have been derived from a critical review of the best measurements up to 1977, and are in complete agreement with other similar reviews by Mortimer (1974) and UNESCO (1973). These concentrations agree with the handbook values in the temperature range 0–10 °C but differ by up to 0.15 mg/ℓ in the range 10–30 °C.

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C. W. HICKEY : What method would you recommend for field calibration of a DO meter?

WILCOCK : Of the three common methods for calibrating electrode systems I favour the moist air method. Experience shows it to be both reliable and convenient. Comparison with the Winkler method should be carried out from time to time, but is not always possible in many situations, while the air saturated water technique requires that one does in fact have a standard solution. Equilibrium times are much quicker for the moist air method.

D. G. SMITH : A comment. Apropos the comment made regarding thermistor failure in DO probes, we have had some recent correspondence with YSI who claim that failure is probably due to mishandling of the probes. Consensus of New Zealand users is that the fault lies with the thermistor type which has been in use for the past few years.

WILCOCK : Yes, I would agree with that comment. Most DO electrode thermistors are well protected by their location on the probe, so that it is difficult to imagine physical (or other) damage being responsible for their malfunction. I suspect that part of the reason for thermistor failure is breakdown of the epoxy resin sealant used to fix the thermistors, allowing water or electrolyte solution to leak through to the inside of the probe and short out or corrode the terminals.

C. D. STEVENSON : A comment. I would agree strongly with Dr Wilcock on the general suitability of air calibration. This leaves Winkler analyses and saturated water tests for quality assurance checks on the DO measurements.

Standard BOD and Other Oxygen Demand Tests
Presented by: C. W. HICKEY

C. D. STEVENSON : It is perhaps unfortunate that studies of rates of BOD exertion in bottles tend to be considered together with the "standard" BOD test. The "standard" BOD test measures only the quantity of biodegradable material in a sample, but says nothing about exertion rates. It is inevitable that attempts to determine rates of BOD exertion which might occur in natural waters by using samples incubated in bottles in the laboratory will often give misleading results. It is not valid to criticise "standard" BOD tests because of these deficiencies in what is really a completely separate type of exercise. Perhaps different names should be used for "standard" tests assessing the quantity of biodegradable materials and BOD exertion rate studies, to minimise possible confusion.

HICKEY : Agreed. My paper on respirometric methods addresses your point to some extent.

M. E. U. TAYLOR : Statement: The author's conclusions are agreed with. However in his discussion he does not fully explore the pros and cons of the use of BOD measurement as a guide to sewage treatment plant operations. One important aspect, where no better alternative has been developed, is in the characterisation of the separate wastes which are coming into a plant where these are separately charged for. Charges are commonly based on the amount of treatment which has to be given to the waste : no better means of estimating this than the BOD test has yet been devised.

Also the problem posed by toxicity is not so great as appears—in fact it is very desirable to be able to detect when wastes are toxic and the BOD test in conjunction with other oxygen demand measurements is one of the ways of establishing the toxicity of a waste.

K. CURRIE : The shortcomings of the BOD test in relation to oxygen balance analysis appear to relate largely to in-bottle rate studies. These do not necessarily bear any relationship to actual river processes. If the BOD test is used *as a test* to compare the concentration at two points in a river, the *difference* is of much greater value and is not subject to many of the short-comings cited.

HICKEY : Agreed, although any significant chemical or biological changes which may have occurred between stations in the river, should be considered in making these studies.

D. OGILVIE : Why not modify the BOD test to suit needs? Why is the test done? If it is to meet a standard, use the standard test. Otherwise relate it to the receiving water—if 2 days to sea, do BOD_2. If time is not critical do BOD_7 so the test can be performed 5 days a week, i.e., no

overtime. BOD_5 without overtime can only be done 3 days a week. To measure load performance on an oxidation pond one could try BOD_{30} if retention time is 30 days.

HICKEY : The test attempts to provide a 'Standard Test' which can be compared between wastes or receiving waters as performed by independant workers and should, I feel, be regarded as such.

I would like to emphasise that the processes which occur in the BOD bottle may in no way be taken as a measure of the rate at which BOD will be exerted in the natural receiving water. Thus a BOD_2 cannot be used as a measure of the BOD removal expected in a river with a 2 day run to the sea.

M. PIPER : In response to Mr Ogilvie's comment on short term BOD for receiving water: short travel time is not valid. I endorse Craig Stevenson's comments that 5 day BOD is a measure of biological oxygen demand. To include uptake rates, and especially to apply these to the receiving water, is to introduce shortcomings to the only sure method of determining the carbonaceous nutrient potential.

M. SPENCER : With reference to the limitation of the "standard BOD_5" test in that one cannot begin on Monday or Tuesday unless the final reading is taken the following Saturday or Sunday, have you considered using the correction factors for BOD measured between 3 to 8 days as given in Merck's "Analysis of Water" Handbook?

HICKEY : I am familiar with the handbook mentioned, and would like to point out that the values quoted in there for adjustment to BOD_5 values were derived from work on primary treated domestic waste water. Thus the use of those values for other effluents is somewhat tenuous and may lead to large errors.

Respirometric Oxygen Demand Tests for Waste Waters
Presented by: J. F. HEDDLE

C. D. STEVENSON : Some respirometric traces show more than one plateau. Does the existence of more than one plateau cause difficulties in the T_cBOD analysis?

HEDDLE : Conceptually the answer is "yes", however most traces which show this two stage uptake involve pure cultures which may not have been acclimated to the substrates in question. We have observed a two stage uptake in the preparation of a mixed microbial seed to be acclimated to *calbiochem serium albumin*. This was prepared by mixing 20% meat waste with 80% albumin solution. (The meat waste had been screened to remove lumps and homogenised in a waring blender to emulsify fats and destroy protozoa). The two component meat waste (fat and protein) showed a single sharp plateau equivalent to 50% of its filterable COD, while the albumin showed its own plateau equivalent to 50% of its COD. When culture was taken from this run and used to inoculate another flask of the same mixture of meat waste and albumin the second plateau disappeared and the single plateau which was seen was the sum of half the soluble COD's of the two components. So in practice a mixed microbial seed which is acclimated to all the components present will only show one plateau, as with sewage and meat waste.

G. B. McBRIDE : Do you ascribe the occurrence of a plateau in the BOD progression to the onset of protozoal predation on the bacteria?

HEDDLE : The plateau's presence is NOT the result of protozoal predation. In fact unless protozoa are at least inhibited the plateau will be either blurred or lost. The abrupt change in gradient seen in the oxygen uptake trace when protozoa are suppressed is due to the transition from exogenous nutrition to endogenous nutrition on the part of the bacteria present, as the substrate is exhausted. If protozoa, whose growth generally lags somewhat behind that of bacteria, are present in sufficient numbers by the time the bacteria run out of food, the slackening of oxygen uptake by the bacteria will, to a greater or lesser extent, be cancelled out by the rising curve of protozoal oxygen uptake.

Ref: Bhatla, A. M.; Gandy, A. F. 1965: The role of protozoa in the diphasic exertion of BOD. *Proceedings of the American Society of Civil Engineers 19 (SA3)*: 63–87.

Electrolytic Respirometric Oxygen Demand Tests for Receiving Waters
Presented by: C. W. HICKEY

C. D. STEVENSON : From a limited examination of literature, it appears that the rapid algal respiration phase over a period of several hours in first incubating algae in the dark corresponds to BOD exertion equivalent to about 3–7% of the dry algal biomass. If we apply a BOD_5 test to an oxidation pond effluent and consider the contribution from algae therein to river BOD after dilution it seems that in many situations the algal contribution will be relatively small (e.g., substantially less than 1 g/m^3) unless substantial discolouration by algae is permitted.

HICKEY : Although algal dark respiration is one addition to the BOD, the cells may also lyse after 2 days in the dark and further add to the BOD_5 as measured. This leads to additional BOD load which may not be exerted if the algae were exposed to natural light conditions.

SESSION III CHARACTERISTICS OF SOURCES OF OXYGEN DEMAND

Characteristics of slaughterhouse effluents

R. N. COOPER

Meat Industry Research Institute of New Zealand, Hamilton

The characteristics of the effluent from New Zealand export slaughterhouses after both primary and secondary treatment are reported and the contribution that fellmongery processing makes to slaughterhouse effluent characteristics discussed.

Information on the oxygen demand characteristics of primary treated slaughterhouse effluent, together with a summary of the secondary treatment practices currently used in New Zealand to reduce this oxygen demand are presented. Specific examples of performance data are given.

Introduction

The New Zealand Export Meat industry processed approximately 37.1 million animals in the year ending September 1978 in 38 export slaughterhouses (New Zealand Year Book 1979). The numbers and types of animals are shown in Table 1.

Table 1 Types and Numbers of Animals Processed in New Zealand Export Slaughterhouses 1978

Sheep	7.3×10^6
Lambs	25.9×10^6
Cattle	2.1×10^6
Calves	1.1×10^6
Pigs	0.7×10^6

Large volumes of water are needed to process this number of stock with the consequent production of a large volume of strong organic effluent as well as solid wastes. Each works has a population equivalent similar to that of some of the larger population centres in New Zealand.

Effluent volumes

The volume of effluent discharged from a slaughterhouse is considerable and is loosely related to throughput. No reliable figures are available on a litres/lamb equivalent or litres/100 kg live or dressed weight basis. Processing day discharge volumes vary, depending on the size of the works, between 500 and 15 000 m^3. These volumes would typically represent between 70 and 80% of the total 24 hour discharge.

Characteristics of slaughterhouse effluents

Slaughterhouse wastes are largely organic in nature and are characterised by the high levels of organic nitrogen and fat they contain. The sources of these organic constituents can be identified as follows:

Paunch contents
Faecal material
Suspended solids and fat
Blood and other soluble material
Pelt processing (fellmongering) effluents

Variations in types and numbers of stock slaughtered, water use, and types of processing employed (e.g., wet or dry rendering) lead to wide differences in slaughterhouse effluent characteristics. The characterisation of such effluents prior to primary treatment is difficult because of the presence of large amounts of readily separable material. Meaningful comparisons can only be made on a 'settled' or 'post primary treatment' basis.

Table 2 shows average processing day composite analyses for several works together with the range of analyses that might be expected. The results were obtained over extended periods when kill levels were high. Night flows are generally only lightly polluted and do not have the characteristics of the effluents in Table 2.

It can be seen that there are wide variations in all parameters of interest. The effluent samples at works A and D included the effluent from peripheral fellmongering operations, such as initial skin washing and wool washing, bate wash effluent was included in the effluent from works A. The effluent from the

depilatory process and its associated washing operations was specifically excluded. The contribution of this effluent to the total oxygen demand of a combined slaughterhouse effluent is discussed later. Works B and C did not have fellmongeries.

Table 2 Average analyses of effluent from different slaughterhouses

Works	A	B	C	D	Expected Range
Parameter			mg/ℓ		
BOD_5	950	..	..	1065	700–1800
COD	1680	1385	2350	2345	1200–3000
COD_f*	880	595	1780	700	..
TKN	129	80	111	122	70–200
TKN_f*	..	..	103	80	..
NH_3–N	30	24	18	23	5–50
TS	2410	1570	1765	2330	1000–3000
VS	..	920	1260	1500	800–2000
Ash	..	650	505	830	..
TSS	450	450	715	1120	200–1200
Fat	145	210	390	400	100–900
TP	..	..	..	12.2	..
IP	..	..	..	10.9	..

*Refers to soluble component

It has been shown (Russell 1980) that the chemical oxygen demand (COD) of primary treated slaughterhouse effluent can be approximated by the following relationship:

COD mg/ℓ = (Organic nitrogen mg/ℓ) x 9 + (fat mg/ℓ) x 3

Where organic nitrogen is defined as follows:

Organic nitrogen mg/ℓ = (TKN – NH_3–N) mg/ℓ.

This relationship can be profitably used to examine and explain quantitatively the reasons for the different effluent characteristics reported above.

Effluents C and D are almost identical with respect to the levels of organic nitrogen and fat they contain and consequently have similar chemical oxygen demands. Effluents A and D have identical organic nitrogen concentrations but markedly different fat levels and the difference in COD levels is attributable quantitatively to the difference in fat concentration.

The differences in effluent characteristics between works after primary treatment will be derived from a number of factors, the major ones being:

(i) Water use and in-plant processing variations.

(ii) The degree of in-plant treatment of specific waste streams undertaken in plant. For example recovery of fat from a rendering department effluent at source should result in reduced total fat levels in the total effluent due to more efficient recovery and reduction of losses due to emulsification.

(iii) Organic nitrogen losses will to a large extent depend on the efficiency of blood collection and processing. This is an area in which a marked improvement has been seen in recent years due to the implementation of new stunning and sticking requirements.

Soluble characteristics of settled slaughterhouse effluent

A significant characteristic of primary treated slaughterhouse effluent is the soluble nature of many of its components (Cooper 1980). The percentage of a settled effluent that is soluble as determined by filtration through Whatman GFC filter paper is shown in Table 3.

Table 3 Percentage of settled effluent that is soluble

Parameter	Mean	SD
COD	59.3	11.0
TKN	79.4	6.9
PN	81.0	7.0
Fat	16.2	9.8
TS	79.6	7.2
VS	65.8	13.3
TP	76.3	11.6
Carbohydrate	61.0	24.2

The table shows that 59% of the COD and 81% of the protein nitrogen are soluble, compared to only 38% of the COD and 30–50% of the organic nitrogen for domestic sewage (Harter & Heukelekian 1965). This factor undoubtedly contributes to the high initial oxygen uptake rates associated with slaughterhouse effluents in respirometric tests.

Oxygen demand characteristics of slaughterhouse effluents

The progression of oxygen demand for primary treated slaughterhouse effluents from 0–5 days is shown in Fig. 1. The variations in oxygen uptake rate in mg/ℓ for each 24 hour period are shown in Table 4.

Table 4 Variations in oxygen uptake rate over 5 days

Effluent	A	B	C	D
Time (hrs)		oxygen uptake mg/ℓ/hr		
0 –24	25.0	30.4	16.7	15.4
24–48	14.6	15.8	18.8	6.3
48–72	10.4	10.0	9.6	5.0
72–96	7.3	4.2	0.4	2.5
96–120	5.0	1.0	0.4	3.0
COD mg/ℓ	2950	2810	2240	1330
BOD_5 mg/ℓ	1500	1475	1100	780

Table 4 shows that slaughterhouse effluent has a high initial oxygen demand when measured over the first 24 hours and that this gradually reduces to much lower levels between 72 and 120 hours. These compare with reported oxygen demand rates (Fletcher 1980) for raw domestic sewage of an initial

rate of 8–9 mg/ℓ/hr reducing to 3 mg/ℓ/hr after 16 hours and 1–5 mg/ℓ/hr after 72 hours.

Influence of fellmongery processing effluent on slaughterhouse effluent

Fellmongery effluent is that produced during the conversion of sheep and lamb skins into pickled pelts and wool suitable for export. Fellmongery effluent usually has a high pH and contains significant quantities of sulphide. What is not generally appreciated is that some fellmongery effluents contribute a significant oxygen demand load to the total works effluent. A schematic diagram of a fellmongery with its various processes is shown in Fig. 2. All the processes are continuous with the exception of the drum or dolly processes which produce effluents from the batch washing of pelts. It is these pelt washing effluents which require separate consideration from other fellmongery processing effluents.

The mass discharge characteristics of the various fellmongery processes are shown in Table 5. For simplicity only the characteristics of the drum process are considered. Table 6 shows quite clearly that the drum wash effluents contribute the largest proportion of COD, TKN, and sulphide of all the fellmongery effluents. This is often used as a basis for segregation of fellmongery effluent as these are the effluents characterised by high pH and sulphide levels.

Table 5 Mass discharge of pollutants from fellmongery (processing kg/1000 skins processed)

	COD	TKN	Fat	S^{2-}	Volume m^3
Skin Wash	67.6	5.6	7.3	..	78.5
Wool Processing	25.7	2.4	2.6	..	29.9
Paint Table	1.5	..	..	0.9	1.9
Drum Effluent					
Wash 1	123.6	12.1	7.4	4.2	7.3
Wash 2	23.4	2.5	1.4	0.6	3.1
Wash 3	47.6	15.8	3.9	0.3	9.7
	289.4	38.4	22.7	6.0	130.4

The effluents from works A and D in Table 2 included contributions from all fellmongery processing operations with the exception of drum wash effluents 1 and 2. Effluent A resulted from the processing of approximately 7000 lambs and had an average flow volume of 2510 m^3 per processing day. At this particular works drum wash effluents 1 and 2 were segregated for separate primary treatment consisting of screening to remove wool, sedimentation to remove suspended lime and manganese catalysed oxidation to remove sulphide. The resultant characteristics of combining the slaughter effluents and the oxidised fellmongery effluents can be calculated as shown in Table 6.

Table 6 Effect of fellmongery effluent on mass discharge characteristics of combined slaughterhouse effluent

	Slaughterhouse		Fellmongery	Combined	
	mg/ℓ	kg/d	kg/d	mg/ℓ	kg/d
COD	1680	4217	1029	2030	5246
TKN	129	324	102	165	426
Fat	145	364	62	165	426
Flow m^3/d	2510		73	2583	

Thus fellmongery effluent can be seen to be a significant contributor to the effluent characteristics of the total effluent from a combined slaughterhouse and fellmongery.

Treatment of slaughterhouse effluents

A wide variation in the type and extent of treatment undertaken by New Zealand export slaughterhouses exists. This variation reflects local circumstances and requirements for discharge. All works undertake some form of primary treatment by sedimentation, dissolved air flotation, screening or a combination of these. The last few years have seen an increasing tendency to use wedge wire screens to pretreat specific effluents, such as stockyards, slaughterfloor and gut shed prior to combination with the total works effluent. Such screens are also used to pretreat the combined effluents prior to discharge to save-alls or dissolved air flotation tanks. A summary of the types of treatment, both primary and secondary, employed by export slaughterhouses in New Zealand is given in Table 7.

Table 7 Treatment methods employed by the New Zealand meat industry

	No. of works
1. Screening for gross solids	38
2. Ocean outfall after screening only	2
3. Primary treatment by sedimentation and fat flotation	36
4. Discharge after primary treatment only	24
(i) Ocean discharge (including into municipal sewers which have no secondary treatment)	10
(ii) River or estuary outfall	11
(iii) Discharge to municipal treatment works	3
5. Works with secondary treatment on site	13
(i) Anaerobic lagoons	1
(ii) Anaerobic-aerobic lagoons in series	5
(iii) Aerobic plastic media tower	1
(iv) Aerated lagoon	1
(v) Physico-chemical treatment (protein recovery)	2
(vi) Irrigation	3
(vii) Irrigation in conjunction with (i), (ii) and (iv)	5

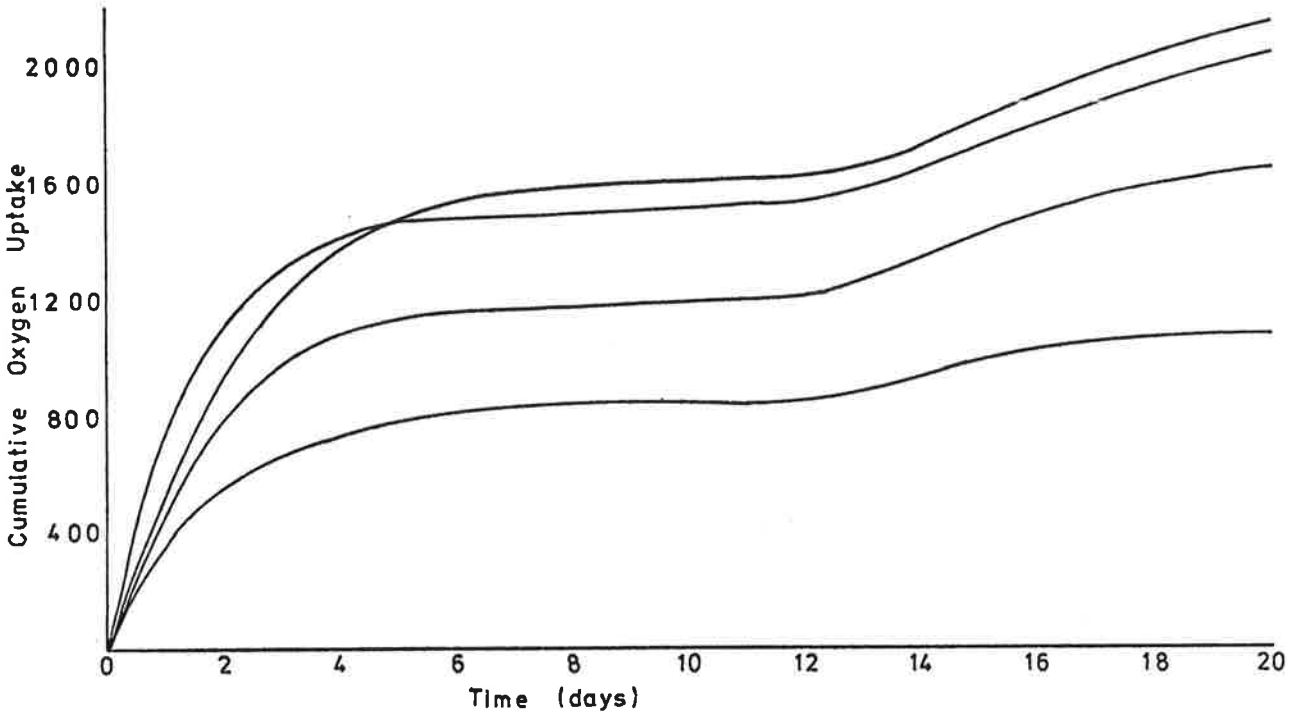

Fig. 1 BOD exertion of primary slaughterhouse effluents.

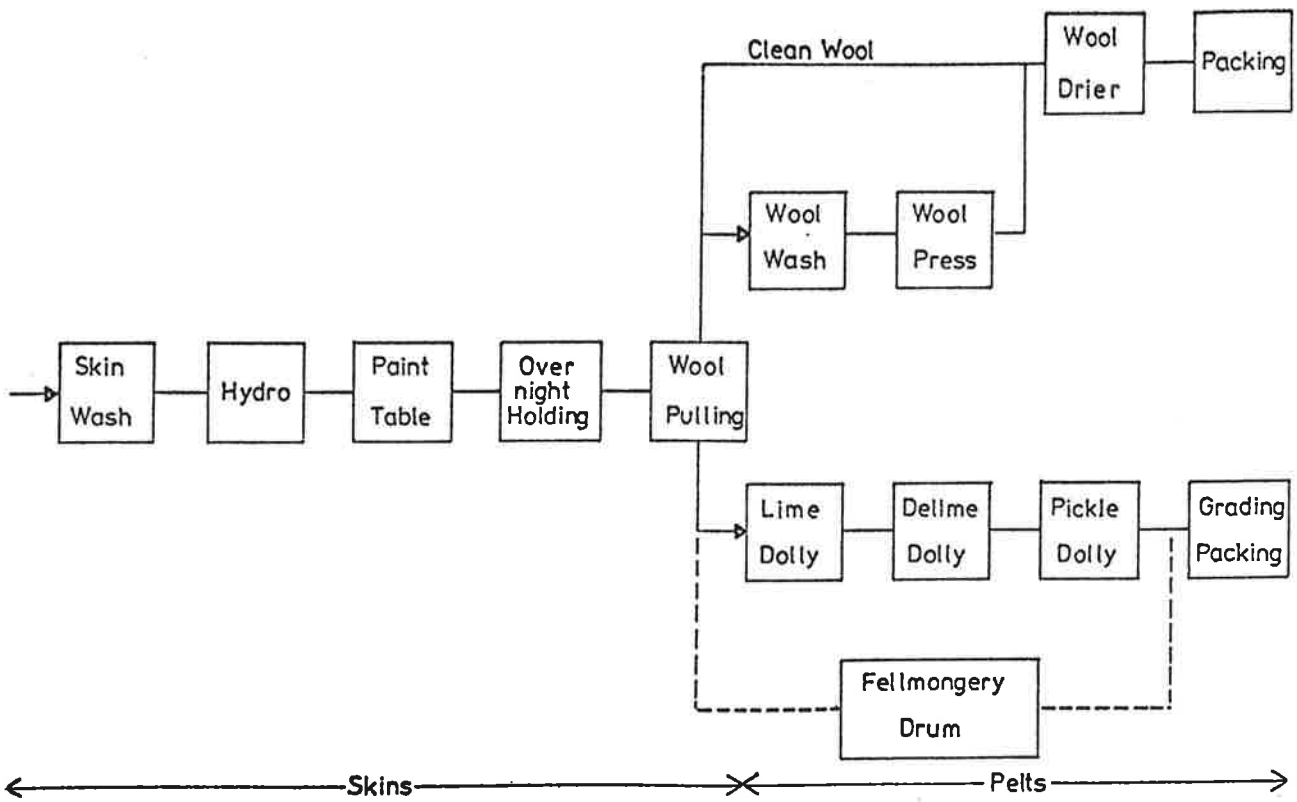

Fig. 2 Schematic diagram of fellmongery process.

Primary treatment

The performance of a dissolved air flotation plant treating slaughterhouse effluents after screening using a 1 mm gap wedge screen is shown in Table 8. It can be seen that such a system is effective in markedly reducing the levels of total fat and suspended solids. The low percentage removal of TKN reflects its largely soluble nature.

Table 8 Purification of slaughterhouse effluent using dissolved air flotation

Parameter	Influent mg/ℓ	Effluent mg/ℓ	Percent Removal
COD	3675	1680	54
TKN	165	130	21
NH_3–N	35	30	14
TS	4050	2410	40
TSS	1950	450	77
Fat	725	145	80

Secondary treatment

If it is assumed that raw domestic sewage has a BOD_5 of 250 mg/ℓ, then reference to Table 3, shows that primary treated slaughterhouse effluent has a BOD_5 of between 3 and 5 times as great (assuming BOD_5 = 0.5 COD). It is therefore obvious that further reduction in the oxygen demand of such effluents will be required in most situations prior to discharge.

The most favoured method of treatment at present is to use anaerobic-aerobic lagoons in series. The principal reasons for this are firstly that most works are situated in a rural environment and have land available and secondly, such systems are cheap to operate, requiring little or no energy input.

Performance of anaerobic lagoons

The performance of an anaerobic lagoon treating slaughterhouse effluent is shown in Table 9. This lagoon uses sludge recycle from the base of the lagoon to seed the incoming effluent. Retention time is 10–12 days at peak season loading.

Table 9 Performance of anaerobic lagoon, average of one year's operation

Influent BOD_5 mg/ℓ	705	324*
Effluent BOD_5 mg/ℓ	123	92*
Percent BOD_5 purification	82.6	

* Standard deviation

The above results are the average of 1 year's operation, detailed results obtained during a 3 month study over a summer are shown in Table 10.

Tables 9 & 10 show that an anaerobic lagoon can achieve substantial reductions in the oxygen demand of an effluent but at the same time no nitrogen is lost from the system. Organic nitrogen in the influent is converted to new biomass and ammonia, resulting in high levels of ammonia in the lagoon effluent.

Table 10 Detailed characterisation of anerobic lagoon influent and effluent

	Influent mg/ℓ	SD	Effluent mg/ℓ	SD	Percent Removal
COD	1385	205	354	72	75
COD_f +	596	104	189	64	68
TKN	80	17	85	16	..
NH_3–N	24	13	58	13	139
TS	1560	230	1120	112	28
VS	920	160	345	106	63
TSS	450	65	154	33	66
Fat	210	60	44	22	79
TP	..	..	9.5	3.0	..
IP	..	..	3.7	1.3	..
Alkalinity	..	..	387	47	..

SD standard deviation
\+ soluble

Anaerobic lagoon effluent usually requires treatment prior to discharge and this is usually achieved by aerobic means or disposal by irrigation. Both techniques either separately or in combination are in use in New Zealand.

Performance of an aerated lagoon treating anaerobic effluent

The performance of an aerated lagoon treating effluent from an anaerobic lagoon is presented in Table 11. The lagoon which is 2.7 m deep has a nominal retention time of 8–10 days and aeration is provided by two 22.5 kW surface aerators.

Table 11 Effluent characteristics aerated lagoon

Parameter	Effluent mg/ℓ	SD	Percent Removal
COD	202	60	43
COD_f*	85	24	55
TKN	78	14	8
NH_3–N	55	9	5
NO_3–N	12	4.8	..
TS	1082	92	
VS	302	81	
TSS	134	33	
Fat	20	7	55
Alkalinity	369	27	
DO	2.5	1.7	

* Soluble

The above results were obtained concurrently with the anaerobic results reported in Table 10. No BOD_5 data were obtained but the following relationship (Price 1980) was derived from subsequent laboratory studies of aerated lagoon performance at temperatures between 12 and 22 °C and retention times of 5–11 days.

$$COD\ mg/\ell = 1.67\ BOD_5 + 216.6$$

This suggests that the BOD_5 of the effluent from an aerated lagoon is likely to be low and furthermore that the effluent contains significant quantities of material that is not degradable in terms of the standard BOD_5 test.

Irrigation

The disposal of treated effluent by irrigation is practised by several slaughterhouses in New Zealand. The effluent is irrigated after primary treatment, anaerobic treatment or aerobic treatment and eliminates the need for discharge to surface waters. One installation has been described in detail (Keeley & Quin 1979) in which primary treated slaughterhouse effluent, including fellmongery effluent, is applied by border dyke irrigation, with cover crop removal by grazing.

More efficient utilisation of the nutrient content of the irrigated slaughterhouse effluent would be obtained if a cropping rather than a grazing regime was practised. This in combination with selection of application rate would enable the recovery of considerable quantities of nutrients (particularly nitrogen) in the form of a cover crop, with minimum contamination of groundwater. Such a scheme implies a change in philosophy from regarding irrigation as a disposal technique to one of utilising the effluent as a resource from which nutrients can be recovered.

Treatment of fellmongery effluent

Segregation of certain fellmongery effluents, principally those from pelt processing, for primary treatment is common practice in the industry. These effluents are treated separately by screening and sedimentation to remove wool, epidermal matter and suspended lime. Subsequent treatment of the effluent to remove sulphide by manganese catalysed oxidation before discharge for further treatment is undertaken at two installations. At those works where no secondary treatment is undertaken a combined primary treated effluent is discharged.

If secondary treatment is to be undertaken, the primary treated fellmongery effluent is treated in combination with the slaughterhouse effluent. Where anaerobic lagoons are used this inevitably leads to odour problems due to the evolution of hydrogen sulphide.

The operation of a lagoon system designed specifically for the treatment of fellmongery effluents has been described (Cooper 1975), which utilises red photosynthetic sulphur bacteria to oxidise sulphide. Metabolism of some of the organic material also occurs resulting in 90% removal of sulphide and 70% removal of COD.

Conclusions

It has been shown that the export meat industry is one of the largest potential polluters in New Zealand, capable of discharging a pollution load well in excess of that from domestic sources. The industry is well aware of this fact and has expended large capital sums in pollution abatement in its works and in the construction of treatment plants, thereby reducing the oxygen demand of its effluents on receiving waters.

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The characteristics and oxygen demand of New Zealand dairy food plant effluent discharges

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Overseas data on effluent characteristics does not necessarily apply to New Zealand because of a number of factors affecting the volume and strength of the effluent from New Zealand dairy plants including the seasonal milk supply, the size and versatility of the manufacturing units and the processing techniques used. Since 1972 the Institute has undertaken a study of effluent characteristics and data are presented on the biochemical oxygen demands and other characteristics of milk products and various dairy waste streams. Measured k-values (from Hach BOD_5 bottle studies) ranged from 0.39 to 0.51 days $^{-1}$. Disposal methods are discussed.

Introduction

The characteristics of the effluent discharged from manufacturing dairy plants in New Zealand are determined largely by the type of milk products being produced. In general the wastes are dilutions of wholemilk and its byproducts, *e.g.*, whey produced when either cheese or casein is being manufactured.

The dairy manufacturing plants in any country of the world have always been visible dischargers of wastes to natural waterways and those in New Zealand are no exception. Even quite large dilutions of milk are turbid, so that relatively small quantities can produce cloudiness in natural waterways, thus eliciting considerable public response. The major pollutant effect from milk waste discharge is the resulting biochemical oxygen demand. Provided dilution is great enough, the wastes do not exert a long-term toxic effect on natural waterways.

There are a number of factors in New Zealand which affect the volume and strength of the discharged effluent from individual plants and so makes them different from overseas units.

(a) Seasonal nature of milk production

Production is very seasonal with the majority of cows (only 10% are involved in producing milk for the market milk supply) calving in late July to early September. Peak milk production is reached in early November. The volume of milk produced then decreases until May when milking is stopped (See Fig. 1). In general the volume of effluent is proportional to the volume of milk being processed for individual manufacturing operations.

(b) Versatility of products able to be manufactured

Almost 90% of the products manufactued are exported and the New Zealand industry has acquired the ability to manufacture a diverse range of products to cope with the vagaries of international trade. This flexibility can result in marked variations in the quantity and strength of effluent produced by any one plant. Milk powder production, for example, results in much less effluent than casein manufacture. Production however is based on market requirements rather than the wish to restrict effluent discharges.

(c) Size of manufacturing unit

Traditionally dairy plants were built near rivers to provide a source of cheap water and to facilitate effluent removal, but the trend now is for large multi-product complexes to be built in the centre of the milk supply area. Thus, individual manufacturing units can be very large, e.g., in 1960, 106 butter plants produced an annual average of 2000 tonnes each. Today there are only 30 plants, averaging 7000 tonnes each with a number producing in excess of 20 000 tonnes annually. This trend has resulted in large volumes of effluent being produced at fewer sites.

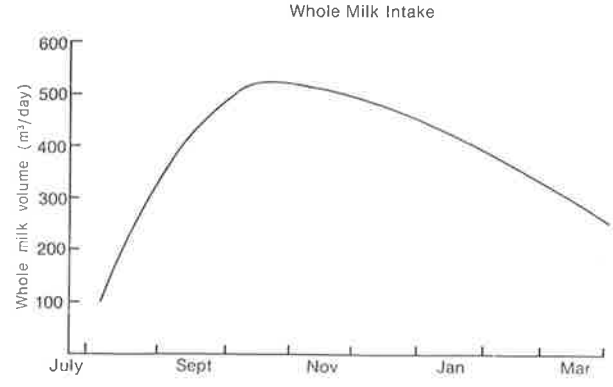

Fig. 1 Seasonal variation in whole milk intake to one large processing plant.

(d) Production techniques

The New Zealand dairy industry uses many unique manufacturing methods and items of equipment.

All these factors combine so that overseas data on effluent characteristics are not necessarily applicable to New Zealand conditions. The New Zealand Dairy Research Institute has, therefore, undertaken a research programme to study the situation in this country. This programme was begun in 1972 and has recently incorporated use of a self-contained mobile analytical laboratory. It has the following objectives:
(a) to determine the quantities and strengths of the effluent discharged from New Zealand dairy plants;
(b) to investigate equipment and processing techniques to determine if changes could bring about a reduction in the quantities and strength of the effluent and, as a result, increase the yields of product being manufactured;
(c) to assist company management and staff with education programmes concerning effluent discharges and means of controlling these;
(d) to investigate and, if necessary, improve present methods of effluent disposal.

Biochemical Oxygen Demand of dairy fluids

The biochemical and chemical oxygen demands of the effluent discharges vary widely with the products being manufactured. Table 1 shows the biochemical oxygen demand (BOD_5) of milk and its by-products.

Table 1 Biochemical oxygen demand of milk products

	BOD_5 g/m³	BOD_5 kg/kg
Wholemilk	103 000	
Skim milk	67 000	
Butter milk	68 000	
Cheese whey	35 000	
Casein whey	32 000	
Lactose		0.69
Milk Proteins		1.03
Milkfat		0.89

The biochemical/chemical oxygen demand ratios for milk, some of its products and from a number of effluent discharges are shown in Tables 2 and 3.

Table 2 BOD_5/COD ratios for dairy products and dairy plant waste waters

	BOD_5/COD	
Wholemilk	0.69	
Skim milk	0.63	
Butter milk	0.66	
Whey	0.52	
Casein	0.53	
Lactose	0.46	
Whey protein	0.23	
Fat	1.28	
Dairy plant waste waters	mean	range
Butter and buttermilk powder	0.69	0.52–1.13
Lactic casein		0.53–1.13
Cheddar cheese	0.66	0.53–0.78
Cheddar cheese	0.50	0.40–0.63
Cheddar and Colby cheese	0.54	0.33–0.68

k-values for dairy plant effluents

As well as having a high biochemical oxygen demand, dairy products and effluents also have a high rate of deoxygenation, as shown in Table 4. Some k-values have been measured using Theriault's least squares analysis applied to data from Hach BOD_5 bottles. The values quoted are to the 'base e'. Because of a small amount of nitrification, BOD_{ULT} values have been interpolated. Measured k-values for dairy fluids range from 0.39–0.51 $days^{-1}$.

Figure 2 shows plots of BOD_5 vs time for various k values. For all dairy products the initial oxygen demand is high with about 50% of the total oxygen demand being exerted in the first 24 h.

Table 4 Rate of deoxygenation of dairy products and dairy factory waste water

	k $days^{-1}$
whole milk	0.42 ± 0.04
skim milk	0.39 ± 0.09
whey powder	0.51 ± 0.10
multi-product factory	0.44–0.62

Table 3 TOC/BOD/COD relationships for dairy products and dairy factory plant waste waters

	TOC/COD		TOC/BOD	
Lactose	0.40			
Lactic casein	0.38			
Rennet casein	0.38			
Sulphuric casein	0.38			
Lactic casein whey	0.76			
Skim milk	0.34			
Dairy plant waste waters	Mean	Range	Mean	Range
Butter	0.32	0.24–0.35	0.53	0.34–0.66
Whole milk powder	0.31	0.21–0.37		
Multi-product	0.32	0.25–0.45	0.49	0.36–0.69

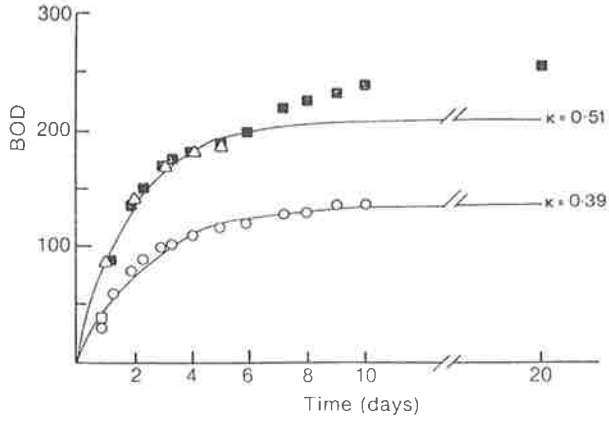

Fig. 2 Deoxygenation rates for skim milk (O), whey powder (■) and a dairy plant effluent (△).

Characteristics of effluent from dairy plants

The characteristics of the effluent discharged from 32 New Zealand dairy plants, as measured by the Institute, are summarised in Tables 5 and 6. The daily volumes of effluent vary widely both between plants and product types. The wastewater volume coefficients, expressed as m^3 effluent/m^3 whole milk processed, average 0.69 for butter and range up to 2.89 on average for casein manufacture.

The biochemical oxygen demand of the waste discharged, expressed as kg BOD_5/m^3 whole milk processed, has a much greater variation between product types than the volume coefficients, and range from 0.22 for butter to 27.6 for casein plants. Thus a plant manufacturing butter and casein from whole milk will have less than 1% of the total effluent organic load being discharged from the butter plant, the remainder being discharged from the casein plant, mostly as whey. The industry is developing a variety of processes to utilise this whey and this will have the effect of a dramatic reduction in the discharge strengths from these plants.

Data obtained from one factory over a complete season related the daily volume of water used to the volume of skim milk processed to make casein. Whilst the correlation coefficient between skim milk intake and water is statistically significant ($r = 0.65$) the data (Fig. 3) show a wide scatter emphasising the relative lack of control of water use typical of dairy plant operation in New Zealand.

Table 7 Chemical and physical properties of some dairy waste waters

suspended solids	7–7200g/m^3
lipid	0–2100g/m^3
phosphorus	4–150 g/m^3
nitrate	0.3–70g/m^3
temperature	11–72 °C
pH	3.0–13.2

Throughout the industry the concentrations of various constituents in waste streams vary widely (Table 7), as do temperature and pH.

Table 5 Characteristics of the effluent from single process plants (mean values and range)

	Casein (includes whey and wash water)	Milk powders	Cheese	Butter
Number of plants	5	5	7	1
Volume m^3/day	(266–1280)	(58–1710)	(33–445)	77
Waste water volume coefficient m^3 effluent/m^3 whole milk	2.89	2.05	2.28	0.69
Biochemical oxygen demand (BOD_5), kg/day	(2500–12400)	(351–3560)	(88–2560)	210
Organic waste coefficient kg BOD_5/m^3 whole milk	27.6 (20.8–37.1)	1.81 (1.4–2.9)	6.64 (4.5–14.8)	0.22

Table 6 Characteristics of the effluent from multi-product plants (mean values and range)

	Butter and milk powder	Casein, butter and milk powder	Milk powder and AMF	Cheese, butter and milk powder	Casein, milk powder and AMF
Number of plants	3	8	1	1	1
Volume m^3/day	(340–2540)	(586–2500)	615	2900	924
Waste water volume coefficient, m^3 effluent/m^3 whole milk	2.53	4.40	1.29	2.68	2.90
Biochemical oxygen demand (BOD_5), kg/day	(400–2465)	(787–1750)	520	3018	970
Organic waste coefficient, kg BOD_5/m^3 whole milk	2.50 (1.6–4.0)	15.48 (1.6–49.0)	1.09	2.79	3.04

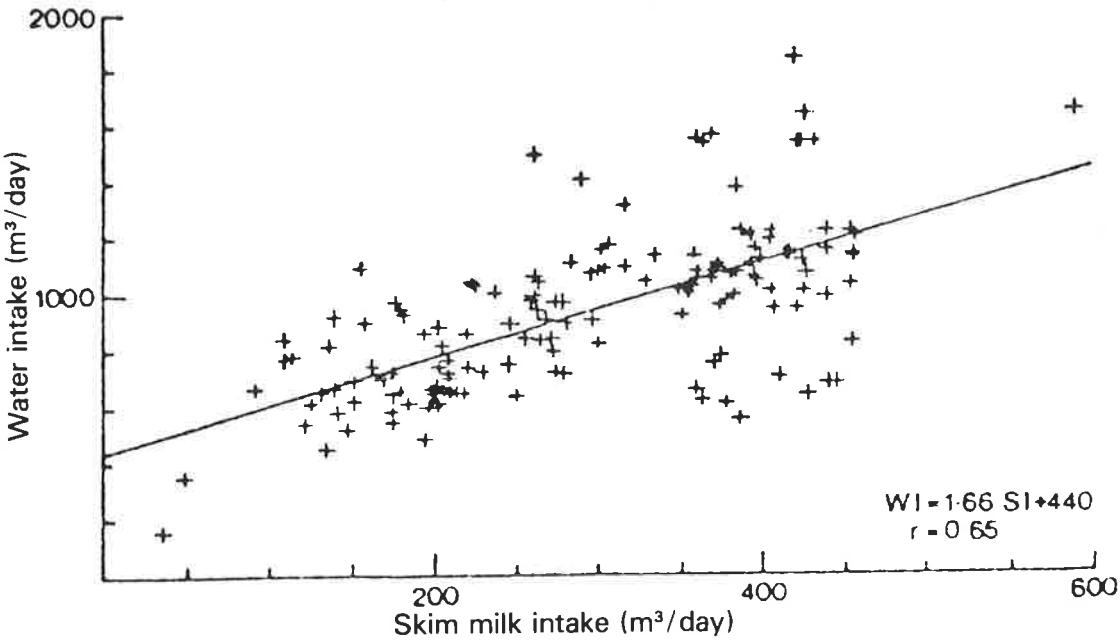

Fig. 3 Ratio of skim milk made into casein to water used in the factory.

Methods of effluent treatment

Table 8 shows the current methods of effluent disposal used in the New Zealand manufacturing dairy industry.

In New Zealand dairy factories have been built mainly in the rural areas, with no access to community sewage plants capable of handling the loads from the dairy plant, thus less than 10% of New Zealand factories use local sewers compared with about 90% in the United States. Biological treatment is little used in New Zealand. Some plants are able to discharge to natural waterways in accordance with discharge rights.

Table 8 Methods of disposal of dairy plant wastes in New Zealand 1979–80

	Number of Factories
River	20
Estuary	3
Sea	8
Spray Irrigation	45
Biological	1
Municipal Sewer	7

Fat traps are used throughout the industry to remove floatable oils and grease. Some balancing of flows and strengths of waste occurs in many factories before discharge. Secondary treatment in New Zealand has been limited to the use of a Flocor trickling filter and aerated lagoons. The lagoons are capable of a 95% reduction in the BOD_5 of the waste before it is discharged.

Overseas, many forms of secondary treatment have been used to obtain a satisfactory effluent for discharge to a waterway. These have included:

chemical coagulation plus biological filtration
activated sludge plant
aerated lagoons
dissolved air flotation plus biological filtration
alternating double filtration

However in New Zealand, it has been found that spray irrigation is the best method for disposal of whey and waste-waters resulting from cheese and casein making, provided that the system is correctly designed and competently managed. Over half the dairy plants in New Zealand use this method. Spray irrigation of wastes is a beneficial adjunct to farming, giving the prudent farmer a significant increase in income coupled with a reduction in expenditure. Irrigation of wastes is an extension of the good farming practice of returning to the soil as much as possible of the nutrients extracted from it.

Studies of the long term effects of spray disposal on soil properties suggest that a more favourable biological and chemical environment is created by the application of wastes. In particular, microbial and earthworm activities are stimulated, and plant available nutrient levels markedly increased. A high availability of water and nutrients at the disposal site enables increased production, particularly over the dry summer period.

Conclusions

In New Zealand, dairy plant wastes are characterised by high strength and high variability both throughout the day and from day-to-day. There is increasing awareness of the fact that high waste strength implies a high loss of milk and its products and many companies have recently initiated programmes to monitor the strengths of wastes and to take steps to reduce losses to the minimum achievable level. This will result in an increased return to the farmer, a lower cost for treatment and less impact on natural waterways.

Pulp and paper industry wastes

MARTIN PIPER

Tasman Pulp & Paper Company Ltd

The basic processes of pulp and paper manufacture are briefly described—debarking; pulping; bleaching; and papermaking.

The major sources of BOD are indicated and the treatment of effluent in this industry is outlined.

Introduction

The basis of the pulp and paper industry is, of course, wood. This seemingly innocuous raw material is however a potential source of aquatic oxygen demand. The trunk of a tree consists of bark, lignin, resin, sap, and the wood fibre which we primarily require. Pulping processes will release biodegradable material (BOD) into the effluent stream.

Wood processing plants are typically large for economic reasons. Tasman, for example, receives 8000 tonne of wood per day. Although only a small fraction of this ends up in effluent the quantity is large and effluent treatment is mandatory for an operation of this size.

This paper briefly describes pulping and papermaking processes, the BOD sources, and treatment methods applied.

Debarking of logs

Twelve percent of the volume of a log is bark and the first stage of processing is removal of this bark. Wet debarking uses high pressure water and produces very clean logs but a lot of sap is washed to the sewer. Dry debarking methods are more widespread and produce less contaminated effluent.

Disposal of bark has presented problems in the past since leachate from bark dumps may be a significant source of pollution. It is now recognised as a valuable fuel. At Tasman we burn 1000 tonne per day of wood waste, mainly bark, to generate steam.

Pulping

There are two broad categories of pulp, mechanical pulp and chemical pulp, and there are several distinct types within these categories.

(a) Mechanical Pulp

Mechanical pulp is produced by macerating a log, or wood chips, to a stage where the appearance is not dissimilar to porridge. It is aptly called groundwood. The older method of mechanical pulping employs enormous grindstones against which short logs are pushed and literally ground to pulp. Today grinders are less popular than refiners in which wood chips are forced between rotating steel discs to separate the wood fibres.

(b) Chemical Pulp

The bonding material between wood fibres can be dissolved chemically to release whole undamaged fibres. Lignin, the material which is dissolved, will be present in the spent cooking liquor together with many by-products of the chemical digestion. The BOD of this liquor is extremely high.

The kraft process is the major chemical pulping method employed in New Zealand, and the economic viability of this depends upon reclaim of cooking chemical and the energy value of the dissolved wood material. The spent liquor is concentrated then burnt, as one would burn oil, in a special recovery furnace. Approximately 5% of the spent liquor cannot be reclaimed and this represents a major BOD source from pulping. Furthermore, the waste liquor is dark brown in colour. Condensates derived from pulping and spent liquor evaporation are the other significant source of BOD.

Bleaching

Groundwood can be brightened with sodium dithionite or hydrogen peroxide. These are neutralised in bleaching and do not constitute a significant effluent load.

Chemical pulp bleaching however, is a source of BOD as well as colour and some toxicity. This is particularly so with chlorine-based bleaching. Bleaching is almost an extension of pulping. The last few percent of lignin, not removed in pulping, is made water soluble in the bleach sequence and is subsequently sewered as bleach wastes.

Papermaking

Papermaking in itself is not a major source of BOD. Pulping is the main offender. The recycled water system usually integrates pulping and papermaking operations and this can in fact reduce BOD discharges. Additives such as alum tend to bind extractives to fibre thus preventing them from being sewered. A gross simplification of papermaking is to describe it as simply the formation of wood fibre into a sheet followed by drying of this sheet.

BOD sources at Tasman

The above is a general outline of pulp and papermaking processes. Operations at Tasman include all

of these and the order of BOD which results is shown in Table 1. BOD is expressed as the approximate discharge per tonne of product and as the total daily contribution to the effluent. Some BOD results from spill losses but most is inherent process loss.

Table 1 Source of effluent BOD_5

Process	kg BOD_5/t	t BOD_5/day
Wood Preparation	..	5
Groundwood and Paper-making	10	11
Kraft Pulping	30	24
Kraft Bleaching	10	5
Total	..	45

Effluent treatment

In addition to 45 t/d BOD some fibre, bark and other solid material is inevitably lost. If fibre and bark are discharged to waterways they may settle, decay and ultimately exert an oxygen demand. Suspended solids must therefore be removed.

The standard procedure for treatment of effluent adopted by the pulp and paper industry is primary treatment for removal of suspended solids followed by secondary, or biological treatment, for BOD removal, detoxification, and spill buffering in some cases. Tertiary treatment is uncommon in the industry.

(a) Primary Treatment

At Tasman bar screens set in the main sewer prevent the larger solid material from entering the effluent clarifier. This clarifier, 100 metres in diameter, incorporates a skimmer for removal of floating debris and separates settleable material as a thick slurry. This underflow is transferred to a land-fill area. Clarified effluent now free of suspended matter is piped to the secondary treatment system. This type of primary treatment can be found in most large plants.

(b) Secondary Treatment

A variety of biological systems may be employed. Activated sludge systems are popular where waste flows are low but BOD concentration is high. Kraft mills which have large effluent volumes and relatively low BOD concentration (150–250 mg/ℓ) typically use more extensive aerated lagoons.

In essence wastes are retained and aerated, nitrogen and phosphorus nutrients are added if necessary, and active cultures of adapted micro-organisms develop and degrade the wastes. This is a natural process which if not carried out before effluent discharge will otherwise occur in receiving water.

Tasman's 45 t/d of BOD is reduced to 10 t/d and in future will be lower. Untreated effluent is often toxic to aquatic life but treated effluent is not toxic.

(c) Tertiary Treatment

Any further treatment will be termed tertiary. This may include sterilisation, filtration, chemical stripping or colour removal. The latter is most relevant to chemical pulping and bleaching effluents but to date no satisfactory process is available. In some cases colour may affect aquatic oxygen by restricting sunlight penetration and therefore plant growth. It may well be the next frontier of water pollution control for the industry.

Domestic sewage and piggery wastes

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Some of the characteristics of raw and treated domestic sewage, with particular reference to biochemical oxygen demand (BOD), are briefly reviewed. A number of problems associated with the BOD test for raw sewage are pointed out. Attention is drawn to the difficulties of quantifying BOD resulting from piggery wastes.

Introduction

Biochemical oxygen demand (BOD) is a measure of the oxygen used by living organisms in converting the organic matter in a waste to more stable compounds. This is affected by a number of variables, probably the most important of which are time, temperature and the composition of the waste. The test has been standardised to reduce the number of variables by carrying out the test at 20 °C over a 5 day period. Much has been written on this subject and many attempts have been made to derive mathematical expressions for calculating the BOD after any period of biological oxidation. This has been complicated by the fact that most of the wastes we are concerned with are a mixture of water inorganic and organic matter. However, in general terms these mathematical expressions do give results that are indicative of the oxygen demand over a given period.

Domestic sewage

This is waterborne waste from the typical urban community with the usual commercial activities but without any large scale industry contributing to the sewer system.

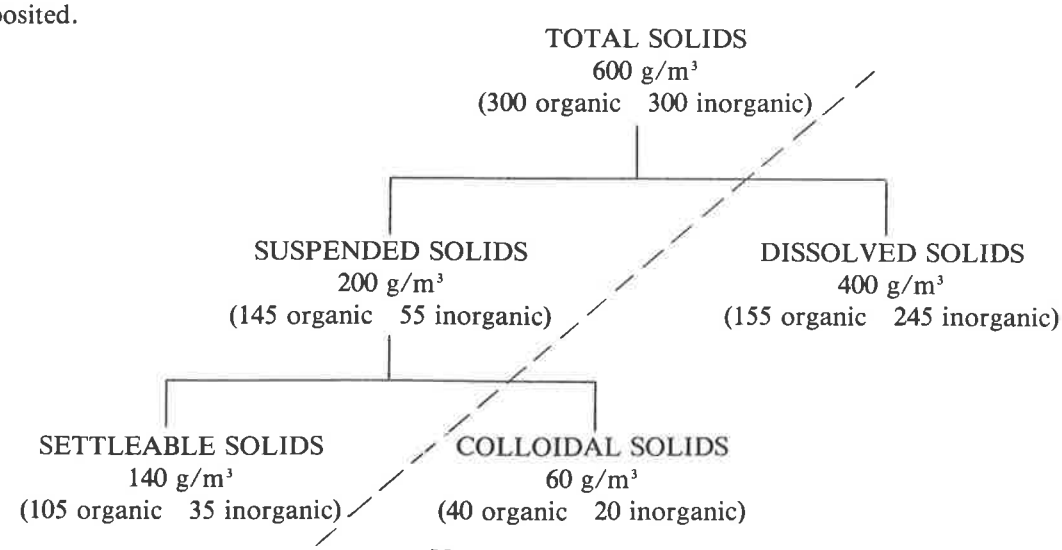
Figure 1 shows the distribution of the solids in a typical domestic sewage sampled over a 24 hour period and composited.

The flow rate of the domestic sewage continually varies throughout the day and the composition varies according to the daily activities of the contributing population, hence the validity of any analytical results is determined by the method used to take the samples and the number of samples analysed.

The sewage from the larger communities is more uniform than from the smaller communities, as the opportunity for blending of the sewage in the sewer is greater. For this reason it is considered that more emphasis should be put on a typical figure for BOD for a sewage, rather than individual analyses for that sewage.

The practice of expressing the BOD in quantitative terms rather than qualitative terms has been adopted, as the qualitative terms are mainly related to sewage flow per capita. The typical figures used in New Zealand are 70 g BOD/capita per day which with sewage flow of 250 litres/capita per day results in a sewage strength of 280 g/m³. It should be noted that the 5-day period BOD test on a raw sewage or a primary settled sewage measures the carbonaceous oxygen demand only; it takes a longer period for sufficient nitrifying bacteria to develop to a level where the ammoniacal nitrogen is oxidised (Fig. 2).

Fig. 1 Typical solids in a typical domestic sewage



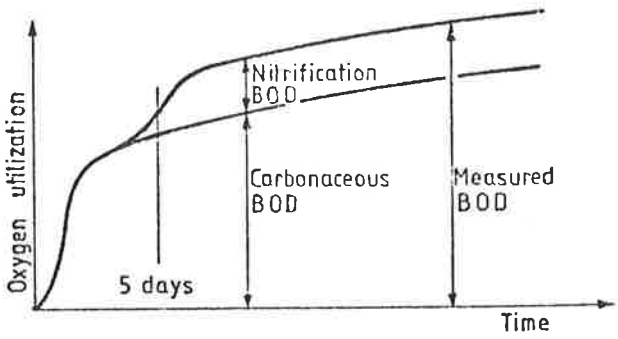


Fig. 2 BOD of raw sewage or primary settled sewage.

BOD of treated sewages

Primary treatment removes the physically settleable solids plus those that rise to the surface of the settling tanks. This process removes various portions of the solids to the left of the dotted line shown in Fig. 1, in particular the settleable solids of which better than 90% are removed. The remaining non-settleable solids, with obviously a high organic content, are removed by biological treatment during which they are converted into living material which is settleable and can be removed in the final sedimentation tank. Both the above processes produce solids (sludge) which must be treated separately. It is the removal of solids that finally reduces the BOD-causing organic matter in the liquid.

In comparing the effectiveness of different treatment processes, the effect of nitrogenous oxygen demand needs to be taken into account. Comparison of the BOD for raw and primary treated sewages with the effluent from secondary biological processes frequently means the comparison is of the carbonaceous oxygen demand of the former with the residual carbonaceous plus some nitrogenous oxygen demand of the latter, depending on the degree of nitrification. There is a school of thought which considers that the use of nitrification inhibitors in the samples of effluent under test gives the true comparison for assessing plant performance. But undoubtedly the test carried out on the natural effluent sample is probably more indicative of the effect on the receiving water.

Typical figures for the removal of BOD by different types of treatment are shown in Table 1.

Table 1 Typical BOD removal figures

Treatment		BOD Removal	Nitrification
Primary Sedimentation		30–35%	Nil
Low Rate Filtration	(1)	90–95%	25–40%
High Rate Filtration	(1)	70–90%	0–20%
Conventional Activated Sludge	(1)	90–95%	Nil
Extended Aeration		95%	90%

(1) includes primary sedimentation

Oxidation ponds are not included in the above list as the interpretation of the results of the BOD test on a pond effluent requires clarification. Oxidation pond effluent contains algae, the numbers of which are varying continually and during the BOD test (incubated in the dark). They either have a respiratory oxygen requirement or they die, creating an organic oxygen demand. The respiratory requirement probably has more significance in the test result. For this reason attempts have been made to modify the test to obtain more consistent results, e.g., filtering the sample or incubating the sample in glass-doored incubators. The filtered samples consistently give results that are about 66% lower than the natural sample, while those incubated in the light give varying results according to the time of the day and the amount of photosynthesis that has occurred. Therefore the BOD test on a pond effluent does not necessarily show the carbonaceous or nitrogenous oxygen demand and is of little value in determining the effect of the discharge on the receiving water. While it is not scientifically proven, there is evidence that a pond effluent has most of the carbonaceous oxygen demand satisfied and that due to nitrification and denitrification 40–70% of the total nitrogen is lost during the process.

The only reported cases I know of where an oxidation pond effluent has caused a problem in the receiving waters have been where there is no dispersion of the algae from the point of discharge.

As can be seen in Fig. 2 the readily biodegradable organic matter in the sewage creates a high rate oxygen demand in the initial period of the test, which reduces as the more stable organic matter is attacked. The typical initial peak rate oxygen demand in a raw domestic sewage is 8–10 mg/ℓ per hour while that for a secondary effluent with a BOD of 20 g/m^3 is in the order of 0.1 mg/ℓ per hour. Various forms of partial treatment, e.g., aerated lagoons, can produce effluents with oxygen uptake rates between the quoted figures. While it has not been common practice to refer to the oxygen uptake rate of a waste, the value of this information is becoming better understood.

Piggery wastes

Work that has been reported on the BOD of piggery wastes tends to be confusing in that it has gone into too much detail as to the age and weight of the pigs and has taken too little cognisance of management and feed material.

Obtaining a representative sample of a piggery waste is extremely difficult as the piggery is generally only washed out once or twice a day to clear the wastes, while at other times there is a trickle of drainage from urine and leaking water hoses, etc. One of the few situations where a representative sample can be obtained is where the waste is collected in a pit prior to spray irrigating. This is done by allowing the waste to accumulate for a day in the pit and circulating the contents with the irrigation pump before sampling.

The practice of quantifying the BOD from pigs of different age and weight could be applicable in a few situations, but usual New Zealand practice is to have a cross section of breeding stock, baconers, porkers, etc., in one unit. Therefore it is more appropriate to express the BOD as the amount per animal per day for a typical unit, as is done for communities of human beings. Work carried out at the Wastewater Treatment Training School, Trentham, established a

figure of 0.14 kg BOD per pig per day with a water usage of 23 ℓ per pig per day. This gives a BOD strength of about 6000 g/m³. The total nitrogen contribution is 3.44 kg per pig per annum, giving a total nitrogen strength of about 400 g/m³.

These results can vary depending on the management of the unit. Where pigs are fed whey the daily BOD is slightly higher, but whey is only available seasonally and by quoting an average figure this compensates for the variations. Spillage of whey or cooked garbage during feeding can dramatically increase the BOD giving misleading results. These variations are minimised in a well managed unit.

It seems that no work on oxygen uptake rates has been carried out in New Zealand, but work reported by Hisset *et al.* (1975) of the West of Scotland Agricultural College near Ayr, on pig slurries with a solids content of 20 g/ℓ shows that during the first day the oxygen uptake rate peaks to about 330 mg/ℓ per hour, falling rapidly to a plateau for the next 2 to 3 days at about a third of the first day peak level before tapering off. While this could be indicative of the oxygen uptake rate for New Zealand piggery wastes the management and feed materials differ markedly.

Summary

BOD information should be based on a series of samplings due to the problems associated with taking a representative sample.

BOD of untreated domestic sewage and piggery wastes should be expressed quantitatively using established figures. Where necessary these can be confirmed by sampling and testing.

The BOD test may not show or only partially show the nitrogenous oxygen demand.

In some cases the oxygen uptake rate can be more informative than the BOD test.

The BOD test on an oxidation pond effluent is not indicative of the carbonaceous or nitrogenous oxygen demand of same.

Reference

Hisset, R.; Evans, M. R.; Baines, S. 1975: The use of respirometric methods for assessing the biodegradability of different components of agricultural wastes. *Progress in Water Technololgy 7 (2)*: 13–21.

Oxygen demand—urban runoff

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The literature on oxygen demand of urban stormwater runoff is reviewed in terms of concentrations and yields, sources, factors affecting water quality, and chemical characteristics of the oxygen demanding substances. Urban runoff in New Zealand is unlikely to significantly affect receiving water DO, except in a few special cases. Data collected from a residential catchment, Hamilton, show that the oxygen demand is from predominantly particulate material, and the potential impact of urban runoff will need to be assessed in the light of this finding.

Introduction

In order to achieve water quality objectives in the United States, EPA have recognised that point sources (such as municipal sewage) are not the only source of potential pollutants, but that there is a wide range of human activities which affect the land surface and which can constitute sources of water pollution. One such example of so-called "non-point" or "diffuse" sources is storm-water runoff from urban areas.

Urban runoff, by virtue of the imperviousness of urbanised areas, is characterised by larger storm flows than an equivalent rural basin. More specifically, urbanisation brings about:

1 drastic decreases in the lag time between rainfall and flow increases in receiving stream;
2 increase in flood peak flows by 2 to 3 times;
3 increase in the number of bank overflows;
4 generation of runoff from quite small rainfall events;
5 decrease of dry weather flows (due to lower infiltration).

The impact, then, on receiving water quality, is largely influenced by this hydrological regime, i.e., mobilisation of potential pollutants during rainfall events and reduction of dry weather flows. The highest concentration of pollutants generally occurs just after the start of runoff, during the rising limb of the hydrograph (first-flush effect).

Concentrations and yields

Measurement of the water quality of urban runoff has revealed that storm runoff can contain quite high concentrations of oxygen demanding substances. Figure 1 shows the range and mean values of COD and BOD_5 concentrations found overseas and in one New Zealand catchment, a small 1.2 km^2 residential area in Hillcrest, Hamilton. Figure 2 summarises average concentrations and annual yields.

There is a wide range of observed mean concentrations and annual loads. Some of the catchments with high concentrations have been implicated in dissolved oxygen deficits (Hammer 1976), although the exact contribution of urban runoff to DO depletion is difficult to gauge in the presence of other diffuse point sources. These catchment studies have led to the oxygen demand of urban runoff frequently being compared unfavourably in strength to secondary treated sewage. Bryan (1972) related the annual BOD yield to population, and found that the annual BOD loading in urban runoff attributable to storms was similar to that for the effluent of an efficient sewage plant servicing the same area. Weibel *et al.* (1964) concluded that urban runoff loads would be 70% of BOD of a good secondary effluent. Whipple *et al.* (1974) calculated a loading of 15 g per person per day in a residential area, in reasonable agreement with Bryan's (1972) 11 g per person per day (cf. a 90% efficient treatment plant effluent which is equivalent to 9 g BOD per person per day).

Other studies have shown quite low BOD and COD in urban runoff (see Fig. 2) and in these cases, the DO downstream of the urban areas rarely fell below 7 g/m^3 (Hammer 1976).

The overall findings have caused water quality planners in the United States to consider treatment of runoff in existing urban areas, at least the first flush component, in order to improve water quality downstream.

Sources of oxygen demanding substances

To assess the implications of these findings to New Zealand one can first consider the sources of oxygen demand in runoff.

Five major sources of oxygen demanding substances can be identified:

1 Precipitation
2 Detritus accumulation on impervious surfaces (trash, oil, combustion products, vegetation, etc.)
3 Stream bank degradation, erosion
4 Gully pots, drainage channels
5 "Non-diffuse" sources (illegal connections, leaky sewerage, leachate from landfills, dumps, etc.).

The first four tend to be ubiquitous in urban areas, and are discussed more fully in the following.

1 Precipitation

Table 1 summarises the COD and TOC values in rainfall. Unfortunately, only Randall *et al.* (1978) and Weibel *et al.* (1966) have specified that they attempted to minimise the dry fallout component.

Comparison of average values give by Weibel *et al.* (1966) and Goettle (1978) in rainfall and runoff indicate that COD in rainfall forms 16% and 71% respectively of that found in runoff, although the latter value may well be enhanced through dustfall.

The source of oxygen demand in precipitation is undoubtably due to the unburnt carbonaceous material resulting from incomplete combustion. Spedding (1974) has pointed out that non-carbonate carbon can form up to 45% of the total particulate aerosol, mostly in the large particle size range (radii 0.1 to 1 μm). This is in good agreement with values of 30–40% as volatile solids in dustfall reported by Goettle (1978). Spedding (1974) reported that a wide range of organic compounds have been found in the atmospheric aerosol. These include all the straight chain hydrocarbons from C_{18} to C_{34}, at least 30 polycyclic hydrocarbons and many heterocyclic compounds. Smoke itself consists mainly of carbonaceous material, particularly tarry hydrocarbons and resins. Apart from aerosols, there is a wide range of gaseous carbonaceous materials, arising from unburnt automotive fuel and its photochemical oxidation products. These compounds would be expected to be precipitated within the first few minutes of rainfall.

Extensive monitoring of COD and TOC in rainfall in Virginia by Randall *et al.* (1978) indicates that non-carbonaceous reductants may exert a considerable COD (see Table 2). Their values are exceptionally high both in magnitude and when compared with theoretical COD/TOC ratios. If they are valid, they could have resulted from SO_2 or NO_x (nitrogen oxides), although levels of these compounds would have to be rather high (the authors noted that the major city near their rain collection

Table 1 BOD_5/COD and COD/TOC relationships in urban runoff. Ranges are given in brackets.

BOD_5/COD	COD/TOC[a]	Source	Reference
0.105[b]		606 ha, mixed urban.	Thompson *et al.*
(0.13–0.21)[d]	(2.1–3.3)[d]	Two storms, small res, comm.	Wanielista *et al.* 1977
0.08[c]		432 ha, mixed urban.	Bryan 1972
0.19[b]	3.0[b]	9 ha. res.	Mattraw & Sherwood 1977
0.14[b]		11 ha, res, comm.	Weibel *et al.* 1964
	4.4[c] (2.4–14)[e]	432 ha, mixed urban, stormwater	Colston 1974
	1.8[c] (1.2–2.8)[e]	432 ha, mixed urban, baseflow	Colston 1974
0.15[b]	2.7[b]	Large urban	Avco 1970

res = residential, comm = commercial

a For comparison, the theoretical factors for CH_4, CH_2O and CO_2H are 5.3, 2.7, and 0.7
b Computed from overall average values
c Computed from annual yields
d Computed from storm mass yields
e Computed from averaged storm values

Table 2 Average concentrations of COD and TOC (g/m^3) in precipitation, together with calculated annual loadings. Ranges are given in brackets.

COD (g/m^3)		Rainfall	TOC	COD	Site	Reference
rainfall	runoff	kg/ha.yr	g/m^3	TOC		
16	99	122			Urban, Cincinnati, Ohio	Weibel *et al.* 1966
9					Rural, Ohio	
12	44				Urban, Florida	Mattraw & Sherwood 1977
(4–22)			(1–3)		(3 events)	
			2.2		Urban, Florida	Wanielista *et al.* 1977
8					Munich	Goettle 1978
16					Tulsa, Oklahoma	
27					Zurich	
37	52	105			Munich	
78			6.8	11.5	Virginia, urban and rural	Randall *et al.* 1978
(20–322)			(2.5–18)			
65					Tenessee, urban	Betson 1978

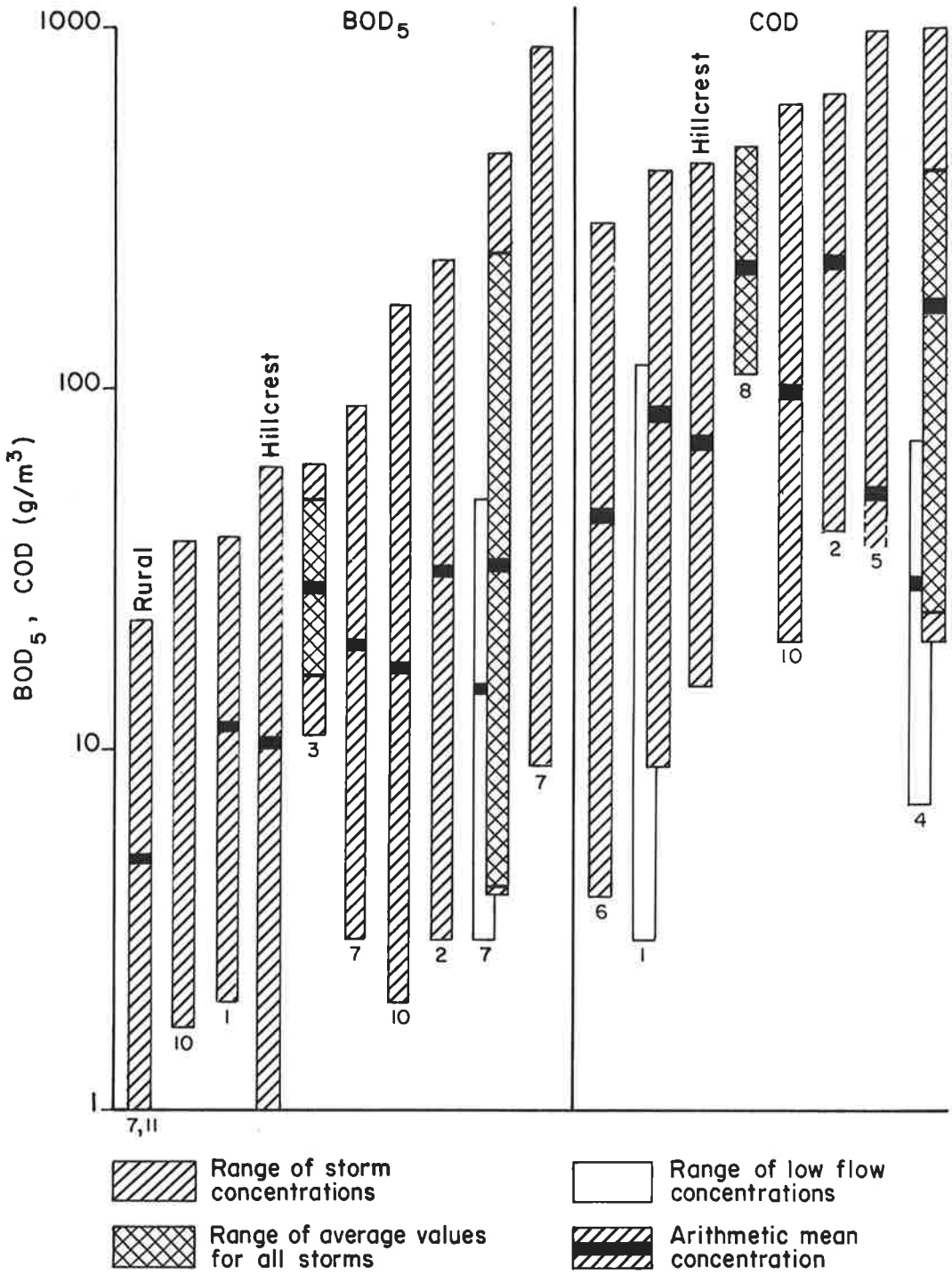

Fig. 1 Range of BOD_5 and COD concentrations in urban runoff. Storm runoff range (hatched) straddle base flow concentrations (unhatched). Cross hatched areas represent the range of average values for all storms. Average values (or range of average values for different subcatchments in any single study) are represented by a solid bar. The data are arranged in order of ascending maximum concentrations (i.e., the x-axis is dimensionless). Data are referenced by a number, corresponding to the list of authors given below.

References

1 Avco (1970)
2 Bryan (1972
3 Burm *et al.* (1968)
4 Colston (1974)
5 Goettle (1978)
6 Mattraw & Sherwood (1977)
7 McElroy *et al.* (1976)
8 Thompson, G. B. *et al.* (reviewed in McElroy *et al.* 1976)
9 Wanielista (1977)
10 Weibel (1964)
11 Weibel *et al.* (1966)

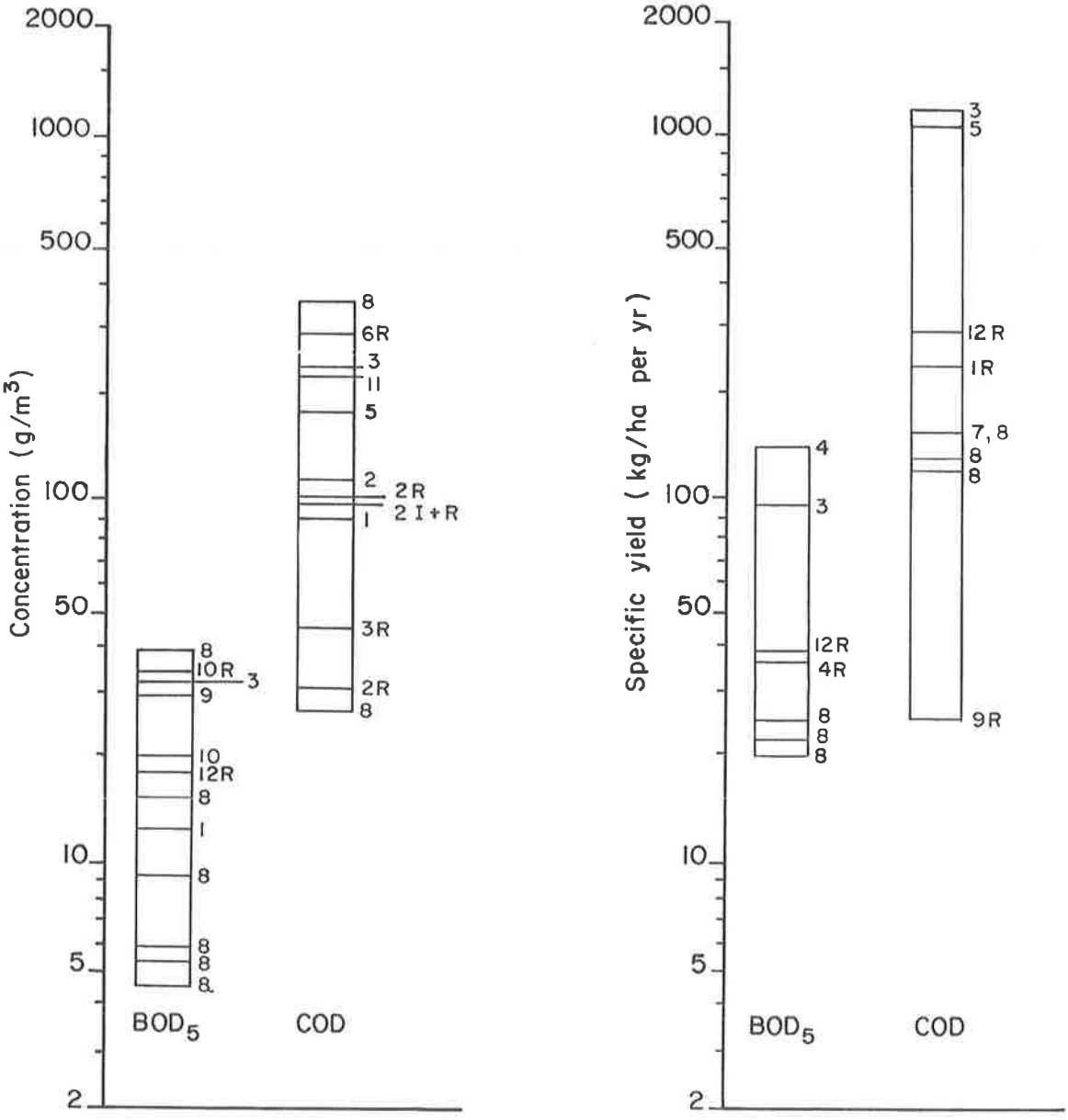

Fig. 2 Range of mean concentrations and specific yields of BOD_5 and COD in urban runoff. Data are referenced by a number, corresponding to the list of authors given below. Where dominant land use is not indicated (by R = residential, I = industrial, C = commercial, D = developing) data is derived from multiple-use urban areas.

References

1 Avco (1970)
2 Betson (1978)
3 Bryan (1972)
4 Burm *et al.* (1968)
5 Coulston (1974)
6 Ellis (1977)
7 Hammer (1972)
8 Hammer (1976)
9 Mattraw (1977)
10 McElroy *et al.* (1976)

sites, Washington, DC, was subject to frequent air pollution alarms).

There is insufficient data in Table 2 to gain a quantitative estimate of the contribution of atmospheric pollution on the oxygen demand of urban runoff. One might suspect that it is likely to be high in heavily industrialised zones such as the north-eastern region of the United States and much of Europe. Because "air pollution" is concentrated in the first few minutes of rainfall it is probably a major contributor to the "first flush" effect observed in urban stormwater.

2 Accumulation on impervious surfaces

Amy *et al.* (1974) found that oxygen demanding substances formed a large fraction of the total solids accumulating on street surfaces. The highest concentrations (weight per weight of dry solids) were found in commercial areas, as compared with residential and industrial areas, and they attributed this to oil from the many parked cars. Roads with traffic densities 500–5000 per day also had lower concentrations than roads with traffic densities 5000–15,000 per day, again suggesting that motor vehicles are a major source of oxygen demanding substances.

Thus from this work, and intuitively, one would expect that oil, grease, tyre wear, and exhaust emission from motor vehicles, together with dead vegetation collecting on impervious surfaces, to be the major contributers to BOD and COD in urban runoff. Unfortunately very little work has attempted to characterise this.

Cordrey (1977) found 900 and 1080 g/m³ of oil in surface samples collected in urban streams in Sydney on two separate occasions. Pope *et al.* (1978) in a study of highway runoff from motorways in England found 29–52 g/m³ total oil in stormwater runoff, but reckoned that their extraction/analysis technique was probably only 25–50% efficient. Unfortunately, no study has systematically examined seasonal effects on yields of oxygen demand from urban areas, and thus the contribution of deciduous vegetation cannot be assessed.

Hunter *et al.* (1979) sampled five storms for hydrocarbon analysis, the procedure used being adapted from oil pollution classification. The total flow-weighted hydrocarbon concentrations varied from 2.2–5.3 g/m³, with an averaged value of 3.7 g/m³, in good agreement with two other studies. Approximately 70% of the hydrocarbons were aliphatic, while 30% were aromatic. On average, 86% was associated with particulate matter and 14% soluble (as distinguished by high speed centrifugation). There was a remarkable similarity in gas chromatography "fingerprints" between the aliphatic component and used crankcase oil. An estimated yield of 26 kg/ha per yr of hydrocarbons from the 616 ha, mainly residential, area was calculated.

3 Stream bank degradation, erosion

Possibly the greatest impact of urbanisation on receiving water quality occurs during the construction period. Here large areas of soil can be exposed to erosion and this can lead to high levels of suspended material during runoff and to aggradation of stream channels. After the construction period, the stream channel will equilibrate itself to the changed hydrological regime brought about by increasing the impervious area (Hammer 1972). This equilibration period can lead to severe degradation in the channel, a situation which is worsened by any aggradation that occurs during construction. Thus the effects of poorly managed urban development can persist for a fairly long time after the construction period. The suspended material will contain a certain proportion of organic material, and because suspended solid concentrations are high, correspondingly high COD levels can be found, even where the exposed soil is dominantly organically-poor subsoil. The importance of streambank erosion would be expected to lessen with the age of the urban area (Hammer 1972).

4 Gully traps, drainage channels

Gully traps are often sited at the intake of stormwater to prevent heavy detritus blocking the drains. These have been shown to be a major contributor to oxygen demand, especially during the initial phase of runoff. Table 3 shows some figures for COD and BOD_5 levels of supernatant liquors in gully traps. Generally, there is an increase in COD, BOD, and NH_4 during dry-spells due to anaerobic "digestion" of waste material in the trap (Fletcher *et al.* 1978). Dissolved oxygen levels have been observed to drop quite rapidly in the traps (1–7 days) after storm events (Fletcher *et al.* 1978; Mance & Herman 1978).

Table 3 Mean and range (in brackets) of COD and BOD concentration (g/m³) in gully trap liquors

COD	BOD	City	Reference
	(35–225)	Chicago	Aitken 1973
6400	110	San Francisco	Lager *et al.* 1977
(153–37,700)	(⩽ 1500)		
(⩽ 965)	(⩽ 350)	Nottingham	Tucker 1974
39	6.8	Nottingham, 4 traps over 1 year	Fletcher *et al.* 1978
(8.7–163)	(0.9–46)		
111	11.4	Nottingham, 25 traps, same day	Fletcher *et al.* 1978
(0–430)	(0.25–42)		

The impact of gully traps on runoff events is highly variable. This is due in part to the highly variable water quality in the traps, their relative volume compared with runoff volume and also to the variable effect on particulate concentration. In one study area in England (Mance & Herman 1978), gully traps were found at times to trap up to 50% of the mass discharged, while in other events as much as 20% of the mass discharged appeared to have originated from the traps. This same study estimated that the traps held a combined volume of 100 m^3 of poor quality water, which formed a significant volume compared with the mean storm volume of 363m^3 of runoff water.

Factors affecting the water quality of urban runoff

Many reasons have been advanced to explain these wide variations in runoff quality between different catchments. Obviously the relative importance of the different sources is one factor. A statistical analysis of the data collected from a number of adjacent catchments in Tulsa, Oklahoma (Avco Economics Systems Corporation 1970), found that land surface characteristics which influence the drainage of a watershed affected the amounts of pollution produced per unit area to a larger degree than the type of environmental deficiencies (e.g., rubbish accumulations, exterior housing quality, exposed human waste—poorly operated septic tanks etc., presence of livestock, poultry and dogs) or the types of land activity. For example, one catchment was a bad environment as determined by a number of deficiencies and ranked the highest of all test areas in the numbers of coliforms. The drainage characteristics of the area were poor, however, and relatively small yields of polluting materials were washed from the watershed in storm runoff. The effect of drainage characteristics are reflected in the data of Mattraw & Sherwood (1977) for a small residential area in Florida. The use of grassy swales for stormwater routing and the excellent drainage qualities of the surficial sands resulted in very low yields of all pollutants, especially those associated with suspended material.

For example, suspended solid loads were 1 to 3 orders of magnitude less than those found for other urban studies. Avco (1970) also remark that in their study, the season which had the greatest rainfall produces the greatest pollutant load.

Other reasons which have been invoked are: size of catchment (Hammer 1976); the susceptibility of catchment soils to erosion (Burm *et al.* 1968); population (Hammer 1976); the numbers of people employed in the catchment (Avco 1970, Hammer 1976); climate (Amy *et al.* 1974).

This wide range of factors makes it very difficult to extrapolate findings from one catchment to another especially from the overseas studies to New Zealand.

Characterisation of oxygen demanding substances

The organic matter in urban runoff is characterised by an apparent low degree of biodegradability, with average COD/BOD_5 ratios of 5–12. This may reflect its nature, e.g., rubber, asphalt, soil humic matter, oil etc. (Ellis 1977), or the inapplicability of the BOD_5 test.

Much of the COD is particulate. This is a direct result of the high suspended solids load with its concomitant organic fraction. Table 4 demonstrates this, with VSS making up 10–40% of suspended solids.

Only one overseas study (Colston 1974) has differentiated between filterable and total COD. This was in a poor quality mixed urban area which has one of the highest COD and BOD loadings and concentrations reported (Fig. 2). Two storms were shown to have quite high filterable COD (61–100 g/m^3), which formed a significant proportion (25–71%) of the total COD (90–280 g/m^3).

A number of researchers (Colston 1974, Amy *et al.* 1974) have questioned the validity of BOD tests in assessing the possible impact of urban runoff, due to the presence of high concentrations of toxic metals. For example, Pb, Cu, Cd, Zn in street detritus have been shown to be sufficiently "available" to exert toxicity effects with certain aquatic micro-organisms under certain conditions (e.g., low hardness water). These authors and others, have suggested that the BOD_5 test is inappropriate and reliance should be placed on the COD test. In the Hillcrest catchment, only Pb and Zn, both predominantly derived from

Table 4 Suspended solid/volatile suspended solid ratios in stormwater runoff

Average (SS)	SS/VSS		TS/VTS	Reference
	Mean	Range[3]		
76	2.6[1]	2.1–3.4		McElroy *et al.* 1976
227	4[1]			Weibel *et al.* 1964
	4.9[1]			Angino *et al.* 1972
2040	6.5[1]	5.4–8.6		Burm *et al.* 1968
1230	10[1], 9.2[2]	6–26	5.2[2]	Colston 1974
			9.2[2]	Bryan 1972
			14[4]	Amy *et al.* 1974

1 Calculated as overall average of mean values for each storm
2 Calculated on annual yields
3 Range of average values for all storms
4 Based on analysis of material accumulated on street surfaces

automobiles, have been found in concentrations exceeding those expected from background levels.

Hillcrest data

There has been very little concern in New Zealand on the possible deleterious effects of urban runoff on DO levels in receiving waters. Any effects would probably have been masked, as most waters which receive storm runoff also presently (or recently) suffer from point discharges (municipal, industrial sewage etc.). With an increasing proportion of trade waste etc. being sewered to treatment plants, the significance of urban runoff in contributing to a general water quality may increase. However, one can conceive of very few situations where significant deleterious effects might be exerted, even if runoff contained a BOD of the same order of magnitude as found in the worse cases in the United States. Most large urban areas in New Zealand are built close to the coast or on large rivers, and there is insufficient travel time or sufficient dilution to minimise DO depletion. Possible exceptions are:

1 predominantly urbanised catchments supplying impounded waters (small lakes or poorly flushed estuaries);
2 small streams during small runoff events, which in some cases can produce extremely high concentrations of pollutants without substantially increasing the flow, e.g., one stream in Sydney contained 120 g/m³ BOD after 1–2 mm of rain (Cordery 1977).

Apart from BOD, we have been interested in the potential impact of urban runoff on receiving water quality in terms of its suspended solids, heavy metals and nutrients. This work was initiated recently and to date we have only looked, in any detail, at water draining the Hillcrest catchment. Tables 5 and 6 summarise these data. Both COD and BOD can be quite high, but most of this is due to particulate material, with filterable COD being quite low.

Table 5 Range of COD concentrations from Hillcrest, Hamilton

Sample	COD (g/m³)	Number of samples
Storm runoff (total)	15–430	13
Storm runoff (filtered)	6–13	12
Dry weather flow	5–28	25

Table 6 BOD and corresponding COD of selected samples from Table 5

	COD (g/m³)	BOD (g/m³)
Storm 1	390	60[a]
Storm 1	230	45[a]
Storm 1	15	4[a]
Storm 2	121	19, 20[b]
Storm 2	22	5[b]
Storm 2	12	3.6[b]

a 6 day BOD measured by COD difference
b 5 day BOD measured by EBOD technique

Table 7 shows the COD of a sample collected over the first flush of a runoff event. COD was analysed at various time intervals during which the suspended material settled out. Nominal particle sizes were calculated assuming Stokes Law and a particle size density of 2.65. Half the COD settled out of the top 20 cm of water within 5 minutes (i.e., it is nominally coarse silt-sized or larger).

In conclusion, a casual assessment of the overseas literature would suggest that urban runoff could exert significant oxygen depletion under a wide variety of receiving water conditions. In reality, not all urban studies show this potential, and in only a few cases has there been evidence that this potential is realised. There is a wide range of BOD and/or COD concentrations and loads and a multitude of reasons are invoked to explain this range. Apart from a few multiple catchment studies, these reasons are still very much at the qualitative level of understanding. Therefore extrapolation of results in order to predict concentrations and loads in other catchments is very difficult.

Close examination of overseas and existing New Zealand data shows that much of the measured BOD is from particulate material. Therefore, the impact of runoff must be assessed in these terms with regard to the existing benthic oxygen demand of the receiving water. The existence of high BOD_5 or COD concentrations or loads, does not in itself lead to significant oxygen depletion.

Table 7 Variation of supernatant COD with settling time. Nominal particle sizes are calculated (a) on basis of Stokes Law and assuming particle density of 2.65 and (b) pore size of filters.

Time settled (minutes)	COD (g/m³)	Maximum particle size (μm)
0	121	..
5	63	26
30	22	7.5
135	12	2.3
2700 (2 days)	10	0.36
GF/C filtered	11	1.2
Membrane filtered	8	0.45

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DISCUSSION FOR SESSION III

Characteristics of slaughterhouse effluents

Presented by: R. N. Cooper

D. G. SMITH : You made fleeting reference only to the use of a plastic media tower for secondary treatment in one plant. Would you comment on the efficiency of this tower especially with respect to BOD removal?

COOPER : The plant referred to is operating at loadings in the range 9–10 kg BOD_5/m^3/day with a BOD_5 removal efficiency of 50–60%. The system has no flow balancing, consequently most of the load is applied over an 8-hour period.

The characteristics and oxygen demand of New Zealand dairy food plant effluent discharges

Presented by: K. R. MARSHALL

G. B. McBRIDE : Can dairy factories using a spray irrigation system continue to use it when there has been heavy rain?

MARSHALL : For a properly designed, managed, and operated system, yes. For recently designed spray irrigation systems, the design irrigation rate is a maximum of 6 mm/h for up to 2–6 h depending on soil type and moisture contents. This rate is less than storm intensity rainfalls. It is also possible at many sites to cease irrigation

for several hours during very heavy rainfall. During periods of heavy rain, such as spring, sprinklers should be moved more often than during dry weather.

M. SPENCER : With reference to your comment that you believed all milk industry waste dischargers were not contravening their discharge rights, could you elaborate on the area(s) sampled for the data presented in Table 7, especially with regard to the upper temperature and pH values?

MARSHALL : The data given in the paper are summaries and show extreme values. The high value of temperature is an extreme and was measured in a small volume effluent stream and hence would have little effect on the natural waterway. Such high temperatures are rare. Normally extreme pH values are balanced out before discharge to the natural waterway. The data on waste streams are taken at the envelope surrounding individual processes and not necessarily at the point of discharge to the waterway.

O. BORLASE : Could Dr Marshall please comment on the suitability of biological methods of treatment of dairy plant wastes?

MARSHALL : Biological treatment methods are being used successfully to treat dairy plant wastes particularly in the United States and Europe. The system in use by one company in New Zealand is an aerobic/facultative lagoon system capable of better than 95% reduction in BOD_5. Effluent quality is generally better than 100 mg/ℓ BOD_5. The biological systems tend to cost more to install than spray irrigation systems and certainly cost more to operate, particularly because of the high power cost.

Pulp and paper industry wastes

Presented by: M. PIPER

H. MORGAN : Is the BOD of Tasman effluent inhibited by deficiencies of other nutrients, in particular phosphorus and nitrogen?

PIPER : Not in the case of phosphorus, possibly because phosphoric acid is used in the process. Nitrogen is only used in a few instances such as startups. However, many mills, particularly chemical pulp mills, do require nitrogen and phosphorus to be continually added to effluent.

Domestic sewage and piggery wastes

Presented by: D. R. CAMERON

C. D. STEVENSON : What type of filter was used in the experiments which showed a 66% reduction of BOD for oxidation pond effluents? Is the filtration removing more than simply the algal material, since literature value for oxygen demands from pure algal culture suggests a relatively small proportion of the algal dry matter will appear as oxygen demands within 5 days?

CAMERON : The pond effluent samples were filtered through Whatman GF/C papers. Tests for chlorophyll extraction from the samples and the nitrogen in typical algae cells gave results that were proportional to the suspended solids removed. Algal cells matter is reported to have a BOD of 0.41 mg per mg of dry cells, but whether this is exerted during the 5-day test period is debatable. It is considered that the 66% reduction in BOD is due to the respiratory requirement of the algae. But the possible removal of other sources of oxygen demand cannot be ruled out.

O. BORLASE : Re use of BOD_5 test as the measure of effluent quality from oxidation ponds. Is it more a question of academic rather than practical concern?

CAMERON : It is considered that the BOD test does not show the effect of an oxidation pond's effluent on a receiving water provided the effluent is dispersed by the flow. I do not know of a case where an oxidation pond effluent from a conventionally loaded pond has created an oxygen deficiency in a receiving water in New Zealand.

A. B. DRYSDALE : A comment. BOD of piggery wastes have been related to weight and age rather than management and feed because the pork industry is now largely based on meal feeding. Whey, skim milk and garbage feeding are decreasing in popularity.

Work involved in characterising piggeries feed on these feed sources is not justified as the problem will be solved when the feed sources stop.

Oxygen demand: urban runoff

Presented by: R. B. WILLIAMSON

D. SMITH : It is one thing to say that OD and SS are correlated but another to say that OD is contained within the SS. Comment?

WILLIAMSON : In the Hamilton catchment the filtered COD is very low even though total COD or BOD_5 can be quite high. There is virtually no overseas data on filtered (so-called dissolved) oxygen demand and so one can only infer the relationship. However, our experience would suggest that this is a reasonable assumption.

D. OGILVIE : Your paper discusses surface runoff volume and quality after rain events. Has any work been done on subsurface flows and composition? In certain areas these subsurface flows must extend the hydrograph and greatly increase the oxygen demand on receiving waters.

WILLIAMSON : This aspect has not received much attention. To some extent the impact of subsurface flows will be reflected in the water quality of low flows. The Hillcrest catchment has high NO_3 concentration, for example. My feeling is that subsurface flow will not contribute much oxygen demand to urban runoff, although the hydrograph will be extended after heavy rain. In essence, I would expect this groundwater contribution to "dilute" the oxygen demand.

SESSION IV SOURCES AND SINKS OF AQUATIC OXYGEN

Aquatic and benthic micro-organisms

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The growth and metabolism of aquatic micro-organisms is a prime cause of oxygen deficit in natural waters. Whilst aerobic heterotrophs are the major group of oxygen consumers, in rare instances chemotrophs may make a significant contribution. Bacteria are able to succeed in aquatic environments, because their efficient substrate transport systems allow them to scavenge for minute amounts of dissolved organic substrate, and they are able to rapidly adapt to imbalances in substrate supply. Their survival is enhanced by adsorption to particulate material. Adsorption enhances the proximity of the bacteria to an increased substrate concentration, and if the particle sediments can prevent wash-out (especially in rivers). The sediment-water interface is consequently the most active zone of bacterial metabolism and therefore oxygen consumption. Anaerobic regions of the sediment indirectly affect oxygen uptake, because the metabolism of anaerobic bacteria results in the release of inorganic nutrients (ammonia and phosphate) as well as small molecular weight substrates. Other than substrate availability, temperature has the greatest influence on microbial oxygen demand. Higher temperatures result in increased bacterial respiration but lower oxygen solubility, and significant responses in the microbial population can occur with small temperature changes. The complexity of biological, chemical and physical factors on benthic oxygen demand is outlined.

Introduction

The posture of bacteria in natural aquatic systems is definitely not the plush existence typified by laboratory cultures. Bacteria in the aquatic environment must endure changes in solar inputs, substrate type, and concentration of oxidisable substrate, nitrogen and phosphorus availability, temperature and oxygen saturation; they are washed from the surface of both living and decaying material; and they are scoured from the sediments (Stevenson 1978).

That bacteria accommodate these hazards to their existence is supported by the mass of information which demonstrates their prime position in oxygen consumption in aquatic habitats. Why should this be so, or what features of microbial physiology allow this group to be so dominant? To gain an insight into this problem we require an understanding of bacterial metabolism and oxygen uptake.

Oxygen requirements of bacteria

1 Why is oxygen required by bacteria?

Not all bacteria require O_2; to the strict anaerobes it is actually toxic. Oxygen consumption is restricted to two large groups—the facultative anaerobes (those that grow best using oxygen but can still grow in its absence) and the aerobes (those unable to grow if oxygen is absent). Oxygen is primarily used as an electron acceptor—it accepts electrons released in the breakdown of substrates from which the cells obtain energy for growth, e.g., in the simple case of glucose breakdown

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + 36ATP$$

the oxygen has accepted electrons (and associated hydrogen protons) transferred from the glucose molecule and been reduced to water. This transfer is

mediated by the cellular enzymes and respiratory electron carriers in an orderly fashion—a process called respiration.

Without substrate to oxidise, the cell will not respire and hence will not consume oxygen. Bacteria are metabolically diverse and use an extremely wide range of substrates. The most important types of substrates are organic, i.e., reduced carbon compounds, but important groups of bacteria (chemotrophs) can use reduced inorganic substrates such as ammonium (reduced N) or sulphur and sulphides.

Whilst the contribution of chemotrophs to the normal aquatic oxygen demand is usually small, in some situations they may become significant or even dominant. Reference has already been made to the contribution of ammonia oxidisers in piggery wastes (Cameron & Williamson 1981; Cooper 1980) has demonstrated that up to 30% of the O_2 demand of the Waiohewa (an inlet into Lake Rotorua) can be attributed to these organisms. We know of no instances where oxygen consumption by sulphide oxidising bacteria is dominant in New Zealand waters. In some strip mining sites in the United States where coal deposits have a small sulphide content, the oxygen demand of effluent runoff can be attributed totally to sulphur oxidisers.

Amongst the heterotrophic bacteria (those that oxidise organic carbon compounds) oxygen is always the preferred electron acceptor because the energy released from the oxidised substrate is greater. Some facultative anaerobes can use other electron acceptors but only in the complete absence of oxygen. Bacteria are efficient at scavenging oxygen, and if substrate is available will reduce the concentration in solution essentially to zero.

The concept of a 'critical oxygen tension' as a distinct and fixed value is obviously somewhat erroneous as applied to different groups of organisms. However, the term is still much used, even for growing bacterial suspensions, as a convenient means of expressing oxygen tension at which the relationship between respiration rate and dissolved oxygen tension changes from being zero order to first order.

Harrison (1976) reports a wide variety of responses to dissolved oxygen tension is possible among micro-organisms. The most general conclusion to be drawn is that for the majority of aerobic and facultative micro-organisms, there is a range of oxygen tensions, usually between 20 and 150 mm Hg, (12–100% saturation), over which the metabolism of the organism is little affected by changes in dissolved oxygen tension. In general, respiration rate might be expected to decrease at extremes of high and low oxygen tensions but this is by no means a universal feature.

2 Why are bacteria more successful at removing oxygen than other organisms?

Oxygen is primarily consumed as a consequence of substrate utilisation. The question could be rephrased as "why are bacteria more successful at removing substrate?", and then, "what substrate is being used?" In aquatic systems two broad substrate groups can be defined, particulate organic matter and dissolved organic matter, of which the latter is by far the greater. Because the turnover time of dissolved organic matter is extremely short in unpolluted natural waters, its concentration as a result is very low (typically of the magnitude of 1 $\mu g/\ell$ for glucose) (Ogura 1975).

Dissolved organic matter is released into aquatic habitats from several sources. Probably all macrophytes and phytoplankton lose a proportion of photosynthetically assimilated carbon and values of up to 30% have been observed (Riley 1970). The autolysis and decomposition of plant material and secretion from invertebrate feeders are also important as are the effluents from processing plants and sewage treatment.

The rapid turnover of dissolved organic matter requires an increase in oxygen consumption by the organism. Because turnover is so rapid and concentrations of the substrate so low only organisms possessing high efficiency uptake systems will be able to compete effectively. A large proportion of aquatic bacteria have been shown to be remarkably efficient at taking up a range of low molecular weight substrates (Crawford *et al.* 1974; Wright & Sliah 1975) and allied to their rapid growth rates, bacteria are the main sink for dissolved organic matter. Wright & Hobbie (1966) have demonstrated the inability of algae to compete with bacteria for substrates in the concentration range found naturally. A similar situation exists with protozoa and ciliates, e.g., *Tetrahymena* feeds on bacteria in nature; it can be grown axenically on peptone solution at concentration above 1 g/ℓ, but growth is slow compared to culture-fed bacteria and the cell yield is reduced by 80% (Sleigh 1973). Saturation constants for glucose with bacteria are of the order of 7 $\mu g/\ell$, but for a range of aquatic invertebrates are 0.94–12.6 mg/ℓ (Fenchel & Jorgensen 1977).

Particulate organic matter is less abundant. Wetzel *et al.* (1972) found proportions of dissolved organic matter, particulate dead organic matter and living biomass of 100 : 10 : 2 in lake water. Particulate organic matter is turned over more slowly, i.e., it is utilised less readily and therefore exerts a lower oxygen demand. Its resistance to turnover reflects the inability of organisms to degrade the complex polymers usually associated with this material. In this situation bacteria again dominate because of the versatility of their enzyme composition. The situation is complex in that although bacteria, and to a lesser extent fungi, are the primary decomposers of particulate organic matter, the size range of these particles renders them amenable to ingestion by protozoa, ciliates and other grazing animals. Many of these organisms consume only the bacteria adsorbed to the particulate material which is then egested for re-colonisation. The oxygen demand derived from the utilisation of particulate materials is therefore attributable to a wider range of organisms.

Substrate supply is not the sole criterion controlling oxygen demand by micro-organisms. Substrate composition is also important and this is because all substrates are used both for energy production and to supply the precursors required for producing more cell material. Table 1 illustrates how substrates vary.

Imbalances in substrate composition impair its rate of decomposition and slow oxygen demand. The most common imbalance is an excess of organic carbon in relation to available phosphorus and nitrogen. Under these conditions successful competitors are those that are adept at scavenging the minute amounts of nitrogen and phosphorus available. Fenchel & Jorgensen (1977) attribute the dominance of bacteria in decomposition and oxygen uptake to their success in this role. Although phytoplankton, at least, seem to be equally efficient at assimilating phosphorus under laboratory conditions, in the natural environment the sites occupied by bacteria allow them first access to sources of these minerals. The work of Neijssel & Tempest (1976) demonstrates increased substrate turnover (and increased oxygen demand) by cultures of bacteria limited with respect to either nitrogen or phosphorus may also be an important feature of bacterial success. By this means, although bacterial growth is slowed the cells effectively still act as a sink for the limiting substrate by "spilling" excess organic carbon.

Growth of an organism on a single substrate will involve the organism in extensive metabolic transformations and so increase the amount of energy needed for growth. In support of this suggestion it has been observed that natural populations for an estuary gave an apparent growth yield on glucose of 64% ± 8 (i.e., 36% respiration) at ambient glucose concentrations (<50 $\mu g/\ell$). When, however, the glucose concentrations were increased to 2–20 mg/ℓ the growth yield fell to 51% ± 2.7 (i.e., 49% respired) (Williams 1973).

Table 2 provides some information on the comparative energetic values of bacterial growth on various carbon sources. It is evident that considerably more oxygen is consumed for cell growth with some compounds than with others. Oxygen consumption has been shown to increase if glucose is added discontinuously (drop-wise) to a glucose-limited culture (Neijssel & Tempest 1976). Increased substrate uptake and rate of oxygen demand have been shown to occur in an intermittently fed activated sludge plant compared to one which receives a continuous feed supply. Organisms which developed in the continuous feed plant were filamentous while those subjected to intermittent feed were floc forming (Houtmeyers *et al.* 1980). No work has been sighted as to the comparative effects on a stream of continuous or intermittent effluent release, although there certainly would be substantial differences in microbial development and oxygen exertion.

In general, increases in substrate supply (organic pollution) besides resulting in an increase in numbers, also result in an increase in the mass of individual cells (approximately double). When organic pollution continuously adds a heavy BOD load *Sphaerotilus* species and associated organisms gain a competitive advantage. This reflects their ability to extract nutrients from flowing water, whilst

Table 1 C:N:P ratios of various wastes compared to that of bacterial cells and laboratory medium.

	BOD_5^{20} (g/ℓ)	Glucose equivalents (g/ℓ)	C : N : P Weight basis
E. coli	..	..	50 : 14 : 3
Theoretical medium for total consumption*	..	..	100 : 14 : 3
Routine lab. medium	7.4	10	133 : 86 : 3
Optimum ratio in waste treatment practice	..	..	146 : 16 : 3
Settled domestic sewage	0.37	0.5	86 : 29 : 3
Brewery waste	1.6	2.2	263 : 87 : 3
Slaughterhouse waste	0.8	1.1	165 : 53 : 3
Sugar beet washing water	4.6	6.2	573 : 16 : 3
Retting waste	2.5	3.4	156 : 46 : 3

*assuming 50% of carbon source is respired for energy. From la Riviere (1977).

Table 2 Comparison of yield coefficients for bacteria grown on various carbon sources (from Bailey & Ollis 1977).

Substrate	Y_S, g cell/ g substrate	Y_O, g cell/ g O_2 consumed	Y_Δ, g cell/ kcal
Maleate	0.34	1.02	0.30
Acetate	0.36	0.70	0.21
Glucose equivalents (molasses, starch, cellulose)	0.51	1.47	0.42
Methanol	0.40	0.44	0.12
Ethanol	0.68	0.61	0.18
Isopropanol	0.43	0.23	0.074
n-Paraffins	1.03	0.50	0.16
Methane	0.62	0.20	0.061

at the same time remaining attached to the substratum.

3 What controls the distribution of bacteria in aquatic environments?

Sites of high bacterial population density will be sites of high oxygen uptake and thus the major sinks for dissolved oxygen. In oligotrophic waters it appears that a majority of the bacterial population exists in an adsorbed state, either to other members of the biomass or to inert particulates. If these particulates settle, either because of density or through the phenomenon of the "algal rains" (Collins 1977) then a large proportion of the bacterial biomass will be found at the sediment surface. There is now a great body of data showing orders of magnitude of increases in bacterial density and activity in surface layers of sediments compared with the overlying water (for a review see Collins 1977). The upper sediment layers must be viewed as one of the major oxygen sinks in aquatic habitats. The physical and hydraulic features of the sediment will of course have an enormous influence on sediment oxygen uptake, and in river situations where sediments may be mobile and particles oscillate between suspended and sedimental stages, this general statement may not hold true.

What advantages do bacteria gain by adsorbing to suspended or sedimented particulates? Three major advantages have been demonstrated for adsorbtion of bacteria and either one or all might apply in any particular situation.

In the first instance concentrations of readily metabolised organic substrates, e.g., glucose, glycollate and amino acids, are extremely low. Many of these substrates adsorb to inert surfaces so that a slightly increased concentration is achieved sufficient to confer an ecological advantage on any organism capable of exploiting this niche. By the use of continuous cultures of mixed and pure cultures of bacteria, Jannasch & Mateles (1974) have clearly demonstrated (i) that bacteria can grow on much lower substrate concentrations in the presence of inert particulate material due to concentration of the substrate at the particle surface and (ii) that the competitive ability of some species is dramatically increased by the presence of surfaces. Figure 1 demonstrates the increased bacterial growth achieved by the presence of inert chitin particles.

Similar influences of surfaces have been demonstrated in natural environments (Paerl 1974, 1977; Seki 1972; Zobell 1943). The ecological importance of adsorption is well established at least in oligotrophic waters and its significance with respect to oxygen consumption is twofold. It facilitates the turnover of dissolved organic matter that would not otherwise be available; and it is the initial step in the formation of detrital particles and the detrital food chain which underlies the oxygen consumption of aquatic invertebrates (Paerl 1977).

A second advantage of adsorption applies predominantly to those organisms adsorbed in the surface sediment layers. The underlying sediment layers are anaerobic. The result of anaerobic metabolism is the release of large quantities of small molecular weight organic molecules as well as the mobilisation of phosphorus and ammonia (Ryding & Forsberg 1977, Neame 1977). Aerobes at the sediment-water interface are in a prime position to exploit the substrate diffusing from the anaerobic zone, as well as particulate substrate settling from the water column. Imbalances in the substrate composition, e.g., macrophyte detritus with C : N ratios of 50–70 : 1, can also be ameliorated by the flux of N and P from anaerobic zones. These features explain the high bacterial activity of sediments and their importance in oxygen consumption (Edberg 1977, Granelli 1977).

Lastly an advantage that may be of more importance to river habitats is the necessity to avoid wash-out. In river situations unless adsorption to sediment or macrophytes occurs, the cell will eventually be washed into saline environments where it is unlikely to compete. Marshall (1976) has shown that laboratory grown cultures of aquatic bacteria differ in the external layers of the cell wall. Natural isolates possess an extensive polysaccharide glycocalyx which is absent from laboratory cultures, though it can be induced when grown in continuous culture on low substrate supply in the presence of inert particles. The role of the glycocalyx is to adhere the cell to particles. In fast flowing streams the production of glycocalyx is profuse; it appears that the cell can respond to increased flow by making itself stickier.

The advantages of adaptation are most pronounced in oligotrophic waters and may diminish as the substrate supply is increased. In eutrophic lakes, or grossly polluted rivers, conditions may exist where free living organisms are competitive, and in these environments the sink of oxygen consumption may be more evenly dispersed throughout the aerated water column. Even then it may still be associated with suspended particles, for in the treatment of settled sewage by trickling filters a greater proportion of substrate is oxidised by cells attached to the filter bed than bacteria suspended in the effluent (la Riviere 1977).

The presence of bacteria in natural aquatic systems suggests that the organisms are well adapted to cope with the problems experienced therein. The metabolic versatility of the bacterial world as a whole is unquestioned; however, this versatility is not a reflection of the multifarious ability of its individuals. Rather an impression of versatility and stability is reflected by considering the population as a whole.

General factors which affect oxygen consumption by bacteria

For the survival of heterotrophic bacteria, living in a natural aquatic environment, a food supply is necessary to provide energy to maintain cellular functions and for synthesis of new cellular material for all growth. Normally this food supply would be provided by allocthonous material (i.e., decomposed organic matter which has leached into the water body) or autocthonous material (i.e., oxidates from the photosynthesis of algae and macrophytes present). A waste effluent will greatly increase the

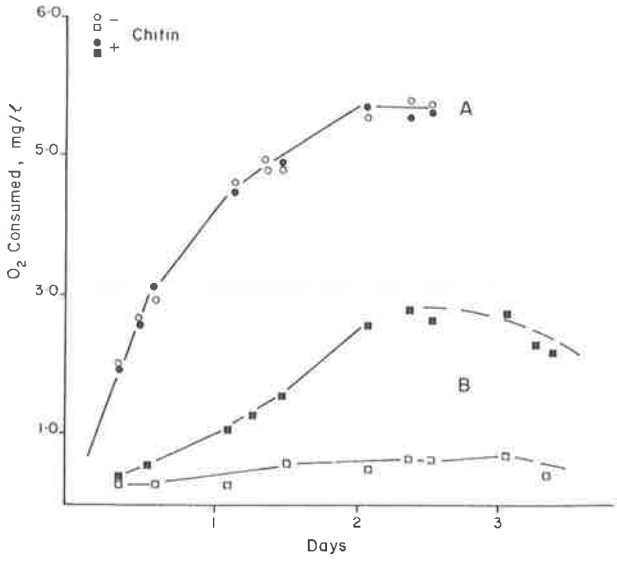

Fig. 1 Oxygen consumption in the presence of 5.0 mg (A) and 0.5 mg (B) peptone/litre in a culture of *Achromobacter* sp. in the absence and presence of chitin particles (7–10 × 10^3/ml) (from Jannash & Pritchard 1972).

concentration of organic substrate present in the aquatic environment. These effluents may contain small organic molecules, e.g., sugars, amino acids, which may be easily assimilated by the bacteria, while larger and more complex molecules require enzymatic degradation prior to uptake by the organisms, e.g., cellulose, proteins, fats. Depending on the size of the bacterial population present the type and concentration of substrate dictates how rapidly the substrate may be metabolised and hence how quickly an oxygen demand will be exerted. Thus an effluent containing a large proportion of small molecules, e.g., milk, will exhibit rapid rates of oxygen exertion when exposed to a microbial population.

Micro-organisms have also been shown to exhibit catabolite repression where the most readily utilisable substrate represses the utilisation of another substrate present. Generally the substrates are in quite high concentrations and will be of similar type, e.g., two types of sugars. This sequential metabolism is known as diauxie and was reported by Monod in 1942. In mixed substrate natural waters with the addition of low concentrations of radioisotope labelled substrates, different substrates have been shown to be metabolised to different extents (Wright 1971). This indicates that some substrates are more readily used for assimilatory growth while others are favoured for energy production, even in mixed substrate systems.

Bacteria have been shown to have varying efficiencies of metabolism depending on the concentration of the carbon source present (Wright 1971; Williams 1973). For aquatic bacteria respiring substrate at concentrations < 50 $\mu g/\ell$ the percentage of glucose respired found is generally between 10 and 30% while isolated bacterial cultures growing on glucose above 500 $\mu g/\ell$ generally respire at least 50% of the substrate. Could it be that the natural populations normally grow on a mixture of substrates, whereas cultures, especially those used for growth yield studies, are grown on single substrates, commonly carbohydrates?

Temperature

The temperature is very important with regard to seasonal effects concerning the microbial population present, and Q_{10} effects (Q_{10} is the respiration increase for a 10 °C increase in temperature). With Q_{10} measurements for bacterial populations ranging from 2 upwards (Wright 1971), a few degrees difference causes a very significant difference to the rate of growth and metabolism.

Temperature appears to have a greater effect on the rate of sediment oxygen demand than on aquatic oxygen demand. Edberg & Hofstein (1973) list Q_{10} temperature coefficients for lake muds at various temperatures (Table 3).

Jorgensen (1977) reports a Q_{10} for oxygen demand of coastal marine sediments of 3.2. No references have been sighted which report temperature effects for high velocity lotic systems. Overall, seasonal increases in temperature tend to result in greatly increased oxygen demand occurring during the summer months in lotic systems (Naiman & Sedell 1979). In general, the question of sediment oxygen demand is complicated because of diffusion and solubility changes in addition to the effect of temperature on the micro-organism.

Table 3 Sediment oxygen demand in relation to temperature (from Edberg & Hofstein 1973)

Temperature Range (°C)	Q_{10}
5–15	3.4
10–20	2.1
15–25	1.5

The microbial population present in a water body would be expected to exhibit a temperature optimum for maximum respiratory rates at approximately the *in situ* temperature. Populations have been shown to require several days' preconditioning to adapt optimally to a temperature change (Carpenter *et al.* 1979).

Increase in temperature also brings about an increase in the rate of total substrate breakdown and increased cellular maintenance requirements.

Other than substrate availability, the *in situ* temperature has the greatest influence on the microbial growth and respiration. In addition to causing an increase in microbial oxygen demand, an increase in temperature also causes a decrease in the solubility of oxygen in water and so further aggravates the dissolved oxygen levels.

Other factors

The presence of trace levels of carbon dioxide is necessary for the metabolism of almost all bacteria, with optimal growth occurring with slightly elevated concentration. However, very high levels of carbon dioxide are very inhibitory to growth and respiration of obligately aerobic micro-organisms (Wimpenny 1969).

Both the pH and the osmotic strength of the medium may markedly influence the metabolic effic-

iency of a micro-organism, resulting in an increase in oxygen required per gram of cell growth (Hempfling & Mainzer 1975).

Inhibitory substances

There are a large number of agents which may markedly impair microbial growth or metabolism. Some compounds are naturally produced by organisms growing in the water body while others are introduced in effluents. These latter compounds include phenols and cresols, organic compounds, aldehydes, halogens, and heavy metals. The release of heavy metals into the environment forms one of the most important types of enduring pollution. Metal toxicity can be greatly influenced by environmental conditions. Binding of metals to organic materials, precipitation, and the formation of complexes through ionic interactions are all important phenomena. In cases of continuous exposure it becomes obvious that microbes possess a range of tolerance mechanisms, most featuring some kind of detoxification mechanism. A number of authors have recently presented reviews covering micro-organism/heavy metal interactions (Summers & Silver 1978; Gadd & Griffiths 1978; Goulder *et al.* 1980).

Physical factors which may affect oxygen removal

The type of river sediments together with the velocity and turbulence of a river, combine to control the availability of oxygen to the benthic micro-organisms. The type of sediment is a major factor which influences interstital flow of water by its particle size. The greater the surface area of the sediment the greater the cell density of aerobic heterotrophic organisms which will be able to develop given a sufficiently large food supply (Jones 1980). In sediment areas where a sludge has developed the rate of oxygen consumption is generally limited by the concentration of dissolved oxygen above the sediments (Fillos & Molof 1972; Polak & Haffner 1978).

Benthic or sediment oxygen demand (SOD) can be divided into two components. The first component involves the diffusion of oxygen and carbon source from overlying waters into the sediment deposits. The transport of oxygen to the interface is generally rapid as eddy currents carry the DO to the interface. Subsequent transport of oxygen into the sediments is governed predominantly by molecular diffusion. The second component is the vertical migration of reduced, oxygen-demanding substances up through the sediments and into the overlying waters where they exert a biological or chemical oxygen demand, or both. This process is also governed predominantly by molecular diffusion, and is rather slow. Consolidation of deposits as they decompose can, however, force interstitial waters into the overlying waters, thus hastening the transport of reduced substances out of the sediments. In addition, gas production in organic-rich deposits may cause further disturbances of the sediments via sludge lifting. A large macro-invertebrate population of borers and detritus feeders can also hasten the release of nutrients and oxygen-demanding matter into the overlying waters and simultaneously permit increased oxygen transport into the sediments. The relative magnitude of each of these components will vary with:

1. dissolved oxygen concentration, turbulence and velocity of the overlying waters;
2. physical, chemical and biological characteristics of the deposits; and
3. diffusion rates of oxygen and reduced substances through the water and sediments.

Benthic oxygen demand incorporates numerous complex physical, chemical and biological processes, including the following:

1. Oxygen diffusion down to the sediment-water interface.
2. Oxygen diffusion down into the sediments.
3. Respiration by micro-organisms and macro-organisms in the aerobic sediment layer.
4. Production and release of reduced substances by organisms in the anaerobic sediment layer.
5. Diffusion of reduced substances up through the sediments.
6. Biological oxidation/utilisation of reduced substances by organisms in the aerobic sediment layer.
7. Chemical oxidation of reduced substances in the aerobic sediment layer.
8. Adsorption/ion exchange of reduced substances in the aerobic sediment layer.
9. Diffusion of reduced substances up into overlying waters.
10. Chemical and biological oxidation/utilisation of reduced substances in overlying waters.

Oxygen concentration-dependent mechanisms include oxygen diffusion to and into the sediments, chemical oxidation of reduced substances in the aerobic sediment layer and in the overlying water, and macro-organism respiration. Oxygen concentration-independent mechanisms include micro-organism respiration (Harrison 1976) and the production, release, and transport of reduced substances in and through the sediments. Therefore, where microbial respiration predominates and only small amounts of reduced substances are present for chemical oxidation, SOD would be expected to be relatively independent of DO concentration (Chiaro & Burke 1980).

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Perspectives for plant metabolism in aquatic oxygen models

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This paper discusses the factors which should be accommodated when measurements of *in situ* oxygen production by submerged water plants are used in dissolved oxygen models.

It is particularly important to establish whether oxygen produced by submerged water plants enters the dissolved oxygen pool or whether conditions of local and transitory oxygen supersaturation result in a loss of photosynthetically produced oxygen to the atmosphere. Water circulation, the degree of saturation of dissolved oxygen in the water surrounding submerged plant communities, plant density and the maximum rate of diurnal oxygen release from submerged plant communities are all relevant to the fate of oxygen produced by plant metabolism.

Methods used to measure primary production of water plants are discussed in relation to these modelling questions.

Introduction

Oxygen is present in lower concentrations and is subject to larger fluctuations of concentration in natural waters than in air. A given volume of water can be expected to contain less than 5% of the oxygen present in an equivalent volume of air and its rate of diffusion is several thousand times less in water than in air. This implies that aquatic plants and animals are more likely to be stressed by oxygen concentration than terrestrial species.

Dissolved oxygen concentrations in a water body are influenced by:

(a) interchange of oxygen through the air-water interface where the direction of transfer will depend upon the degree of saturation of dissolved oxygen;

(b) consumption of oxygen in the water and sediments by direct chemical oxidation and by the respiration of plants and animals (including aerobic decomposition of organic matter by fungi and bacteria);

(c) production of oxygen by the photosynthetic activity of aquatic plants;

(d) flushing of the water body by water with a different oxygen content, oxygen demand, or plant population.

Aquatic plants have the potential to contribute dissolved oxygen to natural waters during periods of carbon fixation by photosynthesis but this potential may not always be realised. Moreover, standard methods for estimating primary productivity in natural waters can give quite misleading impressions regarding the significance of aquatic plants to the dissolved oxygen pool.

The objective of this discussion is to provide perspectives on the significance of plant metabolism to dissolved oxygen models, together with reference to and comment on the assessment of primary productivity in natural waters.

Theoretical considerations

A plant which is aerobically decomposed after its death has made no nett contribution to oxygen concentration in its environment. During its lifetime however, the quantity of free oxygen which is released into the environment is stoichiometrically related to the amount of carbon fixed by that plant which has not been aerobically degraded to CO_2. This will include plant biomass, animal biomass derived from the plant and organic litter. It is common for a proportion of the carbon fixed by a plant to remain as litter or to be in the form of animal biomass after the death of the parent plant; hence primary productivity studies are concerned with the nett accumulation of organic matter with time.

Perhaps a more important consideration in the case of aquatic habitats is the fate of oxygen which is produced by aquatic plants. There are a variety of situations in which the oxygen they produce can be lost to the atmosphere without entering the dissolved oxygen pool.

The effect of aquatic plant life form

The only aquatic plants which are likely to contribute oxygen to the dissolved oxygen pool are those with their photosynthetic tissue in the water.

Free floating aquatic plants may reduce dissolved oxygen levels in a water body. Firstly, when present as a complete surface cover, they prevent wind mixing of the water body; secondly, they shade out submerged plants; and thirdly, it is their respiratory tissue which is in the water—their photosynthetic tissue probably releases oxygen direct to the atmosphere. A complete surface cover of these plants on standing water bodies is normally associated with anoxic conditions.

In shallow closed systems emergent species can have an impact similar to that of free floating species. As with the free floaters, they contribute moribund organic matter; thus BOD may increase and may not contribute to the dissolved oxygen pool.

Submerged species include phytoplankton, periphyton, and macrophytes. The relative importance of phytoplankton versus macrophytes can be established by quantitative surveys but it is frequently related to the proportion of a water body occupied by the littoral zone (macrophytes) compared to the volume of the euphotic zone (plankton). Little quantitative data are available on the importance of periphyton.

Oxygen which is produced by submerged plant communities can, theoretically, increase dissolved oxygen concentrations by a factor of five relative to saturation for an air-water interface (100% O_2 cf 21% O_2 for air). Indeed, 200% saturation for dissolved oxygen is common in water surrounding aquatic plants during periods of active photosynthesis. Such supersaturation is usually local and transitory and it results in a net loss of oxygen to the atmosphere. Oxygen exchange between areas of high and low O_2 concentration depends upon the degree of under- or over-saturation, the area of the interface, the velocity of water currents, and water depth.

In all cases it is the density of the submerged plant community and the rate at which oxygen is produced relative to water mixing which will determine the fate of the oxygen produced. A dense submerged plant community which produces supersaturated conditions for a short period of a diurnal cycle can result in a loss of a major proportion of that oxygen to the atmosphere. The respiratory requirements of that community for the remainder of the diurnal cycle must be met from the dissolved oxygen pool. Dissolved oxygen concentrations can fall to very low levels in dense submerged plant stands immediately before sunrise.

When modelling dissolved oxygen in a water body where aquatic plant metabolism is suspected to be a significant factor, the following questions should be posed:

1. What nett quantity of carbon is being fixed per unit time? It follows that a proportional amount of oxygen has been produced.
2. What is the fate of the oxygen produced with regard to the dissolved oxygen pool and the atmosphere?
3. What are the diurnal maxima and minima of dissolved oxygen which result from the presence of the plants?

Plant metabolism

The majority of studies on aquatic plants have considered primary production (i.e., the production of organic material using an external energy source or the capacity of the community or ecosystem to build up, at the expense of external energy, primary organic compounds of high chemical potentials). The energy source for this carbon fixation is usually sunlight, but can also be energy derived by oxidising chemical compounds (chemo-autotrophs). Such an approach tends to suggest photosynthesis and primary productivity are synonymous. Primary production, however, includes chemo-autotrophic processes as well.

Before considering the techniques available for estimating primary productivity or oxygen budgets for aquatic plants, it is necessary to consider the mode of action of oxygen exchange in submerged aquatics.

Green plants are autotrophic in their mode of nutrition. They have the ability to "fix" (as sugar) carbon derived from atmospheric or dissolved carbon dioxide using radiant energy and the photosynthetic apparatus of the chloroplast according to the generalised equation:

$$CO_2 + H_2O \rightarrow (CH_2O) + O_2 + H_2O$$

with the free oxygen produced being derived from the water entering the reaction.

Due to respiration, the total flux of carbon through the plant during 24 hours is greater than the nett accumulation of carbon. Dark fixation (light independent) of carbon dioxide (via β carboxylation), using metabolically released energy (chemosynthesis) also contributes to the carbon budget of a plant, particularly in drought-adapted succulents with crassulacean acid metabolism (CAM). Many plants also exhibit photorespiration which is an additional metabolic activity occurring only when the plant is illuminated. The substrate for photorespiration is glycolic acid which is formed under conditions of high oxygen concentration and low carbon dioxide concentration and, as with normal respiration, results in oxygen utilisation and the evolution of carbon dioxide.

There has been a great deal of recent work concerning the photosynthetic categories of plants with regard to carboxylation pathways, carbon dioxide compensation points, photorespiration, glycolate metabolism, and carbon isotope ratios. Black (1973) defined the characteristics of three apparently distinct groups of terrestrial plants, the C_3, the C_4, and the CAM plants. These three categories almost certainly represent photosynthetic adaptations to specialised terrestrial conditions. It is not surprising, therefore, that submerged aquatics do not show consistent relationships between carboxylation pathways and characteristics such as the magnitude of detectable photorespiration and $^{13}C/^{12}C$ ratios.

Available evidence (e.g., Stanley & Naylor 1972; Van *et al.* 1976; Winter 1978) suggests that aquatics generally utilise the classical C_3 carboxylation pathway but both C_3 and C_4 pathways can operate in at least some submerged macrophytes under different environmental conditions, for example pH (Brown *et al.* 1974), or at different

times of the year (Bowes *et al.* 1978). Species with the ability to invoke C_4 carboxylation would have the capacity to re-utilise respiratory CO_2 and retain a greater proportion of available CO_2 than species with only C_3 pathways. Photorespiration as indicated by decreased nett photosynthesis with increased oxygen concentration is also widespread in both submerged macrophytes and microphytes. It is particularly significant in the case of light-dark-bottle oxygen studies with phytoplankton and in the case of vascular hydrophytes with internal lacunae. Carbon dioxide compensation points also appear to be variable in submerged aquatics as is their ability to use bicarbonate in addition to free CO_2 as a carbon source for photosynthesis.

It is already clear that the storage and re-utilisation of metabolic gases within the internal lacunae of submerged vascular hydrophytes result in delayed changes of dissolved gases in the water surrounding their photosynthetic tissue. These changes reflect the impact of the plant community on environmental conditions within its immediate vicinity but are not necessarily a true reflection of either the timing or the magnitude of metabolic activity. It is also likely that CO_2 supply from the sediments (via the roots and the lacunal system to photosynthetic tissue) and the downward transport of oxygen to the roots of these species should also be considered when carbon/oxygen budgets are being proposed.

The measurement of submerged plant metabolism

There are three approaches used to describe plant metabolism in water:

(a) isolation of samples of natural communities in enclosures to exclude reaeration and mixing, with monitoring of short term carbon/oxygen budgets;

(b) monitoring of conditions in non-isolated communities using O_2, pH, alkalinity or conductivity as indicators of metabolism;

(c) indirect measures using change per unit time of biomass, nutrient concentration, hypolimnetic oxygen consumption or CO_2 accumulation as indicators of metabolism.

All have inherent problems and it is necessary to define the objectives of field investigations before choosing an appropriate technique. The recommended starting point for a description of techniques is Vollenweider (1974). A discussion of the application of primary productivity techniques for New Zealand conditions is available by Burns (1979).

Phytoplankton techniques

The two methods most commonly used to assess the rate at which new organic matter is formed by photosynthesis and accumulates within a water body are the "Oxygen, Light-and-Dark-Bottle Method" and the ^{14}C Method. The oxygen method is suitable for use in waters of high productivity; the ^{14}C method is more appropriate for waters of low productivity.

A time series of short term incubations at selected depths in a water body can be integrated on a diurnal, seasonal, or annual basis to arrive at oxygen production rates in the euphotic zone. Notwithstanding the precautions required when using these techniques, it is necessary to consider the fundamental assumptions made with regard to plant metabolism.

1 Solar energy is the sole source of energy available for carbon fixation

Fixation of CO_2 may be the result of "dark" carboxylation reactions involving scarcely any gain in potential chemical energy. These reactions may be suppressed by light (Fogg 1963) and cannot be corrected for by subtracting ^{14}C fixation in dark bottles from that fixed in light bottles.

2 The photosynthetic quotient is 1.0

This assumption is true when carbohydrates are the principal products of carboxylation, but the PQ may be less than 1.0 due to the synthesis of organic acids or greater than 1.0 due to the synthesis of fats and proteins. The mineral nutrition of the plant may also be reflected in the photosynthetic quotient for if its nitrogen source is in the form of ammonia, for example, (a reduced state) the PQ may be less than if nitrate is available and used (Ryther 1956).

3 Light and dark respiration occur at the same rate

Errors can be introduced if the rate of respiratory uptake of oxygen varies with light intensity or with oxygen concentration (Gessner & Panier 1958) and so differs between clear and dark bottles or between clear bottles at various levels of illumination.

4 The products of carboxylation remain in the algal cells

The loss of soluble organic compounds from the cells or phytoplankton has been discussed by Watt (1965) and Fogg *et al.* (1965). They report losses of total carbon fixed ranging from 1% in eutrophic waters to 35% in oligotrophic waters.

5 Enclosure problems can be ignored

This assumption should be tested in any experimental programme due to the possibility of buoyant rise or sedimentation of algae in the absence of turbulence and water circulation, population changes during enclosure (particularly bacterial production) and depletion of nutrients. The accumulation of high oxygen concentrations and depletion of CO_2 supply are other problems which may be obviated by limiting the duration of the incubation.

Submerged macrophyte techniques

It is more common to describe indirect measures of primary production for submerged macrophytes (e.g., dry weight increase with time) or to monitor conditions in non-isolated communities. Direct measurements of metabolism may be required in dissolved oxygen models and techniques which are available for this purpose are described by Vollenweider (1974).

The problems listed for algae in enclosures are also applicable in the case of incubating macrophytes. Additional problems associated with the pooling of gases in internal air spaces and the transport of gases to and from the sediments have been mentioned earlier. The latter consideration severely questions the validity of using isolated shoots for short term studies of carbon/oxygen exchange.

The local and transitory impact of submerged macrophytes on dissolved gases as measured in non-isolated communities is depicted in Fig. 1 and 2. These results are for two occasions, February 1971 (summer) and August 1971 (winter) where water samples were collected from the photosynthetic canopy of submerged weed beds, and at open water stations adjacent to these weed beds, in Lakes Whakamaru and Karapiro. The samples were collected at 2-hour intervals over a 24-hour period, to assess diurnal pH and oxygen fluctuations due to submerged macrophyte metabolism.

The pH was lower in the interstitial photosynthetic zone during the hours of darkness, relative to open water stations, but this situation was reversed a short time after sunrise (Fig. 1). The winter maximum was less than the summer maximum, Whakamaru 10.5 cf 11.8 and Karapiro 10.6 cf 11.9; furthermore the timing at maximum pH was later in the day during the winter than in the summer, 1200 hrs cf 1100 hrs.

A lower pH in the weed beds relative to open water stations at night indicates a nett respiratory release of free CO_2 from the weed beds. Conversely a rise of pH above 8.2 during the morning indicates photosynthetic uptake and depletion of all available CO_2 by the weed beds from water adjacent to their foliage.

The same trends were apparent for oxygen (Fig. 2). Within the photosynthetic canopy, diurnal maxima occurred at 1200 hrs (14.3 mg/ℓ) at the Whakamaru station and 1000 hrs (14.5 mg/ℓ) at the Karapiro station during the February 1971 survey. Diurnal maxima during the August 1971 survey were 11.7 mg/ℓ (1400 hrs) for Whakamaru and 13.0 mg/ℓ(1200 to 1400 hrs) for Karapiro.

Diurnal minima for dissolved oxygen within the photosynthetic canopy were lower than diurnal minima at the adjacent open water station suggesting that these dense submerged weeds could make a demand on the general dissolved oxygen during the night.

Open water oxygen values for both pH and dissolved oxygen showed a relatively depressed diurnal fluctuation due to phytoplankton metabolism.

A considerable increase of sophistication is required if a sampling programme is to answer the question posed earlier with regard to the fate of the oxygen produced from such communities.

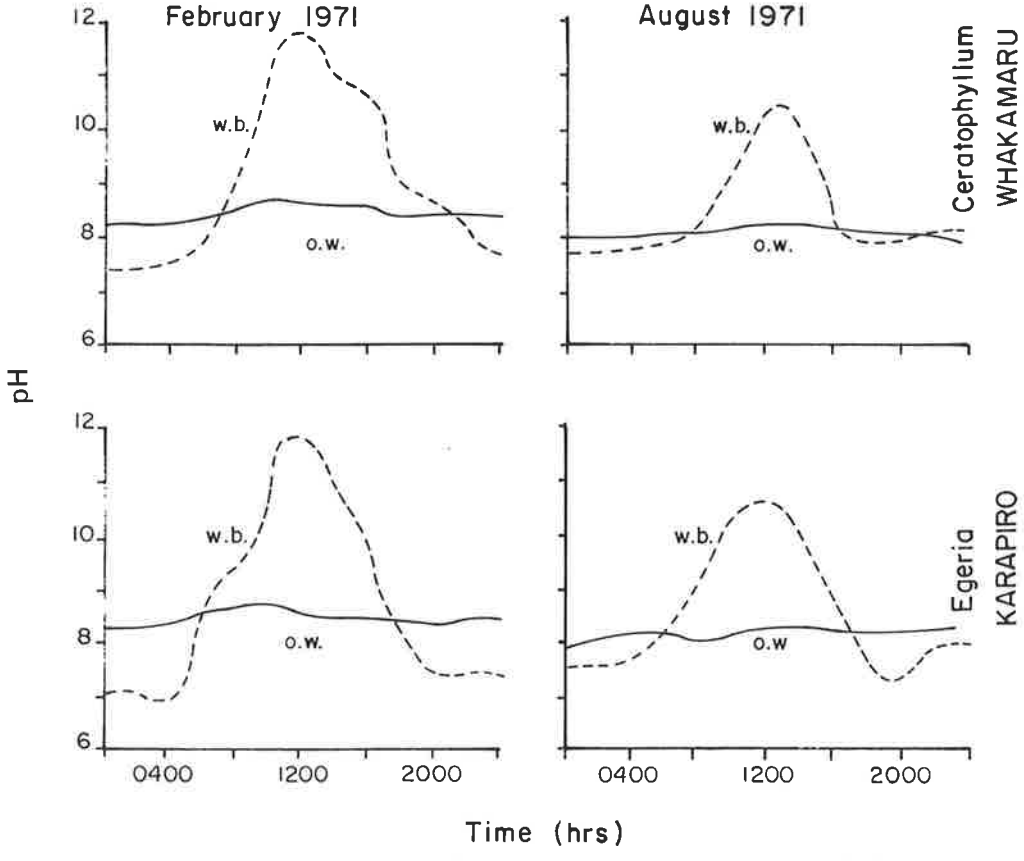

Fig. 1 Diurnal pH surveys (February and August 1971) within the photosynthetic canopy (w.b.) of the dominant plant community in Lakes Whakamaru and Karapiro, and at an open water station (o.w.) adjacent to the plant community.

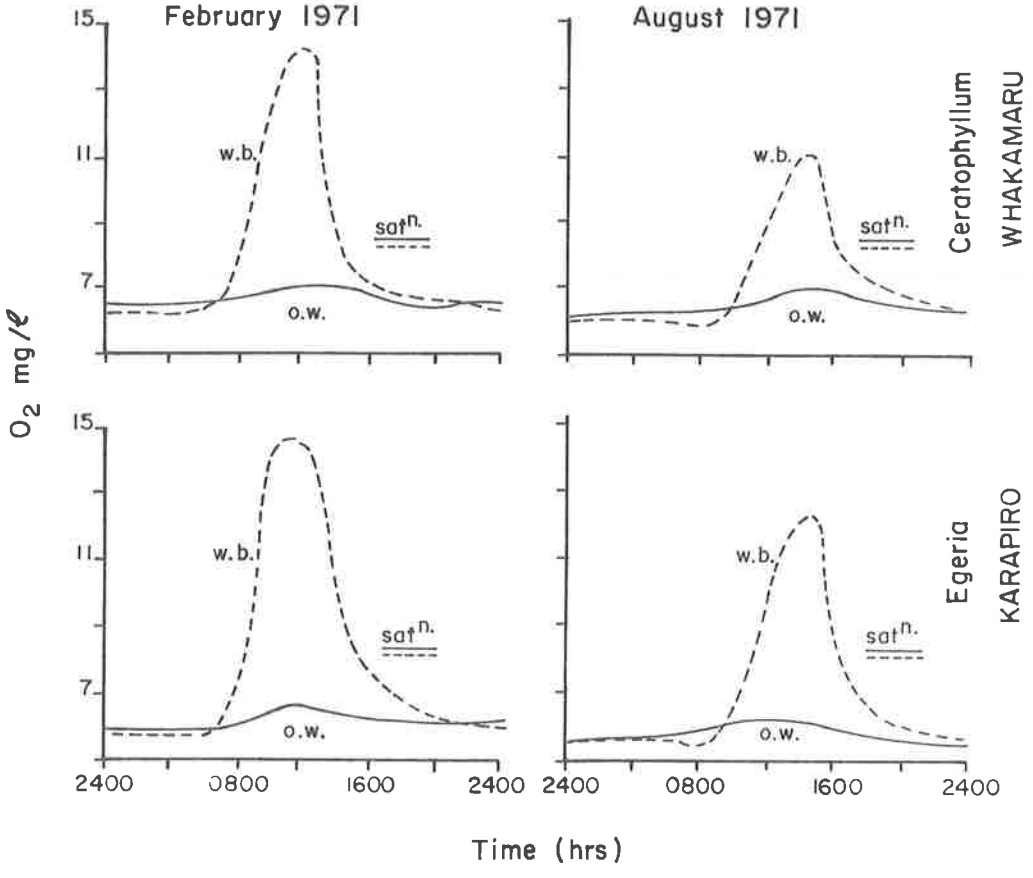

Fig. 2 Diurnal oxygen surveys (February and August 1971) within the photosynthetic canopy (w.b.) of the dominant plant community in Lakes Whakamaru and Karapiro, and at an open water station (o.w.) adjacent to the plant community.

Conclusions

Plant metabolism can contribute oxygen to the dissolved oxygen pool in natural waters where there is a nett accumulation of organic matter with time. This potential is only realised in the case of submerged plants. Emergent and free floating macrophytes represent an oxygen deficit relative to the dissolved oxygen pool.

Where there is free water circulation through low density submerged plant communities and where oxygen produced by these communities is adding to an undersaturated dissolved oxygen pool, plant metabolism may make a significant contribution to that dissolved oxygen pool. Where dense submerged plant communities restrict water movement and/or produce local and transitory conditions of oxygen supersaturation it is likely that a major proportion of the oxygen produced is lost to the atmosphere.

Photosynthesis is a complex of reactions which do not necessarily have fixed relationships with each other. Plant metabolism cannot be inferred from simplistic interpretations of nett or gross changes in dissolved oxygen or free CO_2, particularly in the case of submerged macrophytes.

Management implications

It is a comparatively simple procedure to show the potential contribution aquatic plant metabolism could make to the dissolved oxygen budget in a water body, with standard sampling techniques. It is also a comparatively simple procedure to describe the effect of all contributing factors to the dissolved oxygen budget in a water body, and provided anoxic conditions are not reached or minimum dissolved oxygen standards exceeded on a diurnal or seasonal basis, it may not be necessary to quantify the individual components in the system.

A major increase of sophistication is required both for sampling and for interpretation, if the quantity of oxygen, and the fate of the oxygen produced by plant metabolism, is to be included in dissolved oxygen models.

The removal of dense moribund plant populations (particularly macrophytes which are amenable to mechanical removal) should be considered as a technique for removing oxygen deficits from water bodies where dissolved oxygen levels are of concern.

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Atmospheric reaeration of rivers and streams

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Atmospheric oxygenation in well mixed streams is reviewed, with particular emphasis on the means of estimating the reaeration coefficient, k_2. This is discussed in terms of predictive equations, oxygen balance techniques, and direct measurements. Simple expressions for k_2 in terms of velocity and depth can be chosen for any particular case by adopting the approach of Covar, and choosing the empirical equation derived from the nearest hydraulic conditions. The gas tracer technique is the best direct and independent means of measuring k_2.

Introduction

The presence of organic pollutants in natural waters invariably generates an oxygen demand associated with the biological decay of these substances. Reaeration is the natural process for redressing this imbalance and controls the maximum rate at which a water having a dissolved oxygen (DO) deficit may achieve its saturation, or equilibrium, concentration.

Oxygen balance studies are conducted with a view to understanding better the oxygen dynamics of rivers and streams so that planners and water boards may predict the outcome of pollution incidents, or assess the maximum assimilative capacity (for organic wastes) of these waters. In order to make such predictions it is essential to know the biochemical oxygen demand (BOD) rate coefficient, and the natural reaeration coefficient of the streams in question. The subject of BOD kinetics has been dealt with earlier in the seminar (session III) and this paper will deal only with reaeration, and in particular the reaeration coefficient, k_2.

The rate at which aquatic oxygen exchanges with the atmosphere is determined by both the bulk water diffusion rate (for DO) and the air-water, or interfacial, diffusion rate. In streams there is generally sufficient natural turbulence to ensure rapid mixing within the bulk water, so that the overall rate of aeration is dependent upon the molecular diffusion rate at the air-water interface. From Fick's first law of diffusion Adeney & Becker (1919) were able to show that the rate of change of DO concentration (c) with time (t) is given by

$$\frac{dC}{dt} = k_2 (C_s - C) \qquad (1)$$

$$\ln \frac{(C_s - C_1)}{(C_s - C_2)} = k_2(t_2 - t_1) \qquad (2)$$

where C_s is the saturation DO at the temperatures of the water, C_1 and C_2 are particular DO values at t_1 and t_2 and k_2 is the reaeration coefficient (base e).
(NB: Reaeration coefficients are often expressed to base 10, with k_2 (base 10) = 0.434 k_2 (base e). All references throughout this paper will be to base e coefficients.)

For a given water surface area A, and volume V the reaeration coefficient is related to the oxygen water mass transfer coefficient, k_L (base e) by

$$k_2 = k_L (A/V) \qquad (3)$$

The many theories for gas-liquid mass transfer show k_L to be a function of the molecular diffusivity, D_m, of the diffusing gas, and the state of turbulence of the water. Predictive equations for the reaeration coefficient are similarly based, and the k_2 values derived from them may be critically examined either by substituting them into river-model equations and noting the agreement between observed and predicted values of certain parameters, or by direct comparison with experimentally measured values of k_2.

Oxygen balance equations

The various equations for DO modelling of natural waters will be discussed later in the seminar. These equations generally describe DO profiles in terms of the known sources and sinks of oxygen in each system, and the best known of these equations is that developed by Streeter & Phelps (1925).

1 The Streeter-Phelps equation

This states that the rate of DO depletion is proportional to the amount of organic material present, expressed as biochemical oxygen demand, L, so that

$$\frac{dC}{dt} = k_2 (C_s - C) - k_1 L \qquad (4)$$

where k_1 is the BOD rate constant. The solution to this differential equation is

$$D_t = \frac{k_1 L_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) + D_0 e^{-k_2 t} \qquad (5)$$

where D_0 and D_t are the initial and instantaneous DO deficits $(C_s - C)$ respectively, and L_0 is the initial BOD. The reaeration coefficient, k_2, is chosen to give the best agreement with the observed DO profile.

This approach is not always applicable in natural streams because of the difficulty in identifying or quantifying all sources and sinks of DO, such as algal respiration and photosynthesis or benthic oxygen demands. As a consequence, k_2 values determined by this method are frequently not accurate estimations of solely atmospheric reaeration.

2 Reaeration by productivity analysis

This method was first described by Odum (1956), and later developed by Hornberger & Kelly (1975). The model includes respiration and photosynthesis terms in the oxygen balance, and is based upon the assumption that at night photosynthetic activity is negligible and respiration is at a constant rate. Hence, by measuring $\Delta C/\Delta t$ in a suitably oxygen-depleted stream at two different times (usually just after sunset and just before sunrise) it is possible to calculate both k_2 and the community respiration rate. However, the assumption of constant respiration rate is not always valid and the technique tends to give unreliable answers if the difference between the two measured reaeration rates is not large.

Direct measurements

Direct measurements usually entail monitoring the change in DO with time in a suitably oxygen-depleted stream, and making certain assumptions about the other sources and sinks of DO. The reaeration coefficient is calculated using equation (2).

1 Disturbed equilibrium techniques

In these methods the stream DO is artificially lowered, usually by the reaction with sodium sulphite and cobalt catalyst (Edwards *et al.* 1961; Gameson & Truesdale 1959), according to

$$SO_3^{2-} + \tfrac{1}{2}O_2 = SO_4^{2-}$$

The reaeration rate is studied at a number of different initial DO concentrations so that if C_s, the stream velocity (U) and k_2 are constant for a given reach then k_2 may be deduced from equation (2). Experiments of this kind are often conducted at night to eliminate photosynthesis effects, and are limited for practical reasons to rather small streams (Zogorski & Faust 1973). The mandatory assumption of the technique(s) that respiration is independent of the DO concentration, is questionable (Rathbun 1977).

2 The dome method

This method, developed by Copeland & Duffer (1964), uses a clear plastic dome which floats on the water to measure volumetrically the oxygen lost from the atmosphere to reaeration. The oxygen concentrations of both the gas phase under the dome, and the water, are monitored continuously, and only night time readings are used for calculating the reaeration coefficient. These values are then used for obtaining day time reaeration rates at comparable conditions of turbulence and wind velocity.

The technique requires that the river depth below the "dome" be known, in order to give k_2 in the appropriate units of time. Substantial errors may arise from the volumetric calculations, which are often the difference between numbers of similar magnitude.

3 The gas tracer technique

This technique was first proposed by Tsivoglou *et al.* (1965, 1968, 1976), who reported that atmospheric oxygen uptake in natural waters could be studied, by adding a known quantity of ^{85}Kr and tracing its loss from solution with time. Krypton-85 is a radioactive isotope and may be detected at extremely low levels, by the liquid scintillation counting technique.

The theoretical basis for the formal analogy between the mass transfer rates for ^{85}Kr and O_2 is provided by Einstein's law of diffusion (Moelwyn-Hughes 1971)

$$D_m = kT/\phi \qquad (6)$$

where k is the Boltzmann constant, T is the absolute temperature and ϕ is a function of the size and shape of the diffusing gas molecule and is approximated by the molecular diameter d. Clearly, for the simultaneous diffusion of two gases across the air-water interface of a well-mixed water the relative rates of diffusion, and therefore mass transfer, are inversely proportional to their molecular diameters, or

$$k_L{}^a/k_L{}^b = d^b/d^a \qquad (7)$$

The same relationship holds for the reaeration (gas exchange) coefficients (equation 3) so that for d_{Kr} = 0.369 nm and d_{O_2} = 0.298 nm

$$k_2(Kr)/k_2(O_2) = 0.81 \qquad (8)$$

Tsivoglou *et al.* (1965) have verified this ratio experimentally in laboratory trials and found that it is relatively constant over the range 10–32 °C. (Actually, the temperature dependence of k_2 has been determined empirically for the range 10–30 °C to be (Elmore & West 1961)

$$k_2\,(t°C) = k_2\,(20°C)\,(1.0241)^{t-20} \qquad (9)$$

Other relationships derived either empirically or theoretically give similar results.)

In practice a known quantity of ^{85}Kr is combined with an exact amount of suitable dispersion indicator, such as tritium or rhodamine-WT, and added to the river at a specific site. The tracer and indicator are followed downstream (up to 8 km/dose) and the ratios of their concentrations analysed according to the equations

$$D_t = D_o e^{-k_2 t} \qquad (10)$$

in which D_t and D_o are the oxygen deficits at time (t), and t = 0 respectively, and

$$A_t = A_o e^{-k_{Kr} t} \qquad (11)$$

where A_t and A_o are the corresponding ^{85}Kr activities, or concentration ratios, [Krypton]/[tracer]. It is then a simple matter to calculate reaeration coefficients for selected reaches, without the need for information about other sources and sinks of DO.

The tracer technique has been tested and found satisfactory on a wide range of American rivers with different flow characteristics and pollution loadings. Some objections to the use of radioisotopes has prompted Rathbun *et al.* (1978) to experiment with

non-radioactive tracers, and it is hoped to establish a similar approach to the technique here, at the Hamilton Science Centre.

Predictive equations

Equations for calculating the reaeration coefficient fall into three classes.

1 Conceptual models

These are based upon mass transfer concepts, kinetic theory, eddy diffusion or turbulent flow theories. The models generate parameters such as surface-film thickness, rate of surface renewal, and eddy size, that cannot be readily estimated in the laboratory let alone determined for natural streams. Approximations are necessary for such equations or alternatively, empirically derived coefficients may be employed to give the best fit with observed data.

The most widely used formula from this category is that of O'Connor & Dobbins (1958), namely

$$k_2(\text{days}^{-1}) = \frac{(D_m U)^{1/2}}{H^{3/2}} \qquad (12)$$

where U is the stream velocity and H is average stream depth.

Other examples of this group of formulae for k_2 are given in Table 1.

2 Semi-empirical models

These approaches to the mass transfer process are based upon the application of regression analysis to one or more coefficients to obtain the best agreement between a theoretically derived equation and a set of experimental data. The models include those based upon the rate of energy dissipation and those in which k_2 is correlated with the longitudinal dispersion coefficient. An example of the former case is that of Krenkel & Orlob (1963), namely

$$k_2(\text{days}^{-1}) = 264\ (US)^{0.408}H^{-0.660}(\text{fps units}) \qquad (13)$$

where S is the slope gradient (ft/ft or m/m).

Table 1 Some predictive equations for the reaeration coefficient (base e) in days^{-1}

Reference	Formula for k_2	Units	Temperature	Origin of equation
O'Connor & Dobbins 1958	$(D_m U)^{1/2} H^{-3/2}$	ACU	0–30 °C	film penetration theory
O'Connor & Dobbins 1958	$4.206 U^{1/2} H^{-3/2}$	metric	25 °C	film penetration theory
Dobbins 1965	$\frac{0.276 C_A F E^{0.375} \coth \left[BE^{0.125}/C_4^{1.5}H\right]}{C_4^{0.125} H}$	fps	0–30 °C	liquid film thickness
Thackston & Krenkel 1969	$24.9\ (1 + Fr^{0.25}) U^* H^{-1}$	ACU	20 °C	rate of surface renewal a function of shear velocity
Krenkel & Orlob 1963	$196 (US)^{0.408} H^{-0.660}$	metric	25 °C	energy dissipation
Churchill *et al.* 1962	$0.02446 U^{2.695} H^{-3.085} S^{-0.832}$	metric	25 °C	correlation with D_L
Parkhurst & Pomeroy 1972	$54.5(1 + 0.17\ Fr^2)\ (US)^{3/8} (H)^{-1}$	fps	25 °C	surface renewal
Bennett & Rathbun 1971	$36.8 U^{0.413} S^{0.273} H^{-1.408}$	metric	25 °C	empirical review of data
Churchill *et al.* 1962	$5.013 U^{0.969} H^{-1.673}$	metric	20 °C	empirical
Isaacs & Gaudy 1968	$c D m H^{-2} (N_R)^{2/3} (N_S)^{1/2} (Fr)^{1/6}$	ACU	20 °C	dimensional analysis
Isaacs & Gaudy 1968	$4.754 U H^{-3/2}$	metric	20 °C	empirical
Langbein & Durum 1967	$5.13 U H^{-1.33}$	metric	20 °C	empirical review of data from several sources
Negulescu & Rojanski 1969	$3.79 \times 10^{-5} D_L (U/H)^{1.673}$	fps	20 °C	regression analysis
Negulescu & Rojanski 1969	$10.9\ (U/H)^{0.85}$	ACU	20 °C	regression analysis
Owens *et al.* 1964	$5.34 U^{0.67} H^{-1.85}$	metric	20 °C	regression analysis

NB: Reaeration coefficients at temperatures other than those given may be calculated using equation (9).

Glossary

ACU	=	any compatible units
C_A	=	1.0 + Fr
C_4	=	0.9 + $(Fr)^{0.5}$
Fr	=	U^2/gH (Froude Number)
g	=	gravitational acceleration
F	=	9.08 + 0.054 (τ–20)
B	=	0.976 + 0.0137 (30–τ)
E	=	30.0 SU
U*	=	friction velocity
c	=	a constant
D_L	=	longitudinal dispersion coefficient
N_R	=	ρ UH/μ (Reynolds Number)
N_S	=	ν/Dm (Schmidt Number)
ρ	=	water density
μ	=	absolute viscosity
ν	=	kinematic viscosity (μ/ρ)

An example of the second type, based upon correlation with the longitudinal dispersion coefficient, is the equation of Churchill *et al.* (1962).

$$k_2(\text{days}^{-1}) = \frac{0.03888U^{2.695}}{H^{3.085}S^{0.823}} \text{(fps units)} \quad (14)$$

Many of these equations may only be applied over a narrow range of flow conditions and Wilson & MacLeod (1974) in their excellent review of predictive equations assert that there is a fundamental lack of understanding about which variables have a significant effect upon the rate of oxygenation. This is reflected in the wide range of variables used in the various reaeration equations, in Table 1.

3 Empirical equations

This class of formulae for k_2 are generally of the form

$$k_2 = \frac{aU^b}{H^c} \quad (15)$$

where a, b and c are determined by multiple regression analysis. These equations, like the semi-empirical relationships, are often applicable only over narrow ranges of stream flow conditions, probably as a consequence of the choice of variables.

A number of empirical relationships have been derived from application of dimensional analysis to variables thought likely to have a significant effect upon k_2. These variables are arranged into dimensionless groups, which are then correlated with k_2 to give the best agreement (Wilson & MacLeod 1974).

The diversity of (all) these equations and their uncertain reliability in field situations again indicates that the understanding of the important factors necessary for accurately predicting the reaeration coefficient is far from satisfactory. Table 1 exemplifies the diversity of formulae used for predicting k_2.

It is obvious then that for anyone engaged in oxygen balance studies the question that arises is "which formula should be used for estimating the reaeration coefficient?".

Choosing the appropriate equation

In evaluating which of the predictive equations for k_2 may suit a given set of conditions, it should be realised that this may not be easily accomplished without actually testing the formulae empirically. This is because of the difficulty in relating the conditions of turbulence and mixing used in developing an equation, to those of the system one may wish to study.

Bennett & Rathbun (1971) examined many equations for k_2, using the "standard error" technique, and concluded that the equations giving the best agreement with a wide range of experimental data were those of Dobbins (1965), and Thackston & Krenkel (1969). Wilson & MacLeod (1974), in their review, compared a number of equations with an extremely large body of data, which included both river measurements and laboratory flume data. They concluded that predictive equations expressed only in terms of velocity and depth (i.e., equation 15) were not satisfactory over the entire range of data. In general, the Dobbins equations (1965), and those of Parkhurst & Pomeroy (1972), had the best overall fit with the data.

The conclusions of these reviews, as well as that of Rathbun (1977), in which the rather more complex expressions involving various indicies of turbulence are recommended, are not supported by Tsivoglou & Wallace (1972). They reviewed several equations by comparing them with data gained from tracer studies and concluded that the comparatively simple expressions of Isaacs & Gaudy (1968), and Langbein & Durum (1967) gave the best overall agreement.

The lack of any consensus among reviewers, concerning the best predictive equation for k_2, indicates that no single equation is superior for all hydraulic conditions. It would seem that the experimental data obtained by Tsivoglou from tracer measurements is probably the most reliable set of measured k_2 values and, on the basis of this, the simple equations of Isaacs & Gaudy (1968), and Langbein & Durum (1967), may be the best of a dubious bunch. Table 2 compares these equations, along with those of Churchill *et al.* (1962) and O'Connor & Dobbins (1958) (probably the two most widely used equations for predicting k_2), for a variety of hydraulic conditions. This shows reasonable agreement for some conditions but a rather poor agreement at higher values of k_2.

Covar (1976) has devised a useful means of choosing the appropriate expression for the reaeration coefficient. His approach is to plot the

Table 2 Comparison of different equations for the reaeration coefficient.

Authors	$k_{2(20\,°C)}$ (days^{-1})	value of k_2(days^{-1}) A	B	C
O'Connor & Dobbins (1958)	$3.734U^{½}H^{-3/2}$	22.9	2.94	0.36
Churchill *et al.* (1962)	$5.013U^{0.969}H^{-1.673}$	23.1	3.43	0.36
Isaacs & Gaudy (1965)	$4.754U\ H^{-3/2}$	15.9	3.26	0.44
Langbein & Durum (1967)	$5.13U\ H^{-1.33}$	13.1	3.56	0.62
	mean ± %	18.8 ± 30%	3.30 ± 11%	0.47 ± 31%

Note: Flow conditions for A, B and C are as follows:
A : Velocity = 0.30 m/s ; Depth = 0.20 m
B : Velocity = 0.76 m/s ; Depth = 1.07 m
C : Velocity = 0.91 m/s : Depth = 4.57 m

original experimental U–H data used to derive or test the predictive equations, and show where different equations predict the same results. Agreement between any two equations occurs usually where similar test conditions have existed, and Covar takes this as lending credence to the work of both groups of researchers.

The four equations in Table 2 are based mainly on two independent sets of data, the O'Connor-Dobbins results (1958) and the Churchill-Elmore-Buckingham data (1962). These are shown in Fig. 1, along with families of constant-k_2 curves for the respective predictive equations of these workers, and the line where the k_2 values coincide. The diagram clearly indicates the conditions of stream depth and velocity for which each of these equations is applicable, with the region below the line of coincidence being more appropriately described by the O'Connor-Dobbins equation, while the region above the line is more accurately described by the expression of Churchill–Elmore–Buckingham. It should be noted that for those areas of the U–H diagram that are remote from any data points, neither predictive equation may be justifiably used to predict the reaeration coefficient.

The technique is complicated by the fact that many predictive equations, including some of the more favoured ones such as Langbein & Durum's (1967) or Isaac & Gaudy's (1968) are derived from the same data as other equations. Indeed, because of the scarcity of good field data, most of the predictive equations have been obtained from the results of a small number of workers (O'Connor & Dobbins 1958; Krenkel & Orlob 1963; Churchill *et al.* 1962).

Figure 2 shows the lines of coincident-k_2-values for different pairs of the four equations in Table 2. It is readily apparent that the best agreement occurs in the region where there are several intersecting lines, i.e., at a depth of 0.6–1.7 m and a stream velocity of 0.45–0.7 m/s. It follows then that for any particular conditions of stream depth and velocity the reaeration coefficient should be calculated by considering which of the lines in Fig. 2 is nearest and applying one of the two equations. Again, the errors inherent in extrapolating beyond the primary experimental data should be born in mind.

The three examples used in Table 2 cover the range of stream conditions likely to be observed in New Zealand, and all three fall within the usable ranges of the four predictive equations considered here. Examples A and C are best accounted for by either the O'Connor–Dobbins equation or the Churchill–Elmore–Buckingham expression, while example B is equally suited to any of the four equations.

Conclusions

The reaeration coefficient may be obtained either by direct measurement, or by one of the many predictive equations published in the literature. It would seem that for most conditions the gas tracer technique affords the best direct measurement of k_2.

While some of the more complex equations for predicting k_2 appear to be favoured by some reviewers there is reason to suspect that one is just as likely to be successful with one of the simpler expressions, such as those proposed by Isaacs and Gaudy, and Langbein and Durum.

In choosing a suitable expression for the reaeration coefficient, care should be taken to ensure that the stream conditions match those used to derive the reaeration coefficient equation. The approach of Covar, in which the agreement between pairs of predictive equations is defined, may be used to select the appropriate means of calculating k_2.

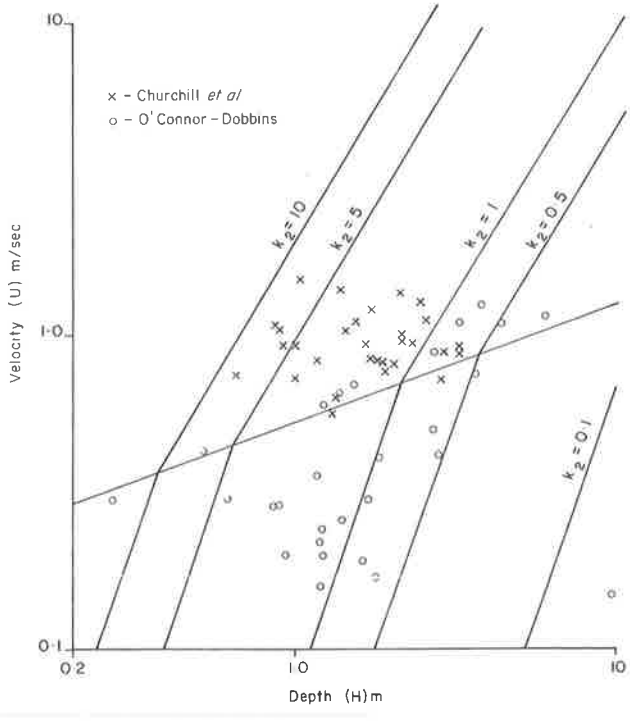

Fig. 1 Data from different investigators.

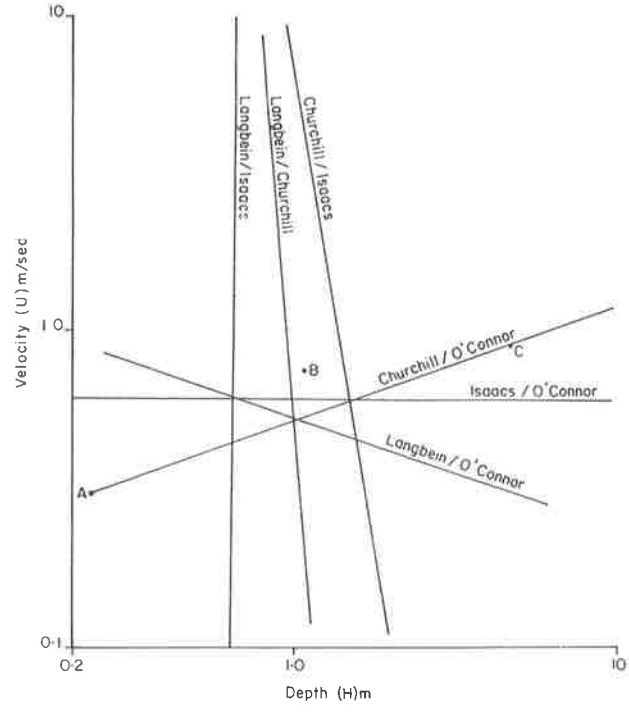

Fig. 2 Stream conditions for equivalent k_2 prediction by different pairs of equations.

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DISCUSSION FOR SESSION IV

Aquatic and benthic micro-organisms

Presented by: H. W. MORGAN

J. MILBURN: In view of the fact that high bacterial levels sometimes indicate areas of high O_2 uptake in aquatic systems is there any possibility of using bacterial levels as an indicator of possible O_2 depletion in natural water systems?

MORGAN: In my view this is unlikely, with the exception of highly eutrophic waters where a large proportion of the bacteria responsible for O_2 uptake may be suspended. Where most bacterial activity is associated with the benthic sediments then problems occur with the desorption of bacteria, the efficiency of which may vary with sediment type. At present it is difficult and time consuming to quantify bacteria on sediments by counting procedures, and indirect measurements of activity (e.g., ATP concentration and dehydrogenase activity) probably are better alternatives.

P. GILLESPIE: In some aquatic systems the proportion of free-living to particulate-associated systems is very high, i.e., 85-95% in marine environments. Could you please comment on this?

MORGAN: I would expect the proportion of free living bacteria to be higher in eutrophic waters. If this is not the case the only alternative I can offer is that the water is surface limited, i.e., the bacteria have no option but to be free living. Results in support of this can be found in the references of Zobell and Jannasch, and could be checked by looking for an increase in activity if inert particles were added to the waters in question.

M. PIPER: Would you expect most bacteria in a river enriched with biodegradable organic matter to be absorbed on surfaces? A study on the Nile River showed that 99.98% of bacteria are absorbed. Is this realistic?

MORGAN: I am surprised at the high numbers of bacteria in this case. I should distinguish between bacterial activity and bacterial numbers. Bacterial activity is regularly associated with surfaces (suspended and benthic) but as a result cells can be shed into the water phase where they may be inactive *in situ* (or show a reduced activity), but may still be counted by culture procedures.

Perspectives for plant metabolism in aquatic oxygen models

Presented by: B. T. COFFEY

J. C. RUTHERFORD: Part 1. You state that when photosynthesising, phytoplankton increase DO concentrations, and when respiring they decrease DO concentration. In your experience when averaged over 24 hours do phytoplankton make a nett contribution, a nett reduction, or have no nett effect on river DO concentrations?

Part 2. When isolated, does a phytoplankton community normally liberate more oxygen than it consumes over a 24 hour period?

COFFEY: Part 1. Phytoplankton will make a nett contribution to dissolved oxygen concentrations where they are fixing a nett quantity of carbon over a diurnal period and they are contributing to a dissolved oxygen pool which is less than saturated.

Part 2. Yes, where it is growing, i.e., its requirements for light and nutrients are being satisfied. The significant difference between enclosures and open, turbulent, river conditions is that dissolved oxygen levels can be raised above saturation levels within an enclosed system whereas in a turbulent river which is saturated with oxygen, the oxygen produced by the plankton may be lost to the atmosphere.

C. HICKEY: Do low DO values present a stress which would result in increased DOM release by macrophytes? Can these low DO values occur within weed beds because of the respiration of the macrophytes?

COFFEY: With regard to the second part of your question, Yes, dissolved oxygen levels can fall quite dramatically due to macrophyte respiration in dense weed beds during the hours of darkness. With regard to the release of dissolved organic matter from submerged macrophyte stands, this is most likely to occur during periods of high light intensity and at high pH values (11.0 and above). These conditions are depicted in the figures included in this paper where by 1100 hours, photosynthetic activity has depleted the available dissolved carbon dioxide pool around the foliage of the plants.

Reaeration

Presented by: R. J. WILCOCK

F. MICHAELIS: Supersaturation can have an adverse effect on fish. Consider water supersaturated with dissolved oxygen as a result of plant photosynthesis or below hydroelectric installations. Can you predict how quickly river water would return to 100% saturation?

WILCOCK: The implication of the diffusion equations is that the rate of recovery from supersaturation to saturation should be the same as for normal reaeration, so that the same reaeration coefficient may be applied. However, turbulence of the kind produced by hydroelectric installations causes air bubbles, and the rate of approach to equilibrium dissolved oxygen is likely to be markedly affected

by the quantity of bubbles (and their size distribution) produced. Few reaeration rates would have been measured in such locations, but one would expect the rate of recovery to 100% saturation to be very fast.

T. F. W. HARRIS: I understand that wind effects are excluded from the equations producing k_2. Wind can increase k_2 by a factor of the order of 10 and since k_2 is an exponent the effect is very powerful.

WILCOCK: Yes I agree that wind can profoundly affect reaeration and in some situations, such as in lakes, it is probably the major mechanism by which oxygen is replenished. Most attempts in the literature at including the effects of wind velocity take the approach of first developing a model for k_2 in terms of stream-flow parameters, and then deriving a correction term for k_2. The correction term is often an empirically derived function of the wind velocity (Mattingly 1977; Banks & Herrera 1977). It is not known how generally applicable these adjustment factors for wind velocity are.

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C. HICKEY: Does a temperature difference between air and water greatly affect the reaeration?

WILCOCK: The rate of reaeration is limited in turbulent waters by the molecular diffusion rate at the air-water interface. This is in turn affected by the water temperature, being greater at elevated temperatures. Consequently it is the water temperature and not the air temperature that affects reaeration.

G. B. McBRIDE: A comment. It is worth stressing that much of the literature on reaeration prediction available to DO modellers is confusing. Many equations may be presented giving somewhat different predictions and formulae are often quoted to the wrong base (10 versus e) : indeed the base may not be quoted at all. Dr Wilcock's paper is helpful in that it identifies equations correctly and provides some guidance as to which equations should be used for given situations.

M. PIPER: Is it valid to determine k_2 at the sag point where BOD uptake must then equal reaeration?

WILCOCK: The sag point indicates where the rate of all oxygen demand equals the total reaeration rate. To calculate the solely atmospheric reaeration contribution requires assumptions to be made concerning other sources and sinks of dissolved oxygen. Furthermore, the oxygen sag method can only be applied in the event of a severely stressed stream, and cannot be used to predict or measure k_2 for waters free from substantial oxygen demands.

SESSION V MODELLING OF AQUATIC OXYGEN

Construction and use of models

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The role of models in prediction of aquatic oxygen is discussed in terms of four basic steps: identification, calibration, verification, and prediction. Examples are given of models of differing complexity.

Introduction

When faced with a proposal to change some use of land or water, especially if the proposal concerns a discharge of waste to a water body, the need arises to predict the effects of that proposal on water quality.

Any such prediction relies on some model of the water body being affected by the proposal. Such models can range from an intuitive understanding, to a sophisticated computer code. The object of this paper is to summarise the salient features of models, to describe methods of construction and to give examples of their use.

What is a model?

A model comprises a summary of the essential features of the processes affecting the quality of the water body in question. It is usually a simplified statement of the array of complex processes operating. Often processes which are shown by available data not to have a significant effect on water quality can be ignored.

A simple illustration of a model for a case of considerable interest to this seminar—the effect of discharging waste organic matter on the dissolved oxygen (DO) concentration of a river—is given in Fig. 1. This shows that the fundamental purpose of the model is to transform the inputs and parameters into the desired output of river DO. "Inputs" are the forcing functions which drive the system and which are likely to be varied between simulations (e.g., BOD inflows). Usually they must be measured directly. "Parameters" are inferred coefficients that describe the rates at which the component processes operate (e.g., reaeration coefficient). Once evaluated, parameters usually remain constant.

Models are developed from a qualitative understanding of the processes affecting water quality. The models are then tested against measurements already made, and if successful under such testing are used for prediction. Predictions are usually made by changing the inputs while holding the parameters constant.

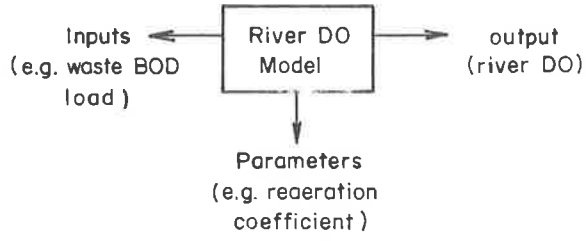

Fig. 1 River DO model.

How is a model constructed and used?

Here we must identify four sequential steps in modelling studies:

1 Identification
2 Calibration
3 Verification
4 Prediction

The first three steps all call for a certain amount of data to be available, and if such are not available they should be collected before the modelling job can be done properly. Indeed it is commonly found that a modelling study being done at the same time as field and laboratory work provides very good guidance as to the amount of such work required.

1 Identification

This refers to the structure of the model. It is important to note that there is always a range of models applicable to any situation, and it is doubtful that any one of these is optimal. It can be highly desirable to have several models available and to compare predictions.

The structure of the model depends on:
- the objectives of the study;
- the important processes operating;
- the desired level of complexity.

Objectives

In aquatic oxygen studies a common objective of modelling studies is to set effluent standards, given that some prescribed receiving water standard is not to be breached. Such "management" models should be as simple and as robust as possible.

Another objective may be to test one's understanding of a system or to develop new techniques. Here realism may be desirable even at the expense of simplicity and robustness.

Important Processes Operating

For the dynamics of DO in water bodies, the mode of water mixing strongly determines the structure of models. Hence quite different model structures may be necessary for rivers, estuaries, and lakes. In addition one must judge, on the basis of available data, what DO removal and replenishment mechanisms are important. Removal mechanisms may include all or some of chemical oxygen demand, aquatic bacterial and plant metabolism, and benthic bacterial and plant metabolism. Replenishment mechanisms may include physical reaeration, tributary inflow and photosynthesis by aquatic plants.

Desired Level of Complexity

In selecting models it has to be borne in mind that no model is perfect. A simple model may give a fairly good prediction, and a more complex model may refine this prediction only slightly. The model may indeed help set desirable effluent standards, but it is too much to expect that models can solve the economic/political problems of achieving them.

2 Calibration

This exercise is aimed at determining the values of the parameters of a model. The value of some of these parameters may be able to be inferred from laboratory or field investigations (e.g., dispersion coefficient, and aquatic plant oxygen production rates) while others may be estimated using standard empirical formulae (e.g., saturation DO). The model is then run with measured input data and the values of the remaining unknown parameters (e.g., deoxygenation, reaeration coefficients) are adjusted until a good fit between observed and predicted DO values is obtained. Care must be exercised to ensure that the set of calibrated parameter values is unique, i.e., that there is not another set of values that would give equally good agreement with the observed DO. For that reason the use of algorithms for automatic fitting of parameters may not be desirable. Clearly complex models containing numerous parameters are likely to give greater problems with uniqueness than simpler models with fewer parameters.

At this point it is desirable to carry out a sensitivity analysis to investigate the uniqueness of the optimal set of parameters and the importance of each parameter and input.

3 Verification

Here the calibrated parameter values are 'frozen' and used with another set of measured input data to see how well the observed and predicted values agree. If good agreement is obtained the model is verified. It must be stressed that the field data used for model verification must be a different set from that used for model calibration.

If agreement is poor, it will probably be necessary to revise the identification of the model and go through the calibration and verification steps again.

4 Prediction

Prediction makes use of a verified model, i.e., the calibrated parameter values are used. The inputs corresponding to the environmental conditions requiring simulation (e.g., BOD_5 load from an outfall, low river flow, warm river temperature) are specified and the model run to obtain the required predictions. Even a carefully constructed model may not make accurate predictions of conditions significantly different from those under which it was developed.

In general it is not possible to invert the problem, i.e., given the parameters and output DO (e.g., as specified by a receiving water standard) then determine the input BOD load to achieve that standard. Rather the allowable input BOD load is found by trial and error predictions. One exception to this is noted below where an inverted problem is solved directly using a nomograph.

Examples

The three examples given are of river DO modelling.

1 Royal Commission model

The first "model" is that of the British Royal Commission on Sewage Disposal (1912), which was based on a semi-statistical summary of river BOD_5 loading and river DO response. The "model" states that river DO is protected if any effluent has a maximum BOD_5 of 20 g/m^3 provided that at least an eightfold dilution of effluent with river water is achieved. Although no "modelling" is required to use these results, the effluent standard is based on the Commission's statistical model of a number of English rivers.

2 General river DO models

Let us suppose that the Royal Commission model results are suspected of being inappropriate (as is often the case, especially for discharges other than sewage) for a study with the object of establishing permissible effluent standards for wastes discharged to a river. In this case thought has to be given to the

types of processes operating in the river. There are many combinations generally possible, including:

—the river flow may be uniform or non-uniform;

—the river flow may vary diurnally (e.g., downstream of power stations as in the Waikato River) and will certainly vary seasonally;

—effluent flows will vary diurnally, weekly and sometimes seasonally;

—bacterial metabolism may proceed at rapid rates, especially if the river bed and banks provide stable sites for bacteria and aquatic plants in contact with the river water (e.g., the Manawatu and Tarawera Rivers);

—aquatic plants may impose diurnal DO variations (e.g., the Waikato River).

The balance of all such processes can be described by use of a differential equation. This equation is derived by dividing the river into segments, performing a mass balance of DO for such a segment, and then supposing that the segment becomes infinitesimally small. The general form of this equation is (Rinaldi *et al.* 1979)

$$\frac{\partial(AC)}{\partial t} + \frac{\partial(AUC)}{\partial x} = \frac{\partial}{\partial x}(AD\ \frac{\partial C}{\partial x}) + S \quad (1)$$

In this equation

A = river cross-section area, C = river DO (assumed uniform over A), U = mean river velocity, D = river longitudinal dispersion coefficient, S = sources and sinks of DO (e.g., reaeration, BOD exertion), x = river distance, t = time.

Inflows are accounted for in this equation either in the term S, or by specifying boundary conditions.

Solutions to equation (1) are usually obtained by use of numerical methods and implemented on a computer. This is especially true for 'research models' such as those discussed in case studies of the Tarawera and Waikato Rivers. Some simplifications can be made so that the equation can be solved using a simple programmable calculator (see case study on the Waikato River). However, in some cases, particularly for estuary flows, use of computers is probably unavoidable.

3 Simple DO river models

In some cases it is possible to simplify equation (1) so that predicitons can be made using relatively simple numerical techniques (see for example the case studies on the Mataura and Tarawera Rivers) or even analytical solutions. It may also be that the limited resources available to the study dictate that only simple models can be used, even if equation (1) cannot strictly be so simplified.

In particular, if longitudinal dispersion is ignored and the river and effluent flows are steady then analytical solutions can be obtained, e.g., O'Connor (1967). If the diurnal DO variation caused by aquatic plants is negligible, then a simple model may be proposed that assumes that the only significant DO processes operating are DO removal by BOD exertion and DO replenishment by reaeration. The result is the well-known model of Streeter-Phelps (1925)

$$\frac{dL}{dt} = -k_1 L \quad (2)$$

$$\frac{dC}{dt} = -\alpha k_1 L + k_2(C_s - C) \quad (3)$$

where now t = river time of travel, and L_o = river BOD_5, k_1 = river deoxygenation coefficient (base e), C = river DO, α = ratio of $BOD_{ultimate}$: BOD_5, k_2 = river reaeration coefficient (base e), C_s = saturation river DO.

Equation (3) may be simplified by defining the DO deficit (DOD) by

$$D = C_s - C$$

In that case equation (3) becomes

$$\frac{dD}{dt} = \alpha k_1 L - k_2 D \quad (4)$$

The analytical solutions to this model (i.e., equations (2) and (4)) for the DOD and BOD_5 distribution downstream of a single outfall are well known and are published in many texts, e.g., Phelps (1944), Velz (1970), Imhoff *et al.* (1971), Linsley and Franzini (1972), Nemerow (1974), Rinaldi *et al.* (1979). A nomograph procedure to calculate the notable features of the "DO sag" predicted by this model has been developed (McBride 1980). In particular, one such nomograph can be used to calculate the maximum permissible river BOD_5 at an outfall, in order that a specified downstream DO standard is not breached. It is assumed that there are no significant inflows downstream of the outfall.

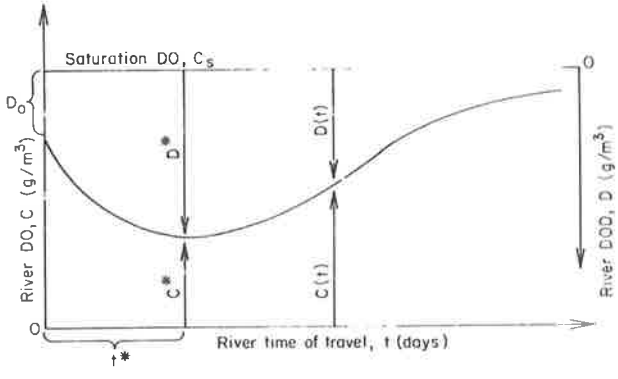

Fig. 2 Definition of variables.

Figure 2 shows the predicted BOD_5 decay and DO sag downstream of some initial river station where the DOD (D_o) is known and the BOD_5 (L_o) is unknown. Suppose that the parameters α, k_1 and k_2 are known and that the downstream DOD is nowhere to exceed 4 g/m³. The required value of L_o can be obtained rapidly as follows:

(a) form the ratios $f = \frac{k_2}{k_1}$ and $d_o = \frac{D_o}{D^*}$

(b) read a value of b_o for these values of f and d_o from the nomograph in Fig. 3

(c) calculate L_o from $L_o = b_o D^*/\alpha$

For example, take a river with the following data:

$D_o = 1.5$ g/m³
$k_1 = 0.6$/day
$k_2 = 0.75$/day
$\alpha = 1.15$

and select $D^* = 4$ g/m³

Then f = 1.25 and d_o = 0.375 so that, from Fig. 3. $b_o \approx 2.65$. The maximum permissible initial river BOD, is thus $L_o = 2.65 \times 4/1.5 \approx 9.2$ g/m³.

This example illustrates what is probably the simplest method of calculation of river assimilative capacity. The procedure shown may be very useful when rapid calculations are required, as in the case of an emergency waste discharge, but is not likely to be valid for most cases when examining the effects of changes in waste loads to a river. In such cases use of some machine for performing the required calculations is probably necessary.

Conclusions

There are two types of water quality models.

(i) Research models are used to test one's understanding of a river system, help design experiments and eventually to develop management models. Research models may be fairly complex and hence may not be robust or simple to use.

(ii) Management models are generally simpler and more robust than research models. They need to be calibrated and verified carefully before being used to make predictions.

The four steps involved in model development are:
identification
calibration
verification
prediction

Even a carefully constructed model may not make accurate predictions of conditions significantly different from those under which it was developed.

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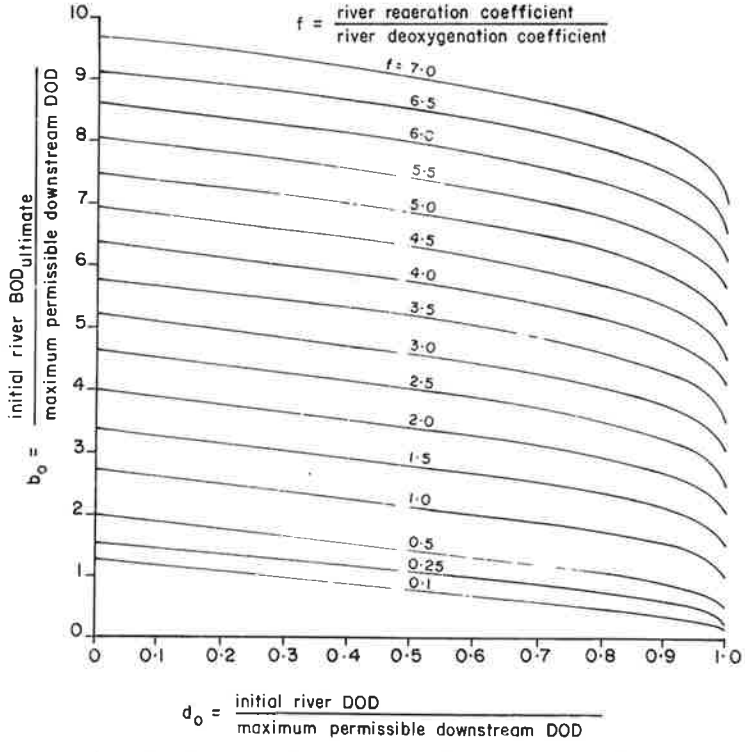

Fig. 3 Streeter–Phelps model solution nomograph.

DISCUSSION FOR SESSION V

Construction and use of models

Presented by: J. C. RUTHERFORD

There was no discussion.

SESSION VI RECEIVING WATER BOD STANDARDS

Rationale for classification standards for BOD

C. D. STEVENSON

Chemistry Division DSIR, Lower Hutt

This discussion paper reviews briefly the relationship between average BOD values in rivers, the types of aquatic communities present and the appearance of the water and river bed. The information available suggests that unacceptable degradation of the appearance and types of aquatic community present is likely to occur if the average BOD is much greater than about 5 g/m^3 over an extended period.

The British Royal Commission on Sewage Disposal (1912, 1913) has set out a river water classification based on observation of numerous river sections and the average BOD in water samples taken from those sections, as follows:

River Condition	Average BOD_5 (g/m^3)
Very clean	1
Clean	2
Fairly clean	3
Doubtful	5
Bad	10

An indication of the actual observations used to decide on the condition of rivers is set out in Table 1.

It may be seen that relatively few of the characteristics noted would be greatly affected by increased flow velocity in rivers.

Further, the Eighth Report of the Commission states

> "Our officers have submitted to (the BOD_5) test a large number of samples drawn from various streams: (a) at points where signs of sewage pollution were observed; and (b) where there were no signs of pollution. By comparing the results of analysis of the two sets of samples it was hoped to arrive at a figure for dissolved oxygen absorption in 5 days, which should represent a limit not to be exceeded without signs of pollution being likely to manifest themselves.
>
> "In view of the variations, both seasonal and local, in the conditions common to streams receiving sewage liquids, it is obvious that such a figure can only be an approximate one. But the data thus obtained, supplemented by the results of channel experiments, justify us in concluding that if 100,000 cubic centimetres of river water do not normally take up more than 0.4 gram of dissolved oxygen in 5 days, the river will ordinarily be free from signs of pollution, and that if a river water normally gives a higher figure than this it will almost certainly show signs of pollution, except perhaps in very cold weather. This figure (0.4) we term the "limiting figure", and in our opinion it should be the foundation on which any scheme of standards should be constructed.
>
> "Temperature, however, is an important factor, and if the 5 days test be carried out at different temperatures which prevail at different seasons in our streams, the results will be found to vary to a marked extent. Our experiments have been carried out at a temperature of 65 °F. Assuming 0.4 to be the true "limiting figure" at this temperature, during the colder months of the year, a river could withstand, without nuisance, much worse pollution. To preserve a wide margin of safety we have adopted the temperature of 65 °F and, for the same reason, the dry-weather flow of the river."

More recent studies (Sladecek 1979) of the relationship between BOD_5 and saprobric zones suggests similar BOD_5 standards to those recommended by the Royal Commission. Saprobric classifications, upper limits of average BOD_5 and the associated water characteristics are listed below for the zones of interest in water management.

Oligosaprobic: BOD_5–2.5 g/m^3; brooks and rivulets, clean lakes and very poor fish ponds, excellent for recreation.

β-mesosaprobic: BOD_5–5 g/m^3; rivers, lakes and fish ponds with medium water quality, with waterblooms and difficulties in water treatment, admissible for recreation.

This paper is also published as an appendix in "The report of the Water Quality Criteria Working Party". Water and Soil Miscellaneous Publication No. 25.

Table 1 Classification of rivers in accordance with their visible degree of cleanness, based on riverside observations under normal summer conditions (from Royal Commission Report on Sewage Disposal, 8th Report).

Observed condition of river water	Very clean	Clean	Fairly clean	Doubtful	Bad
Suspended matter	Clear	Clear	Fairly clear	Slightly turbid	Turbid
Opalescence	Bright	Bright	Slightly opalescent	Opalescent	Opalescent
Smell on being shaken in bottle	Odourless	Faint earthy smell	Pronounced earthy smell	Strong earthy or wormy smell	Soapy, faecal or putrid smell
Appearance in bulk	Limpid	—	Slightly brown and opalescent	Black looking	Brown or black and soapy looking
Delicate fish	May be plentiful	Scarce	Probably absent	Absent	Absent
Coarse fish	—	Plentiful	Plentiful	Scarce	Absent
Stones in shallows	Clean and bare	Clean	Lightly coated with brown fluffy deposit	Coated with brown fluffy deposit	Coated with grey growth and deposit
Stones in pools	Clean and bare	Covered with fine light brown deposit	Lightly coated with brown fluffy deposit	Coated with brown fluffy deposit	Coated with brown or black mud
Water weeds	Scarce	Plentiful. Fronds clean except in late autumn	Plentiful. Fronds brown coloured in places	Plentiful and covered with fluffy deposit	Scarce
Green algae	Scarce	Moderate quantities in shallows	Plentiful in shallows	Abundant	Abundant in protected pools
Grey algae	—	—	—	Present	Plentiful
Insects, larvae, etc.	—	—	—	Plentiful in green algae	Abundant in green algae

α-mesosaprobic: BOD_5–10 g/m³; distinctly polluted waters not suitable for recreation.

Sladecek (1979) reports that higher flow velocities give a more desirable aquatic community for the same water quality. The data reported suggest that at velocities of about 0.8 m/sec the aquatic community in a stream having an average BOD_5 of 5 g/m³ would be comparable with that expected for a stream having a flow velocity of about 0.05 m/sec and a BOD_5 concentration of 2.5 g/m³. On the other hand, European and British observations are likely to be made on streams which are cooler in summer than many New Zealand streams. The effects of increased flow and increased temperature are, intuitively, likely to counteract one another, and it is considered that the likely higher velocities in many New Zealand streams should therefore not justify an increased permissible BOD_5. This is particularly so because salmonids are the predominant sporting fish in our fresh waters and they generally require waters of high saprobric quality.

The Swiss Ordinance for Waste Water Discharge (1975) requires that the concentration of dissolved organic carbon shall not exceed 2 mg C/ℓ and that BOD_5 shall not exceed 4 mg/ℓ in receiving waters. These values apply for water flows exceeding the 95% low flow. The standards are evidently based on research undertaken at the Swiss Federal Institute for Water Resources and Water Pollution Control (1979). These studies suggest that ephemerella (mayflies) are likely to be present in streams receiving a little over 1% of raw waste water (probably corresponding to about 2.5–3.5 g/m³BOD_5), but that hydropsyche (caddis) will predominate if the raw waste water percentage approaches 2% (probably corresponding to a BOD_5 of 4–6 g/m³).

The United Kingdon National Water Council has recently published a classification system for British river water quality (Lester 1979), part of which is set out in Table 2.

The average BOD levels suggested relate to 3-year rolling averages. Accordingly, BOD values for shorter periods are likely to be very close to the class limiting 95 percentile values (e.g., during low summer flows).

It is likely that the general public would find waters of substantially poorer quality than the "fairly clean" class of the Royal Commission or classes 1B (above) unacceptable. The elimination of mayflies from a stretch of river is likely to be an unacceptable change in the aquatic community, at least to the angling fraternity.

For Class R and Class W waters rather more stringent standards for BOD are desirable on general aesthetic grounds and, particularly for Class W waters, to decrease the likelihood of taste and odour problems.

Means of expressing the standard

Any expression of the standard must:

(i) give adequate control of water quality at all times;

(ii) not impose an undue burden on authorities responsible for monitoring compliance;

(iii) not impose unreasonable restrictions on dischargers.

Expression in terms of daily average BOD values is considered to best meet these 3 requirements. Aquatic communities and aesthetic appearance of the river bed will generally respond to "typical" or average BOD values over at least several days, rather than instantaneous values, provided dissolved oxygen levels are always satisfactory (as specified in a separate requirement). Specification of a maximum daily average value will therefore cover these aspects.

Table 2 United Kingdom National Water Council river classification system (from Lester 1979).

River Class	Quality criteria	Remarks	Current potential uses
	Class limiting criteria (95%ile)		
1A	(i) Dissolved oxygen saturation greater than 80%. (ii) Biochemical oxygen demand not greater than 3 mg/ℓ. (iii) Ammonia not greater than 0.4 mg/ℓ. (iv) Where the water is abstracted for drinking water, it complies with requirements for A2** water. (v) Non-toxic to fish in EIFAC terms (or best estimates if EIFAC figures not available).	(i) Average BOD probably not greater than 1.5 mg/ℓ. (ii) Visible evidence of pollution should be absent.	(i) Water of high quality for potable supply abstractions and for all other abstractions. (ii) Game or other high class fisheries. (iii) High amenity value.
1B	(i) DO greater than 60% saturation. (ii) BOD not greater than 5 mg/ℓ. (iii) Ammonia not greater than 0.9 mg/ℓ. (iv) Where water is abstracted for drinking water, it complies with the requirements for A2** water. (iv) Non-toxic to fish in EIFAC terms (or best estimates if EIFAC figures not available).	(i) Average BOD probably not greater than 2 mg/ℓ. (ii) Average ammonia probably not greater than 0.5 mg/ℓ. (iii) Visible evidence of pollution should be absent. (iv) Waters of high quality which cannot be placed in Class 1A because of high proportion of high quality effluent present or because of the effect of physical factors such as canalisation, low gradient or eutrophication. (v) Class 1A and Class 1B together are essentially the Class 1 of the River Pollution Survey.	Water of less high quality than Class 1A but usable for substantially the same purposes.
2	(i) DO greater than 40% saturation. (ii) BOD not greater than 9 mg/ℓ. (iii) Where water is abstracted for drinking water, it complies with the requirements for A3** water. (iv) Non-toxic to fish in EIFAC terms (or best estimates if EIFAC figures not available).	(i) Average BOD probably not greater than 5 mg/ℓ. (ii) Similar to Class 2 of RPS. (iii) Water not showing the physical signs of pollution other than humic colouration and a little foaming below weirs.	(i) Waters suitable for potable supply after advanced treatment. (ii) Supporting reasonably good coarse fisheries. (iii) Moderate amenity value.

**A2, A3 are EEC categories for surface water intended for the abstraction of drinking water as follows:
A2 Normal physical, chemical treatment and disinfection, e.g., pre-chlorination, coagulation, flocculation, decantation, filtration, disinfection (final chlorination).
A3 Intensive physical and chemical treatment, extended treatment and disinfection.
Under extreme weather conditions (e.g., flood, drought, freeze-up), or when dominated by plant growth, or by aquatic plant decay, rivers usually in Classes 1, 2, and 3 may have BODs and dissolved oxygen levels, or ammonia content outside the stated levels for those Classes. When this occurs the cause should be stated along with analytical results.
The BOD determinations refer to 5-day carbonaceous BOD (ATU). Ammonia figures are expressed as NH_4.

Because samples can usually be stored on ice for 24 hours without unacceptable changes in BOD, a daily average value can reasonably be obtained by analysing a single composite sample, preferably collected using an automatic sampler. Specification of the daily average is consistent with common water right conditions controlling BOD discharges and will often avoid the necessity for a discharger to construct effluent storage facilities to smooth out diurnal variations in discharge rates.

Specification of longer-term and particularly annual average values is unsatisfactory because this would permit high BOD values continuously over periods of weeks or months. Estimation of longer-term average BOD values with acceptable accuracy would also increase the monitoring effort required.

Specification of a maximum instantaneous BOD value low enough to ensure protection of the aquatic community and amenity values would either needlessly decrease the BOD loadings on a receiving water, or necessitate construction of effluent storage facilities to achieve uniform discharge rates. Either effect would impose unreasonable restrictions on dischargers.

Proposed standards

For Class G.

The daily average 5-day biochemical oxygen demand at 20 °C shall not exceed 5 g/m³.

For Classes R and W

The daily average 5-day biochemical oxygen demand at 20 °C shall not exceed 3 g/m³.

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DISCUSSION FOR SESSION VI

Rationale for classification standard for BOD

Presented by: C. D. STEVENSON

[The questions and comments for this paper were contained in two separate periods and were not recorded on cards by the participants. Hence what follows is a precis of what was said, as recorded by a chronicler.]

R. H. S. McCOLL Asked that, with regard to the question of whether a standard of 4 g/m³ or 5 g/m³ (as has been recently proposed) daily average BOD_5 should apply to class G, does experimental error in determining the BOD_5 mean that the lower standard is appropriate?

STEVENSON: That may be so, but flow velocities of New Zealand rivers will probably provide adequate safety margin were the higher figure to be adopted.

C. RICHMOND asked if Dr Stevenson could comment on the appropriateness of BOD standards for lakes.

STEVENSON: The BOD standard for low aeration capacity water bodies is probably not necessary since DO standards should provide adequate protection.

M. PIPER asked Dr Stevenson to comment on the very small difference between the standards proposed for drinking and bathing waters (3 g/m³ BOD_5) and for general uses (5 g/m³ BOD_5).

STEVENSON: The drinking water standard applies to the water at source before treatment, not to that water supplied to consumers. Drinking water BOD_5 would be rather less than 3 g/m³, especially after flocculation.

M. PIPER asked if an across-the-board BOD standard is practical.

STEVENSON: Regional Water Boards may choose to classify a water or not to classify it. In the former case, Boards will be free to choose and justify their own standards. If a water is classified, a Board could establish a higher standard for receiving water quality, but I am not sure whether a standard lower than the national classification standards could be adopted.

G. B. McBRIDE commented that 9% of BOD_5 data for the Waikato River at Mercer in the period 1974–76 was above 3 g/m³, these higher values seemingly reflecting high algal biomass in the river rather than waste material. The river in this region is presently classified class B (drinking water supply). Were it to be reclassified using Dr Stevenson's proposed class for drinking water supply (class W for which the daily average BOD_5 should not exceed 3 g/m³), then it would seem that the validity of even present upstream discharges are in question. It is not easy to see why this should be the case.

M. S. CARRIE commented that national standards are nothing more than guidelines. Only water rights are legally binding and it is at the stage of consideration of water right applications that the issue of desirable receiving water standards comes fully into focus.

B. T. COFFEY commented that for aquatic biological systems, good water quality is a key issue. BOD standards averaged over a day might not provide very much protection for aquatic life, minimum or maximum standards may be more relevant.

STEVENSON: The complementary DO standards do however provide a large measure of protection for aquatic life.

Comments made on the proposed BOD standards in the final (general) discussion session of the seminar included:

G. B. McBRIDE who commented that it is desirable that receiving water quality standards be based on criteria in which some confidence can be placed. In the case of BOD being related to the "health" of a water body, it is difficult to find such criteria established, particularly for New Zealand streams. Furthermore, BOD criteria such as those given by the British Royal Commission referred to by Dr Stevenson, are *averages* and exhibit a wide range of values. There seems to be too much inflexibility involved in setting BOD standards that appear to be rather arbitrary. It would seem a better proposition to include some general statement in the national standards to the effect that the water body health should not be unduly impaired by reason of a concentration of organic matter. This leaves the question of desirable BOD standards for a water body to be decided for each case on its merits, exactly as has been (and is still proposed to be) the practice for the management of toxic substances.

A. G. BARNETT pointed out that the introduction of such a BOD standard would involve the country in millions of dollars of expenditure on waste treatment which would not be required, particularly near coasts, to meet existing standards. The issue was therefore very important and a case for BOD standards should be supported by substantial evidence. Dr Stevenson had collected such evidence as he could find from overseas literature but there were many reasons to suspect that New Zealand conditions could be entirely different. If the intention was to preserve the appearance of the receiving water, why not deal with the appearance directly instead of introducing a vaguely related parameter which is both tricky to sample and preserve, and expensive to analyse? What about cases where the appearance of receiving waters was conspicuously unacceptable even though the BOD standard was being met? Dr Stevenson's report should be followed up with extensive local research before any final decisions were taken.

Further discussions concerned the possible relationship of BOD to stream appearance or health, based on Seminar participants' experience or on overseas literature. Dr STEVENSON stated that he found considerable conformity between the results given in various papers.

SESSION VII CASE HISTORIES—RIVERS

Mataura River

L. R. McKENZIE

Southland Catchment Board, Invercargill

G. B. McBRIDE

Hamilton Science Centre, MWD, Hamilton

A steady state model was constructed to predict an average dissolved oxygen (DO) profile for the Mataura River under summer low flow conditions, so as to enable a decision to be made in 1976 regarding the possible location of a pulp mill downstream of Mataura. Predictions were made on the effect of adding the pulp mill discharge to the Mataura River with and without a reduction in BOD_5 loading from the existing Southland Frozen Meat Company discharge.

It was concluded that a pulp mill could be accommodated without breaching the D Classification DO limit of 5.0 g/m³ only with a substantial reduction in the BOD_5 loading from SFM. The model predictions for the case where the SFM BOD_5 loading was reduced by 85% have generally been verified by subsequent surveys. Though treatment of effluent by SFM did go ahead, the pulp mill proposal did not.

Introduction

In early 1975 a Government Interdepartmental Working group was evaluating a number of proposals put by the New Zealand Forest Service for the utilisation of Southland beech forests.

One of the proposals was for the establishment of a bleached kraft pulp mill adjacent to the Mataura River just downstream of Mataura Borough.

The Southland Regional Water Board was requested to evaluate this, and the alternative proposals from the point of view of both the supply of water to the industries and the disposal of waste from them. The main question to be answered was whether or not such an industry's waste could be accommodated in the river, then or in the future, and what changes to existing discharges were required to make this possible. A computer model was used to predict values of dissolved oxygen (DO) and biochemical oxygen demand (BOD_5) in the Mataura River, since it was thought that introduction of this kraft pulp mill effluent could have a significant impact on the DO in the river (and also on the colour).

The pulp mill proposal had to be considered in the light of the existing heavy loading of organic wastes placed on the river, primarily by the Southland Frozen Meat and Produce Export Company's (SFM) freezing works discharge at Mataura. The contribution of BOD_5 from this waste source was measured in February/April 1976 as part of the field data input to the model. The average daily loading of BOD_5 in the waste was found to be approximately 24 000 kg/day. At that time the BOD_5 loading contribution from all other discharges would not have exceeded 2000 kg/day. The contribution from the combined Edendale Dairy Factory/Lactose Company discharge to the Mataura River at Wyndham which is included in the latter figure, was 800–1000 kg/day.

Despite the high BOD_5 loading, the river was not regarded as having a particular DO deficit problem prior to the mid 70's. However, as was fairly typical, few measurements were made.

The information available suggested that a DO concentration of 7–9 g/m³ was normal downstream of Mataura except under summer low flow conditions when the DO concentration could be reduced to 4 g/m³ near Wyndham.

No fish kills were reported during this time.

While the DO concentration of the river indicated a reasonable standard of water quality many other factors did not. Below Mataura Borough the river was turbid and discoloured. Solids were visible in the water column and surface foaming was frequently a problem.

As a result of a combination of administrative action (initiated by the Pollution Advisory Council and followed up by the Southland Regional Water Board), the field surveys and computer modelling

and to a large extent the attitudes and efforts of the dischargers themselves, we now have an improved situation with regard to river DO levels, colour, and turbidity, suspended solids and foaming.

Historical Background

The whole of the Mataura River Catchment was classified by the Pollution Advisory Council in the late 60's, mainly as a response to pressure from local organisations concerned about the quality of the river. The classification was made under the Waters Pollution Regulations 1963 and was publicly notified in April 1969. As a consequence of this action every existing outfall from which pollutants were discharged to the river was required to be registered and a permit to continue discharging applied for.

The Pollution Advisory Council issued a number of temporary permits to dischargers to the Mataura River including the Southland Frozen Meat and Produce Export Company, New Zealand Paper Mills, the Edendale Dairy Factory, the Lactose Company of New Zealand, the Boroughs of Mataura and Gore, and the town of Wyndham.

It was a requirement of permit No. 775/11T issued to Southland Frozen Meat (SFM) that the Council be notified of steps taken by the company to meet the following effluent standards.

(a) Volume = 3 million gallons per day (13.6m³/day)
(b) 5-day BOD at 20°C = 200 ppm, i.e., 6000 lbs/day (2700 kg/day)
(c) Suspended solids = 100 ppm, i.e., 3000 lbs/day (1400 kg/day)

It is to be noted that these limits require about a 90% removal of BOD_5 and suspended solids from the waste. The Company commenced investigations about that time with the Meat Industry Research Institute of New Zealand with a view to meeting the requirements of the temporary permit. It proved to be necessary for the Company to obtain a number of regular extensions to its permit while this investigation, and more lately, the construction and commissioning phases of effluent treatment went on.

The proposal to establish a pulp mill on the Mataura River was put to the Southland Regional Water Board, about the same time as SFM brought forward a firm proposal to install an Acid Coagulation/Dissolved Air Flotation Treatment system at their Mataura freezing works. The method of treatment (Butler 1973) was to be designed to achieve an 85% reduction in waste BOD_5. Knowing what SFM planned to do simplified the assessment of the effects of the discharge of pulp mill effluent on the Mataura River.

The production output of the pulp mill was initially to be 200–270 tonnes/day of bleached kraft pulp, later expanding to 500 plus tonnes/day. On this basis it was estimated that the initial water requirement would be 43 000 m³/day, and the residual waste after treatment would contribute to the river 2700 kg/day suspended solids, 3900 kg/day BOD_5 and 15 000 kg/day COD.

An adequate supply of water was considered to be available to meet the 0.5 m³/s pulp mill demand. This figure is 8% of the lowest gauged flow at Gore of 6.16 m³/s measured in March 1956.

The question of the effect of an additional 3900 kg/day of BOD_5 on the river was less easily resolved. During the summer of 1975/76 the Southland Regional Water Board began a survey of the river, a large part of which was designed to assess the effect of existing discharges on the DO concentration of the river.

Ministry of Works and Development staff co-operated in this survey and were responsible for the modelling work which was necessary if predictions were to be made regarding the effect of the pulp mill discharge both with and without an 85% reduction in the BOD_5 loading from the SFM freezing works discharge.

It became apparent early in this work that river DO could be maintained above 6.0 g/m³ with the pulp mill discharge to the river, providing the BOD_5 loading from SFM was substantially reduced.

Towards the end of the 1978 freezing works killing season SFM commissioned an AMINODAN effluent treatment plant. The plant is an acid coagulation/dissolved air flotation unit somewhat similar to that developed by the Meat Industry Research Institute of New Zealand. The plant was operated during the 78/79 and 79/80 seasons. The freezing works now contributes an average of 1500 kg/day of BOD_5 to the river.

At the present time we have the situation where the BOD_5 loading from SFM has been substantially reduced and the pulp mill proposal not been proceeded with.

The Southland Regional Water Board continued to monitor water quality in the Mataura River during and after plant commissioning. Since 1978 the summer flow in the Mataura River at Gore has not dropped to below 24 m³/s compared to a design flow at Gore for model calculations of 14 m³/s.

Although masked by higher than usual summer flows a considerable improvement in river water quality is suggested by the results obtained since the AMINODAN plant was commissioned.

Survey Results

Prior to 1975 the Southland Regional Water Board had not made any DO measurements on the Mataura River. SFM had indicated (McMillan 1974) that river DO concentrations were normally in the range 7–9 g/m³ and only fell below 5.0 g/m³ during summer low flows and then only in the early morning.

1 Dissolved Oxygen

The first evidence that the 5.0 g/m³ minimum dissolved oxygen standard of the river's D classification was under threat was not obtained until surveys were carried out by the Board in March and April 1976. (See Fig. 1 and 2 for survey sites.)

By 15 March 1976, the flow in the river at Gore had dropped to 15 m³/s with a mid-morning DO concentration at Wyndham Bridge of 5.6 g/m³ (55% saturation), down from 9.3 g/m³ at Gore (91% saturation). For the next 5 weeks the Wyndham DO concentration remained low. The lowest recorded DO concentration was found to be 5.2 g/m³ (48%

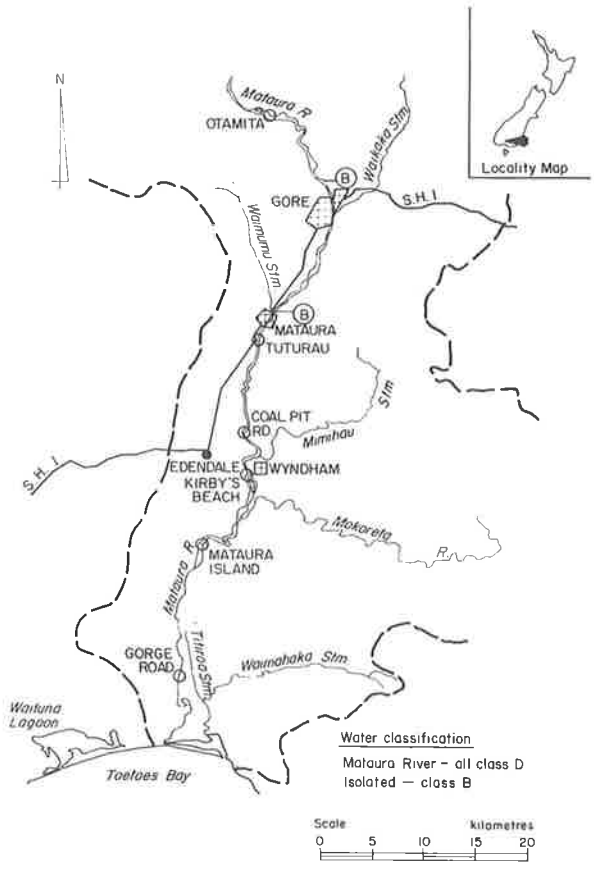


Fig. 1 Location of survey sites on the Mataura River.

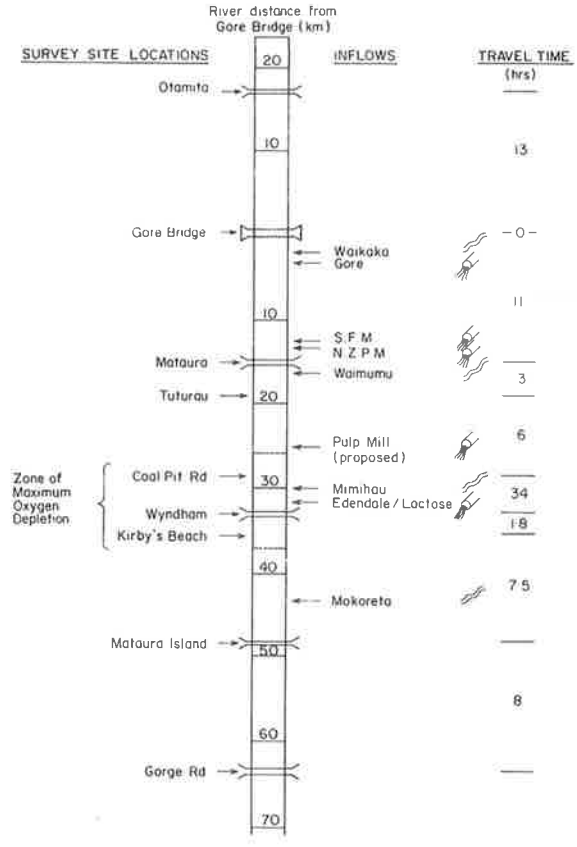


Fig. 2 Mataura River distance and inflow sketch. River distance from Gore Bridge (km)

saturation) at the Coal Pit Road site (Fig. 2) at 0940 hours on 15 April 1976 (Gore flow = 13 m³/s).

These surveys showed that a dissolved oxygen sag of 4.0 g/m³ at a point 20 km south of Mataura occurred when SFM were discharging close to 20 000 kg/day of BOD_5 to the river.

A 24 hour DO sampling survey was carried out on 9 March 1976 to provide information for the setting up of the computer model. Some effort was made to assess the magnitude and distribution of photosynthetic oxygen production (P) and benthic oxygen demand (B). However, as it was not possible to obtain consistent results the terms were assumed to be making equal contributions (i.e., P - B = 0).

The three sites used were at Otamita, 17 km upstream of Gore; at Tuturau, 5 km downstream of Mataura; and at Mataura Island, 34 km downstream of Mataura. The diurnal DO curves obtained for these three sites are given in Fig. 3. Some evidence was obtained from this survey to indicate that diurnal DO fluctuations were being influenced by the varying inflow from the SFM freezing works. The river DO profile taken during the early afternoon of the same day is given in Fig. 4.

On 7 April 1976 a calibration survey was carried out for the model giving river DO data only for a Gore flow of 14 m³/s. A further survey, for model verification, was carried out under very similar conditions on 15 April 1976. The results of these surveys together with the predicted results for April 1976 conditions are discussed in the next section.

Notable features of these surveys are that there was a rapid DO depletion in the Mataura—Wyndham reach and a very rapid rise in DO downstream of Wyndham due to vigorous reaeration of the river induced by a number of rapids in the area.

Further field information for comparison with results predicted by the model in 1976 was collected during the summer of 1977/78. SFM had undertaken some operating trials with their treatment plant in the 1977/78 killing season; however, the BOD_5 loading had not been significantly decreased. Three diurnal oxygen surveys were undertaken at the Otamita, Coal Pit Road and Kirby's Beach sites. Samples were also taken at Tuturau. The Mataura Island and Tuturau sites used in 1976 were not used on this occasion as they were considered to be outside the zone of maximum oxygen depletion (see Fig. 2), particularly Mataura Island.

The results of these surveys are presented in Fig. 5.

On 6–7 December 1977 with a flow at Gore of 47.2 m³/s and SFM operating for only 2 weeks the dissolved oxygen sag downstream of Mataura was only about 1 g/m³. By mid February 1978 the flow at Gore (13 m³/s) was close to the April 1976 value as were the DO concentrations.

Diurnal variation was more pronounced than earlier surveys had indicated, being 3–4 g/m³, and there was more visual evidence of attached growths on the river bed. The diurnal curves for Coal Pit Road and Kirby's Beach were out of phase on 16–17 February 1978 by between 4 and 5 hours, which is the time of travel between the sites at a flow of 14 m³/s. This again suggests that waste inflows influenced the expression of diurnal DO variation.

The feature of the final survey for that season,

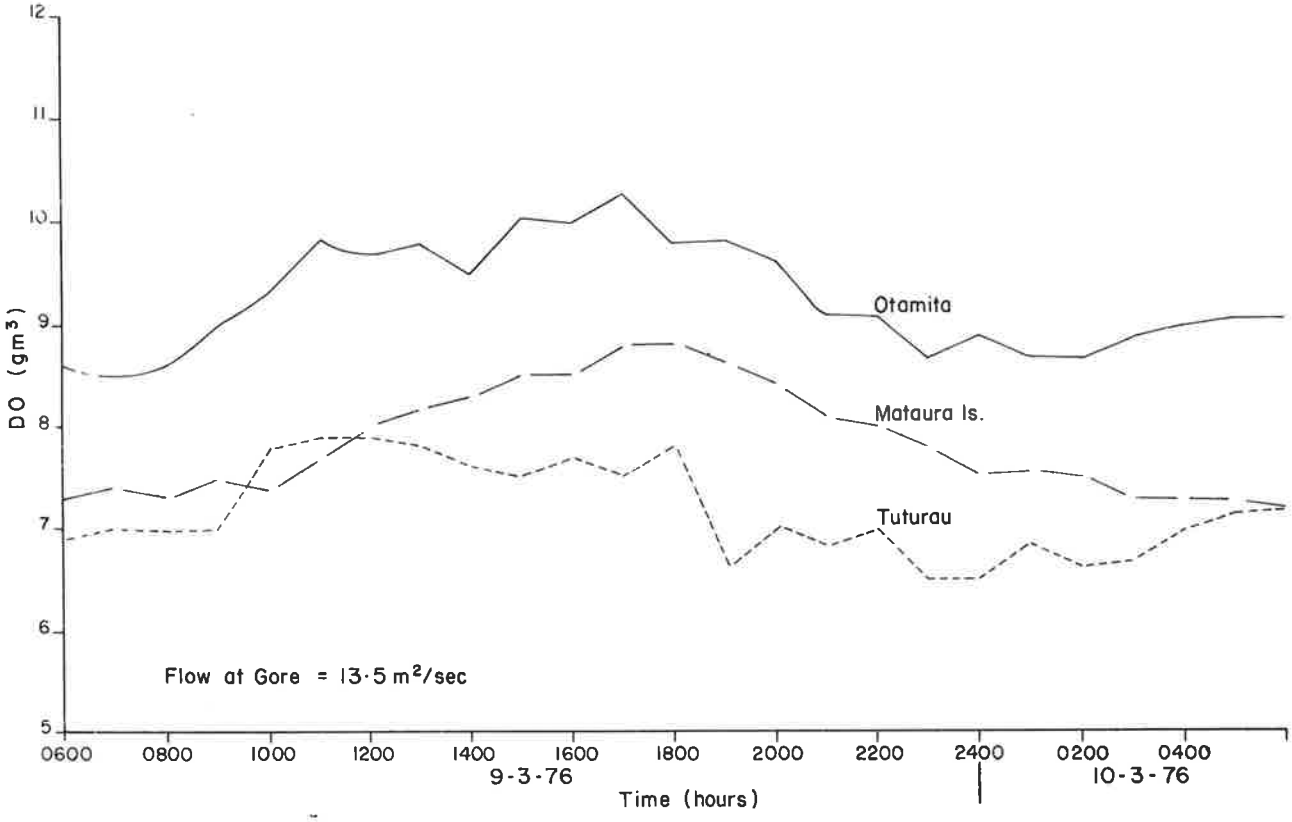


Fig. 3 Diurnal dissolved oxygen profile, 9–10 March 1976.

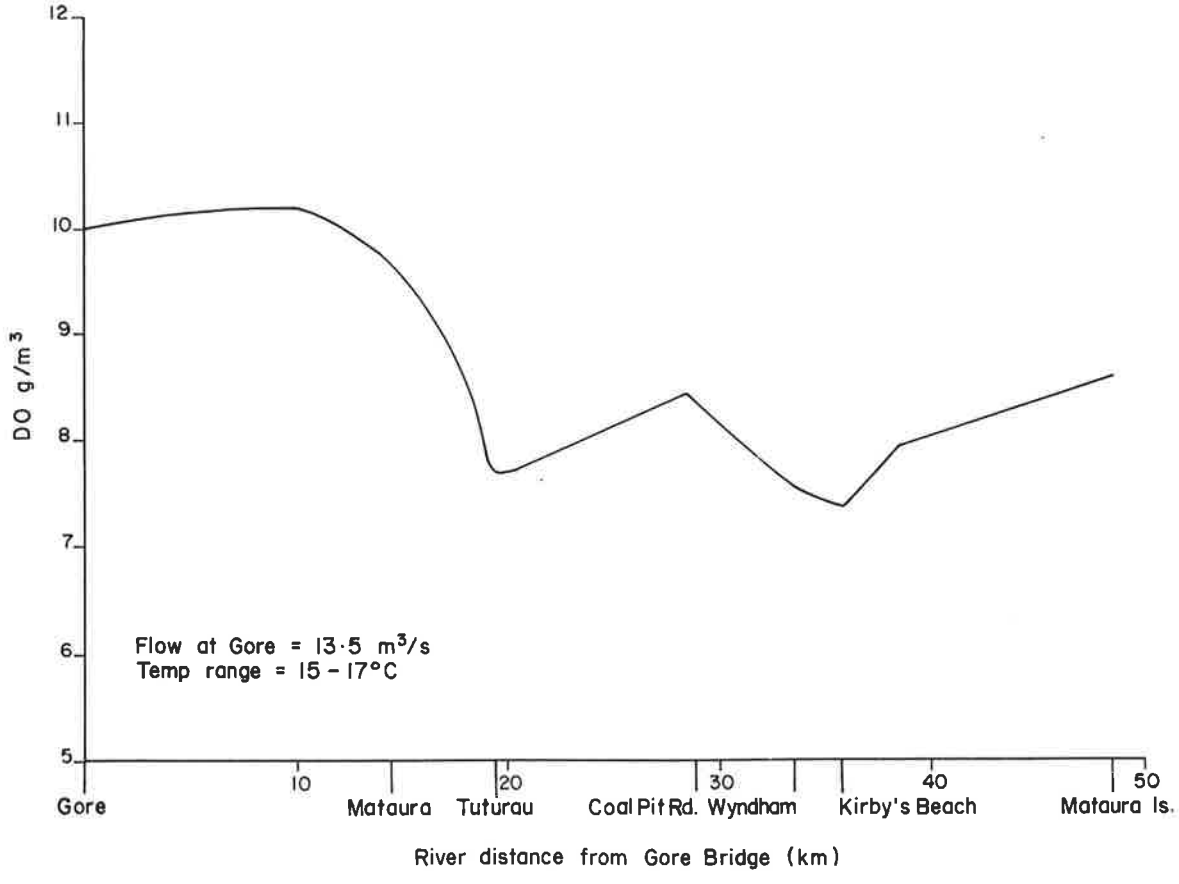


Fig. 4 Mataura River dissolved oxygen profile, 9 March 1976.

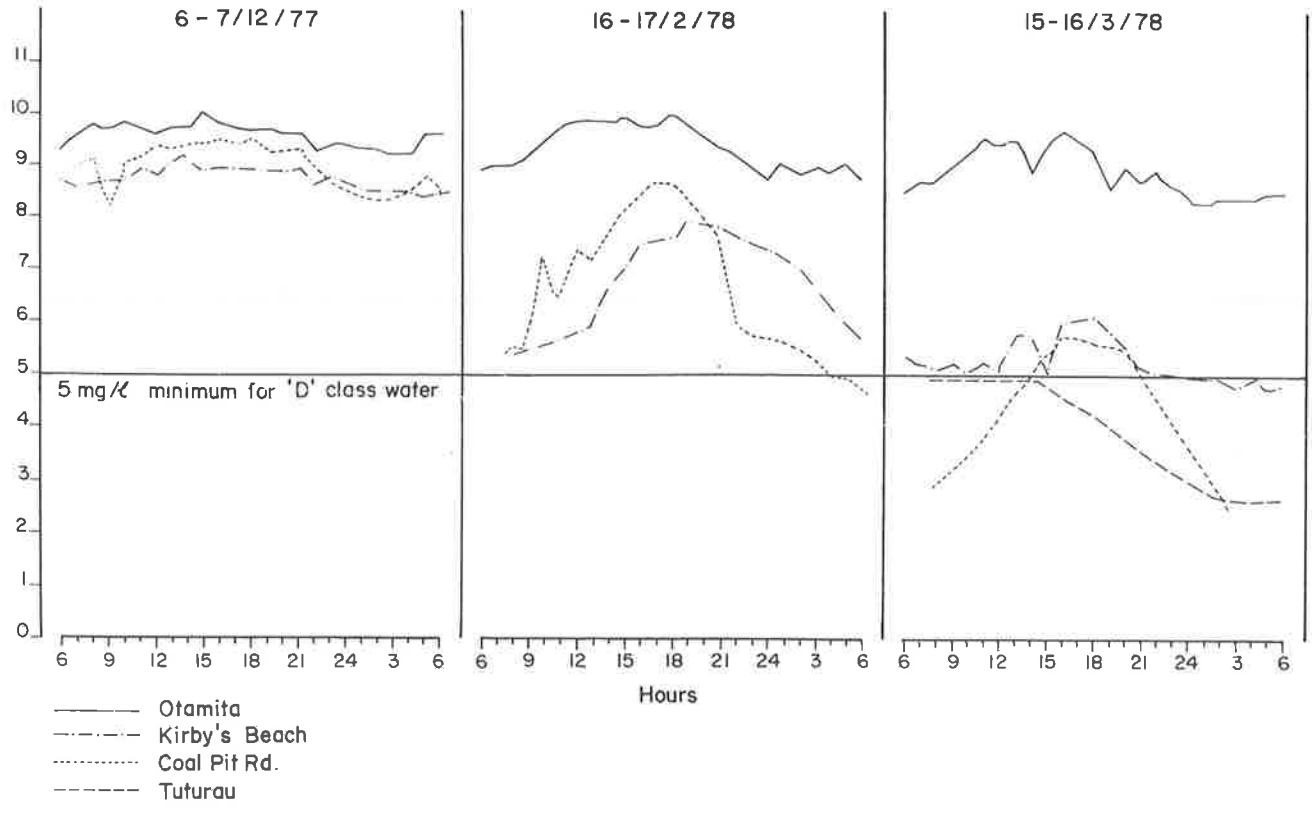


Fig. 5 24-hour dissolved oxygen sampling, Mataura River.

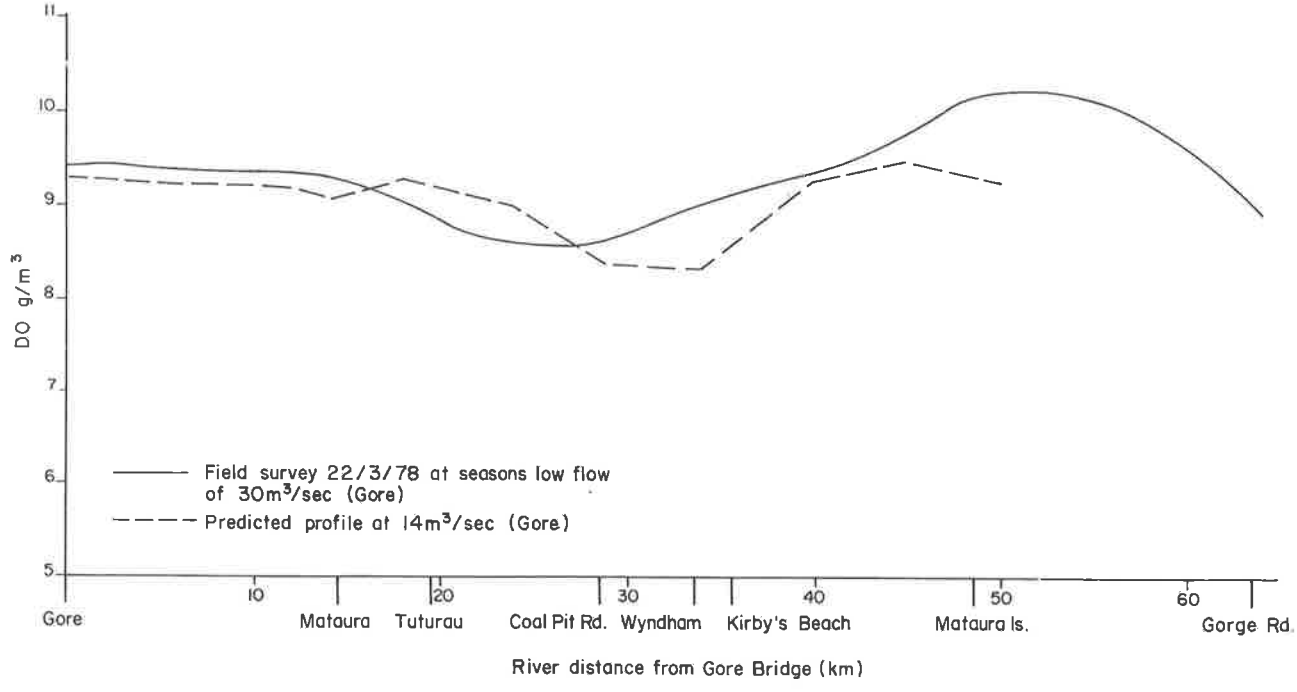


Fig. 6 Mataura River dissolved oxygen profile with about 85% removal of meatworks waste.

taken on 15-16 March 1978 at a Gore flow of 8.1 m^3/s, was the low DO concentrations recorded at Coat Pit Road and Tuturau of 2.7 and 2.8 g/m^3 respectively.

These values compare quite favourably with a predicted minimum concentration of 2.0 g/m^3 between these two points for a Gore flow of 7 m^3/s. This result was predicted for the conditions which existed prior to 85% removal of SFM BOD_5 loading.

Higher than normal summer flows in the Mataura River since March 1978, about the time of commissioning of SFM's effluent treatment plant, have not provided any real opportunity to monitor the river DO concentrations under the reduced waste loading conditions which now exist. Flows at Gore have generally exceeded the model design flow of 14 m^3/s by a factor of two.

A DO profile for the 1979 summer low flow of 30 m^3/s is given in Fig. 6 and is compared with the predicted profile at 14 m^3/s.

2 Biochemical Oxygen Demand

Sampling of effluent discharges and of the river was undertaken in early 1976 to provide effluent BOD_5 loading and river BOD_5 concentration data. A summary of waste loadings is given for BOD_5 in Table 1.

Table 1

Major waste sources	Average volume m^3/day	Average BOD_5 g/m^3	BOD_5 kg/day
SFM — Mataura	11 000	2 200	24 000
New Zealand Paper Mills — Mataura	7 000	70	490
Edendale Dairy Factory/ Lactose Factory — Edendale	1 000	800	800

Relatively few surveys of river BOD_5 have been undertaken. A survey on 15 March 1976 showed a rapid reduction in river BOD_5 concentrations downstream of Mataura, a trend which has subsequently been shown to be fairly typical of the river. The BOD_5 loading from SFM since effluent treatment plant commissioning has been in the region of 1 500 kg/day. River BOD_5 concentrations reflect this change as is evident on Fig. 7. It is notable from this figure that substantial removal of BOD_5 occurred in the Mataura—Wyndham reach prior to commissioning of this plant.

Modelling of dissolved oxygen

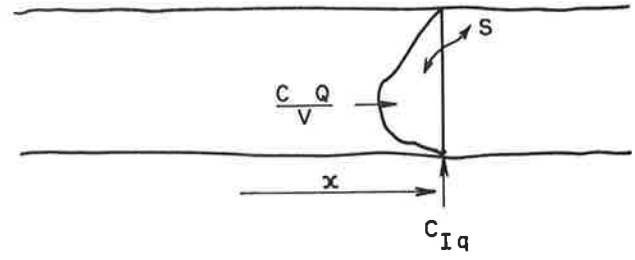
As noted above, by 1976 there was an active proposal to site a pulp mill in the Southland region, possibly on the Mataura River. It was therefore important to determine whether the river could assimilate the waste discharge of 4 t BOD_5/day from such a mill and maintain its D classification (minimum DO = 5 g/m^3). The Catchment Board was also concerned to predict the effects of improved waste treatment by the then existing dischargers to the river. The Board carried out some surveys in this period, the major conclusions of which are given under Survey Results. These data were used by the latter author (G.B.M.) to construct and verify a DO model for the river.

1 Model Identification

Though there was some evidence of diurnal DO fluctuations because of varying waste inflows from the meat works, a steady state model was proposed There were insufficient data available at that time to verify a dynamic model, this being particularly true of waste discharge and river BOD_5 data. The model therefore predicts an average DO profile, about which some variation could occur. It should be noted that the installation of waste treatment will have the effect of ironing out much of this variation.

Since the maximum effect of waste discharges on river DO is observed considerably downstream of the point at which the waste is fully mixed with the river water (this being especially true at Mataura where the river is narrow and swift) a one dimensional model was adopted. The effect of longitudinal dispersion can be expected to be small for steady state conditions and was ignored.

The general form of the model can be described with reference to the figure below which shows a cross-section of the river at which the fully-mixed concentration of DO or BOD_5 is given by the variable C(x).



In the figure

- x = distance from some reference point
- C_I (x) = concentration of DO or BOD_5 in tributary or waste inflow
- Q (x) = river flow rate
- q (x) = inflow rate per unit length of river
- v (x) = mean river velocity
- S (c,x) = source or sink of DO or BOD_5 due to in-river processes

The mass balance for the river may be written in differential form as

$$\frac{dC}{dx} = \frac{S}{v} + \frac{q}{Q}(C_I - C)$$

For the equation to be solved values of S, v, q, Q, and C_I must obviously be given as functions of x. Because of the variability of these terms for this river, analytical solutions could not be simply obtained and a numerical solution was sought using a computer programme written for the Ministry of Works and Development IBM 360/168 Machine. Details are given in McBride (1976).

The form of the source/sink term, S, was taken as follows:—

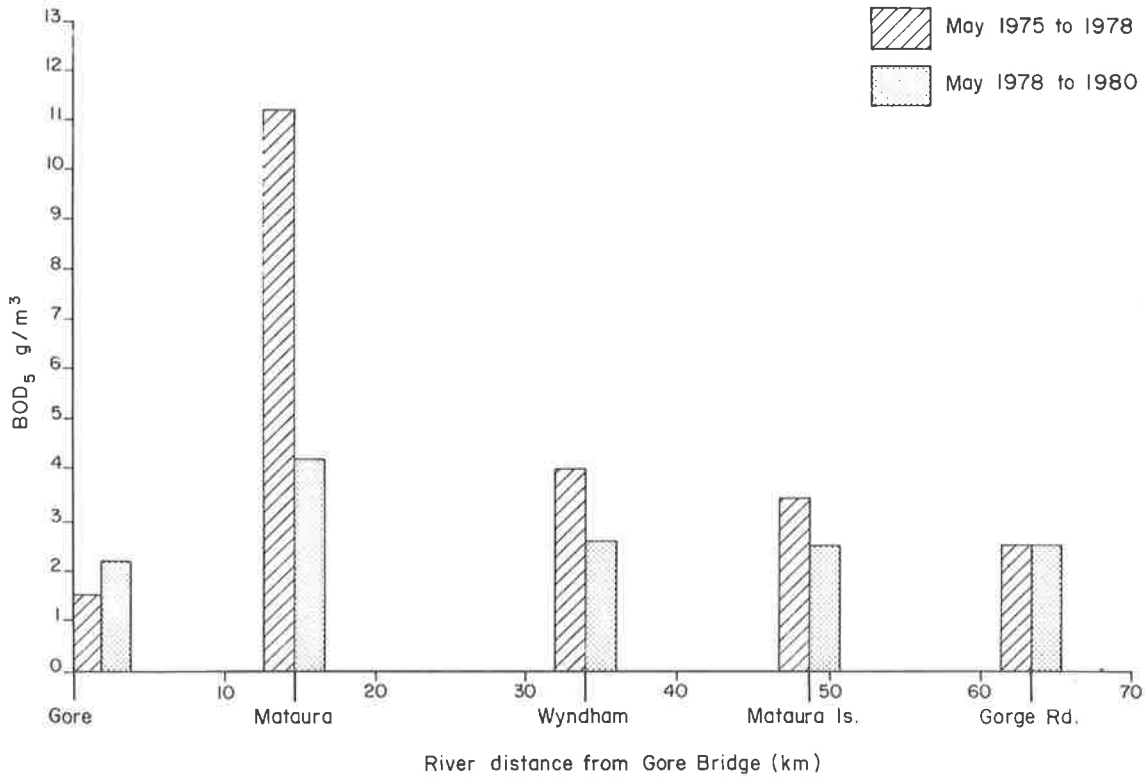


Fig. 7 Mataura River BOD_5 concentrations (Average of measured concentration).

BOD It was assumed that the only significant in-river process was the removal of BOD by aquatic bacteria, modelled by the usual first-order law, i.e.

$$S_{BOD} = -k_1 L$$

where k_1 = prescribed river deoxygenation coefficient (base e)

and L = ultimate river carbonaceous BOD (assumed equal to BOD_5)

the BOD equation is thus

$$\frac{dL}{dx} = -k_1 L/v + q(L_I - L)/Q \qquad (1)$$

DO The average net contribution of photosynthesis and respiration of aquatic plants for this steady-state model was taken to be zero, so that the two significant in-river processes were the source of DO from surface reaeration and the sink of DO by exertion of the oxygen demand, i.e.

$$S_{DO} = k_2 (C_s - C) - k_1 L$$

where k_2 (x) = river reaeration coefficient (base e)

C_s (x) = saturation river DO related to river temperature T(x), by

$$C_s = 14.48 - 0.36T + 0.0043T^2$$

C (x) = river DO

The DO equation is thus

$$\frac{dC}{dx} = \{k_2(C_s - C) - k_1 L\}/v + q(C_I - C)/Q \qquad (2)$$

Finally, the values of k_1 and k_2 at the given river temperature T were related to their given values at the usual reference temperature (20 °C) by standard formulae, e.g., Fair *et al.* (1968)

$$k_1 = k_1^{20}\, 1.047^{T-20}$$
$$k_2 = k_2^{20}\, 1.016^{T-20}$$

It may be seen that the model given by equations (1) and (2) is the same as that of Streeter and Phelps (1925) except that longitudinal variation of parameters such as k_2 and C_s is now allowed.

2 Model Calibration and Verification

Since it was intended to use the model for low flow predictions, river surveys were carried out by Southland Catchment Board staff when the river was at about the 96% low-flow.

The 7 April and 15 April 1976 surveys were used as calibration and verification surveys respectively. These surveys were carried out from Mataura to just upstream from the Mokoreta tributary confluence, and the model was run for the 50 km reach downstream from Gore. Eleven inflows were accounted for in this reach, as measured by the Board's surveys. These included four tributaries (Waikaka, Waimumu, Mimihau and Mokoreta) and five waste discharges (Mataura Meatworks, New Zealand Paper Mills at Mataura, Mataura Borough, Edendale Lactose and Dairy Factories, and Wyndham Town). The river water temperature and velocity varied from 15 °C and 0.36 m/s at Gore to 17 °C and 0.44 m/s at the end of this reach. River discharge, BOD_5 and DO at Gore were 14 m^3/s, 2.0 g/m^3 and 9.5 g/m^3 respectively.

For the calibration run the best fit of predicted and observed river DO was obtained for $k_1^{20} = 1.0$/day and a variable distribution of k_2^{20} as shown on Fig. 8. These latter values were obtained by assigning typical values of velocity and depth at various reaches of the river and computing k_2^{20} from the Churchill - Elmore - Buckingham formula

$$k_2^{20} = 2.3\, vy^{-5/3}$$

where v = river velocity in metres/second

y = river depth in metres.

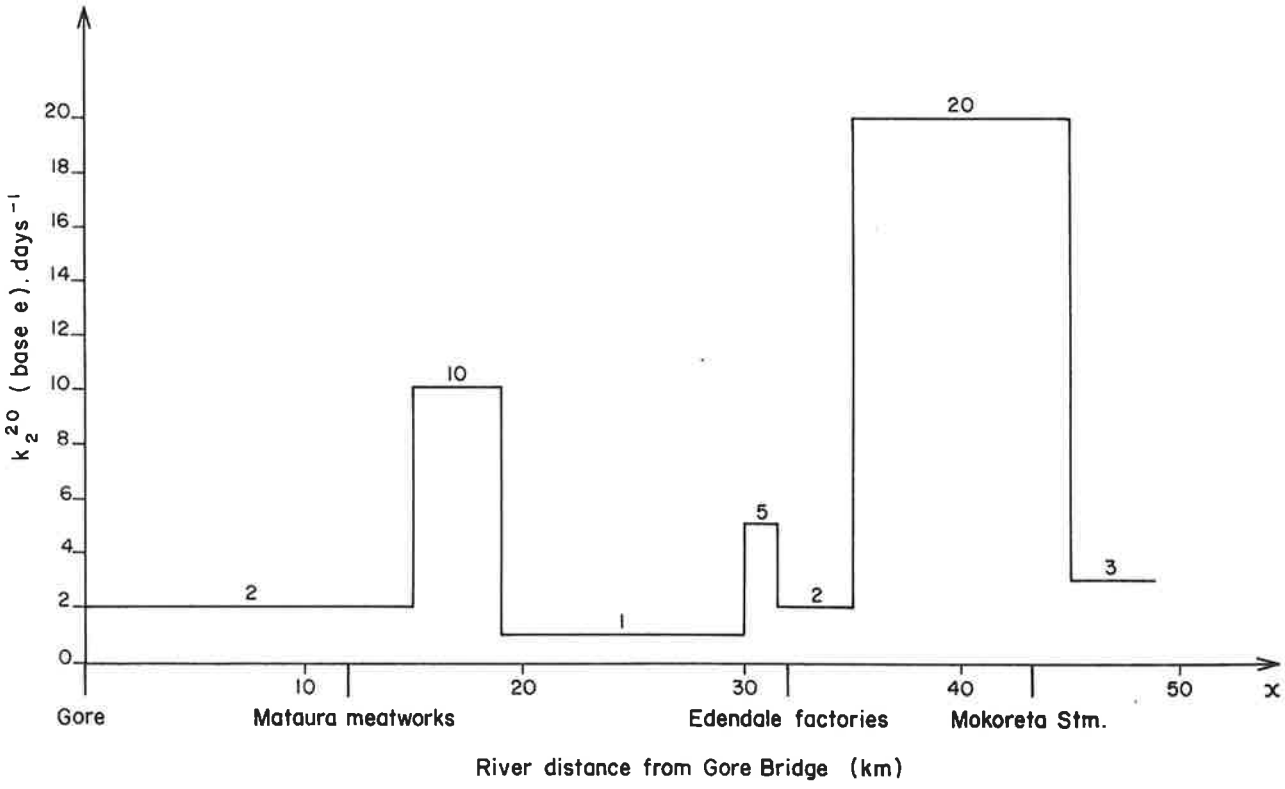


Fig. 8 Assumed variation of reaeration coefficient (k_2^{20}) with downstream distance.

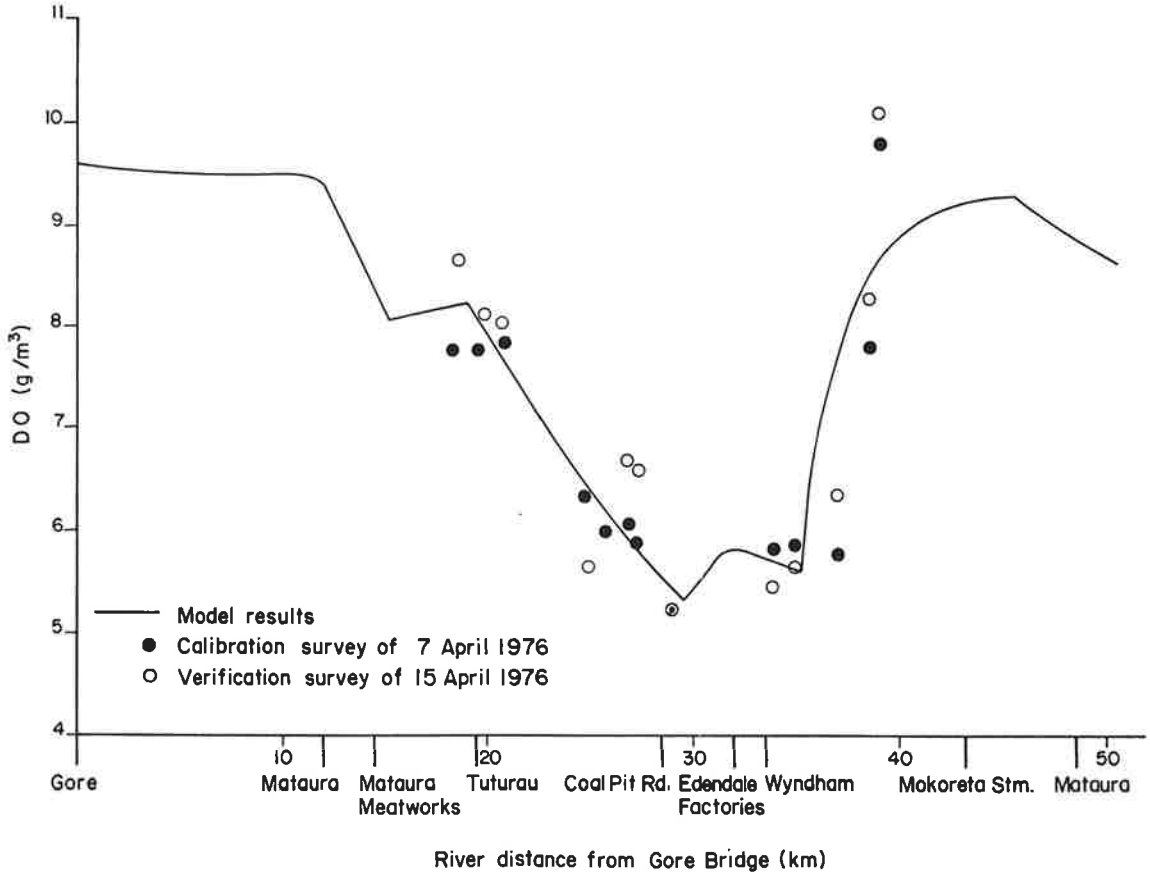


Fig. 9 Model DO results for April 1976 conditions compared to survey results.

The three regions of high coefficient values reflect the rapid regions of the river.

Figure 9 shows the results of the model predictions using the above parameter values (continuous line) and also the results of the calibration and verification surveys. Agreement between observed and predicted DO is seen to be quite good. Notable features of these results are:

—a sag of 4.5 g/m³ occurs some 20 km downstream of Mataura;

—the meat works and Edendale factories are the major point sources of waste to the river;

—the combined effects of tributary inflows and high reaeration coefficient downstream of Mataura and Edendale serve to lessen the impacts of oxygen demand exertion in the river.

The latter effect is quite spectacular downstream of Edendale, and is even under-estimated by the model. Presumably if this region of the river were not rapid and shallow the DO in the river would have substantially breached the classified standard.

The river BOD_5 predicted by the model for these survey conditions shows a value of about 22 g/m³ at Mataura, reducing to about 12 g/m³ near Wyndham. Few measurements of river BOD_5 were taken, but those available suggest that the former figure is about right, but that the latter is about double that measured. The reason for this discrepancy is not clear, and in the absence of more detailed field work, can only be speculated upon.

3 Model Predictions

The model was run with the above values of k_1 and k_2 for an extreme low flow of 7 m³/s at Gore Bridge. A minimum DO of 2 g/m³ was predicted at 30 km from Gore, clearly an unacceptable situation compared to the classified minimum standard of 5 g/m³.

The effect of a pulp mill was assessed by running the model for conditions pertaining during the surveys of April 1976, but with a discharge from Gore Borough's new oxidation ponds (which were filling up in 1976) and with a discharge of 3.9 t BOD_5/day from a pulp mill situated at the proposed site (some 11 km downstream from Mataura). The results are shown in Fig. 10, for both the 1976 waste loading from the Mataura meatworks, and with the meatworks loading reduced by 85%. As is evident from the figure, the introduction of a pulp mill under 1976 conditions lowers the DO in the river by up to 0.5 g/m³. However with the reduction of waste loading from the meatworks, the minimum DO in the river was raised to 8 g/m³. Even at the extreme low flow, the minimum DO predicted was 7.2 g/m³, considerably above the classified minimum standard.

From these modelling studies, it was concluded that a very substantial improvement in river DO would be effected by implementation of secondary treatment of the waste discharge to the river. Even the inclusion of treated pulp mill effluent would not cause serious DO depletion in the river.

Conclusions

Prior to the commencement of this investigation into DO concentrations in the Mataura River, SFM had indicated that the lowest concentrations of DO would be encountered in the vicinity of Wyndham some 20 km downstream of Mataura Borough. Both the field measurements and computer predictions

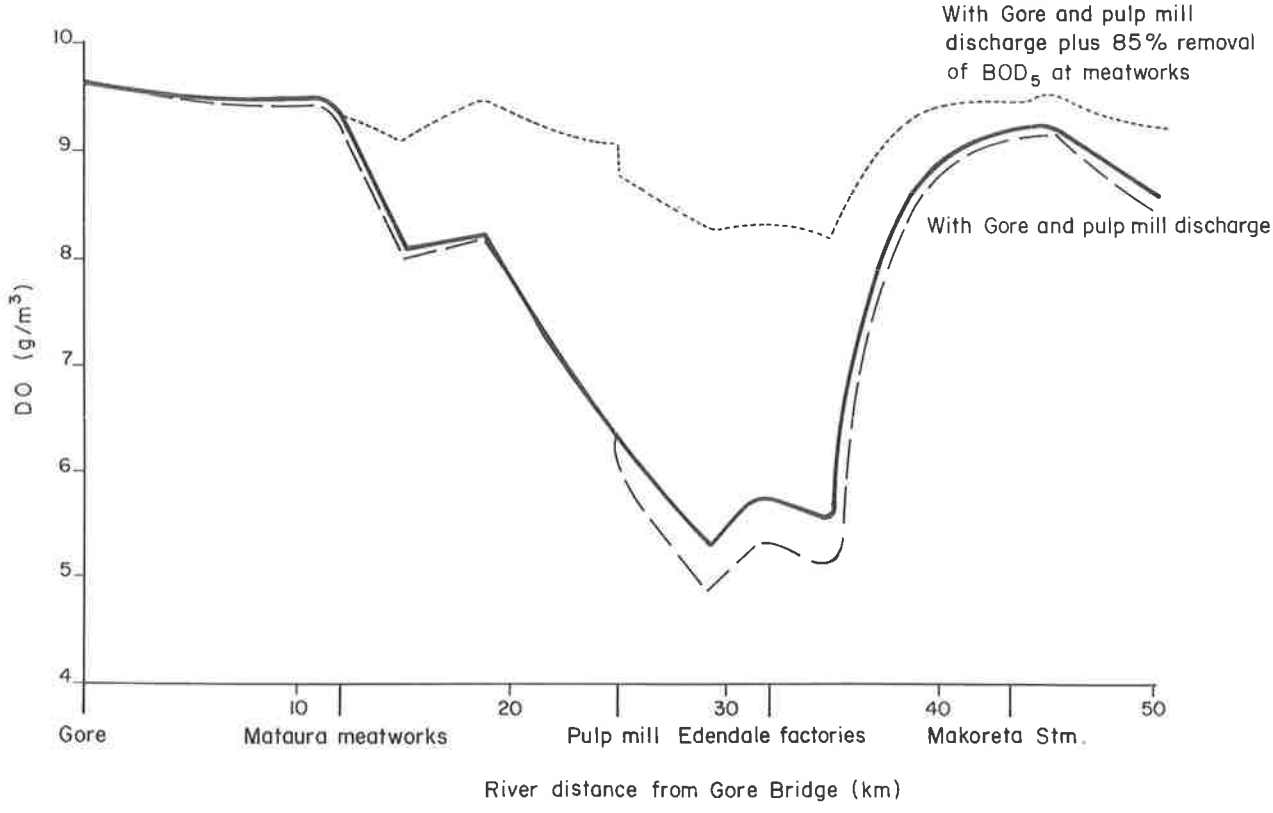


Fig. 10 Model predictions for April 1976 low flow with pulp mill discharge, including effect of 85% reduction of meatworks waste.

subsequently made confirmed this to be the case.

Under the conditions which existed in March 1976, when calibration and verification surveys were undertaken, the minimum DO level of 5.0 g/m³, specified in the Mataura River D classification, was close to being breached. These conditions included a flow in the river at Gore of 14 m³/sec (close to the 96% exceedence value), and the discharge of around 20 000 kg/day of BOD_5 to the river by SFM.

On the basis of the information obtained from these two surveys the computer model predicted that the addition of 3900 kg/day of BOD_5 from the proposed pulp mill would have caused the D classification to have been breached.

If an 85% reduction in BOD_5 waste loading could be achieved by SFM then it was predicted that under March 1976 conditions, the DO would not drop below the higher Class C limit of 6.0 g/m³.

In a report (McMillan 1976) on the location of the proposed pulp mill 25 km downstream of Gore these predictions were used to conclude:

(1) that under the conditions which prevailed at the time (March 1976) a pulp mill would cause the D classification to be breached;

(2) that with suitable upgrading of existing waste discharges, i.e., an 85% BOD_5 removal by SFM, the pulp mill discharge would not breach the dissolved oxygen provisions of either Class D (5.0 g/m³) or Class C (6.0 g/m³).

The field work and model predictions had served their initial purpose.

The effect of extreme low flows in the river, such as occurred in 1956, 1971 and 1978, was determined by re-running the model with a flow at Gore of 7 m³/s.

A minimum DO concentration of 2 g/m³ was predicted for the situation where no reduction of SFM's BOD_5 loading occurred. If an 85% BOD_5 removal was achieved it was predicted that the pulp mill could be accommodated with a resulting DO concentration of 7.2 g/m³, 29 km downstream from Gore. The former of these two predictions was substantially verified in March 1978 when the DO concentration at Coal Pit Road, 29 km from Gore was measured at 2.7 g/m³ (Gore flow = 8.19 m³/s).

These low flow predictions have been of value to the Board in its water quality management programme on the Mataura river.

In addition to the management value of the initial survey there are a number of aspects of the survey results themselves which are worthy of some comment.

(1) It appears that the Mataura River was receiving up to 30 tonnes/day of BOD_5 when all discharges are accounted for.
This loading was being assimilated without the occurrence of serious DO depletion problems, the exceptions being the years of extreme low flow including 1978.

(2) There was a remarkable rise in DO concentration in the river downstream of Wyndham. The rise which was evident in all model predictions and in field data obtained by the Board, is due to vigorous reaeration of the river induced by a number of shallow rapids in the area. Without these conditions, which exist over a distance of about 5 km, there is no doubt that the DO sink would have continued and the D classification substantially breached.

(3) BOD_5 values in the river were predicted and measured to be about 22 g/m³ at Mataura Borough. It was predicted that near Wyndham the river BOD_5 would reduce to 12 g/m³ whereas the few field values available at the time suggested this figure was high by a factor of two. Subsequent field surveys support the latter figure. This discrepancy remains unexplained.

Since the model was completed there has been a significant (about 85%) reduction in BOD_5 loading discharged to the river. The effects of this were discussed in the sections on Survey Results and Modelling. With the lowest recorded DO concentration since 1978 being 8.6 mg/ℓ at a flow of 30 m³/s there is every indication that even under extreme low flow the DO concentration can be maintained above 7.0 mg/ℓ.

These surveys, together with the administrative actions of the Pollution Advisory Council and the Southland Regional Water Board and to a large part the commitment of dischargers to improve effluent quality, has resulted in the elimination of serious oxygen depletion in the Mataura River.

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Appendix I

The Mataura River and catchment

The headwaters of the Mataura River lie in the Eyre Mountain Range, west of Kingston on Lake Wakatipu, where the highest point in the catchment is around 2,040 m. The catchment area, including tributaries is 5,360 km².

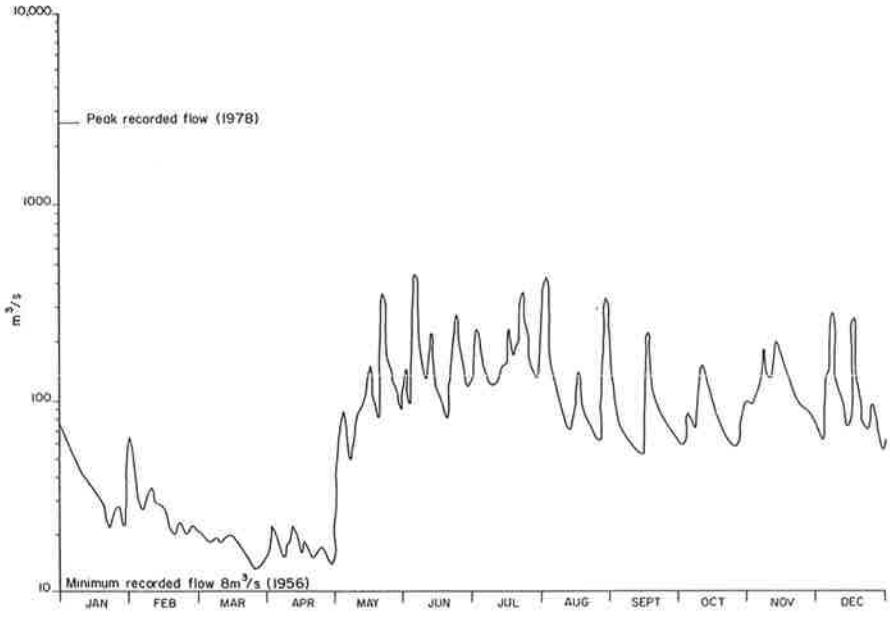
Flow records extend back to 1955 for Parawa in the upper catchment, and to 1961 at Gore. Since 1973/74 the continuity of hydrological data is good.

The lowest gauged flows at Gore are:—

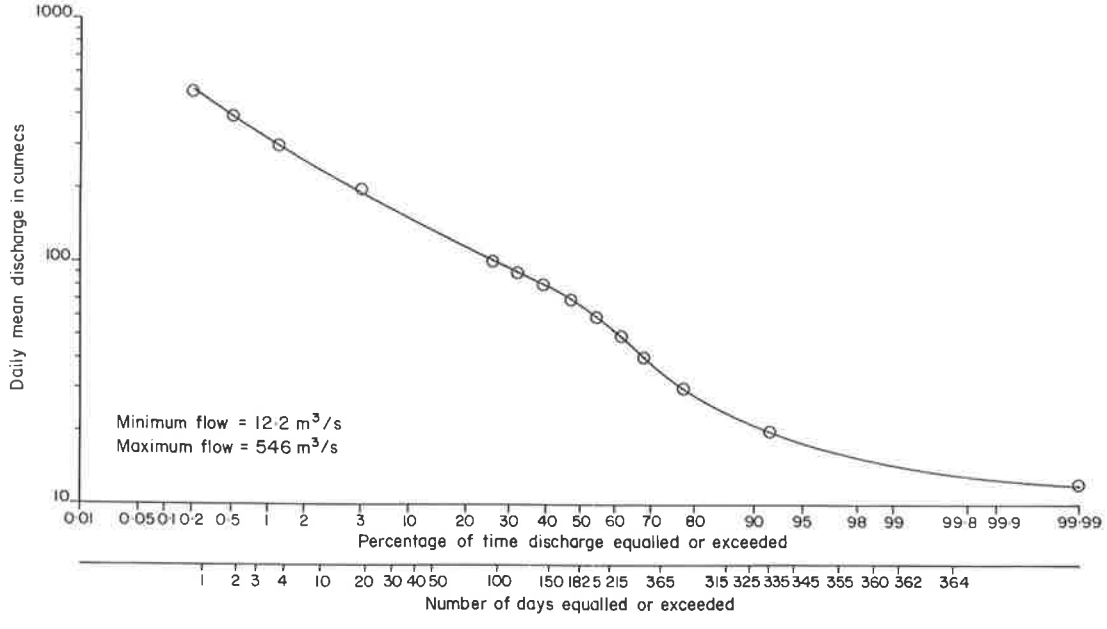
Date	Flow
15/3/56	6.16 m³/s
16/2/71	7.76 m³/s
15/3/78	8.19 m³/s

The annual low flow period occurs, as with most Southland rivers, during the January–March period. Flood flows are considered by most to be a feature of the river. There have been seven "major" floods in the last 10 years. Of these the October 1978 flood was the largest with a peak flow at Gore of 2225 m³/s and at Mataura Island 2600 m³/s.

An annual flow hydrograph for the Mataura River at Mataura Island forms part of this appendix to indicate the seasonal flow patterns in what could be considered a fairly typical year. A flow duration curve for the same site is also given.



Appendix I Annual flow for Mataura at Mataura Island 1976.



Appendix I Flow duration curve and regional catchment data.

Management of BOD in the lower Manawatu River

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A maximum river BOD_5 concentration standard of 5 g/m³ is thought likely to reduce sewage fungus infestations and maintain adequate DO concentrations in the Manawatu River below Palmerston North. The method of apportioning effluent treatment between the three major discharges to meet this standard (established by a technical committee which included representatives of the dischargers) is described and the effluent treatment requirements given. BOD removal between outfall and control site is taken into account.

Background

The Manawatu River is approximately 226 km long, is extensively branching, and drains some 6000 km² of predominantly agricultural land. At Palmerston North (79 km from the sea) the mean flow is 54.6 m³/s with a range of 9–2430 m³/s (period of record: 16 December 1971 — present). Close to Palmerston North City the river is steep (1 m/km), shallow, fairly swift, meanders extensively and has a shingle bed. Some 10–20 km downstream from the city, the gradient decreases (0.1 m/km) and finer sediments deposit on the bed.

In a 5 km reach immediately downstream from Palmerston North, the river receives effluent from five installations (Table 1 and Fig. 1).

The combined effect of these effluents presently causes some degradation of water quality in the river. Dissolved oxygen concentrations are satisfactory for much of the time, notably in winter, but severe oxygen depletion has been observed in summer and a major fish kill caused by anoxic river conditions occurred in January 1978 following a period of prolonged low flow and warm water temperatures.

Another consequence of the discharges is to promote the prolific growth of benthic slimes on the river bed, so called "sewage fungus". These growths are unsightly, produce an unpleasant odour when the river recedes and exclude or smother other aquatic life. Sewage fungus is confined to a comparatively short stretch of river below the three major discharges.

The quality of the river was seen to be unsatisfactory and a technical committee was established in December 1979 comprising representatives of each of the five dischargers, the Wellington Acclimatisation Society, and the convenors — the Manawatu Regional Water Board. The committee's brief was to make recommendations on improvements in effluent treatment required to upgrade river conditions. This approach meant that not only was the combined expertise brought to bear on the problem, but the dischargers and other bodies were a party to the decision-making process and thus were in a better position to appreciate the reasoning behind the fairly stringent effluent limits produced.

Table 1 Discharges to the Manawatu River near Palmerston North.

Discharger	Volume m³/day	Raw BOD kg/day	Treated BOD kg/day	Population Equivalence*
Palmerston North Sewage	16000	6700	4500	66000
Linton Military Camp	365	80	5	7.3
Manawatu Co-op Dairy Co.	1610	12600	12600	185000
New Zealand Pharmaceuticals	10	136	136	200
Borthwicks/CWS Freezing Works	5000	10000	6500	96000
Total	23000	30000	23700	350000

(*Raw sewage from this number of people would contain the equivalent amount of BOD as is discharged from each installation. Based on 0.68 kilograms per person per day.)

Processes operating in the river

The results of surveys carried out during 1975–1977 indicate that sewage fungus growths are prolific within 3–5 km of the major outfalls. Besides being unsightly and causing odour problems, sewage fungus appears to have three effects on river water quality.

(i) Sewage fungus causes an unexpectedly high rate of removal of BOD from the river water in the immediate vicinity of the outfalls (Fig. 2). Although detailed BOD and DO budgets have not been drawn up, it is suspected that a substantial portion of the BOD removed by the sewage fungus is not exerted immediately because either
   (b) organic matter may be stored in plant tissue and flushed from the river during high flows, or
   (b) sewage fungus sloughed off during times of low to medium flow may not break down as rapidly as the effluents. Thus the sewage fungus may have a beneficial role to play in river self-purification.

(ii) Sewage fungus sometimes causes rapid deoxygenation of the river water, especially at high temperatures and low flows (Fig. 3). It is clear that under low flows and high temperatures some of the BOD stored by the sewage fungus is exerted and the effect of the attached growths may be to cause a higher than normal rate of deoxygenation. By comparison with the reach infested with sewage fungus, the lower reaches of the river exhibit low BOD removal and deoxygenation rates.

(iii) Sewage fungus causes a large diurnal variation in DO concentration.

Curtis' work in English rivers (Curtis & Curds 1971; Curtis 1972) indicates that prolific growths of sewage fungus do not establish unless BOD_5 concentrations consistently exceed 5 g/m³. This appears to be validated in this country by the observation that in the Oroua River (a tributary of the Manawatu) sewage fungus proliferated below the Feilding freezing works when the river BOD_5 concentrations ranged from 5–10 g/m³ but substantially disappeared when improved effluent treatment reduced river BOD_5 concentrations to an average of 3 g/m³.

Setting effluent standards

A maximum mean daily and night-time BOD_5 concentration of 5 g/m³ at a control site downstream from all three discharges was adopted as the target receiving water standard. Aerial photography of dye released at the Borthwicks/CWS outfall was used to select a control site where complete lateral mixing was attained (Fig. 1).

The three discharges are close enough together so that the river does not return to ambient conditions between them, and it was necessary to consider the three discharges as contributing to a single effect. Thus the problem facing the committee was to apportion the acceptable BOD massflow at the control site between the three dischargers. Although there are serious deficiencies in our knowledge of the behaviour of sewage fungus in the Manawatu River, it was felt that an effort should be made to allow for its beneficial effect in removing BOD when setting effluent standards. To this end the BOD removal between each outfall and the control site was taken into account.

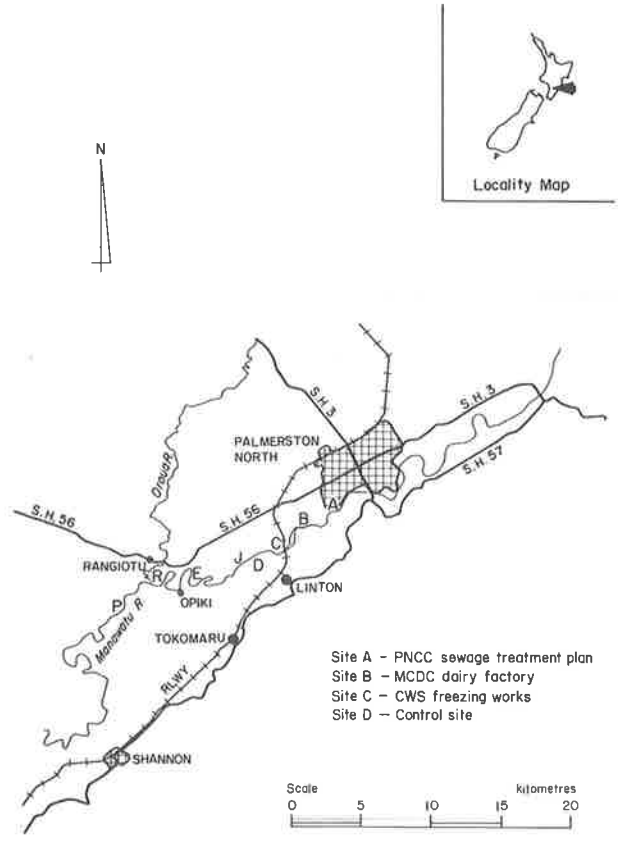

Fig. 1 Location Map.

Clearly the BOD mass flow rate which the river can tolerate increases with increasing river flow rate. It was agreed that higher BOD mass inflows should be permissible at high river flows than at low river flows provided always that the BOD concentration at the control site does not exceed 5 g/m³. This approach enables considerable savings to be made in effluent treatment costs. A minimum design flow of 13 m³/s was adopted.

Effluent standards were set on the basis of anticipated mean daily raw BOD load together with an allowance for a 10% contribution in BOD load for expansion and from other minor sources.

Model for BOD concentration

Assuming the channel is uniform, BOD inflows are steady, lateral mixing occurs rapidly below each outfall, BOD removal can be approximated as a first order process and the BOD removal rate depends only on the effluent, then the BOD concentration at the control site is given by

$$S = \frac{M_1}{Q}e^{-k_1t_1} + \frac{M_2}{Q}e^{-k_2t_2} + \frac{M_3}{Q}e^{-k_3t_3} + S_0 \quad (1)$$

where S, S_0 = BOD_5 concentration at the control site, and above Palmerston North; M_1, M_2, M_3 =

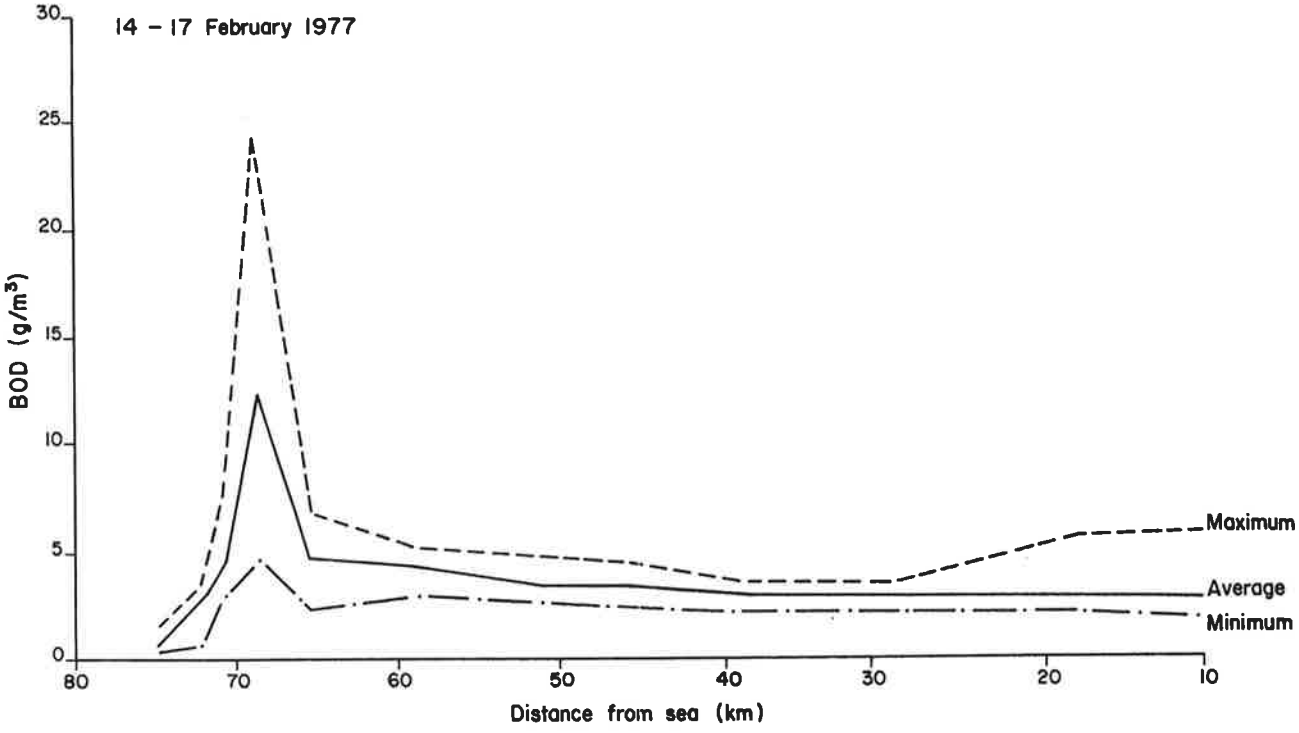

Fig. 2 Data showing the high rate of BOD removal near Palmerston North.

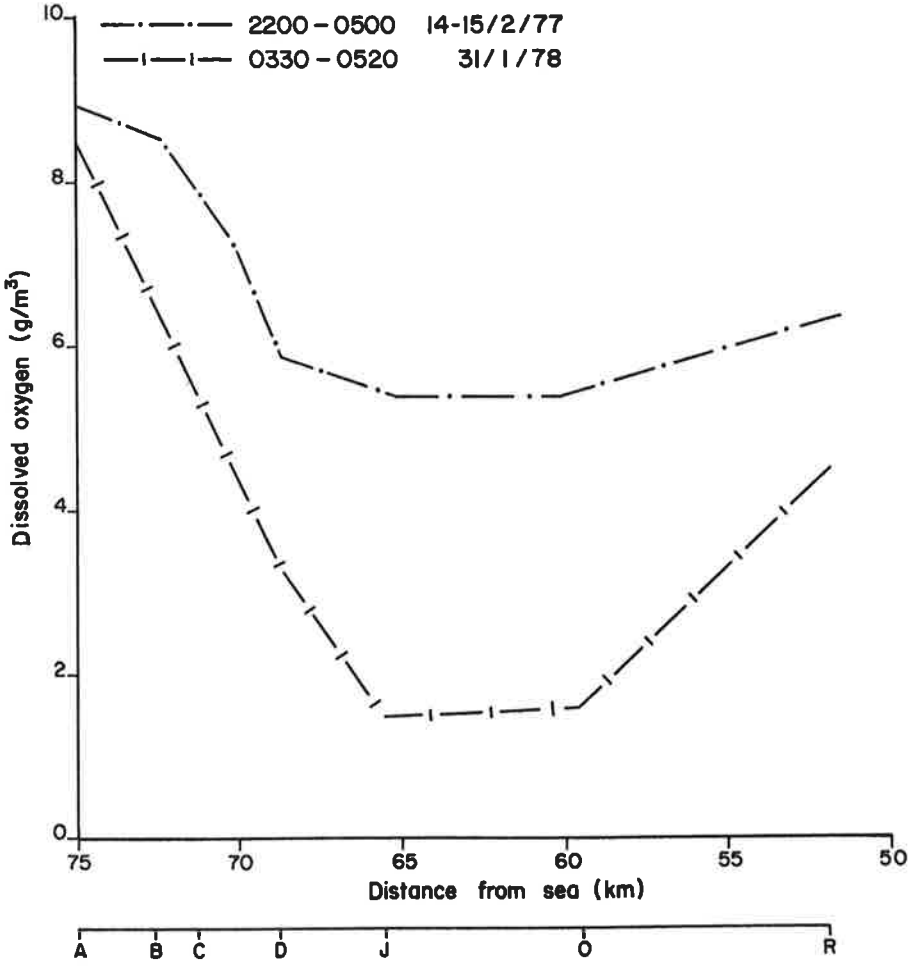

Fig. 3 Data showing the high rate of deoxygenation near Palmerston North.

BOD_5 massflow at outfalls 1, 2, and 3 respectively; Q = river flow rate; k_1, k_2, k_3 = BOD removal rate coefficients for effluents 1, 2, and 3 respectively; t_1, t_2, t_3 = times of travel from outfalls 1, 2, and 3 respectively to the control site.

Travel time varies with river flow rate according to

$$t_b \cong t_a \left(\frac{Q_a}{Q_b}\right)^{2/5} \quad (2)$$

where t_a, t_b = travel times at river flows Q_a, Q_b respectively.

If the BOD massflow at each outfall is taken as a proportion of the raw BOD massflow, and an allowance is made for a 10% contribution to river BOD massflow from expansion and minor sources, then in order to meet the target receiving water standard:

$$\left(1 - \frac{a}{100}\right)(S^* - S_o) > \frac{1}{Q}\sum_{i=1}^{3} f_i R_i \exp(-k_i t_i) \quad (3)$$

where a = contribution from expansion and minor sources (about 10%); S^* = target receiving water standard (adopted as 5 g/m³); R_i = raw BOD_5 load of discharger i; and f_i = % BOD load remaining after treatment.

The committee agreed that the most equitable method of apportioning effluent treatment costs between the three main dischargers was to require that

$$f_1 = f_2 = f_3 = f \quad (4)$$

This required that

$$fR_i = M_i < Q(S^* - S_o)\left(1 - \frac{a}{100}\right)\frac{R_i}{\sum_{i=1}^{3} R_i \exp(-k_i t_i)} \quad (5)$$

In order to determine f and hence M_i from equation (5), k_i and t_i must be known. Data from surveys carried out on 12 February 1977 and 16 December 1975 (Currie 1977) gave some indication of k and t values but to obtain more precise values a joint experiment was conducted on 22 March 1979 involving some 30 people from Manawatu Regional Water Board, Palmerston North City Council, Dairy Research Institute, Borthwicks/CWS Ltd, and Hamilton Science Centre. 5.4 kg of Rhodamine WT dye was released from the PNCC sewage treatment plant. Samples of river water were collected from five sites and analysed for dye, BOD_5 and DO. BOD massflows were measured regularly at each of the three major outfalls. Travel times and BOD removal rate coefficients were estimated from the results of this and other experiments (Table 2). Also shown in Table 2 are the k values which might be expected in the Manawatu River if sewage fungus were absent based on the observation that 70% of the BOD removal in the channels studied by Curtis (1972) was due to sewage fungus. In the absence of other information the committee adopted values midway between the figures based on Curtis (1972) and those measured on 22 March 1979 (Table 2).

Figure 4 shows the permissible BOD loads and required treatment to maintain the target receiving water standard as a function of flow. The percentage treatment required is fairly high at low flows but decreases substantially as flow increases. Figure 5 shows the percentage of time that a particular level of treatment is required.

Discussion

This study has produced a set of recommendations based on a fairly limited understanding of the behaviour of sewage fungus which nevertheless should ensure a substantial improvement in river appearance and hopefully will eliminate the severe oxygen depletion which results from high respiration rates in the sewage fungus beds.

Two changes may occur in the river if sewage fungus is eliminated. Firstly, it appears that under some flow conditions sewage fungus removes BOD from the river and stores it until high flow scours and removes it from the river. Eliminating sewage fungus may result in exertion of a higher proportion of the BOD load than at present. However, adoption of the committee's recommendations should limit BOD_5 concentrations to the level where serious DO depletion will not occur. Secondly, it has been suggested (Cooke *et al.* 1980) that sewage fungus may be replaced by benthic algae which will cause a large diurnal DO variation and aggravate DO depletion at night. Surveillance of the effectiveness of the proposed control measures together with studies on the benthic communities will indicate whether any additional effluent treatment is required to maintain adequate water quality in the Manawatu River.

References

Cooke, J. G.; Tilman R. W.; Syers J. K. 1980: Characterisation of municipal sewage and meat works effluent discharges into the Manawatu River. *New Zealand Journal of Science 23:* 387–97.

Currie, K. J. 1977: Water Quality Management Report — Manawatu River below Palmerston North. Manawatu Regional Water Board.

Table 2 BOD removal rates in the Manawatu River.

Reach	Travel time on 22/3/79 at 25 m³/s	BOD removal rate, k				
		12/2/77	16/12/75	22/3/79	30% of 22/3/79 based on Curtis (1972) see text	Design values
	hrs	hrs⁻¹	hrs⁻¹	hrs⁻¹	hrs⁻¹	hrs⁻¹
A–B	2.7	0.05	0.04	0.15	0.04	0.10
B–C	1.4	–	0.19	0.44	0.13	0.29
C–D	1.0	0.05		0.17	0.05	0.11

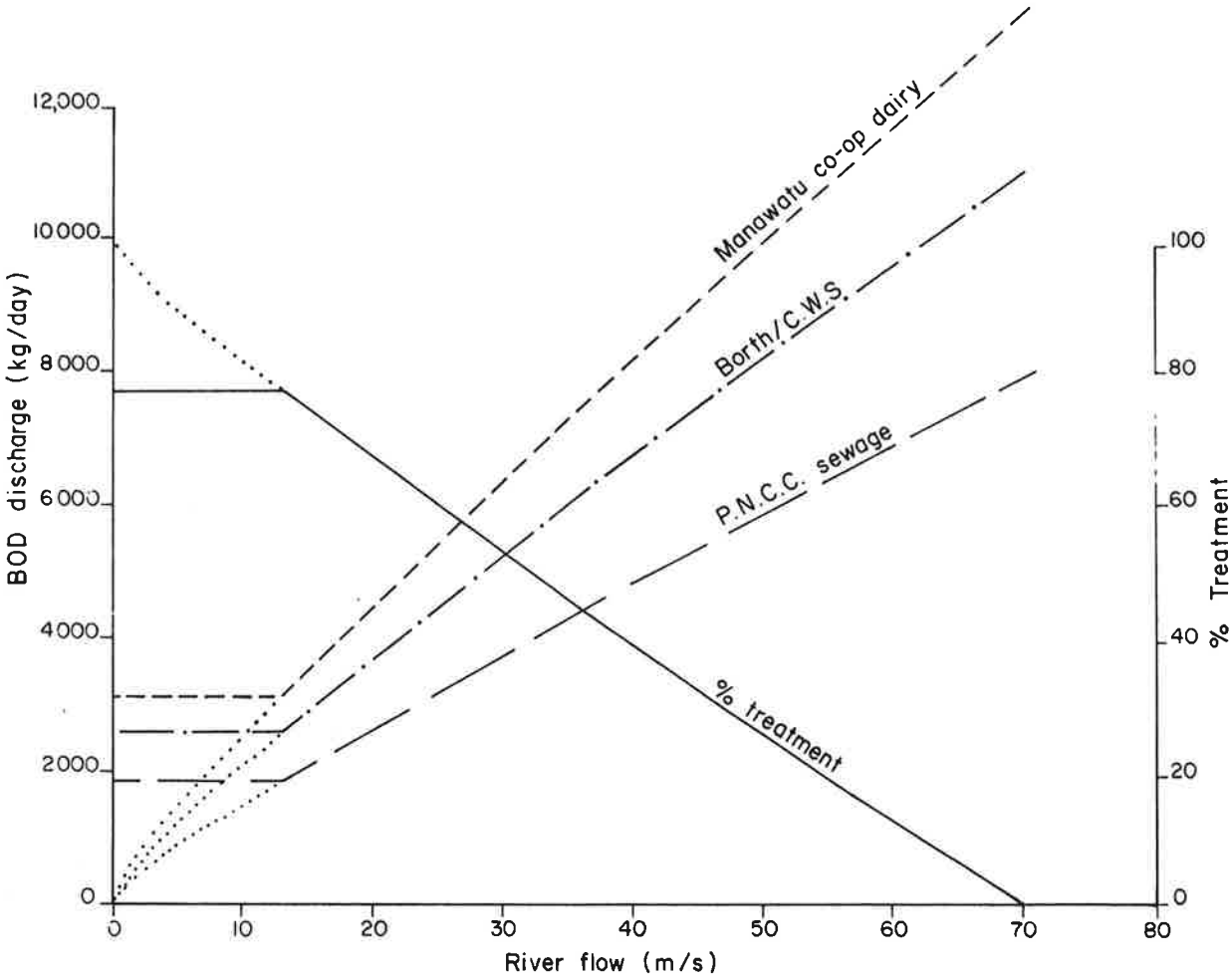

Fig. 4 Recommended permissible BOD loads and required treatment.

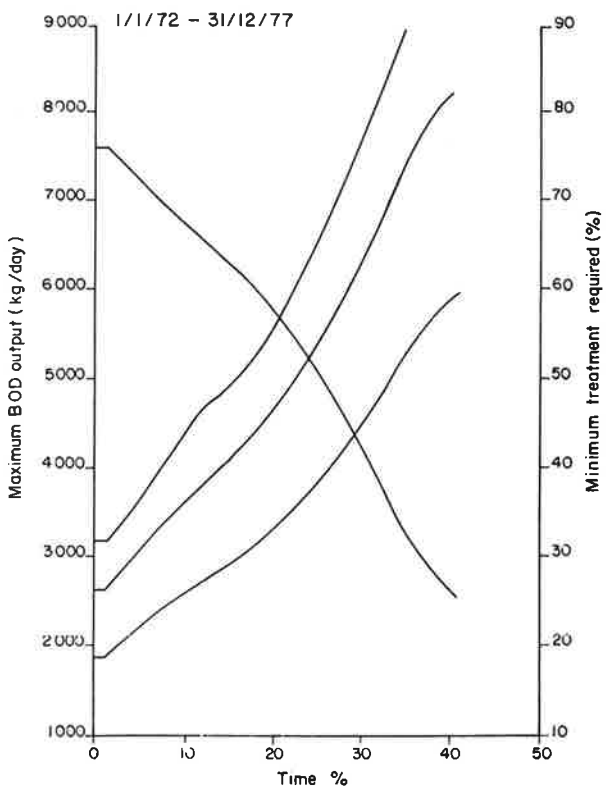

Fig. 5 Estimated frequency distribution of treatment, based on river flows recorded 1 January 1972–31 December 1977.

Curtis, E. J. C.; Curds, C. R. 1971: Sewage fungus in rivers in the United Kingdom: the slime community and its constituent organisms. *Water Research 5:* 1147–59.

Curtis, E. J. C. 1972: Sewage fungus in rivers in the United Kingdom. *Journal of the Water Pollution Control Federation Pt.6:* 673–85.

Waikato River DO simulations

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A 5 year study of water quality in the Waikato River has recently been completed which included development of a 'research' model for simulating dissolved oxygen. The objectives and structure of this model are reviewed and examples given of how the essential components of the 'research' model have been distilled to produce two 'management' models.

Introduction

Water quality of the Waikato River has been the subject of a recently completed 5 year study. This study aimed to "provide information about the river in a form in which it could be used as a basis for management". It was envisaged that this could be achieved by "carrying out a comprehensive water quality survey" and producing "a model that predicts changes in dissolved oxygen, coliform bacteria, nutrient material and biological populations" (Ridall in Strachan 1979). It was also envisaged that expertise developed during this study could be usefully employed on other New Zealand rivers. The majority of the field work and all of the modelling work was done on the lower part of the river between Lake Karapiro and the sea. To date only dissolved oxygen has been modelled.

Initially the modelling work sought to help interpret field measurements and test our understanding of how the river behaved. This resulted in what can be termed the 'research' model, and was completed in 1975. At present, steps are being taken to distil the essential components of the research model to produce what can be termed 'management' models which can be used to predict the effects of changing effluent load and river flow. The objectives and structure of these two models are somewhat different.

Research Model

The research model needed to include all of the processes with the potential to influence BOD and DO concentrations, since initially we did not know what mechanisms were important in the Waikato River. It also needed to be flexible so that it could be changed easily as required.

Details of the model are given elsewhere (Rutherford 1975) but its main features can be summarised as follows:

1 BOD and DO concentrations were predicted from a pair of coupled one-dimensional unsteady mass conservation equations which included the effects of advection, longitudinal dispersion, tributary inflows, point sources, BOD exertion, atmospheric reaeration, and aquatic plant metabolism.

2 River flows were assumed steady and non-uniform. Mean velocities and cross-sectional areas were obtained from backwater curves predicted using the extensive surveyed cross-section data on the Lower Waikato River. Predicted water levels were checked against measured profiles at several river flows.

3 Longitudinal dispersion was assumed steady and non-uniform. Rates of dispersion were estimated from cross-section velocity distributions measured at five regular gauging sites using the method developed by Fischer (1966). This method was found to give good results when compared with those measured using dye in a 30km stretch below Hamilton City. Longitudinal dispersion was found to influence BOD concentrations close to major inflows which exhibited large diurnal fluctuations in flow (notably the AFFCO freezing works at Horotiu), but was found to have only a minor influence on DO concentrations.

4 BOD concentrations in the river seldom exceed 3 g/m^3 and consequently it was considered sufficient to model BOD exertion using simple first order kinetics. It was difficult to decide on a value for k_1, the BOD exertion rate, for two reasons. Firstly field measurements of both BOD and DO were affected by the presence of aquatic plants, notably phytoplankton, and secondly laboratory derived values were considered unreliable because the same turbulence and contact with the sediments which occur in the river could not be produced in the laboratory. The best fit between observed and predicted DO profiles was obtained with k_1 (base e) values between 0.050 and 0.075/hr.

5 The reaeration rate coefficient, k_2, was difficult to evaluate from field data for the same reasons given in 4 above. Estimates were made from empirical formulae published by O'Connor & Dobbins (1958), Churchill *et al.* (1962), and Isaacs and Gaudy (1968). Initially k_2 (base e) was taken as 0.025/hr but it is now considered that at low flow k_2 lies in the range 0.035–0.065/hr.

6 The effects of macrophytes were estimated using WVA data on the extent of weed beds and various published figures on rates of photosynthesis and respiration. It was concluded that macrophytes have very little effect on cross-section average DO concentrations under normal circumstances,

contributing less than 0.5 g/m³ to the diurnal variation in DO even under summer low flows.

7 The effects of phytoplankton were estimated using algal counts together with oxygen production and consumption rates measured *in situ* using light and dark bottles. It was found that the diurnal DO variation of 1.5–3.5 g/m³ observed during summer low flow could be explained satisfactorily by modelling phytoplankton metabolism.

8 It was inferred that periphyton have very little effect on DO concentrations in the river.

The conclusions which were reached on the basis of this modelling were:

1 BOD exertion causes a comparatively small oxygen sag, about 1 g/m³ in summer low flow. The largest discharger of organic waste matter, AFFCO freezing works at Horotiu, causes at most about 0.5 g/m³ DO depletion; Hamilton City and the NZCDC dairy factory at Te Rapa jointly cause at most about 0.25 g/m³ and the tributaries jointly cause about 0.25 g/m³. Diurnal variations in effluent load have only a minor effect on DO concentrations. The changes in BOD load on the river likely in the near future as a result of increased urbanisation or increased treatment of effluent appear unlikely to alter the oxygen sag markedly.

2 Aquatic plant metabolism causes a large diurnal variation in DO with an amplitude between 1.5 and 3.5 g/m³ during summer low flow. DO has been recorded below 6 g/m³ on one occasion in the early morning near Rangiriri. (Much of the river is classified class D for which the lowest acceptable DO concentration is 5 g/m³.) Modelling indicates that phytoplankton are largely responsible for the diurnal variation and that macrophytes and periphyton have a comparatively minor impact.

3 Modelling studies indicate that if phytoplankton populations were damaged severely (for example by toxic wastes or thermal shock) and BOD concentrations increased as a result, then more severe oxygen depletion could result (Rutherford 1975 and Rutherford in Strachan 1979). This model does not predict how much damage might occur in any given situation but if such information were available from other sources then the model can predict the DO sag likely to result.

Management Models

On the basis of experience gained using the research model, various simplifications can be made. Two models are described here: a steady load model and an unsteady load model. Both models are simplified by first simulating BOD exertion and reaeration in isolation and then superimposing on this sag the effects of aquatic plant metabolism. This approach is felt to be valid in a river such as the Waikato where BOD exertion is comparatively small.

Steady Load Model

The standard Streeter-Phelps model can be modified to account for aquatic plant metabolism as follows. First BOD and dissolved oxygen deficit (DOD) profiles are calculated from

$$B(x) = B_o e^{-k_1 T} \quad (1)$$

$$D(x) = \frac{k_1 B_o}{k_2 - k_1}\left(e^{-k_1 T} - e^{-k_2 T}\right) + D_o e^{-k_2 T}$$

where x = distance down channel; T = time of travel from x_o to x; B_o,D_o = BOD and DOD at x_o; k_1, k_2 = BOD exertion and reaeration rate.

As written, equations (1) and (2) hold in a uniform channel reach with no inflows. Where k_1 or k_2 change and/or inflows are important, the channel must be divided up into uniform segments with boundaries at each important inflow or change in parameter value. Equations (1) and (2) are then applied to each segment in turn starting at the most upstream and a mass balance done at each boundary to determine the appropriate values of B_o and D_o (Velz 1970).

The effects of aquatic plant metabolism can be approximated by

$$D^*(x,t) = D(x) + \tfrac{1}{2}A(x)\cos\left(\frac{\pi t}{12}\right) \quad (3)$$

where t = time (hrs) measured from the time of minimum DO (in early morning); A(x) = amplitude of diurnal DO variation (g/m³). In particular the maximum DOD is D(x) + ½A(x) and the minimum is D(x) − ½A(x). Figure 1 illustrates the methodology.

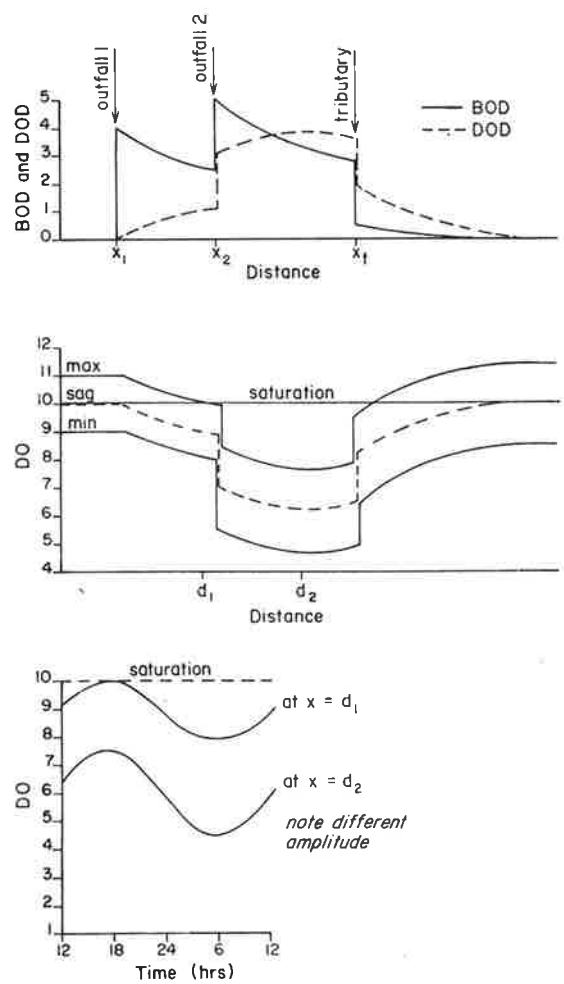

Fig. 1 Incorporating aquatic plant metabolism on steady load models.

A(x) was estimated from diurnal surveys conducted in the Waikato River by MWD and ARA. It varied depending on the numbers of algae present as shown by Fig. 2. As a first approximation other factors such as water temperature and flow can be neglected and then

$$A(x) = \frac{0.10P}{0.20 + 0.025P} \quad (4)$$

where P = phytoplankton biomass (g/m³).

Equations (1)–(4) are readily solved on a small programmable calculator such as an HP 33E.

Figure 3 shows simulations made using equations (1)–(4) with the parameters and input data given in Table 1. Also shown are DO data measured during a diurnal survey on 23–24 January 1974. Agreement is fairly good except perhaps in the vicinity of kilometre 150 where predicted DO depletion is less than that observed.

Non-Steady Load Model

The BOD and DOD concentrations in a uniform channel reach are (Bennett 1972)

$$B(x,t) = \frac{W}{A\sqrt{4\pi Et}} \exp\left\{-\frac{(x-Ut)^2}{4Et}\right\} \exp\{-k_1 t\} \quad (5)$$

$$D(x,t) = \frac{W}{A\sqrt{4\pi Et}} \exp\left\{-\frac{(x-Ut)^2}{4Et}\right\} (\exp(-k_1 t) - \exp(-k_2 t))\frac{k_1}{k_2 - k_1}$$

$$+ \frac{W_1}{A\sqrt{4\pi Et}} \exp\left\{-\frac{(x-Ut)^2}{4Et}\right\} \exp(-k_2 t) \quad (6)$$

where W = mass of BOD at x = 0, t = 0; W_1 = mass of DOD at x = 0, t = 0; A = channel cross sectional area (m²); E = longitudinal dispersion coefficient (m²/s); U = mean velocity (m/s).

Where several inputs occur either at different times or different locations solutions for BOD and DOD as functions of x at a specified t can be obtained separately using equations (5) and (6) and because the governing equations are linear, these can simply be added to obtain the complete solution.

A non-uniform channel may be sub-divided into uniform reaches and equations (5) and (6) used to calculate BOD and DOD concentration versus time profiles anywhere in each reach including the downstream boundary of the reach (see Fig. 4). This technique is only valid for small $\frac{k_1 E}{U^2}$.

An alternative method of handling non-uniform channels is to average coefficients along their length, and to locate all inflows and tributaries at the upstream boundary. This method was adopted here.

As before, the effects of aquatic plants can be approximated by adding a sinusoidally varying term, see equations (3) and (4).

Equations (5) and (6) can be solved on a programmable calculator such as an HP 33E.

In March 1979 emergency discharges of milk were made to several rivers in the Waikato and Hauraki Plains region. Discharges to the Waikato River were intermittent and therefore could not accurately be simulated using equations (1) – (2). On 5 March 1979 some 666 m³ of raw milk were released between about

Table 1: Parameters used to obtain predictions shown in Fig. 2

	Distance from sea (km)	Flow (m³/s)	BOD_5 (g/m³)	DO (g/m³)
Waikato : Hamilton	115	150	0	8.0
: Mercer	40	200	..	..
Waipa : Ngaruawahia	95	50	1	6.5
		BOD load (kg/d)		
Hamilton City NZCDC Dairy Factory	110	6500	combined	
AFFCO Freezing Works	100	12000		
		Symbol	Value	
BOD decay rate		k_1	0.075/hr	
Reaeration rate		k_2	0.050/hr	
Amplitude of diurnal fluctuation		A(x)		
: Hamilton			1.00 g/m³	
: Mercer			1.50 g/m³	
(linear variation between)				

0900 and 1900 hours (NZCDC *pers. comm.).* Two synoptic surveys of the river were conducted from bridges by a team travelling by car, one on the afternoon of 5 March 1979 and the other early in the morning of 6 March 1979. Samples were collected over a 3–4 hour period, but using known river times of travel approximate instantaneous COD and DO profiles were calculated. These are shown in Fig. 5. High COD's can be seen between kilometres 80 and 100 in the first survey and the DO depletion which this caused can be seen between kilometres 60 and 80 in the second survey. The two DO profiles are not directly comparable because algae metabolism has affected them as can be seen at kilometres 100–115 and 30–80.

Simulations were made with the following assumptions:

1 666 m³ of milk were discharged uniformly between 0900 and 2100 on 5 March 1979.
2 Milk has a COD = 150,000 g/m³ and BOD = 100,000 g/m³.
3 River flow was 150 m³/s at Hamilton and 200 m³/s at Mercer. The difference was assumed equivalent to a 50 m³/s inflow in the Waipa River at kilometre 95, which had a DO of 7.0 g/m³ and a COD of 7.5 g/m³.
4 Background COD in the river was 7.5 g/m³ which was not exerted.
5 Algal metabolism caused a diurnal DO fluctuation of 1 g/m³ and 0.5 g/m³ was added to DO predictions made at 2100 hours 5 March 1979 and 0.5 g/m³ was subtracted from predictions made at 0800 hours 6 March 1979.
6 k_2 was 0.050/hr.

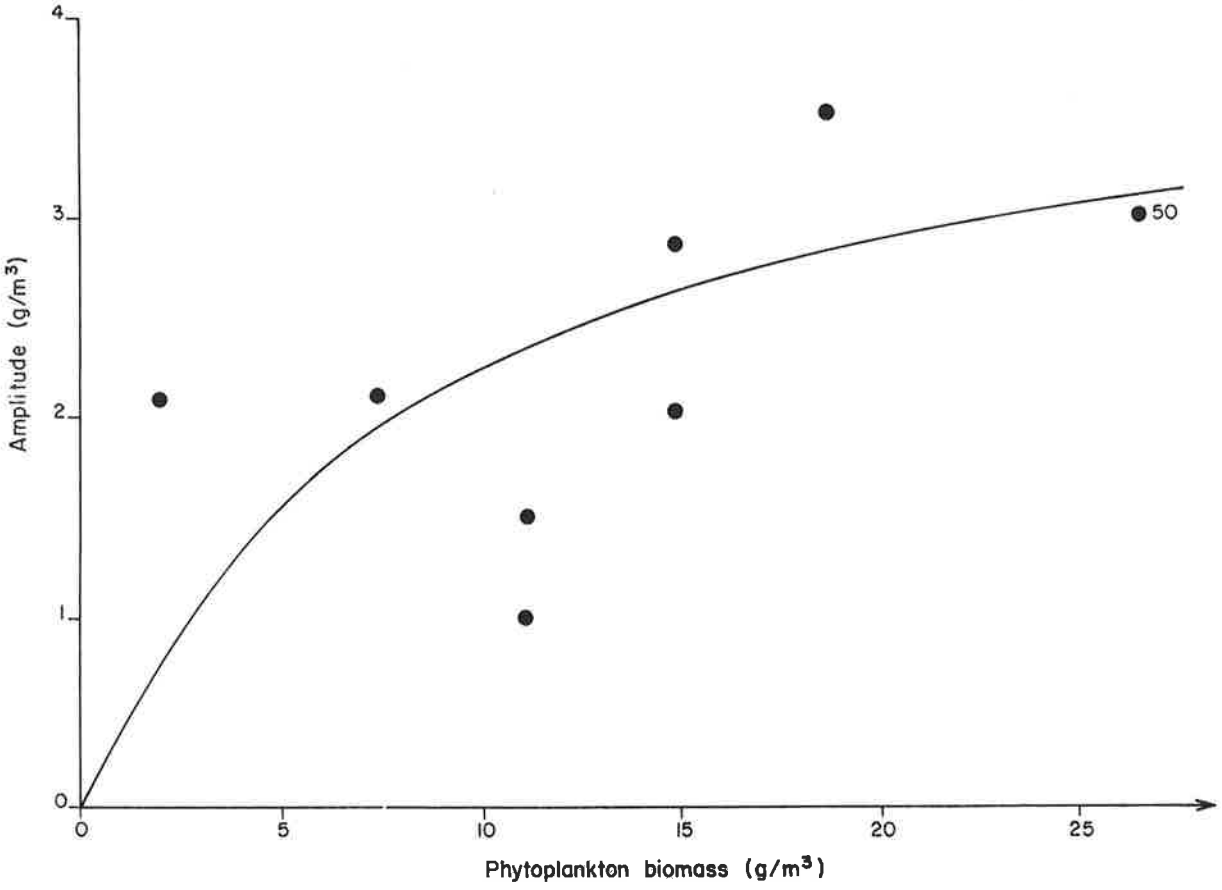

Fig. 2 Amplitude of diurnal DO variation versus algal biomass, Waikato River.

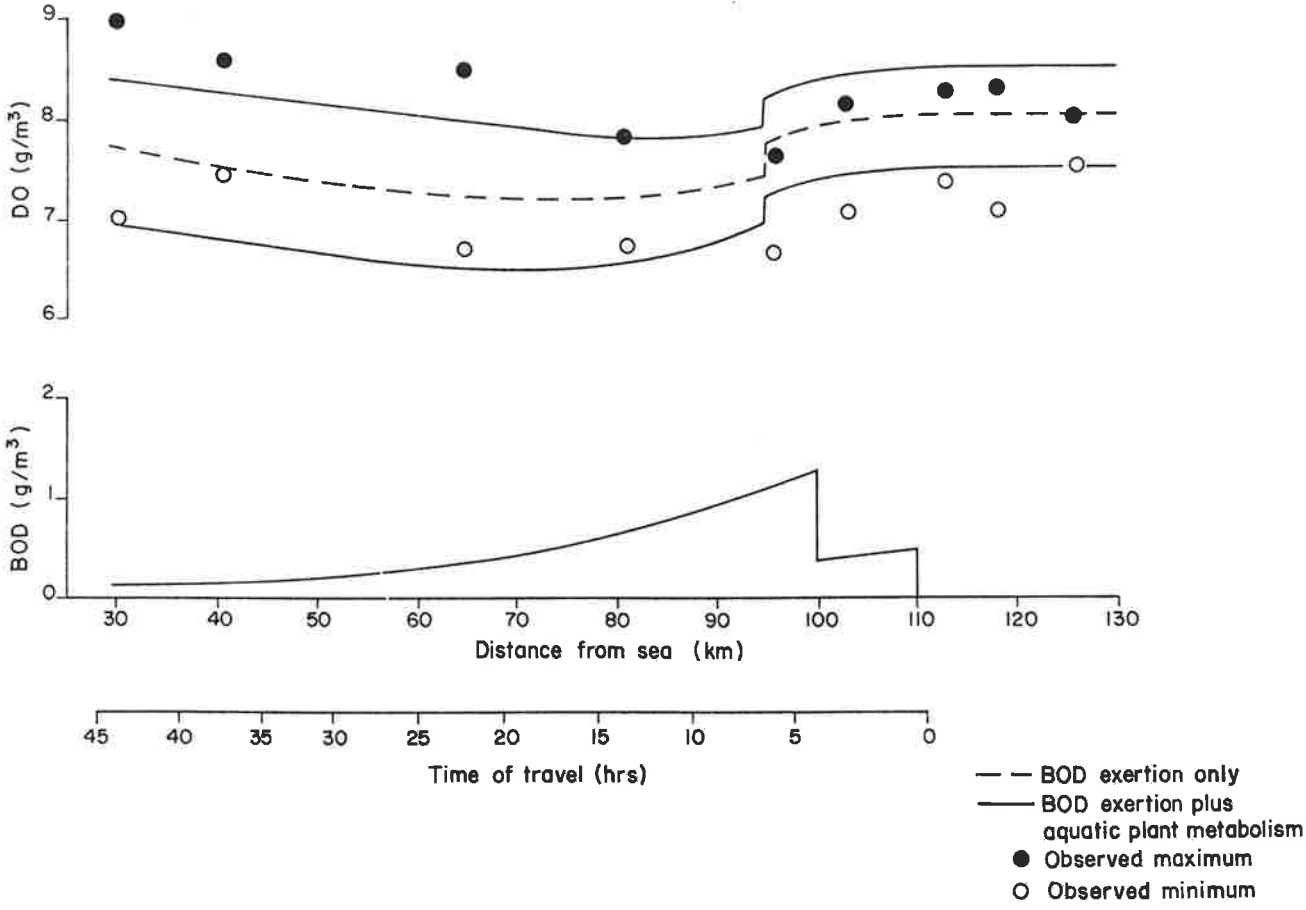

Fig. 3 Observed and predicted DO, steady load model.

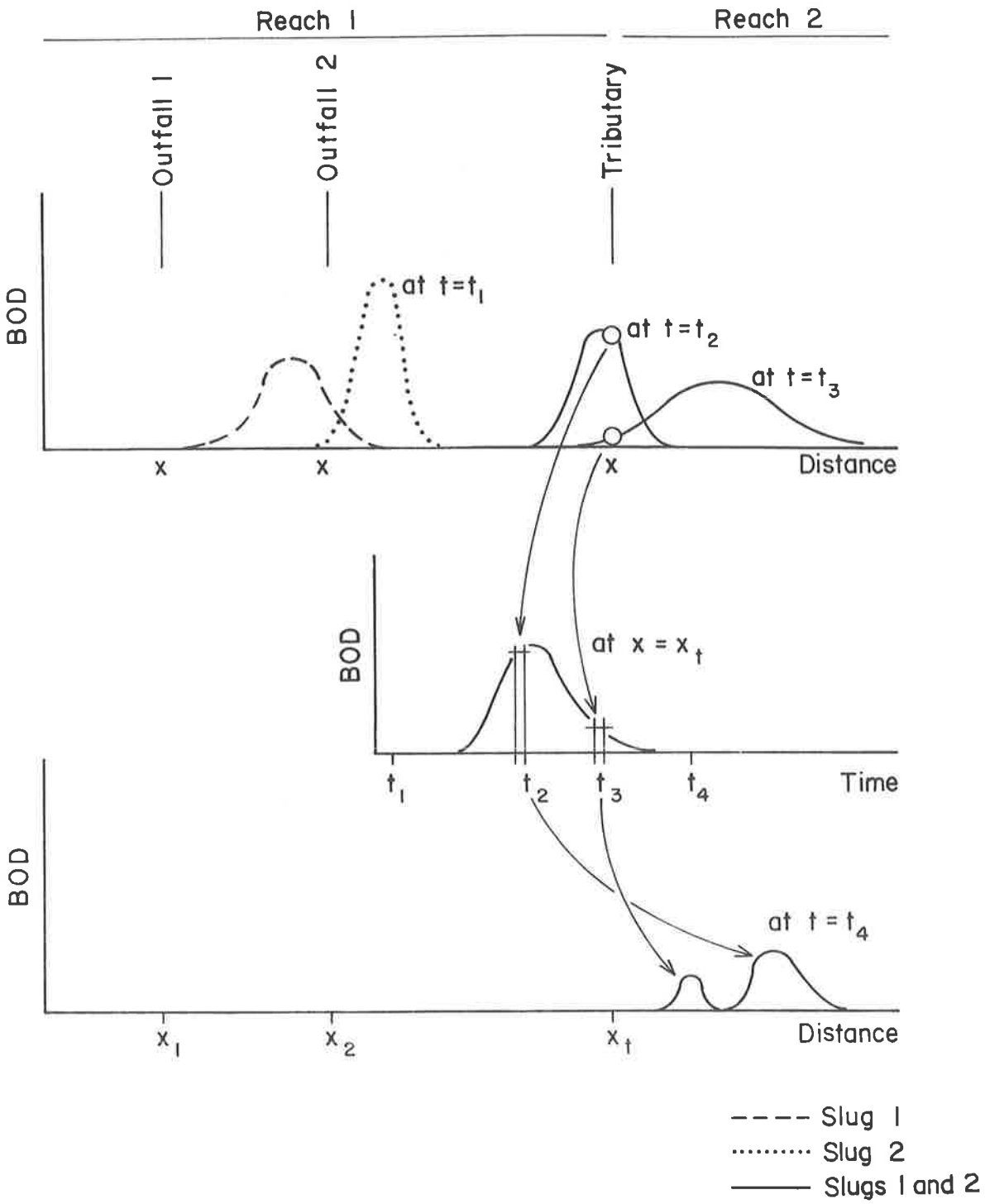

Fig. 4 Non-steady load model.

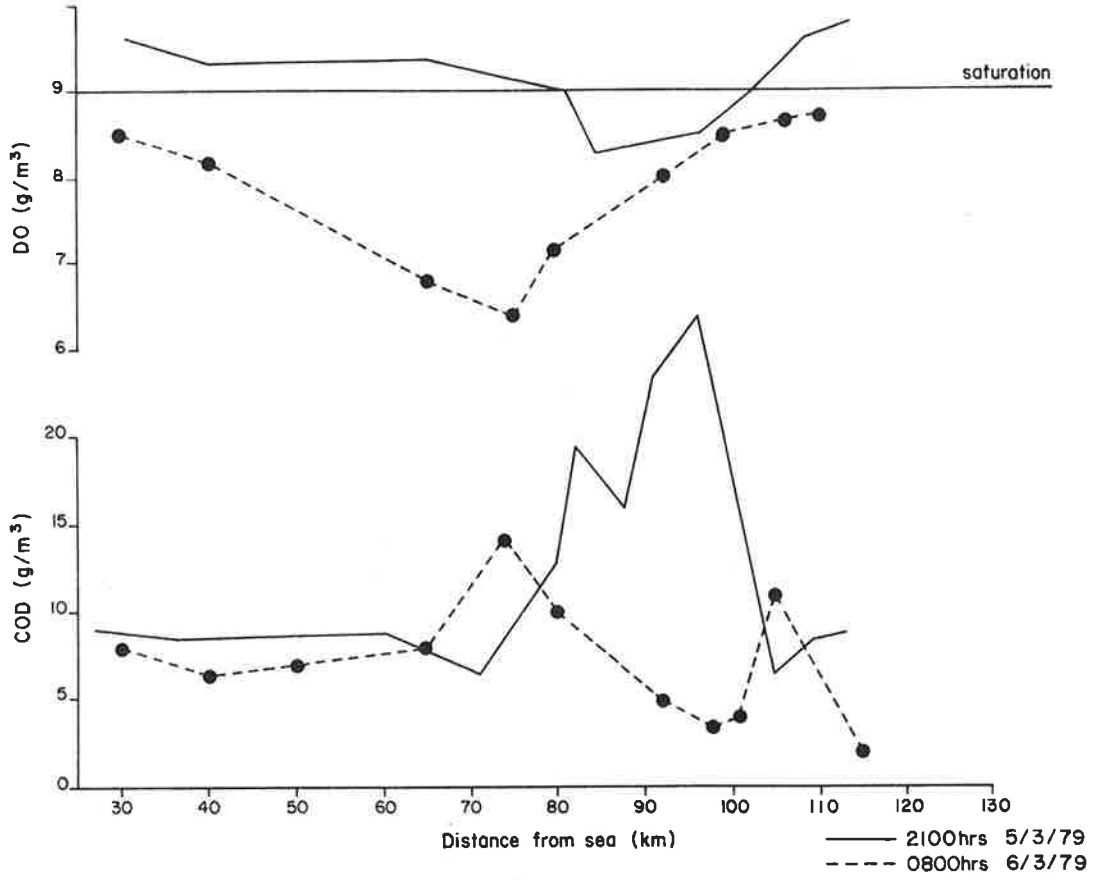

Fig. 5 Observed COD and DO, 5–6 March 1979.

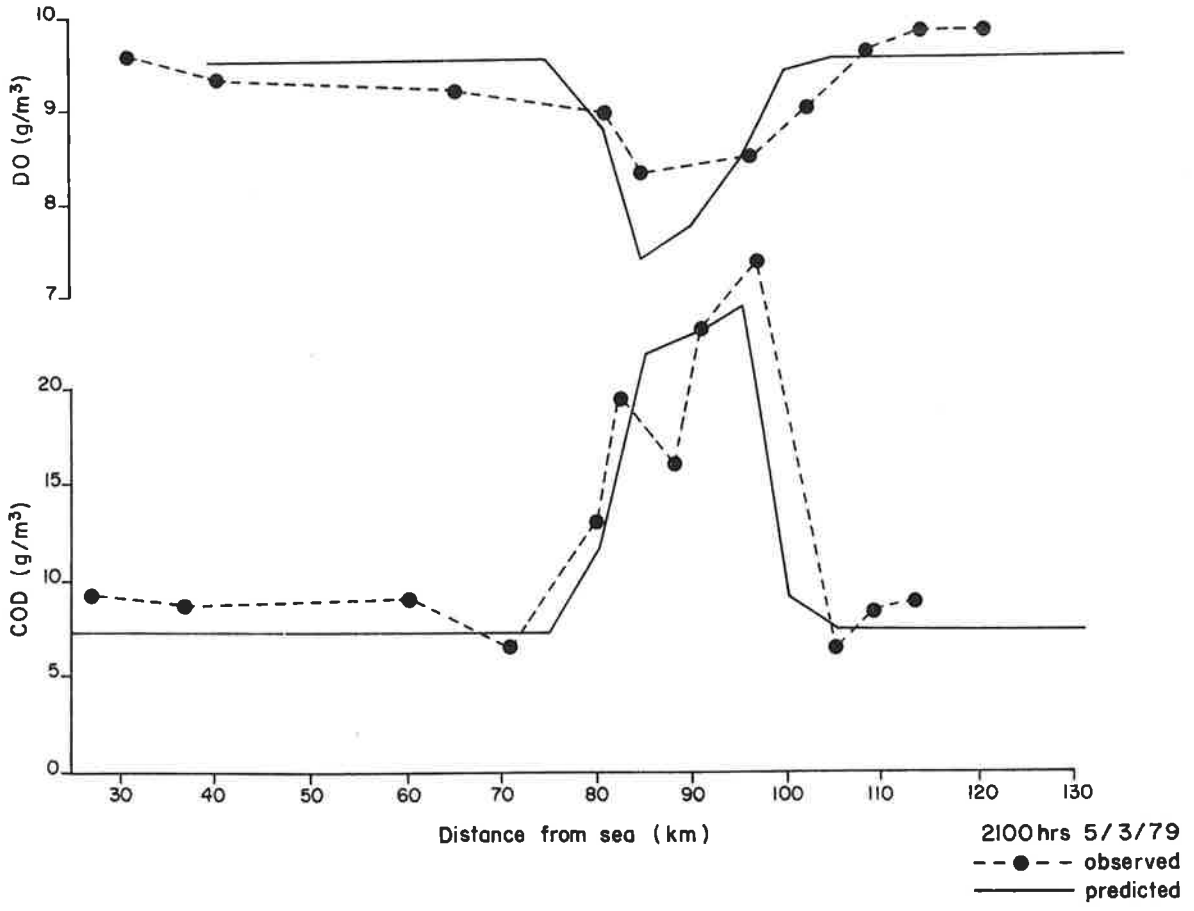

Fig. 6 Observed and predicted COD and DO, 5 March 1979.

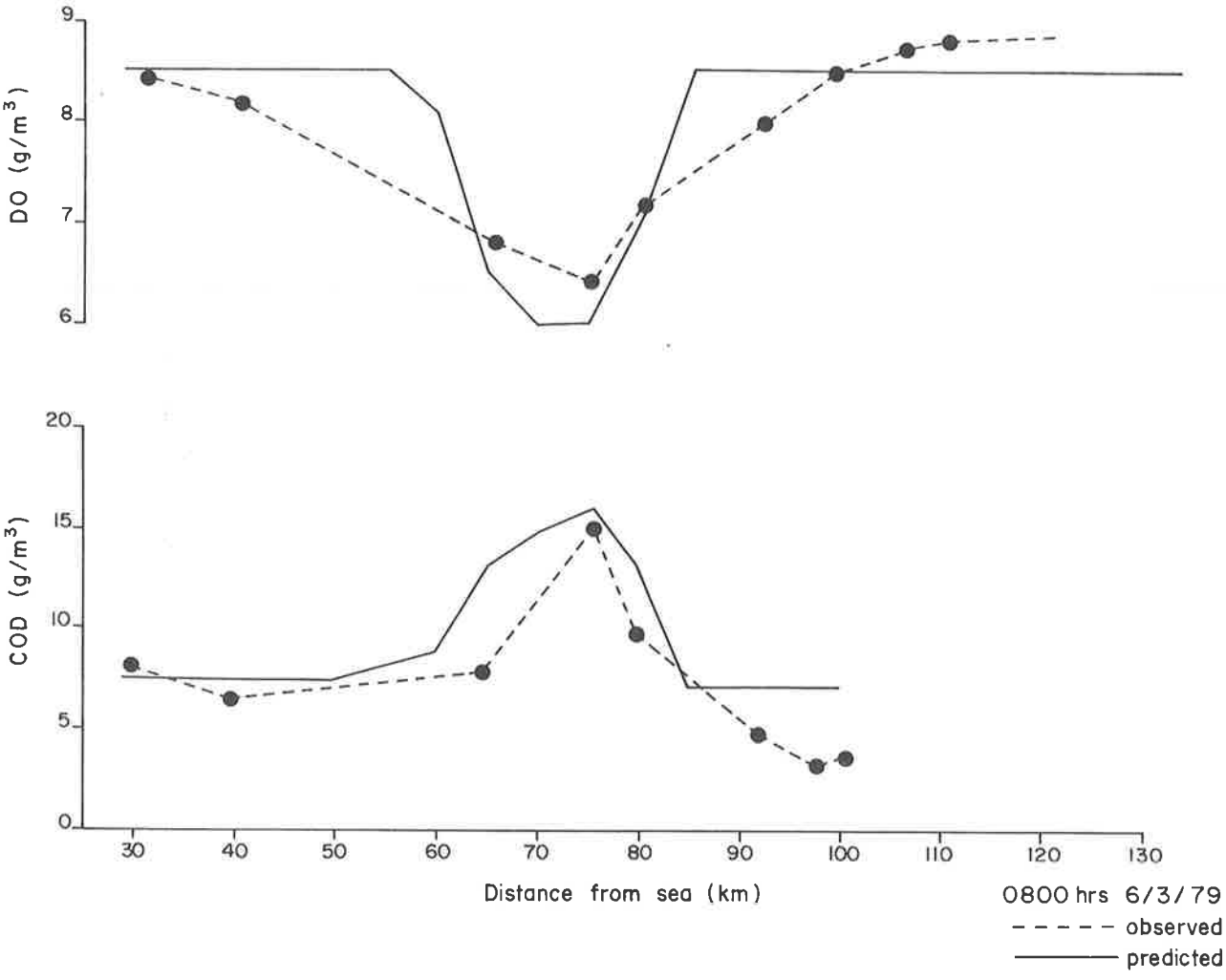

Fig. 7 Observed and predicted COD and DO, 6 March 1979.

Results of the simulations are shown in Fig. 6 and 7. Given that there are comparatively few observations and that the exact pattern of discharge is unknown, the fit between observed and predicted COD and DO is satisfactory.

A good fit could not be obtained between observed and predicted DO and COD using a single value for k_1. A value of $k_1 = 0.025$/hr was used to simulate the first survey and $k_1 = 0.035$/hr for the second. A possible explanation for this is that a lag occurred when milk was first discharged into the river before bacteria began to break it down. This suggestion is supported by laboratory work in which a mixture of milk and Waikato River water with a BOD of about 10 g/m³ exhibited a lag phase of 6 hours followed by an oxygen uptake rate of 0.4 g/m³.hr (equivalent to $k_1 = 0.040$/hr). When after several days a second 10 g/m³ of milk BOD was introduced into this mixture, an immediate oxygen uptake rate of 1.2 g/m³.hr occurred (equivalent to $k_1 = 0.120$/hr), (Hickey pers. comm.).

The k_1 values used for these simulations, 0.025–0.035/hr, are somewhat lower than those used in earlier simulations, 0.075–0.050/hr. This illustrates that k_1 is not necessarily constant in any given river but may vary with the volume and nature of waste discharges, and the numbers and activity of bacteria in the river water and/or river bed.

Conclusions

Two types of model of DO depletion in the Waikato River have been developed.

(a) A research model was used to help interpret field measurements and understand the factors influencing DO. This model was comprehensive, flexible and was operated on a large computer.

(b) Management type models can be developed, on the basis of experience gained with the research model, which are less flexible but are simpler and can be operated on a programmable calculator.

The research model was helpful in reaching the following conclusions about the Waikato River.

(a) BOD exertion causes a comparatively small oxygen sag, approximately 1 g/m³ at low flow.

(b) Phytoplankton metabolism causes a diurnal variation of between 1.5 and 3.5 g/m³ during low flow which is superimposed on this sag.

(c) Forecast changes in BOD load on the river are unlikely to greatly affect DO concentrations.

(d) If severe damage occurred to phytoplankton populations (e.g., as a result of toxic effluents or thermal shock) and BOD concentrations in the river increased as a result, then more severe oxygen depletion could occur.

Two management models are described which predict DO profiles under steady and non-steady effluent loading conditions. These are both two step models which predict the effects of BOD exertion in isolation using Streeter-Phelps equations and then superimpose the effects of phytoplankton metabolism with an empirical formula. This approach is considered valid in the Waikato River where BOD exertion is comparatively small and both models give results which match fairly well observed concentrations.

There is some evidence that the BOD decay rate, k_1, is not constant but varies with time and location presumably as the numbers and activity of bacteria in the river water vary.

Acknowledgements

G. B. McBride and C. W. Hickey contributed ideas on the development of the management models.

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Dissolved oxygen depletion of the Tarawera River

MARTIN PIPER

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The history of dissolved oxygen in the Tarawera River is reviewed. A model to simulate the dissolved oxygen response to waste loading is presented and the unusual mechanism which operates in the Tarawera River is discussed.

Introduction

The Tarawera River flows from Lake Tarawera via Kawerau to the Bay of Plenty at Matata. Kawerau is a major pulp and papermaking centre and wastes from this industry, the township and geothermal activity are discharged to the Tarawera River. These cause a dramatic reduction in dissolved oxygen of the river below Kawerau.

Many attempts to explain the unusual response have been made over the past two decades and a variety of theories and modelling attempts have been promulgated. Despite extensive investigation the Tarawera gained a reputation as a complex and unpredictable river.

This paper discusses our present understanding of oxygen depletion in the Tarawera River. We believe that the river is simply an extreme example of natural stream purification, and as such there may be much which we can learn about this process which is common to all rivers.

A brief history

The Tasman Mill commenced operation in 1955 and since that time Tasman has monitored its effluent and the response of the Tarawera River continuously. By 1965 a trend of decreasing dissolved oxygen had emerged and several unusual features of the river were apparent.

The shape of the oxygen profile below Kawerau was well documented, and showed the rate of oxygen depletion below Kawerau to be twenty times greater than standard values predicted, then, after a few kilometres, the profile remained relatively flat. When waste discharges ceased an oxygen sag persisted. Attempts to correlate BOD with river oxygen were unsuccessful, as were early attempts to model DO in the river.

The most significant research on the river was that by Dr W. J. Mitchell in 1965. His experiments indicated that the mechanism which is dominant in the Tarawera is a biofilm on the pumice river bed. This provided the key to most of the phenomena of the river. However several interpretations of this work have arisen in the past 15 years.

On the best advice available Tasman installed primary effluent treatment in 1970 and secondary treatment in 1973. Discharge of suspended solids ceased and BOD loading to the river was substantially reduced. In spite of this, DO of the Tarawera continued to decline through the 1970's. Not surprisingly even BOD was questioned as a valid control parameter and the need to explain the Tarawera River had now become paramount to making sensible decisions on river management. This objective dominated in the late 1970's but not far behind has been a successful effort by the industries at Kawerau to reduce effluent loading to the river. Unfortunately river flow decreased to extremely low levels which has partially obscured the improvements which have been achieved.

The downward trend in DO has however been reversed, and we enter the 1980's with some confidence in knowing what further action is necessary, and more importantly, why.

Tarawera Technical Committee

In 1975 this committee was set up by the Bay of Plenty Catchment Commission primarily to review discharge limits for the Tarawera River. Under the very able chairmanship of Mr Dale Revington the committee recognised a need to elucidate the oxygen depletion mechanism.

Input from all members of this committee and subsequent discussion of often conflicting ideas has been valuable to the understanding of the Tarawera River, and possibly to the understanding of stream purification in other rivers.

The Tasman Model

Despite the failure of earlier attempts this author has concluded that a simple first order BOD decay model most accurately describes oxygen depletion in the Tarawera River.

The model states that the change in dissolved oxygen per kilometre equals 0.02 times the oxygen deficit (reaeration) less 0.08 times river BOD_5 concentration (BOD exertion) i.e.,

$$\frac{d\ (DO)}{dx} = 0.02\ (Ds - D) - 0.08\ (BOD_5)$$

This equation is solved numerically to predict DO between waste inputs and tributary inflows. At hydraulic confluences, river DO and BOD are recalculated by simple mass balance.

BOD_5 prediction for the river is inherent in the solution for DO but the change in BOD can be expressed separately as

$$\frac{d\ (BOD_5)}{dx} = -0.08\ (BOD_5)$$

Figure 1 shows the model prediction and observed oxygen sag for 1965 data as used by Rutherford & O'Sullivan (1974). At this time wastes were untreated and discharged at Kawerau.

Figure 2 shows the predicted and observed DO sag for a survey in 1976 conducted by M.W.D.. Treated Tasman effluent now enters the river at Onepu but other waste loads enter at Kawerau.

The Tasman Model successfully predicts both situations.

Limitations of the Tasman Model

1 Steady state

The model can only describe a steady-state situation. This is a limitation of virtually all models but for the fixed biomass mechanism in the Tarawera River the effect is accentuated. A true steady state condition of constant river BOD will rarely exist since both river flow and BOD loading are not stable. One must treat spot survey data with caution, and the river microbiology should be considered.

2 Predicted BOD

The predicted BOD will not necessarily match survey BOD. Non steady-state can explain some of this, but measured BOD of the lower river is usually higher than predicted BOD. The inability of the river water to support slime growth suggests that predicted BOD is a more correct indication of available nutrients. The standard BOD test will include the endogenous oxygen demand of sloughed-off micro-organisms which will not be exerted in the river. There is also the probability that digestion of material which is not readily assimilated may occur in a BOD bottle over 5 days but will not readily occur in the river.

3 Minor influences on DO

Minor influences on DO are intentionally neglected to facilitate simplicity and clarity.

The model was produced to demonstrate that BOD_5 is a relevant control parameter, single substrate first order BOD decay simulates BOD exertion, and no benthic oxygen demand exists.

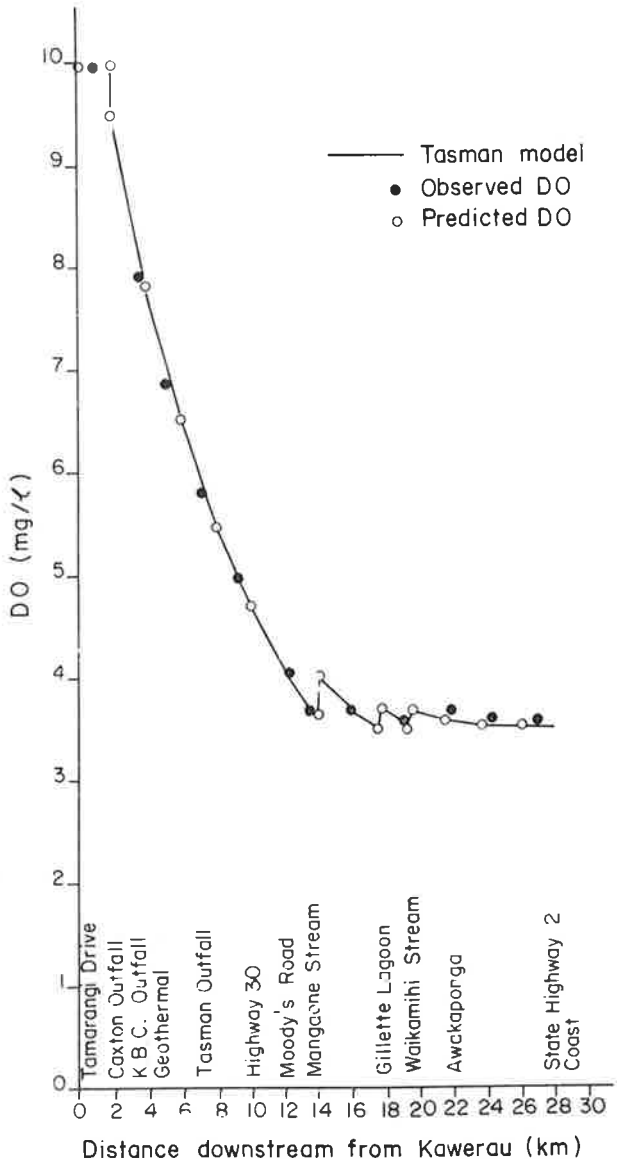

Fig. 1 Tarawera River. Observed and predicted DO for 1965 survey.

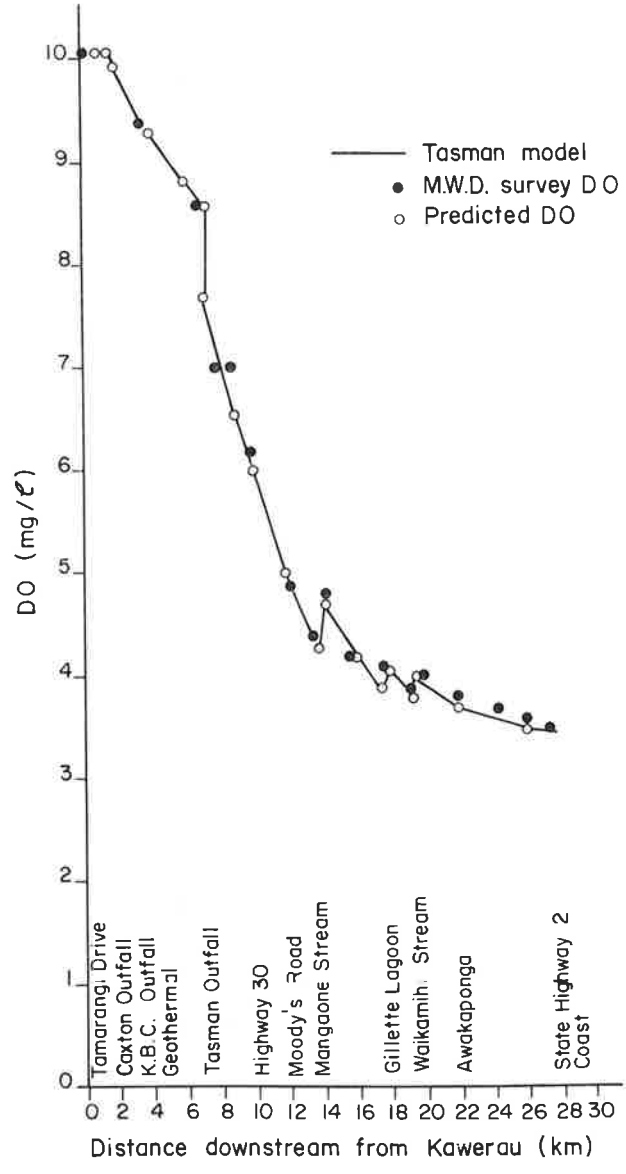

Fig. 2 Tarawera River. Observed and predicted DO for 26 August 1976 survey.

General comment on river modelling

There have been several approaches used to model DO in the Tarawera River, and these together with our present views on the river highlight several aspects of river modelling which may be of general interest.

1. Tributary inflows and waste input flows. These must be considered when predicting an oxygen sag. They were neglected in all early models of the Tarawera and this is a major reason why early models were not successful.

2. BOD — what is it? BOD is a measure of the food potential of a solution, the concentration of sugar for example. For human foods we refer to calorific value. For polluted water we refer to the oxygen required to consume the food rather than the energy value.

Both are indirect measures of the food concentration. A potential source of error is to read more into BOD than the test provides.

3. BOD assimilation rates. Rate coefficients for BOD should be obtained from field surveys of the receiving water since rates determined in laboratory studies or even those determined in other rivers are not necessarily valid. The Tarawera River vividly demonstrates that rate coefficients are more a function of the river than of the wastes.

The ecological model assumed different components of BOD, assigned laboratory rates to these fractions and varied biomass and metabolic rate in the river to match DO. The modified Streeter & Phelps model used similar BOD components and rate coefficients and added a benthic term to match DO and BOD. The Tasman Model used BOD as measured and a rate obtained from field surveys. No theoretical factors were then necessary to match DO.

4. River Microbiology. BOD assimilation is carried out by micro-organisms and to disregard these and treat BOD exertion as simply a chemical reaction is to neglect a major consideration in river modelling.

There is some confusion regarding fixed or planktonic micro-organisms and their roles. Some authors consider that Streeter-Phelps type models apply only to planktonic micro-organisms. This in part was a justification for the benthic term of the modified Streeter-Phelps model. Eckenfelder (1970) puts sewage fungi into the oxygen sink of autotrophic respiration yet the sewage fungus is a fixed heterotroph and more properly belongs in the BOD sink term.

This author believes that heterotrophic micro-organisms, fixed or planktonic, belong in the BOD term. Virtually all oxygen demand in the Tarawera is by fixed micro-organisms yet standard first order kinetics do apply. The fixed micro-organisms affect the rate coefficient for the river and account for the phenomena which occur at non steady-state (e.g., the 'permanent' oxygen sag).

5. Benthic Oxygen Demand. Benthic means bottom dwelling as opposed to planktonic or drifting. On this definition virtually all oxygen demand in the Tarawera River would be a benthic demand. However the term is normally reserved for oxygen consumed in decay of sediments or to BOD released in the decay process. Adequate study of river sediments is desirable to ascertain the nature and extent of a benthic demand before it is introduced into an oxygen model.

6. Complexity. The desired complexity of a model must depend on the river system and the use for which the model is developed. This author believes that a model should however be as simple as is possible.

Mechanism of oxygen depletion

The unusual feature of the Tarawera River is the river bed. This consists of pumice granules which are loosely packed and very porous. There is a nett downstream movement of this pumice and the dune effect created causes a high degree of turbulence within the river.

Dr W. J. Mitchell's experiments in 1965 demonstrated that oxygen depletion of the Tarawera River results primarily from the development of an active biofilm on the pumice bed of the river. Biofilms will develop on any submerged surfaces if food is available in the water so this in itself is not unusual. The interesting features are the high surface area of pumice, the porosity of the material and possibly the turbulence of the river. A high rate of interchange between water above and water within the river bed can occur. Mitchell likened the Tarawera River to a trickling filter, an analogy which describes the mechanism of the Tarawera very well.

If one views the river water/river bed as one system rather than as two entities the unusual responses of the river become clearer. Think of the river as flowing through, rather than over, a mass of pumice on which large concentrations of micro-organisms are attached. The water itself has relatively few bacteria but imagine the pumice suddenly disappearing. We would then be left with the nett situation in the river — a huge concentration of micro-organisms in the river water.

Surfaces play important roles in microecology. The Tarawera River demonstrates an extreme situation in this respect.

The "permanent" oxygen sag

When waste discharges cease an oxygen sag still occurs in the Tarawera River. Dr Mitchell in his experiments in 1965 showed that pumice from the river bed would consume oxygen from distilled water. Clearly, the biomass on the pumice does not cease to metabolise as soon as the food supply is removed from the water. Metabolic rate will slow down and the bacteria revert to their stored food reserves. If we do not eat for a period of time we do the same. We utilise food reserves and keep on breathing.

A "permanent" oxygen sag will characterise any river system which includes fixed heterotrophic micro-organisms. It is of course not permanent since in time the micro-organisms will be starved out. It is a non steady-state effect.

Correlation of BOD and river DO

The "permanent oxygen sag" is one extreme of what is occurring in the river continuously. The microbiological populations will tend to be in a state of flux, increasing or decreasing in response to changes in the food supply. However, the response of biomass and therefore of oxygen depletion is slow compared to changes which can occur in BOD concentration.

The opposite extreme is a step change in BOD loading from zero (or at least very low) BOD to a very high loading. If the fixed biomass is slow to respond then there should be little DO change with a short-term high BOD loading.

Experience at Tasman has shown this to be the case. For example our BOD loading to the river may be 10 t/d and DO in the river may be 5 mg/ℓ. If BOD increased to 50 t/d for one day DO would remain virtually unchanged, yet if the 50 t/d was maintained for a second day DO begins to decrease.

A third day at this loading would see DO dropping rapidly. If BOD load was then reduced back to 10 t/d there would be a slow return to 5 mg/ℓ over 1 or 2 weeks.

If one tried to correlate BOD and DO for such a situation it would prove confusing. We have two BOD loadings and a full range of DO figures for each loading. To complicate this type of superficial data even further, if 25 t/d BOD was discharged continually for approximately 2 weeks then, at present river flow, DO would be almost zero.

Before effluent treatment was implemented by Tasman, wastes from the mill were discharged directly to the river, and researchers found little correlation between BOD and DO. The delayed biomass response explains much of this but, in addition, river flow was considered to be stable and changes were not usually taken into account.

The treatment system has stabilised BOD discharge rate and now we find that BOD and river DO correlate reasonably well. Five day averages of BOD and DO give the best results. Monthly averages dampen the variations too much and daily figures are often unsatisfactory for reasons explained above.

Intermittent effluent discharge

Our observations in the mid 1970's had shown that oxygen depletion was a function of the quantity of fixed biomass, and that this in turn was a function of the continuous BOD loading.

Extending this thinking one could reason that a non-continuous food supply may be detrimental to the fixed bacteria, and anything detrimental to them should be beneficial to the oxygen level of the Tarawera. Dr Mitchell facetiously stated in the early 1970's that "what the river needs is a good dose of slimicide." In 1976 and 1977 we experimented with intermittent discharge of effluent. High loading of BOD was followed by very low loading. The "slimicide" effect did occur. Sphaerotilus growth near the effluent outfalls reduced and dissolved oxygen in the river increased for the same average BOD loading.

We found that zero discharge by Tasman for 1 day per week had a beneficial effect on DO. Low discharge for 1 day in 5 was even better. However, 8 hours/day at zero discharge had no beneficial effect on the minimum DO, but, despite the 50% increase during the time of discharge, there was no detrimental effect either. The literature holds several references to intermittent discharge as a means of controlling sewage fungi, which is basically an unsightly fixed heterotrophic bacterium. Our own experimentation confirms this and gives us some indication of the potential for the Tarawera River.

Trials with intermittent effluent discharge were suspended when our treatment system was modified for other environmental considerations. We have chosen lower total BOD as our control option, but intermittent discharge may have a place in future and it is a possible alternative or complement to treatment for some situations in New Zealand.

Effluent treatment — a poor response?

Tasman spent several million dollars in the early 1970's on treatment facilities. Before biological treatment commenced BOD averaged 22 t/d. For the 2 years after treatment BOD was halved, to 11 t/d. DO of the river increased, but only by a small margin. DO for the 3 years before treatment averaged 4.8 mg/ℓ. DO for the 2 years after treatment averaged 4.9 mg/ℓ which was well below expectations. There are two reasons for this:

1 As required by our discharge conditions, after treatment our waste is a stable loading on the river. Earlier discussion indicates that such provides the optimum condition for heterotrophic bacteria and thus the maximum oxygen depletion which can occur for any given waste loading.

2 Biological treatment was commenced in February 1973. In this year, flow in the Tarawera decreased drastically. Average flow for 1973 was 26.5 m^3/s, which was the lowest average flow on record, and only 70% of the average flow for the previous 3 years. Implementation of treatment may seem to have been ineffective at first glance, but in reality it was a timely exercise.

Tarawera River flow

River flow has a direct influence on river pollution in terms of dissolved oxygen.

In 1973 we installed secondary treatment facilities and have upgraded these three times since then. Also in 1973 we got the combined effect of the droughts of 1972 and 1973. River flow remained low for the next 3 years then plummetted again in 1977 and 1978 and hit record low flow in early 1979. Figure 3 shows river flow for the past 30 years.

Tasman has increased production by nearly 120% over the past 8 years but has reduced its water pollution significantly over the same period. Nature it seems intends to make the task of maintaining river DO difficult. We simply have to realign our sights at lower river flows, and the machinery to cope with this is in progress. A little more rainfall would be helpful, but we have decided not to count on it.

Assimilative capacity of the Tarawera River

The purpose of DO modelling of a river is generally to determine its capacity to assimilate wastes. This can be done with the Tasman Model or it can be achieved by direct observation over a period of time.

At Tasman we have recorded the effect of our effluent on the river over many years. Although other wastes have a significant effect our aim has been to determine what we must achieve, irrespective of other influences, to restore DO to the desired level.

Extensive observation over the past 4 years shows that

$$\text{mg/}\ell \text{ Total DO Depletion} = \frac{12.7 \times \text{Tasman BOD}_5\ (\text{t/d})}{\text{River flow}\quad (\text{m}^3/\text{s})} + 0.5$$

This relationship predicts the same results as the Tasman Model does, but has the advantage of credibility for it is simply what has happened over the past 4 years. It is, of course, only valid within a narrow range, but then this range is that in which we are interested.

Figure 4 shows a predictive graph which can be constructed from the above formula. This indicates our target BOD for various river flows. Any assistance by way of reduction of other wastes will be beneficial. Any increase in other wastes will mean our target treatment levels may become difficult to attain. Our present targets require more than 80% BOD removal, and in future we may be aiming for 90%.

Tasman policy regarding the Tarawera River

Tasman Pulp and Paper Company is New Zealand's largest single sited industry and our wastes are discharged to a small and unusual river. The treatment system has the capacity to serve a city such as Wellington. We have recently modified the system to improve potential treatment and are awaiting delivery of equipment for further improvement. Production personnel are river-conscious, and over recent years have done much to reduce the ex-mill pollution loading.

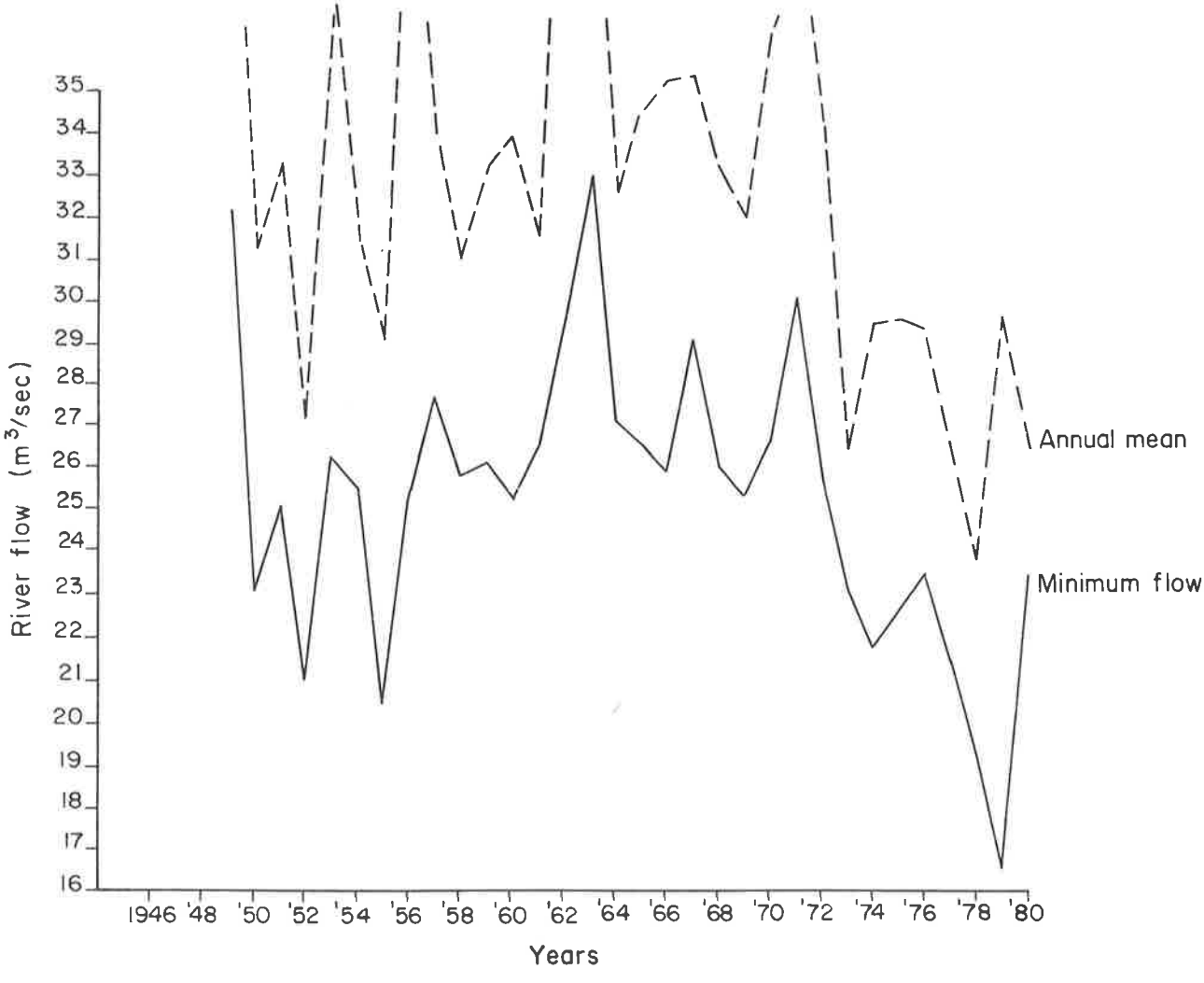

Fig. 3 Tarawera River flow at Awakaponga.

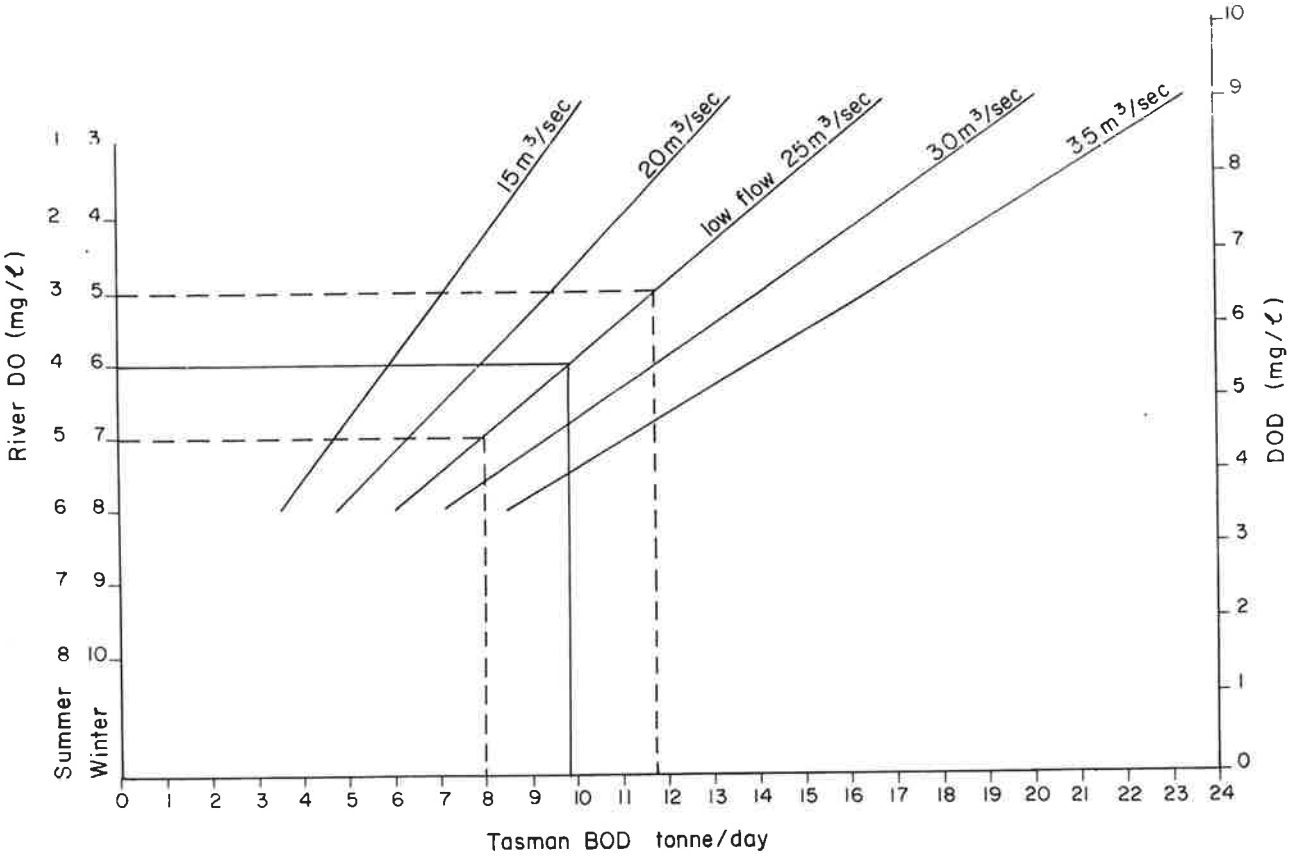

Fig. 4 Effect of Tasman BOD on Tarawera River dissolved oxygen.

Dissolved oxygen as a control parameter

This seminar is on dissolved oxygen (DO). Implied in this is that DO is the most satisfactory measure of pollution. There are however other aspects of pollution which should be considered along with DO.

To highlight this consider a swimming pool and your response to various conditions:

(a) Crystal clear spring water of premium quality for town supply such as that at Kawerau which has never required any form of treatment. It has between two and three mg/ℓ of DO. DO as the criterion would rate this very low quality.

(b) Murky green water due to algae as occurs in pools which are not chlorinated. In daytime at least, such will be supersaturated with dissolved oxygen, hence the DO criterion will rate this high. Inorganic enrichment of natural waters will encourage this condition.

(c) Grey/brown slime growth on the periphery with suspended bacterial growths throughout the water. In a pool this may lead to low DO but in many rivers this condition can exist without significant DO depletion. No slime but lower DO will generally be more acceptable. Slime growth results from organic enrichment under suitable conditions of flow and temperature.

(d) Toxic materials in a river may have no effect on DO but can be deleterious to plant and animal life.

The above are some aspects of pollution which are not fully covered by DO considerations alone. DO is an important criterion but is only one of several.

Acknowledgements

Discussions with Mr Graham McBride have been extremely valuable, and the assistance of colleagues at Tasman, particularly Jim Mitchell and John Keene, is much appreciated.

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Tarawera River DO models

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Over the years a number of models have been proposed for the distribution of dissolved oxygen in the lower Tarawera River below sewage and pulp mill discharges. This paper describes these models and compares their performance. It is notable that the simplest model appears to give the best results for assimilative capacity prediction. Two of the models have been used to arrive at a recommended allowable waste load to the stream from all discharges of 10 t BOD_5/day, in order to keep the downstream dissolved oxygen above the classified minimum of 5 g/m^3.

Introduction

The lower Tarawera River has been the subject of a number of dissolved oxygen (DO) investigations because the river has often been in breach of its classification (Class D, for which the minimum DO is 5 g/m^3). Substantial DO depletion, down to 2 g/m^3, has occurred in the 30 km from Kawerau to the sea. This depletion is attributable to the discharge of sewage and pulp and paper mill wastes near Kawerau. Of these discharges that from the Tasman Pulp and Paper Company Mills Ltd is much the largest, presently being in the order of 10–12 t BOD_5/day.

The degree of deoxygenation in this 30 km reach of river is quite in excess of that which may be inferred from standard works, due to the stimulation of micro-organism activity within the pumice sediments.

This paper reviews the various attempts that have been made to model DO in the lower Tarawera River. The location and sampling sites referred to are displayed in Fig. 1. A history of the state of the river since the 1950's and Tasman's waste treatment developments are given in Mr Piper's paper to this Seminar, along with a more detailed account of the simplest (Streeter-Phelps) model described herein.

Oxygen transfer in the Tarawera River

Fieldwork to date (mostly by Tasman Pulp and Paper Co. and Ministry of Works and Development) shows that:

- substantial oxygen depletion occurs in the 30 km (approximately 8 hours travel time) from Kawerau to the Bay of Plenty;
- there is a normal level of microbiological activity in the river water;
- there is a low organic content but high biological activity in the pumice sediments downstream of outfalls, presumably allied to the high specific surface area of pumice sediments;
- there is little visible evidence of cellulose or other organic materials accumulating on the bed (though there may have been some on the banks prior to the commissioning of Tasman's aeration pond treatment system in 1973);
- diurnal DO variations due to plant metabolism are not very significant;
- the river DO does not immediately respond to a change in waste inflow loading, the lag between inflow change and river DO response being of the order of one week;
- a considerable DO deficit persists in the river downstream of Kawerau after cessation of waste discharges from Tasman, probably lasting for more than 1 month;
- the treated Tasman effluent is usually anoxic at the point of discharge to the river, with the result that there is an immediate DO drop in the river at the outfall as the discharge is mixed with the river water;
- tributary inflows result in significant amounts of oxygen being added to the river downstream of the outfalls (this point has not always been appreciated);
- the "decay" of BOD_5 downstream of the outfalls is not exponential (i.e., first order), and is concave when plotted on semi-log paper.

DO models

There have been four distinct approaches of varying complexity to modelling DO in the Tarawera River. It is notable that the simplest of these models (the Streeter–Phelps model) appears to give the best results for prediction of river assimilative capacity. Each approach is described below in terms of objectives, model structure and use, and model validity.

Churchill–Buckingham Model

Objective: This model is described in a report of the Pollution Advisory Council (Anon. 1962). The objective in developing this model was to indicate likely trends in river quality.

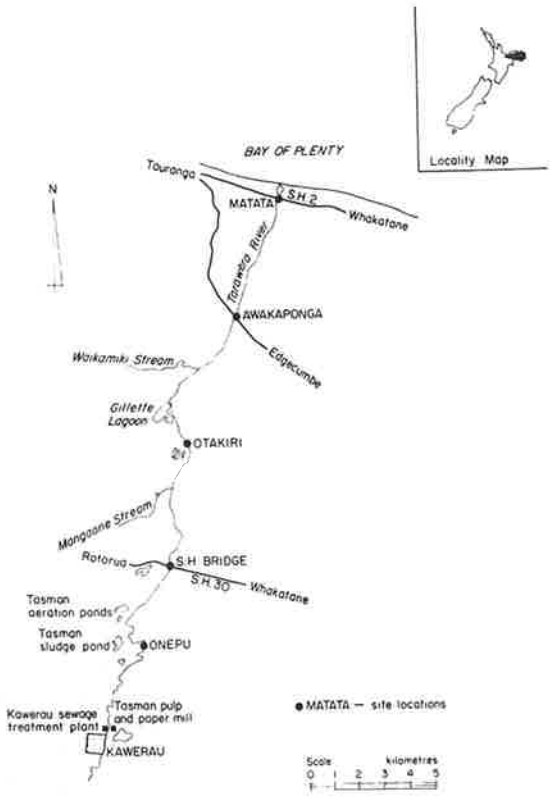

Fig. 1 Site and location maps.

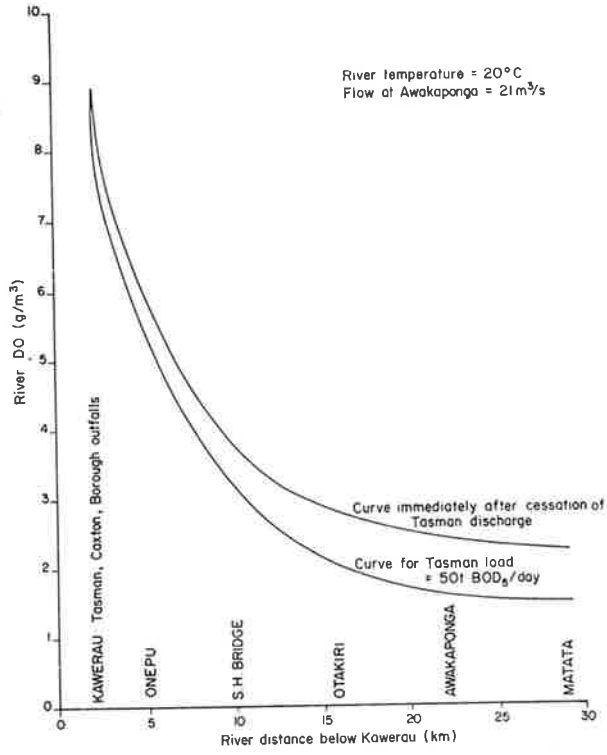

Fig. 2 Typical low-flow DO predictions of Churchill-Buckingham model.

Structure and Use: The model was based on data collected in the period January–May 1962. An initial attempt was made to use the Streeter–Phelps model (see Session V) but was abandoned because the authors could not make that model explain either the observed non-exponential BOD exertion or the persistent DO sag when discharges ceased.

Instead the statistical technique of Churchill & Buckingham (1956) was used. This method seeks a statistical correlation between the observed DO deficit (DOD) at some river station and the BOD_5, temperature and flow at that station. The equation for DOD at a station is thus

$$DOD = a + b.BOD_5 + c.T + d.\frac{1000}{Q} \qquad (1)$$

where a, b, c, and d = constants; T = river temperature, °C ; Q = river flow, cusecs.

It will be noted that the inverse of flow (normalised to 1000 cusecs) was taken, since it had ". . . been found by experience that a linear relationship exists between this variable and the dissolved oxygen drop". The data collected for January–May 1962 at five sites downstream from Kawerau was used to estimate values of the coefficients a, b, c, and d for those sites. These are shown in Table 1.

Use of equation (1) requires foreknowledge of the station BOD_5. An equation of similar form to equation (1) was therefore developed to predict the station BOD_5, given some upstream BOD_5, i.e.,

$$\text{station } BOD_5 \text{ load} = e + f.\text{upstream } BOD_5 \text{ load} + g.T + h.\frac{Q}{1000} \qquad (2)$$

where BOD_5 load is expressed in 1000 lb per day and e, f, g, and h = constants.

Table 1 DOD equation coefficients

River station	Coefficient value			
	a	b	c	d
Onepu	0.4	0.22	0.029	0.33
S.H. Bridge	−9.0	1.18	0.406	0.16
Otakiri	−0.5	0.48	0.0153	0.395
Awakaponga	0.7	−0.167	0.0304	0.41
Matata	0	0.9	0.021	0.277

Here it will be noted that the normalised flow, rather than its inverse, is used directly. For some reason Onepu, rather than Kawerau, was selected as the upstream station. The values of the coefficients for the reaches so defined are given in Table 2.

Table 2 BOD_5 equation coefficients

River Reach	Coefficient value			
	e	f	g	h
Onepu–S.H. Bridge	−10.66	0.052	0.233	22.0
Onepu–Otakiri	− 2.5	0.227	0.044	9.7
Onepu–Awakaponga	4.6	0.148	−0.475	8.3
Onepu–Matata	40.8	0.134	−1.57	−2.35

These equations were used to make predictions of river DO under various waste loads. In particular, the non-exponential BOD exertion and persistent DO sag for zero Tasman discharge were predicted. Typical predictions are shown in Fig. 2.

Validity: This model is simple to apply and is probably a good description of the data upon which it is based. However, being a statistical model, it is not based on much physical understanding of the mechanisms operating. It is therefore not clear what confidence can be placed in the predictions of such a model for conditions beyond those prevailing in 1962, especially since some of the coefficients of the model shown in Tables 1 and 2 are anomalous. This is especially so for the effect of temperature on river DOD at the S.H. Bridge site (c in Table 1) and on river BOD_5 at Matata (g in Table 2).

Ecological Model

Objective: This model is described by Rutherford & O'Sullivan (1974). The objective of this work was to show that the very high rate of river deoxygenation could be explained by using laboratory data on micro-organism metabolism, assumed to occur in the river sediments.

Structure and Use: It was assumed that most of the oxygen was being removed from the river water by the action of micro-organisms living on pumice particles in an "active layer" of bed sediments. The importance of such sediment activity was demonstrated in experiments carried out by Tasman staff in 1965, as reported in Rutherford & O'Sullivan's paper. A model was developed that predicts the biomass of these micro-organisms in the sediments (and hence is an "ecological model" according the definitions of Rinaldi *et al.* 1979). From these sediment biomass predictions, the deoxygenation of the overlying water was calculated.

This is a highly complicated model involving exogenous bacterial metabolism and predation by protozoa on the bacteria. The Monod model (e.g., Rinaldi *et al.* 1979) was used to model the micro-organism interactions. The BOD_5 input from waste discharges was taken as the measure of substrate to the river. The substrate was assumed to be comprised of two basic components (sugars and organic acids) that were able to be assimilated at different rates by the sediment micro-organisms. The rates for all these reactions were based on laboratory data on micro-organism growth rates. The effects of tributary inflows were ignored. No data were available on substrate concentrations or on micro-organism biomass and so the model was tested using river DO data alone.

The typical form of solutions obtained for DO are shown in Fig. 3 (solutions for substrate and micro-organism concentrations were not given) plotted with averaged DO data for the period January 1965–February 1966. The solutions were obtained by numerical methods for the set of model simultaneous partial differential pollution transport equations.

Validity: This model does provide reasonably valid estimates of river DO, as seen from Fig. 3, except that results for the critical lower 15 km of the river predict that the DO rises somewhat, whereas field data show that the DO profile in this region is flat. This lack of agreement would presumably be exacerbated were the effect of tributary inflows taken into account. The model does explain, as endogenous

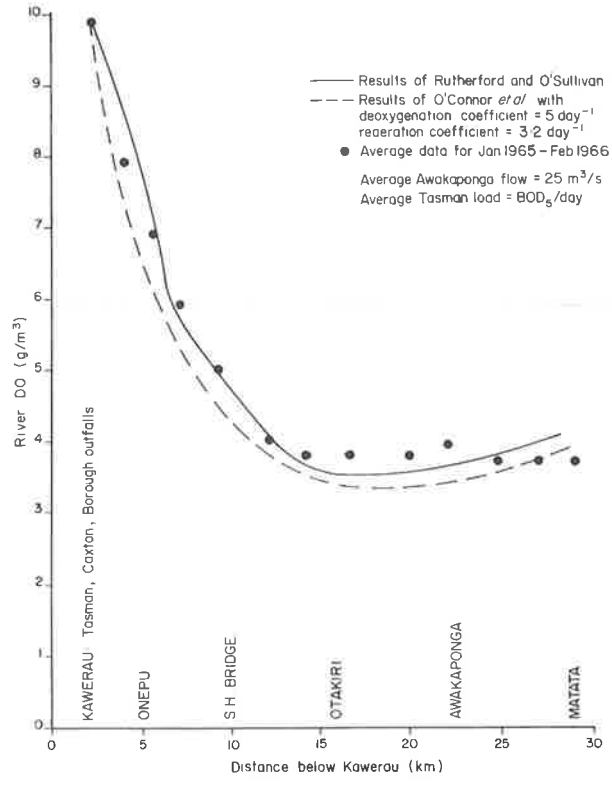

Fig. 3 Low-flow predictions of Rutherford & O'Sullivan (1974) and O'Connor *et al.* (1975).

micro-organism metabolism, the observed persistent DO sag on cessation of Tasman's waste discharge. However, more data would be needed before such a complicated model could be fully verified and considered for use in river water quality management.

Streeter–Phelps Model

Objective: This model has been used by O'Connor *et al.* (1975), in a discussion of Rutherford and O'Sullivan's paper, to show that this simple first-order model can give results as good as those obtained from the ecological model. It has also been described by this author, and by Mr Piper of Tasman Pulp and Paper Company, in submissions to the technical committee on the Tarawera River of the Bay of Plenty Catchment Commission. Mr Piper has advocated its use to predict the assimilative capacity of the river.

Structure and Use: O'Connor *et al.* used dimensionless number arguments to claim that the complex Monod model system proposed by Rutherford and O'Sullivan could be replaced by a first order model as incorporated in the classical Streeter-Phelps model. They used a low-flow reaeration coefficient (base e) of 3.2/day, derived from the empirical formula of O'Connor & Dobbins (1958). A deoxygenation coefficient (base e) of 5/day was assumed, very much higher than the normal value of 0.23 for this coefficient reported in standard works (e.g., Nemerow 1974) for sewage in laboratory BOD tests (value = 0.1 to base 10). Using analytical

solutions to the model equations, the classical shape of DO sag curves was obtained. These are also shown on Fig. 3.

This simple approach has also been described by this author, and more particularly by Mr Piper of Tasman Pulp and Paper Company in submissions to the technical committee on the Tarawera River. Both submissions have included the effects of tributary inflows and solutions to the model equations have been obtained by numerical methods. The latter used a low-flow reaeration coefficient (base 3) of 1.3/day and a river deoxygenation coefficient (base e) of 5.2/day. The anomalously high deoxygenation coefficient was assumed to reflect the high bacterial biomass in the river/sediment system as compared to other rivers receiving similar wastes, rather than reflecting the chemical nature of these wastes. Values of the two coefficients were calibrated from Tasman's own river data and from a Ministry of Works and Development river survey in July 1976. Figure 4 shows observed and predicted river DO for a verification survey in December 1976. In this modelling it was assumed (based on Tasman's extensive data) that the rate of river oxygen depletion does not immediately respond to changes in inflow BOD_5 load, because an increase (or decrease) in load precedes an increase (or decrease) in sediment biomass production. This point is considered further in Mr Piper's paper to this Seminar.

Validity: The validity of predictions of the model as proposed by O'Connor *et al.* is about as good as that previously noted for the ecological model.

Results presented by Mr Piper show an impressive agreement with river DO as measured on Ministry of Works and Development survey in December 1976, and also for the data used by Rutherford and O'Sullivan. This improved performance over that given in the paper of O'Connor *et al.* appears principally due to the large reduction in the value assumed for the low-flow reaeration coefficient (1.3/day versus 3.2/day). This latter value is not in agreement with present methods of estimation of reaeration coefficients (e.g. Rathbun 1977) and may require some explanation. It has also to be noted that this model with a deoxygenation coefficient in the order of 5/day predicts that the BOD_5 in the lower part of the river is only about one half of that measured. To maintain that this model is a proper description of the DO dynamics in the river, one must argue that only 50% of the measured BOD_5 in this region represents substrate available to micro-organisms (such an assumption would explain the non-exponential decay of BOD_5, an effect that is not accounted for by this first-order model). Such lack of agreement of observed and predicted BOD_5 is not uncommon in overseas studies. The observed persistent DO sag on cessation of Tasman's waste discharge can be explained by postulating some level of endogenous bacterial activity in the river sediments causing a BOD load on the river.

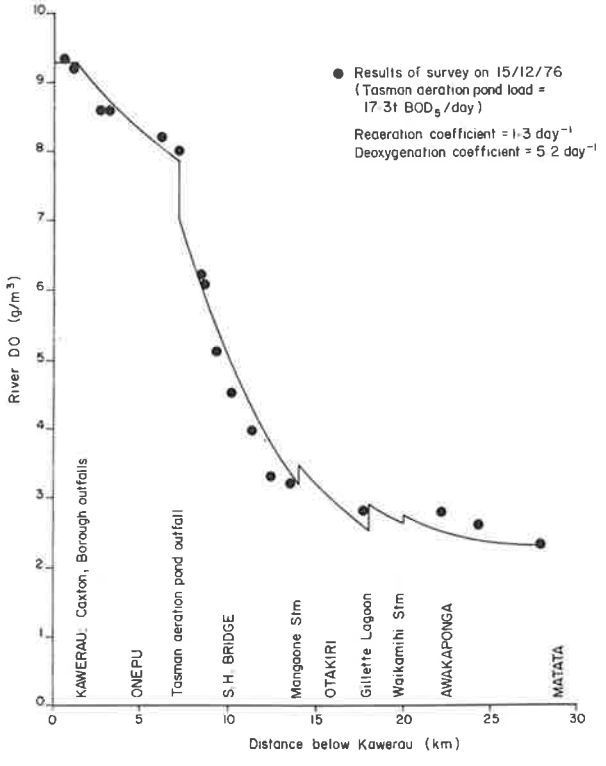

Fig. 4 Verification of Streeter-Phelps model for low-flow DO.

Modified Streeter-Phelps Model

Objective: The objective with this work has been the prediction of river assimilative capacity based on a model that successfully predicts both river BOD_5 and DO.

Structure and Use: In a further submission to the Tarawera Technical Committee this author proposed a model that is of similar form to the Streeter-Phelps model, except that a "benthic oxygen demand" term was added to the DO transport equation. By this means a lower value of the river deoxygenation rate can be taken so as to match observed river BOD_5 and also the observed river DO. Also, the deoxygenation coefficient was presumed to decrease with distance downstream of outfalls in a prescribed manner to account for the observed non-exponential BOD exertion.

Two river surveys carried out at low river flow in the latter part of 1976 were used to calibrate the model, and a further survey in December 1976 (the same data as shown on Fig. 3) was used for verification. The low-flow reaeration coefficient (base e) was about 3.2/day and the deoxygenation coefficient (base e) varied from 3.5/day at Tasman's outfall to 2/day at the mouth. The "benthic oxygen demand" term was calibrated at 12 g/m³ per day.

Predicted and observed river DO and BOD_5 for the verification survey are shown in Fig. 5. The predictions were obtained by applying a standard numerical method to the model's ordinary differential equations.

Validity: This model has an advantage in that it matches both observed river DO and BOD_5 with some accuracy. However, the physical nature of the mechanisms described by such a model is poorly understood. The observed persistent DO sag on cessation of Tasman's waste discharge can be

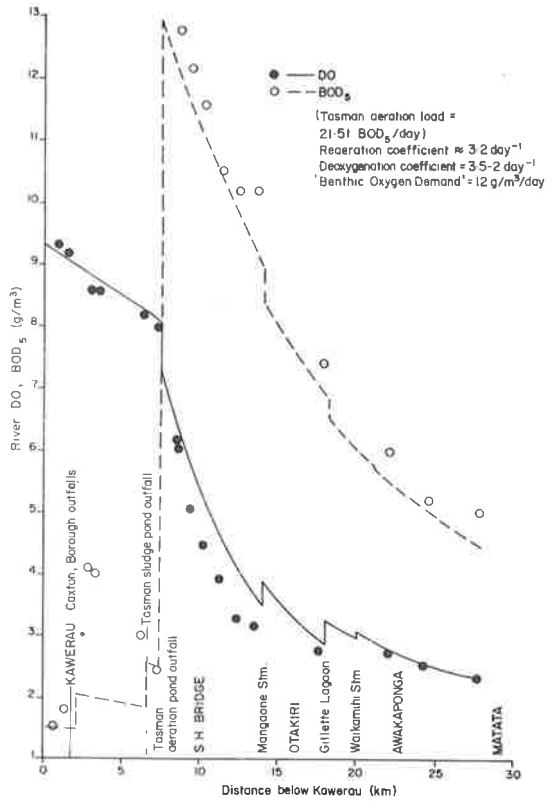

Fig. 5 Verification of modified Streeter-Phelps model for low-flow DO and BOD_5.

explained by this model using the benthic oxygen demand term, but the value that this term should take is not clear.

Discussion

The choice among these models is not simple and, as discussed in Session V, must depend on the objectives of the model study, the desired level of complexity, and the important processes operating.

Each model has advantages and disadvantages in these categories. For assimilative capacity prediction, the choice lies between the simple and modified Streeter–Phelps models. The former model would appear to be more appropriate. Although it appears to underestimate reaeration and overestimate BOD removal it none the less appears to have a more rational physical basis. The overestimation of BOD removal may be more to do with the shortcomings of the BOD test, rather than a fault with the model: it may be that the BOD test measures substrate concentration near the outfall, but also measures bacterial biomass further downstream.

Both models require the same amount of data for construction, calibration and verification. The solution technique for the former model is somewhat simpler, and the model involves a minimum of parameters. In fact both models have been used to make similar estimates of assimilative capacity of the lower Tarawera River.

The ecological model provides a spur for future research work on microbiological oxygen metabolism on pumice sediments, especially in association with field and laboratory microbiological work such as recently carried out by Cawthron Institute.

Conclusion

Research into oxygen depletion in the sediments and water of the Tarawera River such as recently conducted by Cawthron Institute (as reported in Dr Gillespie's paper to this Seminar) should be continued. In time that should show which of the proposed models, or variants of them, can best describe DO dynamics in this river. Work to date appears to show that the simplest model (Streeter–Phelps) is in fact the best model for making assimilative capacity predictions.

In the meantime the Streeter–Phelps and modified Streeter–Phelps models have both been used to estimate the river assimilation capacity (in keeping minimum river DO > 5 g/m³) from the combined discharges at 10 t BOD_5/day, recognising that the actual figure could be ± 20% of this figure. The effect of further research should be to refine this confidence bound.

A figure in the order of 10 t/day appears to be confirmed by recent data collected by Tasman for 5 day average BOD loading and river DO response.

In these modelling studies intensive surveys of the river within its travel time are necessary to verify models. Since this river also displays only slow responses to changes in loading, longer term data are desirable also. It is fortunate that Tasman have taken the trouble to collect such data.

Acknowledgements

Many discussions on oxygen depletion mechanisms in this river have been had with Mr Martin Piper (Tasman) and Dr Kit Rutherford (MWD). The MWD surveys were ably carried out by Mr J. W. Nagels (MWD) with assistance of MWD Rotorua staff and also staff of the Bay of Plenty Catchment Commission.

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Investigation of the mechanism of oxygen depletion in the Tarawera River

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The mechanism by which oxygen depletion occurs in the Tarawera River under the influence of high organic loadings from urban and wood processing industry effluents was examined. The rates of oxygen consumption at various locations on the river by free-living and attached benthic micro-organisms were related to parameters describing microbial biomass (ATP, total counts) and activity (^{14}C-glucose metabolism). Chemical analyses of water and effluent samples were done to determine the nature of the organic material entering the river. A flow-through incubation chamber to simulate *in situ* conditions and provide a means of relating oxygen consumption to the area of river bed was designed. The main stimulus to microbial activity and oxygen depletion was associated with effluent from the Tasman Pulp and Paper Company mill. Rates of oxygen consumption in water samples ranged from < 2 g/m^3 per day above, to a high of 9.1 g/m^3 per day below the Tasman outfall. A similar pattern of oxygen consumption occurred in the sediments, with a high of 10.1 g/m^2 per day a short distance below the outfall. In general the rates of glucose metabolism and microbial biomass parameters showed a similar distribution. A significant proportion of the carbohydrates in the Tasman effluent are in the form of simple sugars. This together with the porous nature and mobility of the pumice particles of which the river bed is composed, provides an ideal environment for the development of an extremely active heterotrophic microbial community.

Introduction

The Tarawera River appears to function somewhat uniquely in the mechanism by which it "processes" organic waste materials. The river bed is composed to a large extent of a mixture of coarse and fine pumice which, because of its porous nature and large surface area, provides an ideal habitat for the development of an extremely active heterotrophic microbial community. The surface of the pumice bed appears to be in constant motion as it is agitated by the currents, giving it a continually renewed supply of organic nutrients and oxygen necessary for a rapid rate of aerobic decomposition.

The objective of this study was to obtain information characterising this suggested mechanism of oxygen depletion. It was therefore necessary to examine the rates of oxygen consumption at various locations on the river by both free-living and attached benthic micro-organisms and relate them to other parameters describing microbial biomass and activity.

Methods

Sampling locations and procedures

Water and sediment samples were obtained on two occasions from either seven or eight stations on the Tarawera River between Kawerau and the sea (28 km). The specific locations are shown in Fig. 1. Water samples were collected in hand-held glass or polyethylene bottles. Sediment samples were collected using a 2-litre stainless steel scoop attached to the end of a 215 cm stainless steel rod. Each sample was a composite of at least three scoops taken at the same station. After mixing the samples thoroughly they were worked through a sieve excluding particles >2 mm to obtain relatively comparable samples. For certain experiments, however, unsieved samples were used to more closely simulate natural conditions. On one occasion (January 1980) stations 4–8 were sampled from the main channel with the aid of a jet boat. The remainder were sampled by wading as far into the main channel as practical. Water samples to be used for chemical analyses were preserved immediately with 1 ml of 6% $HgCl_2$ per litre. Biological experiments were carried out at the Environmental Laboratory of Tasman Pulp and Paper Company within 2 to 3 hours of sample collection.

Oxygen uptake experiments

The rates of oxygen consumption of both water and sediment samples were estimated using a YSI

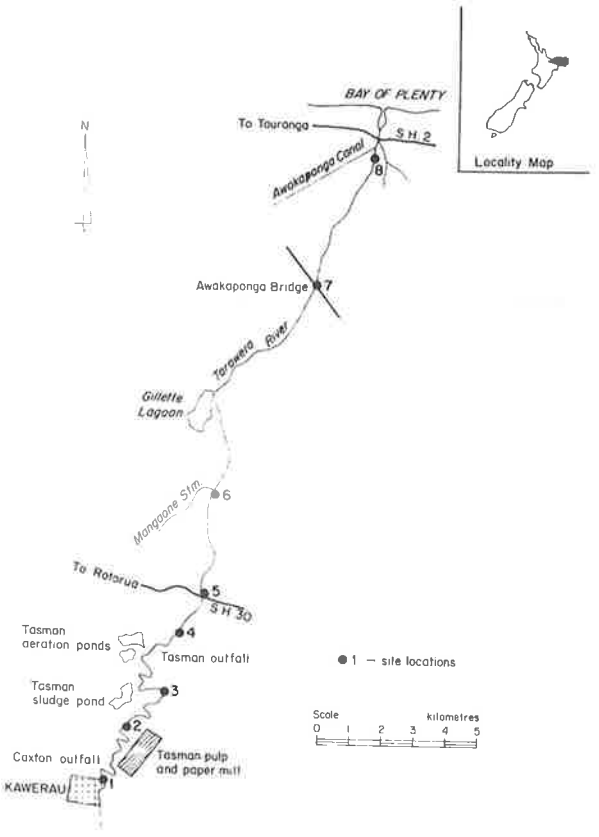

Fig. 1 Tarawera River sampling site locations.

Model 57 Oxygen Meter with a Clark-type electrode and one of three different incubation techniques.

The first method involved incubation in standard BOD bottles and dissolved oxygen measurements were made with a stirring BOD-probe at approximately 10 minute intervals until a satisfactory rate could be established. In this manner the rate of uptake by micro-organisms in the water alone was first determined prior to the addition of 20 cc of sediment from the same station. The rate of uptake was again established and corrected to exclude the background level of oxygen consumption in the water. Because of the vigorous stirring employed with this method the results probably represent maximum rates of uptake as might occur in the top layer of the river bed pumice.

Additional information was obtained by incubating unsieved sediment samples in 2.2ℓ perspex chambers (Fig. 2). Water was circulated over a 2.5 cm bed of sediment from the same station using a Cole-Parmer Masterflex peristaltic pump (2 litres per min.). DO levels were again monitored with a probe fixed to the top of the chamber. Since the flow rates obtainable in this manner were much lower than under natural conditions, rates of uptake were compared to those observed with a gentle rocking of the chambers prior to recording of DO. Thus we were not able to duplicate the natural conditions of flow but we were able to measure oxygen consumption at what might be considered maximum and minimum rates.

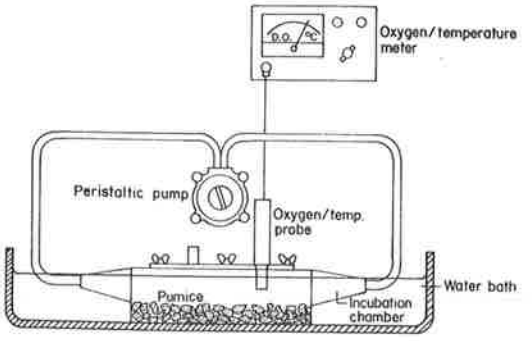

Fig. 2 Apparatus for measuring oxygen consumption by pumice sediments.

^{14}C-glucose uptake

The rate of microbial uptake of ^{14}C—labelled glucose in both water and sediment samples was used as a relative index to the activity of the heterotrophic population. We measured ^{14}C-glucose uptake using a simplified version of the technique described by Wright & Hobbie (1966). Additions of 0.1 μ Ci of ^{14}C-glucose (U) were made to a series of 20 ml subsamples of river water with additions of ^{12}C-glucose to give a range of concentrations (in duplicate) up to 8 μg glucose per litre. The subsamples were incubated in the dark for 45 minutes along with one formalin-killed control. The rest were then also killed with formalin and the amount of radioactivity taken up into microbial cells was measured using liquid scintillation techniques. The kinetics of glucose uptake thus obtained are expressed in terms of the maximum velocity of uptake (V_{max}) as described by Gillespie (1976) according to the equations of Wright & Hobbie (1966). It should be noted that V_{max} is not a measure of the *in situ* rate of glucose metabolism but a maximum rate which is characteristic of the existing heterotrophic population.

ATP Determinations

Adenosine triphosphate (ATP) is a constituent of all living cellular material and its concentration in water or sediment is directly related to the amount of living material present. Consequently in this study ATP concentrations were used to estimate the total living biomass in samples of river water and sediments. The procedures of Holm-Hansen & Booth (1966) were used for the extraction and assay of ATP in water samples and the phosphate buffer extraction procedure described by Bulleid (1978) was used for sediments.

Total microscopic counts of bacteria

One ml of pumice from each composite sample was mixed with 2.5 ml of sterile distilled water and 0.1 ml 10% glutaraldehyde (fixative). They were then stored on ice or in a refrigerator (4 °C) until the counts could be made. The samples were shaken vigorously to dislodge the majority of cells from the pumice and further dilutions were made with sterile distilled water. Bacterial cells were counted using acridine orange staining and epifluorescence microscopy according to the methods recommended by Ramsay (1978).

Chemical analyses

Chemical analyses of the preserved water and effluent samples were done by the Cawthron Institute Chemical Services Department. Total organic carbon analyses were done using a Dohrmann Envirotech Organic Analyser. Total soluble carbohydrates were measured using a standard anthrone procedure and expressed as glucose equivalents. For individual sugar analyses, samples of effluent were lyophilized and silylized to form trimethylsilyl ether derivatives. The derivative concentrations were then estimated using a Tracor 560 Gas Chromatograph with a flame ionization detector.

Results

The rates of oxygen depletion in water samples from the Tarawera River (January 1980) are compared in Fig. 3 with other parameters characterising the microbial community. The corresponding numerical data is given in Table 1.

Oxygen consumption varied from < 2 g/m³ per day (the approximate detection limit for our method) at the three stations above the main Tasman outfall to a high of 9.1 g/m³ per day at a point 2 km below the outfall. Surprisingly enough these rates appeared to be increasing again in the lower reaches of the river after an initial decline.

Table 1. Measurements of microbial activity and biomass in water samples from 8 sites in the Tarawera River (Jan. 1980)

Site No. and Location	(g/m^3 per day) O_2 uptake	($\mu g/l$ per hr.) V_{max} glc.	% ^{14}C-glc uptake	($\mu g/l$) ATP
1. Kawerau Bridge	N.M.[a]	0.26	0.7	0.019
2. Pipe Bridge below Caxton O.F.	N.M.	0.90	1.8	0.095
3. 2 km above Tasman O.F.	N.M.	0.85	1.5	0.075
4. 2 km below Tasman O.F.	9.1	40.0	45	2.03
5. SH 30 Bridge	6.7	30.3	44	2.45
6. Above Mangaone Stream	4.5	47.6	37	2.60
7. Awakaponga Bridge	6.7	25.0	33	2.24
8. Above Awaka-ponga Canal	7.4	25.0	30	2.77

a. < 2 mg/m³ per day.

Correlation coefficients

O_2 Uptake vs. V_{max}	=	0.82
O_2 Uptake vs. ATP	=	0.90
V_{max} vs. ATP	=	0.89

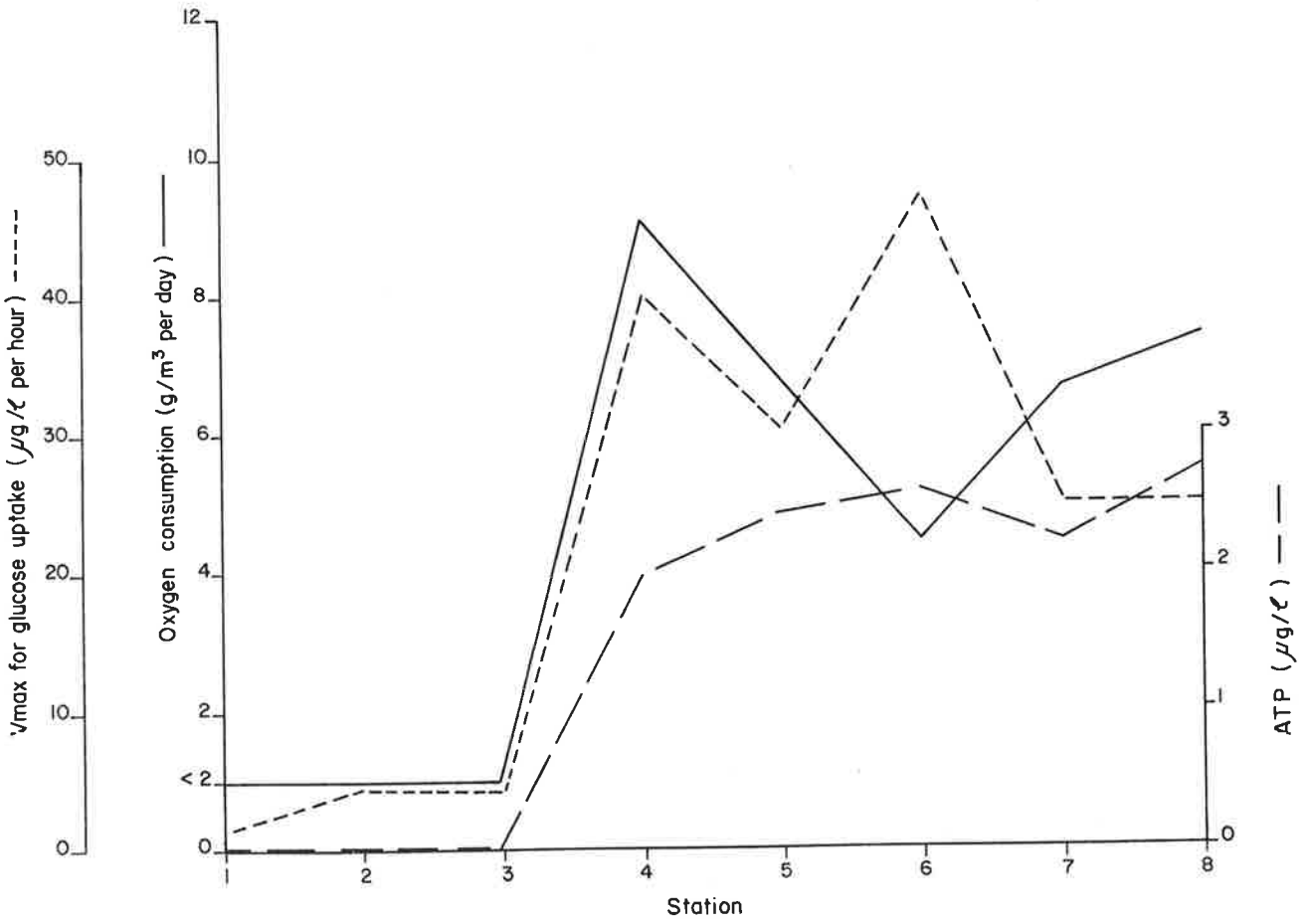

Fig. 3 Oxygen consumption and related microbial parameters in water samples from the Tarawera River (January 1980).

V_{max} for glucose uptake, which is sometimes referred to as the heterotrophic potential of the microbial community, increased by a factor of 3.5 between station 1 at Kawerau Bridge and station 2 below the Caxton outfall. A further 47-fold increase occurred below the Tasman outfall. Thus there was an overall increase in heterotrophic potential of approximately 150 fold between stations 1 and 4. Rates of glucose uptake at stations 5–8 remained high varying from 25–48 $\mu g/\ell$ per hour.

ATP concentrations gave roughly the same downstream increasing pattern except that a gradual increase was detected in the total biomass of water from the lower stations with less fluctuation than the activity measurements.

The corresponding activity and biomass relationships of benthic samples (Jan. 1980) are shown in Fig. 4 and Table 2.

The marked stimulation in benthic O_2 consumption between stations 1 and 2 is somewhat curious in that similar increases were not observed in either bacterial numbers or ATP concentrations. This may be the result of non-homogeneity of the sediments due to a deposition of particulate organic material and an inadequate mixing of the composite samples. Additional study will be necessary to verify this. There does appear to be a significant increase in benthic microbial activity, however, upstream of the Tasman outfall. From station 3 (immediately above Tasman) to station 4 (2 km below) a 3-fold increase in the rate of O_2 consumption occurred with a corresponding increase of 5-fold at ATP and 12-fold in bacterial numbers. The percentage of added ^{14}C-glucose taken up by the benthic community increased by 1.4 times between the same two stations. This parameter, however, is not as sensitive as V_{max}

Table 2. Measurements of microbial activity and biomass in pumice from eight sites on the Tarawera River (Jan. 1980).

Site No. and Location	(g/m^2 per day)[a] O_2 uptake	% ^{14}C-glc uptake	($\mu g/g$)* ATP	(Cells/g)[b] Bacteria
1. Kawerau Bridge	1.3	4.4	0.17	2.9×10^7
2. Pipe Bridge below Caxton O.F.	8.2	6.5	0.25	4.6×10^7
3. 2 km above Tasman O.F.	3.7	7.1	0.35	8.0×10^7
4. 2 km below Tasman O.F.	10.1	9.6	1.89	9.9×10^8
5. SH 30 Bridge	8.9	9.5	1.67	5.0×10^8
6. Above Mangaone Stream	7.4	8.4	2.26	6.2×10^8
7. Awakaponga Bridge	4.5	6.7	1.43	4.0×10^8
8. Above Awakaponga Canal	2.8	4.8	0.52	5.5×10^8

a. Calculated assuming the active depth of pumice to be 2 cm.
b. Dry weight basis.

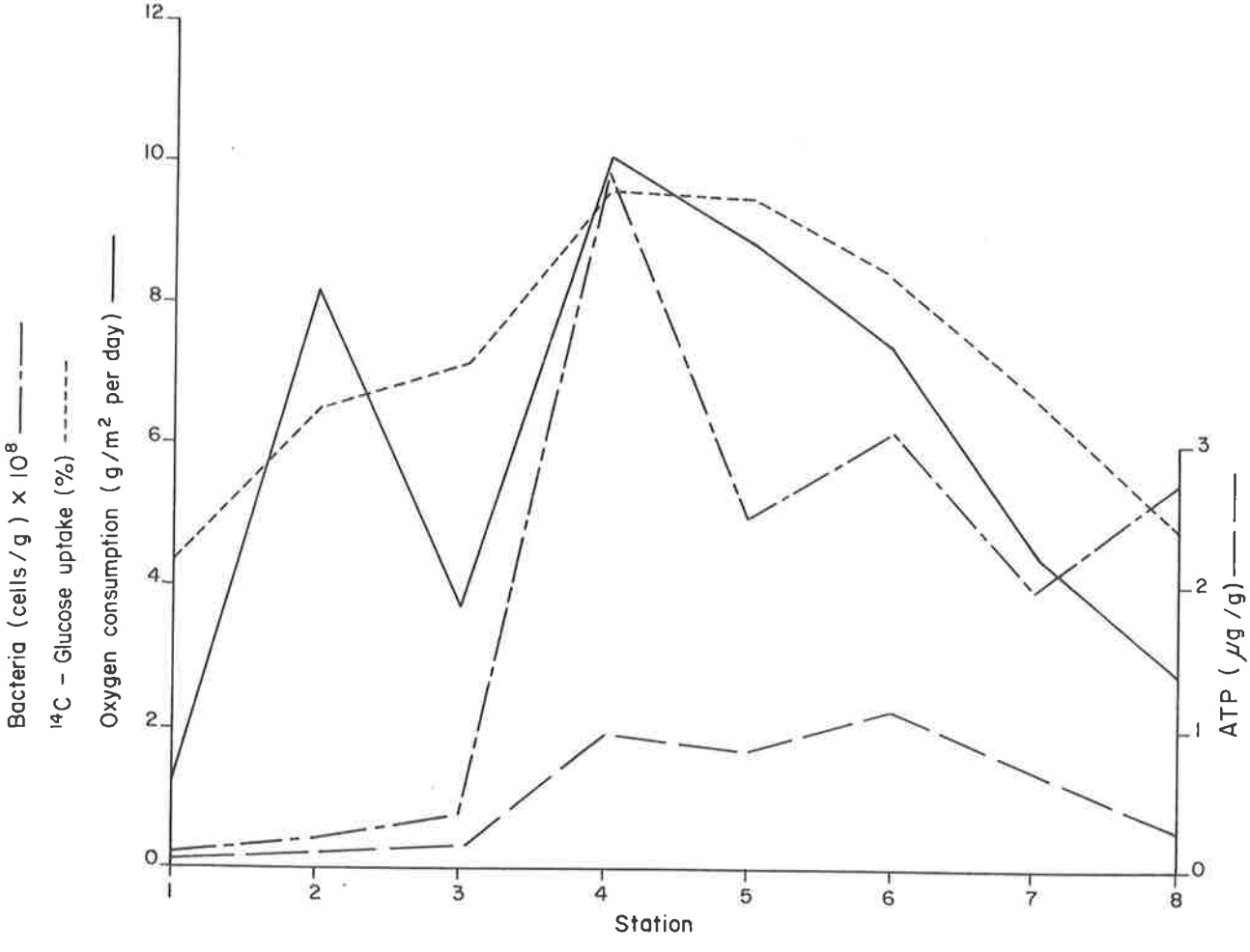

Fig. 4 Oxygen consumption and related microbial parameters in sediment samples from the Tarawera River (January 1980).

and probably does not warrant a great deal of discussion except that it follows the general trend of the other parameters. One interesting trend which can be seen in Fig. 4 is that all of the parameters, both activity and biomass measurements, decreased significantly downstream from the highest levels observed at station 4.

Benthic oxygen consumption data generated using the flow-through chamber technique are compared in Table 3 with total microscopic counts of bacteria and ATP concentrations. During this survey sediments of different types were sampled and they were not sieved prior to oxygen uptake experiments. Likewise samples were collected by wading and in some cases the main channels were not accessible. Consequently these measurements were intended mainly to demonstrate the variability which is likely to occur under natural conditions depending on the nature of the sediment and the degree of mixing by water currents. Sediment oxygen consumption rates were considerably lower using this technique and a marked stimulation was observed as a result of intermittent rocking of the chambers. In the shaken chambers the O_2 consumption rate was stimulated by an average increase of 2.6 times but the degree of stimulation varied depending upon the nature of the sample. For example in a mud sample collected below the Tasman outfall (4a), a rate of only 0.2 g/m² per day was observed. Since the sample was compact, allowing a minimum nutrient and oxygen exchange with the water, shaking caused an 18-fold increase in this rate. The downstream pattern of ATP concentrations and sediment bacterial numbers were also quite variable depending upon the sediment texture but they follow a pattern similar to the January sampling (Fig. 5). ATP concentrations in the water were considerably higher than during the previous sampling but again the downstream pattern was similar.

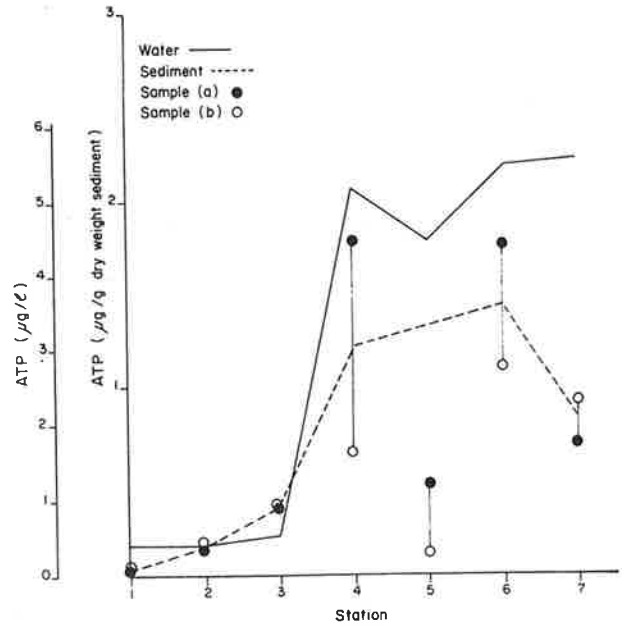

Fig. 5 Sediment and water ATP concentrations in the Tarawera River (May 1980).

Chemical analyses: The main stimulation of microbial activity and corresponding oxygen depletion in the river appears to be associated with the effluent from Tasman Pulp and Paper Company. For this reason we were interested in the nutritive capacity of the effluent. We found the total organic carbon (TOC) content of the effluent to be 140 g/m³. Of course a large proportion of this would be expected to be refractive in nature and not readily available to the microbial community. Approximately 5% of this total, however, was made up of soluble carbohydrate material. If this carbohydrate fraction is largely available to the microbial population it certainly represents sufficient organic loading to explain the observed downstream increases in microbial activity. Additional measurements were made of the individual wood sugars which are normally found in chemical pulp mill effluents of this

Table 3. Benthic oxygen demand at seven locations on the Tarawera River and associated total bacterial counts and ATP concentrations (May 1980).

Site No.	Location	Substrate type	Oxygen consumption[a] (g/m² per day)		Bacteria (cells/g)	ATP (μg/g)
			Unshaken	Shaken[b]		
1 a	Kawerau Bridge	Fine pumice	0.5	..	5.8×10^7	0.04
b	Kawerau Bridge	Fine pumice	0.3	..	6.7×10^7	0.05
2 a	Below Caxton O.F.	Fine pumice	0.4	..	1.5×10^8	0.14
b	Below Caxton O.F.	Fine pumice	0.1	..	9.2×10^7	0.19
3 a	Above Tasman O.F.	Coarse pumice	0.6	..	1.2×10^8	0.37
b	Above Tasman O.F.	Fine pumice	0.4	..	9.6×10^7	0.37
4 a	Below Tasman O.F.	Mud	0.2	3.6	2.8×10^8	1.80
b	Below Tasman O.F.	Coarse pumice	1.8	4.7	..	0.67
5 a	SH 30 Bridge	Fine sand	1.2	2.8	3.6×10^8	0.48
b	SH 30 Bridge	Fine sand	0.4	3.0	1.4×10^8	0.12
6 a	Above Mangaone Stream	Coarse pumice	2.4	2.8	1.4×10^8	1.79
b	Above Mangaone Stream	Fine pumice	1.0	1.2	7.8×10^8	1.12
7 a	Awakaponga Bridge	Fine pumice	1.7	4.4	1.1×10^8	0.72
b	Awakaponga Bridge	Fine pumice	1.4	3.6	0.9×10^7	0.95

a Calculated using data from flow-through chamber experiments.
b Gentle rocking of chamber prior to DO measurements (mean increase due to shaking, excluding site 4a, was 2.6 times).

type (Table 4). Most significant of these were galactose and glucose which at a total concentration of 1 g/m³ (5.4% of the total carbohydrates) would result in concentrations in the river of from 10 to 50 times that which would normally be found in unpolluted waters.

Table 4. Chemical analyses of effluent from Tasman Pulp and Paper Company (Jan. 1980)

Analysis	g/m³
Total Organic Carbon	140
Total Carbohydrates	18.5
Sugars	
Rhamnose + Arabinose	0.19
Xylose	0.025
Mannose	0.15
Galactose + Glucose	1.00

The mean TOC concentration below Tasman outfall was 7.8 times greater than that of stations 1-3 above it. Similarly total carbohydrate concentrations were an average of 3.6 times greater below the outfall (Table 5). In both instances the concentrations were approximately one tenth of those observed in the effluent but no significant decreases occurred in downstream samples between stations 4 and 8.

Table 5. Chemical analyses of water samples from the Tarawera River (January 1980).

Site No.	Location	(g/m³) Total Organic C	Total Carbohydrate (g/m³ as glucose)
1	Kawerau Bridge	2	0.5
2	Below Caxton O.F.	1	0.5
3	Above Tasman O.F.	2	-
4	Below Tasman O.F.	12	1.7
5	SH 30 Bridge	14	1.8
6	Above Mangaone Stream	12	1.6
7	Awakaponga Bridge	13	2.0
8	Above Awak. Canal	14	2.0

Discussion

Because of the high degree of deoxygenation in the Tarawera River and subsequent attempts to model DO levels, the relative importance of the benthic versus the aquatic oxygen demand has been a major question. The results presented here suggest that both are important and that we should consider the sum of the two contributing mechanisms of oxygen removal.

Certainly the benthic oxygen demand is greater than I would have anticipated, due to the efficiency of the pumice-associated microflora. Maximum daily rates of from 10 to 15 g O_2/m^2 consumed by the upper 2 cm of pumice were observed approximately 2 km below the main Tasman outfall (station 4). This agrees reasonably well with the benthic oxygen demand of 12 g/m³ per day suggested by McBride in the previous paper, although the conversion from a m² to a m³ basis may cause some discrepancy. It should be emphasised here that the actual *in situ* rates are highly dependent upon the nature of the sediment. In areas where the pumice is of a fine grain size or where interstitial spaces are filled with silt, thus cutting down water movement, the rates of O_2 consumption are much lower. A more accurate estimate of benthic oxygen demand will therefore require further classification of the sediments.

Rates of oxygen consumption in the water layer at station 4 were also quite high varying from 9 g/m³ per day (January 1980) to 3.5 g/m³ per day (May 1980). Likewise the V_{max} values observed here were consistent with extremely high rates of heterotrophic activity. By way of comparison, V_{max} values observed in water samples 2 km below Tasman were 30 times greater than those reported for a polluted lake in Sweden (Allen 1968) and twice as great as a eutrophic section of the Waikato River at Mihi bridge (Spencer & Ramsay 1978).

We might hypothesize as to the possible changes in the relative importance of these two mechanisms in the lower reaches of the river. All of the parameters measured in the benthic samples followed a decreasing trend at stations downstream from Tasman. This may be due to a decrease in available organic substrates as we move progressively downstream. The same decreases were not observed in the water samples. This pattern may be the result of a continual sloughing off of the pumice-associated flora in response to nutrient limitation. This is a common phenomenon in slime-associated communities. The growing population may limit the nutrient availability to underlying cells inducing a liberation of mobile swarmer cells which then contribute to the "aquatic" oxygen demand. This is known to occur in the case of sheathed bacteria such as *Sphaerotilis natans*. I should mention, however, that both microscopic inspection of the pumice and plate counts using a medium capable of supporting *Sphaerotilis* growth showed a rich and diverse microbial flora composed mainly of rod-shaped bacteria and fungi. It may be that the constant movement of the pumice prevents the build up of a slime layer with the characteristic sheathed bacteria. Characteristic "sewage fungus" growths have been observed by others along the banks of the river on submerged streamside vegetation such as fallen willows (M. Piper, Tasman Pulp and Paper Company, pers. comm.). During the sampling periods of this study, however, such growth was not obvious.

Nagels (1978) reported a lengthy lag in the recovery of DO levels in the Tarawera River after cessation of waste discharges from Tasman. This is presumed to be due to a storage of organic materials within the bottom sediments. During the present study we measured the rates of oxygen consumption (using the flow-through chambers) of samples taken from depth intervals of 0-5, 5-10 and 10-15 cm in the pumice bed at station 4. All three depth intervals were found to be equally active when exposed to oxygen-containing river water. We also observed a sharply declining oxygen profile within the pumice bed suggesting that at this location water movement

is sufficient to maintain an aerobic zone of metabolism only in the surface 1 or 2 cm. Thus in the deeper layers of pumice, microbial activity occurs under anaerobic or microaerophilic conditions at a much reduced rate. Consequently an endogenous nutrient supply may remain buried for a long period of time. After cessation of waste discharge the river flow would gradually (or periodically) expose new layers of pumice containing potentially active microbial populations thus exerting a continual or renewable oxygen demand on the river.

Conclusions

The results of this survey indicate that there are sufficient organic nutrients in the form of soluble carbohydrates entering the Tarawera River via the Tasman Pulp and Paper Company effluent to cause a critical stimulation of microbial activity and associated oxygen depletion. A significant proportion of these carbohydrates are simple sugars such as glucose and galactose which can be utilised directly by the bacterial population without requiring the slower sequential oxidation necessary for the breakdown of many complex organics. Both benthic and free-living aquatic microbial populations exert a significant pressure on the dissolved oxygen levels of the river. The coarse pumice river bed which is in constant agitation from current action provides an ideal environment for a highly efficient microbial removal of organic nutrients and oxygen from the overlying water. The sediments, however, are not completely uniform and differences in grain size or the degree of siltation can alter the efficiency of removal. Thus to achieve mean values which would accurately describe the natural situation would require a more thorough field survey particularly with respect to characterisation of the bottom sediments.

Acknowledgements

This research was supported by the Bay of Plenty Catchment Commission and Regional Water Board, Whakatane, and Cawthron Institute Research Department, Nelson. Laboratory space and facilities were provided by Tasman Pulp and Paper Company and the helpful co-operation of Mr Martin Piper of the same company is greatly appreciated. I wish to acknowledge the technical assistance of Mr A. L. MacKenzie during this survey.

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Dissolved oxygen levels and waste discharges: a case study of the Taylor — Opawa River, Blenheim

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A survey of water quality in the Taylor and Opawa Rivers near Blenheim identified two point source discharges of wastes as being important in reducing dissolved oxygen levels in the rivers. Dissolved oxygen was monitored along the rivers on several occasions. The flow and biochemical oxygen demand of the wastes was also monitored in order to determine the effect of these on oxygen levels downstream..

Introduction

The Taylor and Opawa Rivers begin flowing from hilly regions south of Blenheim (Fig. 1). They flow in partly controlled channels across the lower Wairau Plains to join in Blenheim. The Lower Opawa River then flows east to join the Wairau River approximately 1 km upstream of its entry to sea.

During 1977 a survey of water quality in the Taylor and Opawa Rivers was carried out by the Marlborough Regional Water Board. The survey identified point source discharges as being the most important causes of low water quality. In particular, continuous discharges of raw sewage (from about half the town of Blenheim) and the discharge of wastes from a vegetable processing factory caused oxygen depletion in the river.

As a result of the 1977 survey the Blenheim Borough Council was requested to extend the town's sewerage system in order to prevent sewage discharge to the Opawa River. The discharge of sewage ceased in mid February 1980. The vegetable processing waste discharge ceased in early 1979.

This paper presents the results of investigations into the strength and flow of wastes into the Taylor–Opawa River and the effects of these on dissolved oxygen levels in the river. Readers are referred to the Marlborough Regional Water Board 'Taylor–Opawa River Water Quality Survey — 1977' for additional information and a water quality management strategy.

Survey methods

Dissolved oxygen was monitored along the Opawa River on a number of occasions. Waste discharge flows were measured and sampled on several occasions to determine various parameters and in particular the 5-day biochemical oxygen demand (BOD_5). River flows at various points on the Opawa River were correlated with flow at the Taylor River flow recorder, sited 17 km upstream of the survey area. In this way estimates of flow were made for the days on which these surveys were conducted.

Dissolved oxygen was determined using a Yellow Springs ARC–54 portable meter. Biochemical oxygen demand of wastes was determined over a 5-day period using standard methods. Some BOD_5 information was supplied by the Blenheim Borough Council and the vegetable processing company concerned.

Results of survey

1 Waste Discharges

Over the periods that these dissolved oxygen surveys were conducted there were only two effluent

TABLE 1. River and waste flows

Date	Flow (ℓ/s)			Average water temp.	Effluent BOD_5 (g/m³) and flow in brackets (ℓ/s)		Dissolved Oxygen (g/m³)	
	Taylor	Opawa	Downstream (estimated)	°C	Processing wastes	Sewage	Max.	Min.
26.1.77	4933	1200	6500	17.5	704(22)	90(35)	9.6	7.0
2.2.77	2889	900	4000	16.0	704(22)	110(25)	9.9	2.3
18.4.77	1757	600	3000	14.0	704(22)	140(25)	10.0	3.3
16.1.80	2976	750	4100	15.2	ceased	130(25)	8.7	3.8
19.3.80	2900	700	4000	16.0	ceased	ceased	11.2	9.8

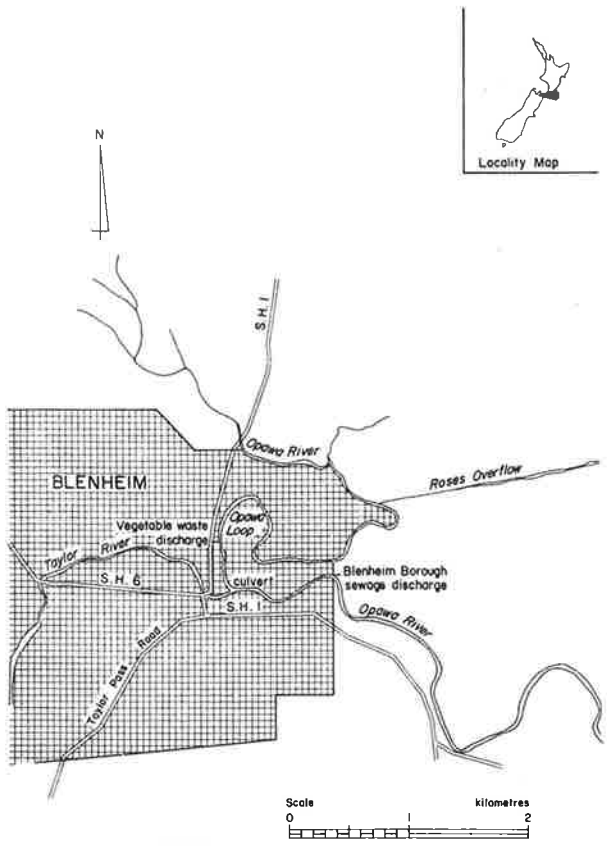

Fig. 1 Location map, showing rivers and waste discharges.

discharges into the Taylor–Opawa River. The nature of these discharges is discussed below. Some minor pollution of the river from diffuse sources may have been occurring but this was not reflected in dissolved oxygen concentrations which were at optimum levels upstream of the two point source discharges discussed below.

(a) Vegetable Processing Wastes

Vegetable processing wastes were discharged from the factory at a constant rate of 22 ± 5 ℓ/s. The wastes consisted predominantly of screened pea and corn processing water. To obtain an average BOD_5 value two sets of figures were used. Firstly, values were obtained from analyses of samples taken by the food processing company. The average of these was 402 ± 185 g/m³. The Marlborough Regional Water Board also conducted tests on the effluent and the BOD_5 was found to be 1854 ± 867 g/m³. The average BOD of the combined sets of values is 704 ± 700. Water flow through the Opawa Loop into which these wastes were discharged (Fig. 1) is controlled by inlet and outlet culverts.

The loop section functions as an urban runoff water storage area during floods when both culverts are closed. Roses Overflow channel marked on Fig. 1 is an artificial channel enabling flood waters to bypass Blenheim instead of them being routed along the loop channel into the Taylor River. During low flows the amount of water flowing through the Opawa Loop depends on low flows in the Opawa River but is generally about 800 ℓ/s (see Table 1). The vegetable processing wastes were discharged into the lower end of the loop some 200 m upstream of the Opawa Loop–Taylor River confluence.

(b) Sewage Discharge

Raw domestic sewage was being discharged into the Opawa River 1 km downstream of the vegetable processing waste discharge. The BOD_5 concentration of this sewage varied between 90 g/m³ (wet weather flows) and 200 g/m³ (dry weather flows). Sewage samples were not analysed for BOD_5 on the specific days that the dissolved oxygen surveys were conducted. For the purposes of this paper, estimates of BOD_5 have been made (see Table 1) for the days on which surveys of dissolved oxygen were made.

Sewage flow to the river varied between 10 ℓ/s and 50 ℓ/s (maximum pumping rate). It is of note that the Blenheim sewerage system has now been extended and sewage no longer enters the river, but is piped to an oxidation pond near the Opawa River outlet to the sea. Discharge of the oxidation pond effluent enters the Opawa River at that point.

2 Dissolved Oxygen Levels

Figure 2 presents dissolved oxygen levels in the lower Opawa River as a result of waste inputs of sewage and vegetable processing matter as outlined in Table 1. The following points are of interest in interpreting these results.

The effect of river flow on dissolved oxygen levels

The difference in dissolved oxygen levels between the days 26 January 1977 and the 22 February 1977 appears to be directly related to flow. The variation in river water temperature could only account for about a 2% difference in dissolved oxygen. The differences in waste load inputs (measured as BOD_5) were quite small on 2 February 1977. As a result of a minor flood in the river system which had peaked 3 days earlier, flow along the lower Opawa on 26 January 1977 was estimated at 6500 ℓ/s while on 2 February 1977 was 4000 ℓ/s — a 40% reduction in flow. This lower flow would have reduced the organic waste assimilation capacity of the river.

Differences between dissolved oxygen levels on 2 February 1977 and 18 April 1977 appear to be due to a combination of factors. Firstly, river flow on 18 April 1977 is 25% less than on 2 February 1977. Water temperatures are 5% cooler on 18 April 1977 thereby compensating, in part at least, for the reduced organic waste assimilation capacity of the river due to the lower flow on that day.

The effect of photosynthesis/respiration on dissolved oxygen levels

The lower Opawa channel is notable for the prolific growth of water weeds. *Lagarosiphon major* (oxygen weed) and *Elodea canadensis* (Canadian pondweed) are the most abundant. An attempt was made on 18 April 1977 to determine whether there were significant differences in dissolved oxygen levels between night and day. Vegetable processing waste

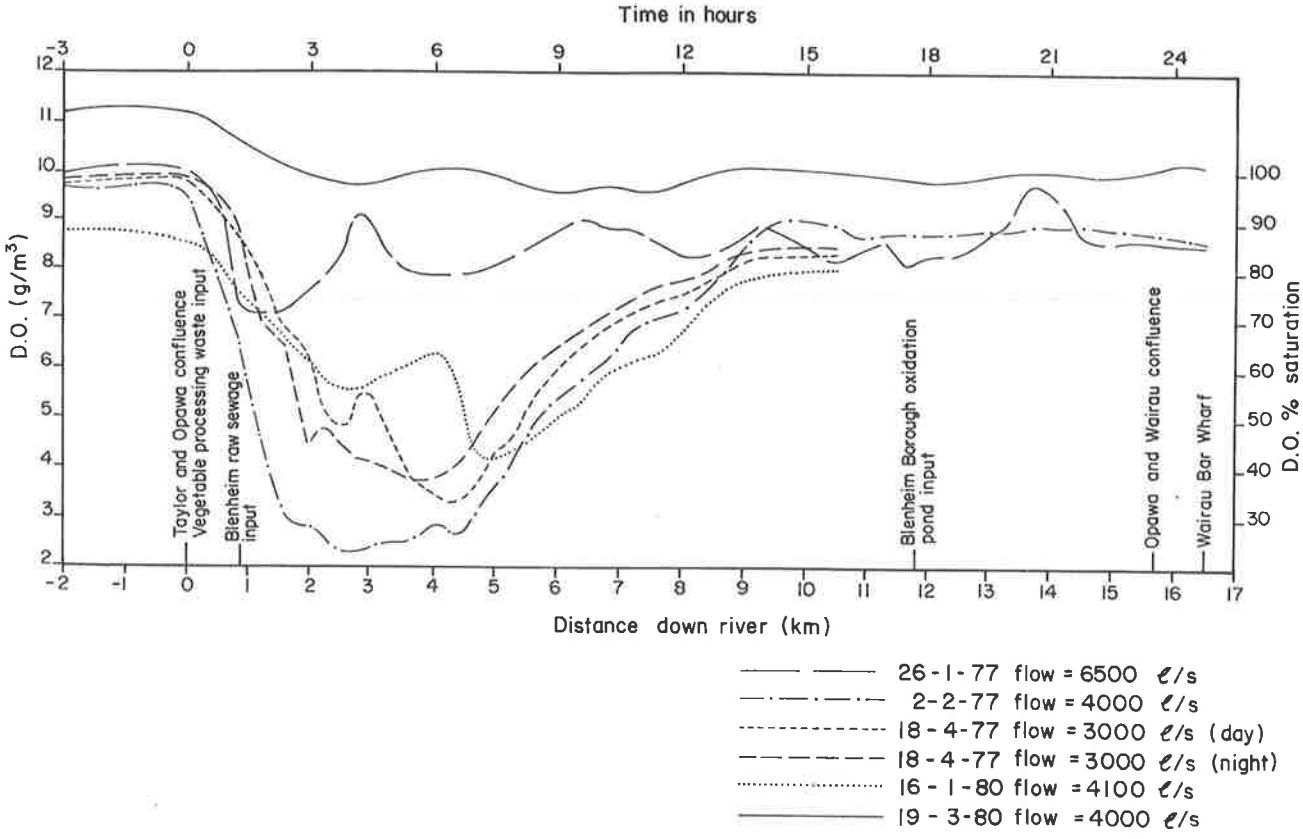

Fig. 2 Dissolved oxygen concentrations in the lower Opawa River. The scale for dissolved oxygen percentage saturation is correct for a survey carried out at 16 °C, when 100% saturation corresponds to a dissolved oxygen level of 10 g/m³. The surveys were carried out at average temperatures of 17.5 °C (26/1/77), 16 °C (2/2/77), 14 °C (18/4/77), 15.2 °C (16/1/80) and 16 °C (19/3/80).

discharges ceased over night. Initially, it appeared (from the curves in Fig. 2) that plant respiration requirements for oxygen had reduced dissolved oxygen levels below that obtained during daytime. However, further downstream, night-time dissolved oxygen levels were slightly higher than daytime levels. This could be related to the travel time. At night the vegetable processing waste flows were reduced causing the critical point to move downstream. However, the results of this exercise were inconclusive.

The effect of food processing waste discharge cessation on dissolved oxygen levels

A survey of dissolved oxygen levels in the river was conducted on 16 January 1980 after the vegetable processing wastes ceased flowing to the river.

Figure 2 shows that the discharge of sewage alone created a reasonably large sag in dissolved oxygen levels.

The effect of sewage discharge cessation on dissolved oxygen levels

The survey of dissolved oxygen levels conducted on 19 March 1980 following a month's cessation of the sewage flow indicated that dissolved oxygen levels in the river had recovered completely. The levels were at or about saturation point.

General comments

A simple mass balance applied to the BOD_5 loading of wastes and river flows indicates that the sag in dissolved oxygen levels cannot be adequately accounted for. Either a simple mass balance approach is an inadequate method to use to explain downstream levels or the BOD_5 of the effluent discharges is underestimated. The survey results indicate that the BOD_5 of vegetable processing wastes may have been underestimated. Unfortunately, BOD_5 levels of the river waters were not determined. The river bed was composed of mud and fine sand containing high amounts of organic matter. It is possible that this factor could also influence dissolved oxygen levels adding to the difficulties of interpretation.

Several of the curves in Fig. 2 show an initial decline in dissolved oxygen followed by a partial recovery then a further fall. This apparently short-lived recovery is possibly due to differences in the rate of waste discharge during the night, when the food processing wastes ceased and sewage discharge was considerably reduced.

Waipa River

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The results of surveys carried out when patches of anoxic water were being conveyed down the Waipa River are presented. These unusual conditions prevailed after the dumping of some two million litres of milk into the river in March 1979. A model has been calibrated and verified using these data. Comparatively low rates of longitudinal dispersion and deoxygenation occurred in this river.

Introduction

Industrial action which commenced on 2 March 1979 and ended on 7 March 1979 at six factories of the New Zealand Co-operative Dairy Company (NZCDC) situated in the Waikato and Hauraki Plains districts resulted in the dumping of several million litres of raw milk into nearby rivers and streams. The milk had a dramatic visual impact on water quality in the receiving waters and attracted considerable public attention. Severe deoxygenation occurred in several rivers with consequent adverse effect on taste, odour, appearance, fish, and benthic invertebrate populations.

The opportunity was taken by the Hamilton Science Centre (HSC) working in conjunction with the Waikato Valley Authority (WVA) and Aquatic Weeds Section, Ministry of Agriculture and Fisheries (MAF) to study the response of the Waipa River to shock loads of organic pollutants. The stretch of river studied covered the 60 km from Pirongia to Ngaruawahia, as shown on Fig. 1.

Preliminary field surveys

A preliminary field survey carried out on 5 March 1979 with WVA staff, using only the few sampling sites accessible by motor car, revealed very low DO concentrations in the Mangapiko Stream (approximately 1 g/m^3). The stream was obviously discoloured with large quantities of milk. Samples taken from the Waipa River showed little signs of deoxygenation, although some were later found to have a BOD_5 concentration as high as 12.5 g/m^3 indicating that some milk had found its way into the Waipa River. Presumably insufficient time had elapsed for bacteria to break down the milk constituents and so remove river oxygen.

A further survey was carried out at sites accessible by road on 7 March 1979, when it was found that the Waipa River was seriously depleted of oxygen between Pirongia and Whatawhata Bridge. It is normally a well-oxygenated river. Two samples were completely anoxic. Distressed eels and small fish were seen from the bank at sites where the water was anoxic. The BOD_5 concentrations of these anoxic waters were later found to be as high as 46 g/m^3.

These preliminary surveys showed that the milk spill was obviously having a major impact on oxygen levels in the Waipa River, with a long stretch of the river being completely anoxic. This provided an unique opportunity to study the response of a river system to a large shock load of organic matter with the subsequent deoxygenation and recovery. Accordingly it was decided to mount a more intensive sampling programme to investigate changes of DO, BOD_5 and COD concentrations in the Waipa River. The objective of this programme was not only to determine the state of the river under these conditions, but also to gather sufficient data to develop a model of the oxygen dynamics of this unique situation.

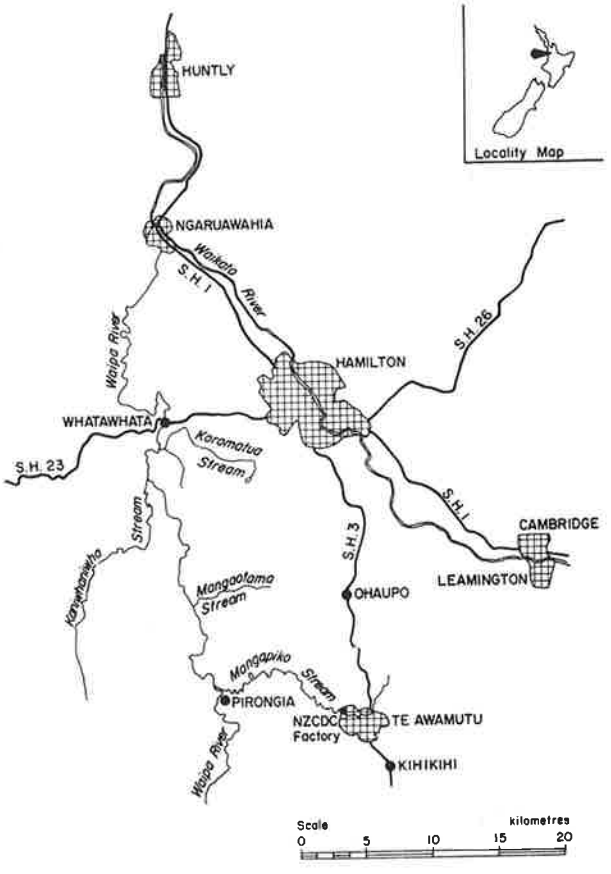

Fig. 1 Location map.

Intensive longitudinal surveys

Three longitudinal boat surveys of the Waipa River were conducted during the passage of the anoxic water:

Run 1: 1947–2355 on 7/3/79.
Run 2: 0620–1026 on 8/3/79.
Run 3: 1730–2135 on 8/3/79.

Two two-man boat teams were used for Runs 1 and 2, both boats being launched at Whatawhata, one travelling upstream and one downstream. For Run 3 one boat was used, being launched at Whatawhata.

These surveys were carried out before details of the pattern of milk discharge from the dairy factory could be obtained. Water samples were collected at fixed sites, analysed for temperature and DO in the field, and returned to the laboratory for BOD_5 and COD analysis and some check DO analyses using the modified Winkler method. Sampling sites were established during the first and second surveys (using landmarks visible from the river), and were located on maps and aerial mosaic photographs during a subsequent survey. A total of 50 sites were used.

The results of these surveys, for DO and BOD_5 only, are shown on Fig. 2, where the data have all been plotted at a run reference time (as explained in the next section, under Calibration . The COD results were 8–10 g/m³ higher than the BOD_5 results. River temperature was approximately 20 °C, and river flow rate at Whatawhata was 26.5 m³/s. Tributary inflows amounted to 3 m³/s.

Run 1 Results

The first boat survey established that there was a patch of anoxic water approximately 20 km long stretching from 15 km below Pirongia to 5 km below Whatawhata Bridge. BOD_5 concentrations were highest near the tail of this patch. DO concentrations dropped very quickly at the head of the anoxic patch and recovered more slowly in its tail. A stretch of water extending some 5 km upstream of Whatawhata Bridge had lower BOD_5 concentrations and higher DO concentrations suggesting that the rate of release of milk load had not been uniform.

Run 2 Results

Run 2 (see Fig. 2) showed that there were, in fact, two patches of anoxic water separated by some 10 km of water in which BOD_5 concentrations were low (less than 2 g/m³) and DO concentrations quite high (about 5 g/m³). The full extent of the older patch of anoxic water was not established during Run 2 but subsequently the patch was found to be about 5 km long. The tail of the younger patch of anoxic water was tracked upstream to within 2 km of the Mangapiko confluence.

Comparison of the results of Runs 1 and 2 indicates that the front of the younger patch of anoxic water had moved downstream 5 km overnight while the tail had moved down some 8 km. The difference reflects non-uniform mean velocity in the Waipa River caused by changes in bed slope of the river channel. The BOD_5 concentrations appeared to have decreased overnight (although no samples were taken between 28–36 km).

Run 3 Results

Run 3 (see Fig. 2) established that the older patch of anoxic water had a peak BOD_5 concentration of 23.5 g/m³ and was 4–5 km long.

Comparison of the results of Runs 2 and 3 indicates that the younger patch of anoxic water had remained about 15 km long and had moved about 5 km downstream during the day. Peak BOD_5 concentrations had decreased to about 18 g/m³. The patch of aerated water had remained much the same shape while travelling downstream 5 km, and the peak DO of about 5 g/m³ was unchanged.

Fish Kill

Many dead small fish were seen near the river bank at Whatawhata Bridge at 1600 hours on 7 March 1979: of the order 10–20 per square metre. These were predominantly bullies (*Gobiomorphus* spp.), smelt (*Retropinna retropinna*) and shrimps (*Paratya* sp). Very large numbers of small fish (predominantly) bullies (*Gobiomorphus*)) were seen floating in the main stream during the course of Runs 1, 2, and 3. No attempt was made to count or estimate the numbers seen.

Numerous large fish were also seen floating in the main stream or snagged on logs and branches. These included brown trout (*Salmo trutta*), grey mullet (*Mugil celphalus*), gold fish (*Carassius auratus*), catfish (*Ictalurus nebulosus*), and eels (*Anguilla* spp.). A very rough count of 104 large dead fish was made during passage at high speed between sampling sites from Whatawhata Bridge to 12 km upstream during Run 2.

An eel was observed resting in very shallow water near the bank at the boat launching site near Whatawhata Bridge and appeared to survive the passage of the anoxic slugs. Occasionally during Runs 1, 2, and 3 eels were seen swimming on the surface in stretches which were anoxic.

Dissolved oxygen model

The data obtained from these surveys can be used to calibrate and verify a river dissolved oxygen model.

Identification

Objective: To infer the rates at which important processes affect the river dissolved oxygen.

Important processes: These were judged to be tributary inflows containing high DO and low BOD_5, longitudinal convection, longitudinal dispersion, reaeration and aerobic bacterial decomposition of milk organic material.

BOD_5 breakdown was assumed to occur only when DO was above 0.1 g/m³. It was assumed that there was neither sufficient time, nor nitrates and sulphates, for anaerobic bacterial activity to be important. Aquatic plant metabolism was known to be small and was neglected.

Desired level of complexity: The model constructed solves partial differential equations for river BOD_5 and DO. Some care had to be taken to ensure that the

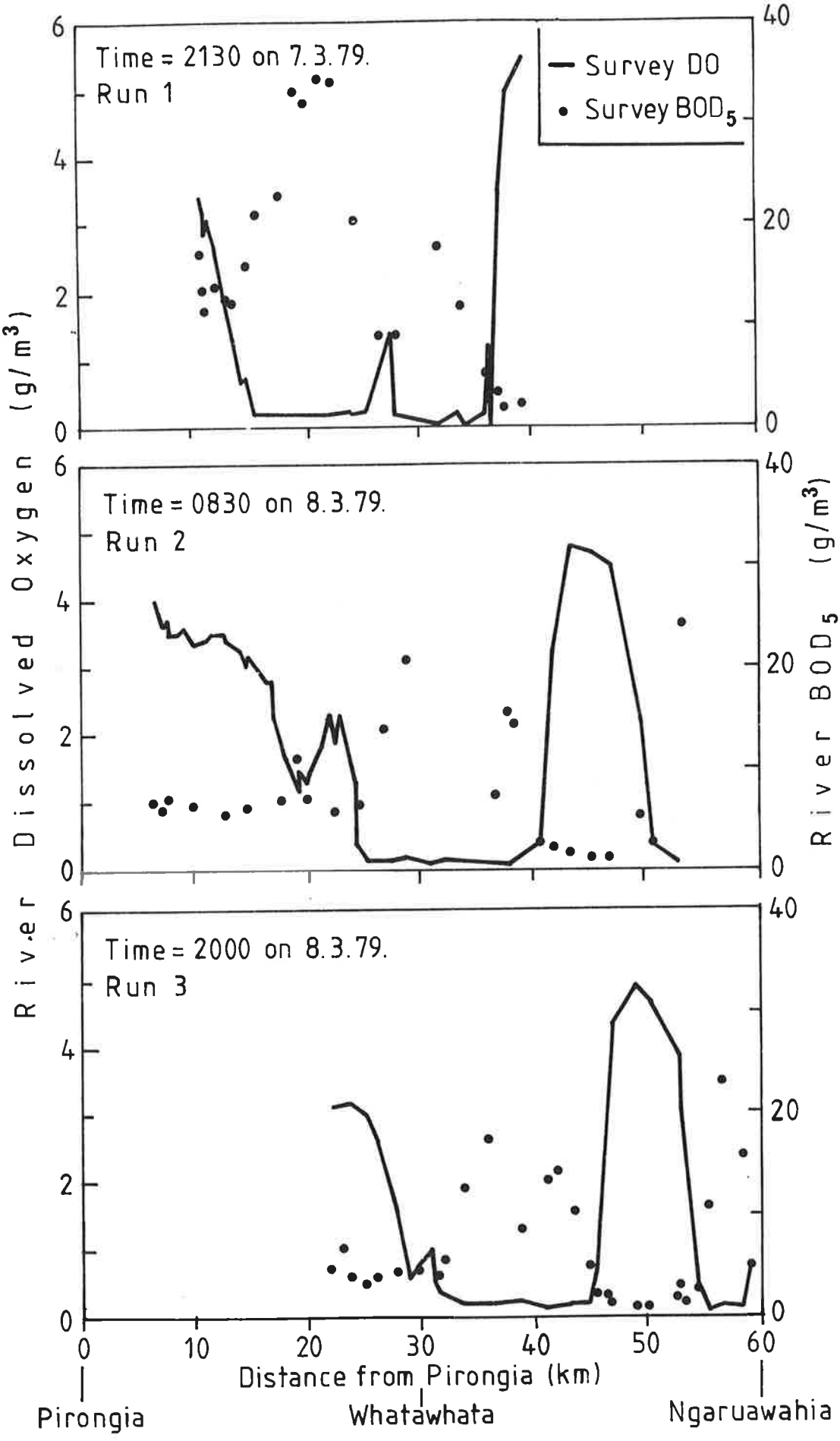

Fig. 2 DO and BOD_5 results for Runs 1, 2, and 3.

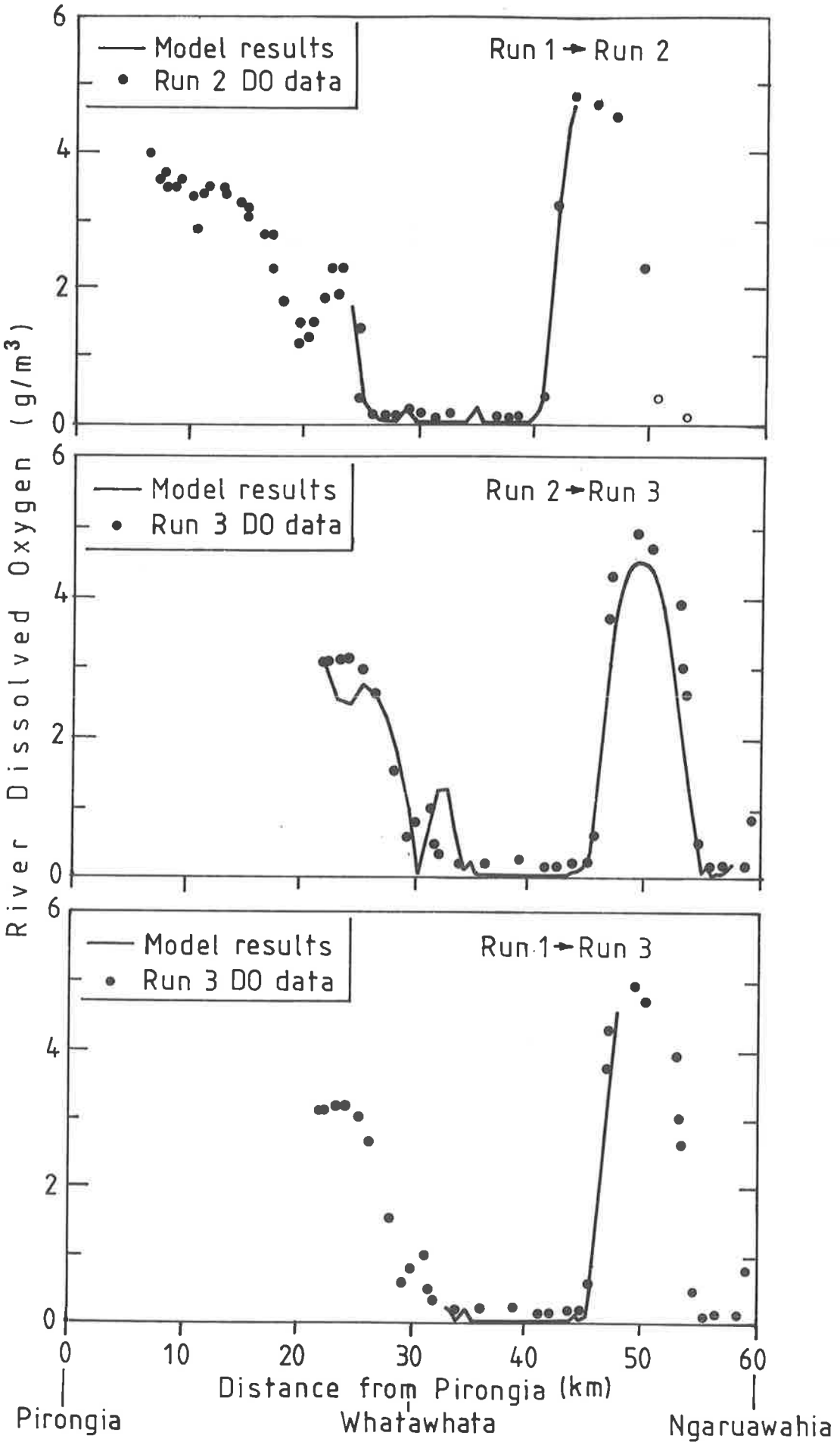

Fig. 3 Model DO calibration and verification (k_1 = 0.7 day^{-1}, ξ = 3.7, D = 10 m^2.s^{-1}).

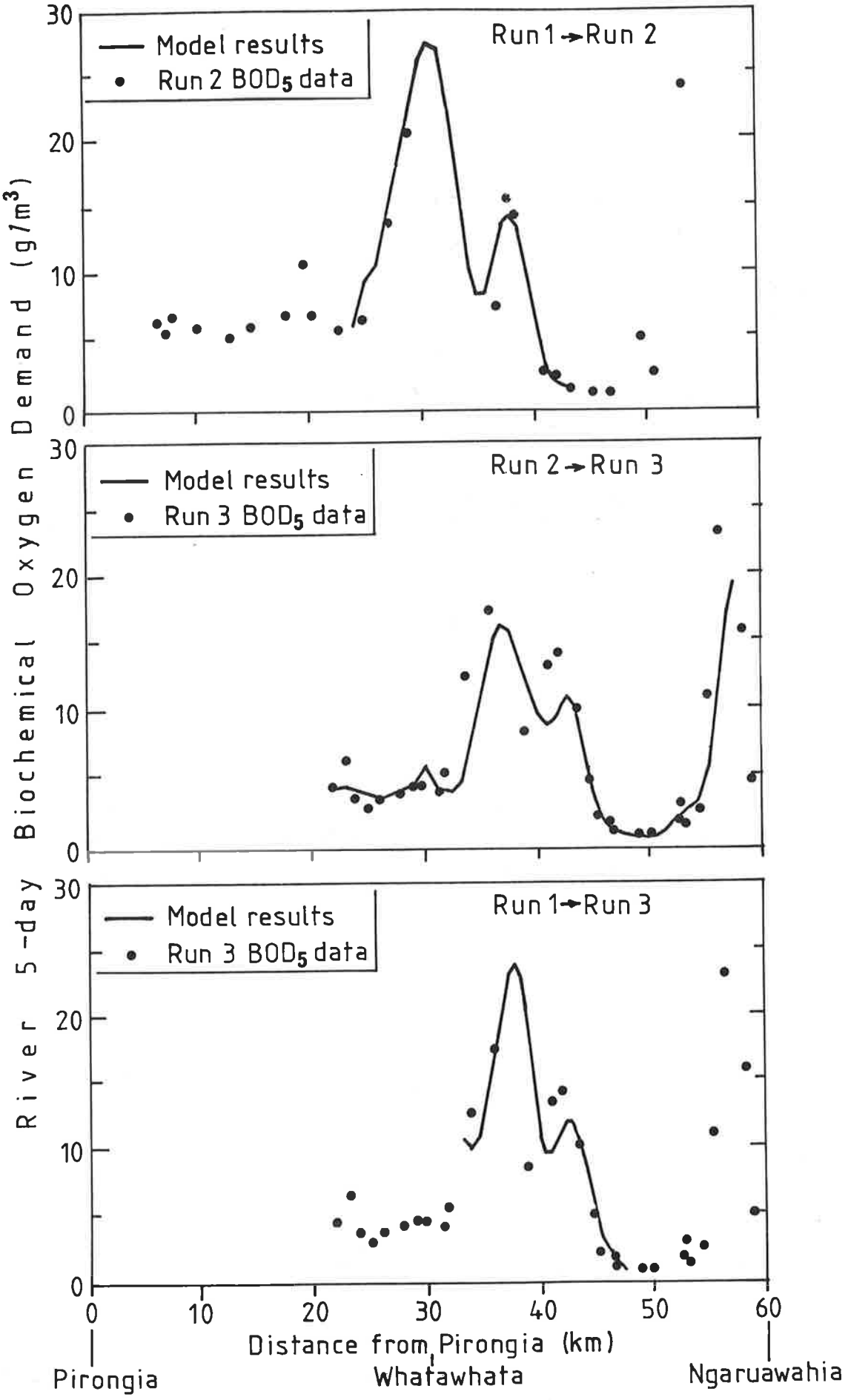

Fig. 4 Model BOD_5 calibration and verification ($k_1 = 0.7\ day^{-1}$, $\xi = 3.7$, $D = 10\ m^2.s^{-1}$).

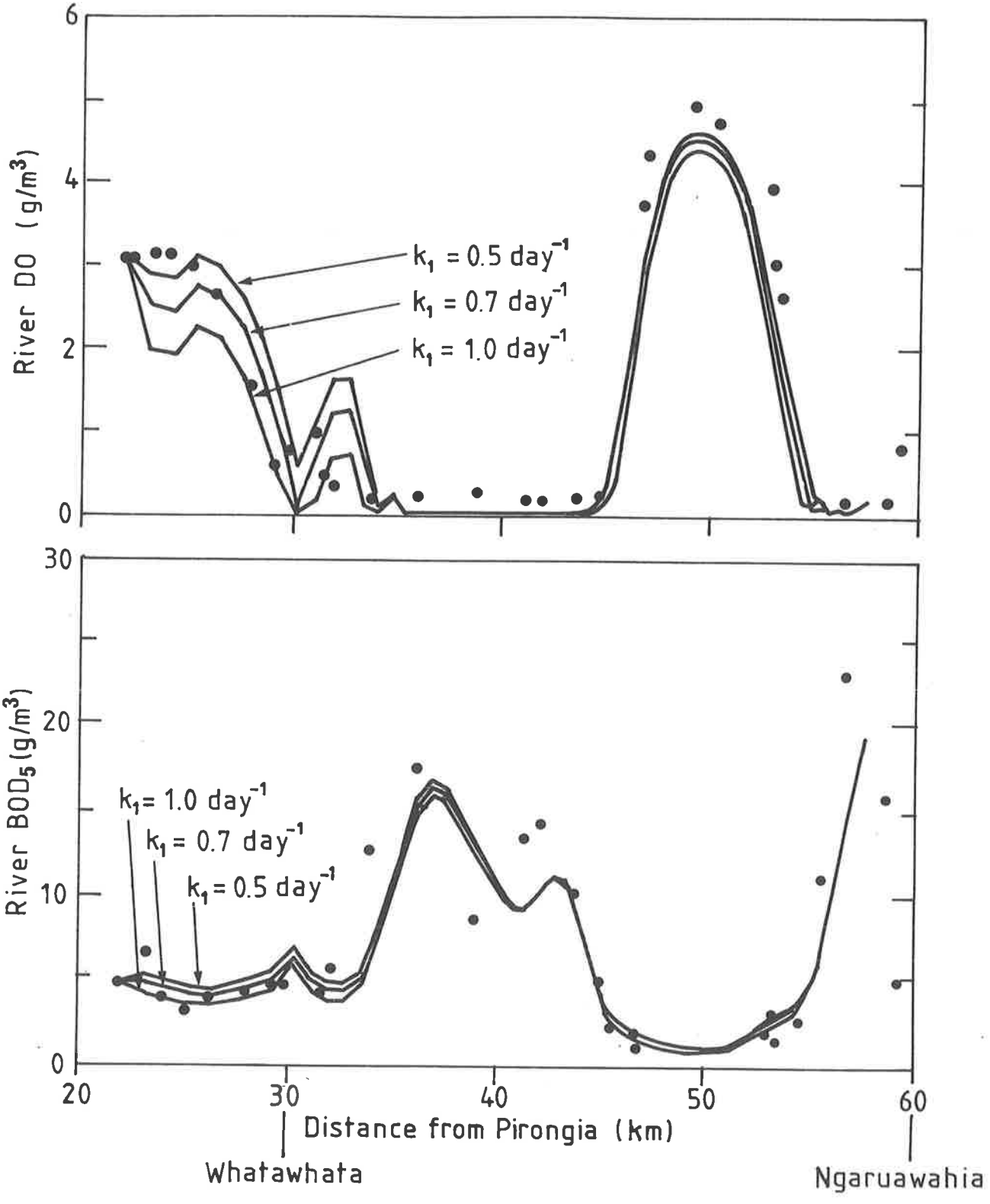

Fig. 5 Effect of variation of deoxygenation coefficient on model DO and BOD_5 predictions for Run 2→Run 3 (ξ = 3.7, D = $10 m^2.s^{-1}$).

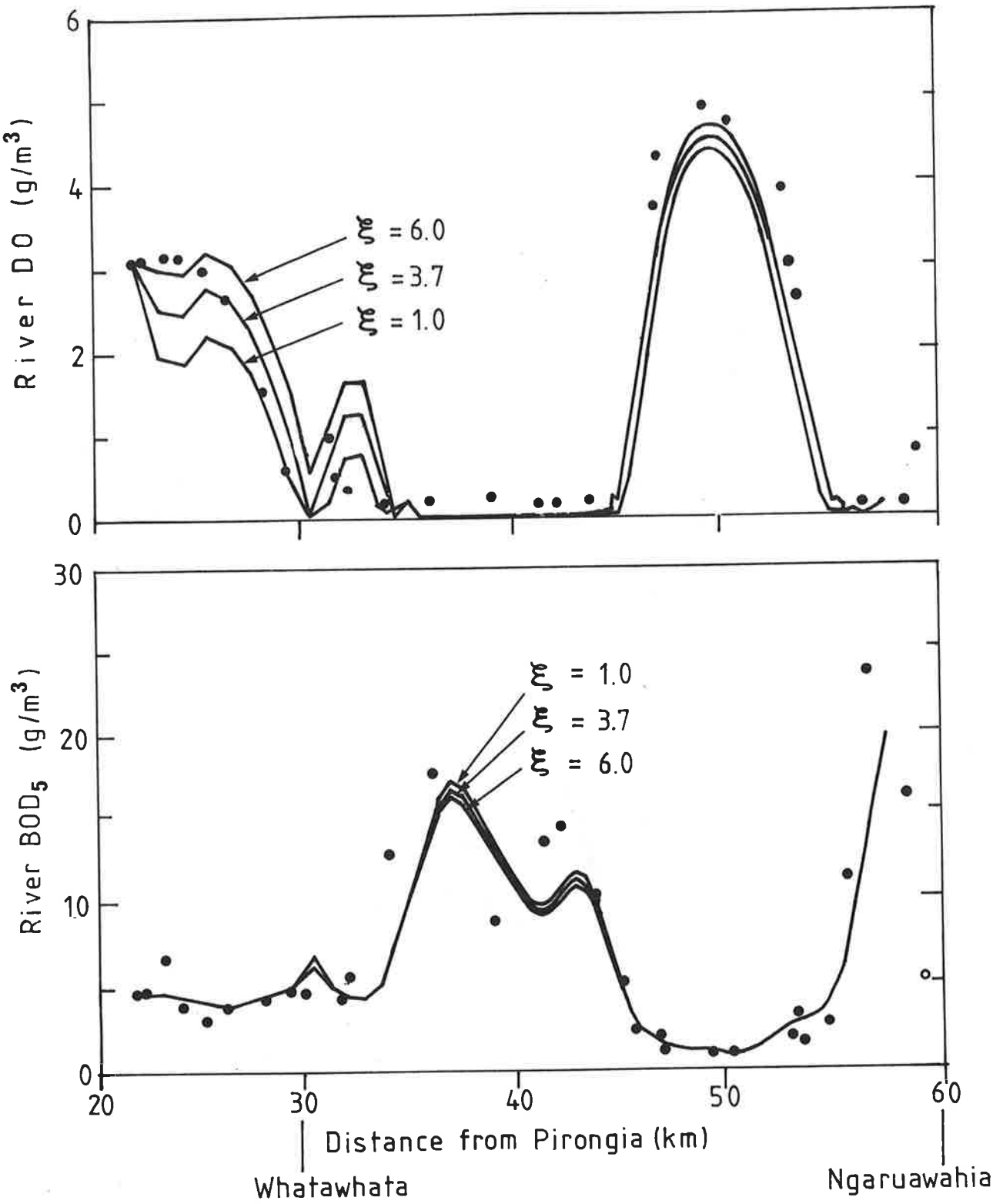

Fig. 6 Effect of variation of reaeration coefficient on model DO and BOD_5 predictions for Run 2→Run 3 (k_1 = 0.7/day, D^{-1} = 10m².s⁻¹).

numerical solution method used did not introduce errors into the results. The method used is somewhat similar to the approach of Bella & Dobbins (1968) and Fischer (1972). Details of the model equations are given in the Appendix. The numerical technique will be described at a later date.

Calibration

The "peaks and troughs" in the data from Runs 1, 2, and 3 were first used to estimate a velocity distribution in the river from Pirongia to Ngaruawahia. This distribution was taken as

$$v = \begin{cases} 0.0005x + 0.1 \text{ for } 0 \leqslant x < 20 \\ 0.0105x - 0.1 \text{ for } 20 \leqslant x \leqslant 60 \end{cases} \quad (1)$$

where v = river velocity (m/s)
x = river distance from Ngaruawahia (km).

The data for each run were then corrected to apply at a "run reference time" for each run. This reference time is at approximately the mid-time for each survey period. For these corrections the survey DO and BOD_5 data were each simply shifted up or downstream according to:

(a) the difference between the time at which the sample was taken and the run reference time; and
(b) the above velocity distribution.

Apart from the above velocity distribution, which was assumed to hold for all the modelling, the model has three parameters to be fitted during calibration:
deoxygenation coefficient (base e) — k_1 ($days^{-1}$)
reaeration coefficient (base e) — k_2 ($days^{-1}$)
longitudinal dispersion coefficient — D (m^2/s)

The reaeration coefficient was evaluated for the appropriate formula for this river, that of O'Connor and Dobbins:

$$k_2 = \xi \, v.h^{-1.5} \quad (2)$$

where ξ = 3.7
and h = river depth (m)

For calibration purposes, data for Run 1 were modelled over the 11-hour period between Runs 1 and 2. The combination of k_1 = 0.7/day, and D = 10 m^2/s was found by trial and error to give the best visual fit between observed and predicted DO and BOD_5. These results are given in the first graph of Fig. 3 and 4. Note that predictions can only be made for that part of the Run 2 data that includes the region occupied by the Run 1 data region when convected downstream for 11 hours according to the above velocity distribution.

Verification

The second and last graphs on Fig. 3 and 4 give the verification results for modelling Run 2 → Run 3 and Run 1 → Run 3 using the calibrated parameter values. The agreement between observed and predicted DO and BOD_5 is rather good.

Sensitivity Analysis

The response of the model to small changes in parameter values was also assessed. In brief, the model is not very sensitive to increases in D, the main effect of which is to decrease the slopes of predicted concentration. The model is however fairly sensitive to variations in deoxygenation coefficient (k_1) and reaeration coefficient (effected by changing ξ in equation (2)).

Figure 5 shows the effect of variation of k_1 for Run 2 → Run 3 predictions. The main effect is seen in aerobic regions; in particular, the position of the tail of the older anoxic patch is shifted upstream by increasing k_1.

Figure 6 shows the effect of variation of ξ for Run 2 → Run 3 predictions. A very similar effect to that observed in Fig. 5 is observed for DO. Note that increasing ξ has the effect of decreasing BOD_5 concentrations in the anoxic patch. This follows from the fact that in this patch the rate of exertion of BOD_5 is limited by the amount of free oxygen available to be consumed by aerobic bacteria, i.e., by the reaeration rate.

Discussion

The value of k_1 inferred from this modelling (0.7 $days^{-1}$) may be compared with k_1 values reported for other rivers at this Seminar:

— Mataura River, k_1 = 1.0 $days^{-1}$
— Manawatu River, k_1 from 1.2 $days^{-1}$ to 10.6 $days^{-1}$
— Waikato River, k_1 from 0.6 $days^{-1}$ to 0.84 $days^{-1}$
— Tarawera River, k_1 from 2 $days^{-1}$ to 5 $days^{-1}$

Reasons for this range of k_1 values have yet to be clearly demonstrated, but it appears reasonable at this stage to suggest that k_1 is materially affected by channel geometry, sediment type, and availability of sites for attached growths of sewage fungus and other aquatic organisms. Presumably the rather deep and slow moving waters of the Waipa, especially toward Ngaruawahia, account for the value of k_1 inferred herein being at the lower end of the above ranges.

This value of k_1 must, however, be regarded as provisional only as there is some suggestion in the results on Fig. 3 and 4 that the inferred velocity distribution may not be sufficiently accurate. Some further time-of-travel studies in the Waipa River may be necessary before firm conclusions are reached.

The value of the longitudinal dispersion coefficient is unlikely to be changed. Only a combination of a low coefficient and a decreasing velocity toward Ngaruawahia is capable of maintaining the sharp concentration gradients observed in all these data.

We hope in the future to be able to independently verify the reaeration rate (given by equation (2)) using the gas tracer technique discussed in Dr Wilcock's paper.

Although not reported in this paper further data are available (collected at Ngaruawahia Bridge over 4 days during the passage of anoxic water) and will be used to further test the model.

Acknowledgements

Several staff members from the Waikato Valley Authority (WVA) were involved in some of the sampling described herein and they kindly made available laboratory equipment, an aluminium dinghy with outboard, and their jet boat.

The Aquatic Weeds Section, Ministry of Agriculture and Fisheries (MAF) kindly made available an aluminium dinghy with outboard motor.

It is a pleasure to acknowledge the assistance and enthusiasm of a number of Hamilton Science Centre staff involved in field and laboratory work during the days and nights of the second week of March 1979.

The excellent computer graphics software was supplied by Dr R. A. Hoare (Fig. 2-6 are direct copies of the display of graphics screens on the University of Waikato's PDP 11/70 machine).

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Appendix

The equations for distribution of BOD_5 and DO down a river channel are taken as

$$BOD_5 : \frac{\partial L}{\partial t} + v\frac{\partial L}{\partial x} = D\frac{\partial^2 L}{\partial x^2} + L_I + S_L$$

$$DO \quad : \frac{\partial C}{\partial t} + v\frac{\partial C}{\partial x} = D\frac{\partial^2 C}{\partial x^2} + C_I + S_C$$

where L = river BOD_5
C = river DO
t = time
x = distance
v = river velocity
D = longitudinal dispersion coefficient
L_I, C_I = addition of BOD_5 and DO by tributary inflow
S_L, S_C = internal sources and sinks of BOD_5 and DO

For **aerobic conditions:**

$$S_L = -k_1 L$$
$$S_C = k_2(C_s - C) - \alpha k_1 L$$

where
k_1 = deoxygenation coefficient (base e)
k_2 = reaeration coefficient (base e)
C_s = saturation DO
α = ratio of $BOD_{ultimate}$: BOD_5

These are the standard Streeter-Phelps assumptions.

For **anaerobic conditions:** Gundelach & Castillo (1976) show that

$$S_L = -k_2 C_s$$

$$SC = \begin{cases} 0 & \text{if } k_1 \geq \dfrac{k_2 C_s}{\alpha L} \\ k_2(C_s - C) - \alpha k_1 L & \text{if } k_1 < \dfrac{k_2 C_s}{\alpha L} \end{cases}$$

The former equation states that for anoxic conditions the rate of exertion of BOD is controlled by the reaeration rate. The latter equation states that the DO begins to increase from zero only when the deoxygenation rate ($\alpha k_1 L$) is less than the reaeration rate ($k_2 C_s$).

DISCUSSION FOR SESSION VII

Mataura River

Presented by: L. McKENZIE

C. D. STEVENSON: To a degree, the modelling exercise has not had to make a management prediction in terms of an acceptable BOD loading on the river because of the voluntary introduction of treatment by SFM. Acceptability of the river conditions is clearly not determined by dissolved oxygen and how, therefore, would acceptable discharge conditions have been determined had this been necessary?

McKENZIE: The question with which the Regional Water Board was confronted was whether the DO classification of the Mataura River would be breached by the addition of 4 t/day of BOD_5 to the river. The model was therefore used to predict river DO levels given various combinations of river flow and waste load, including an 85% reduction in BOD_5 from SFM. Given the opposite situation where the Board had to state what lesser waste load was required to maintain acceptable river conditions, DO levels would probably have still been a major consideration. In-river BOD would have been another as this relates to the effect of the appearance of the water column, the deposition of solids and growth of benthic organisms and the effect on the ecology of the river as a whole.

D. CARTER: In the 1973 situation the SFM were discharging via a point discharge and it would appear this is still the case. Was it felt that there was no need to install a diffuser and is there any localised depletion in O_2 with BOD concentration adjacent to the bank?

McKENZIE: The present discharge is a diffused discharge but not because of any localised DO depletion problem in the region of the outfall. Natural turbulence from the Mataura River Falls upstream of the discharge point aids mixing of this discharge which is relatively complete within 300 m of the outfall. I have no information on a localised DO depletion problem in the vicinity of the river bank downstream of the outfall but doubt very much if one exists.

I. GUNN: Given that in the future DO may not be limiting, what ecological studies were carried out to assess effects of BOD on the river, bearing in mind the proposals put forward by Dr Craig Stevenson in a case for BOD standards for receiving water?

McKENZIE: Dr Scott of Otago University has had responsibility for a research project on the Mataura River which has included ecological studies. This project was commenced in 1976 and is to conclude in early 1981. The Southland Regional Water Board has had an input to the project through water and wastewater analysis. It should be possible to relate in-river BOD_5 to the ecological studies which were carried out concurrently. So far as in-river BOD_5 levels are concerned, the average value downstream of SFM has dropped from 11.2 g/m^3 to 4.2 g/m^3 as a result of the installation of treatment facilities by that Company.

J. RUTHERFORD: Is the plateau on the DO profile in Fig. 9 in the vicinity of Tuturau attributable to high reaeration in the rapids? If so, would the DO depletion have been about 0.5–1.0 g/m^3 more severe in the absence of those rapids?

McKENZIE: The plateau on the DO profile in Fig. 9 is a reflection of the high reaeration coefficient (10 $days^{-1}$) generated by the Tuturau rapids. The inference is that had a reaeration coefficient of say 2 $days^{-1}$ applied downstream of Mataura borough then DO depletion would have been about 1.0 g/m^3 more severe.

Management of BOD in the Lower Manawatu River

Presented by: K. J. CURRIE

I. GUNN: (a) Figure 5 shows a percent treatment line. Does this apply to the accumulated total discharge quantities?
(b) Given that each discharger then has the opportunity to vary his treatment standard or discharge quantity to suit this graph of percent treatment versus river flow, how does PNCC propose to vary the effluent quality of its domestic waste discharge?

CURRIE: (a) The principle of apportioning the allowable load adopted was on the basis of *raw* BOD load handled by each discharger. Hence, each discharger must provide the same percent treatment. The percent treatment line in Fig. 4 and 5 applies to each discharger.
(b) PNCC propose to install (in addition to present 1° sedimentation) a chemical precipitation plant operated on a cell principle whereby additional treatment can be employed as river flows decrease. Overland irrigation of grass plots will provide additional treatment in dry periods.

J. C. RUTHERFORD: Comment. Three alternatives were considered by the technical committee:
1 equal BOD massflow to the river from each discharger;
2 equal contribution to BOD massflow at the control site;
3 equal percentage BOD removal.
Alternative 3 was adopted as being feasible and the most equitable.

G. B. McBRIDE: How was the concept of selecting a design flow, that may be breached for some small percentage of time, accepted by fishing representatives of the technical committee?

CURRIE: The design flow was selected on the grounds that:
(a) flow would be below design only infrequently;
(b) flow would rarely (if ever) remain below design for a week, hence there is limited time available for sewage fungus populations to respond to higher BOD concentration;
(c) should the flow fall to the theoretical absolute minimum, resulting BOD concentration should not cause excessive deoxygenation.

The Wellington Acclimatisation Society was agreeable to the principle of a design flow and the figure selected. Had direct toxicity or similar effects been involved, their response may have been different.

J. C. FLETCHER: How will the Manawatu River management plan cope with the introduction of a significant new discharger?

CURRIE: Before the allowable river BOD load was apportioned between the three existing dischargers, 10% was reserved for possible future discharges. In allocating the new discharger a portion of this reserve, the newcomer would be required to provide at least the same level of treatment that present dischargers must now install.

Waikato River DO Simulations

Presented by: J. C. RUTHERFORD

M. E. U. TAYLOR: Were you able to predict in advance the extent of the oxygen sag in the Waikato River due to emergency milk discharges?

RUTHERFORD: Unfortunately we had no warning about the impending milk spill and therefore no attempt was made to predict the oxygen sag in advance.

M. E. U. TAYLOR: Were you able to use the management model to devise discharge strategies which would minimise the deleterious effects of the emergency milk discharges which occurred in the Waikato River?

RUTHERFORD: The exercise was principally a simulation to check the adequacy of the model. As yet it has not been used by management although we feel we have demonstrated its potential usefulness.

Supplementary Note: G. B. McBride has developed nomographs which enable rapid estimation of permissible discharges to maintain a specified DO level. These were presented to a dairy wastes committee and could be useful in minimising deleterious effects of future emergency milk discharges.

C. D. STEVENSON: Noting the period required for bacterial acclimatisation before major BOD consumption occurs, are there some situations, particularly where flow times to the sea are short, where it may be advantageous to discharge an effluent as a slug, rather than continuously? This might be particularly helpful where highly discolouring effluents are concerned.

RUTHERFORD: There may be the potential for manipulations of this sort and I believe that M. Piper and G. B. McBride will discuss this point further in the case of the Tarawera River.

F. MICHAELIS: Comment. Surely we must not be so limited in our outlook. Consider the discharge of Bubbling Springs Salmon Farm effluent into the Waikoropupu River just above the Takaha estuary. It was suggested that effluent would be "out to sea in 1½ hours". Such a fast throughput is not possible because there would still be tidal refluxing in the estuary. In discharging effluent into freshwaters near the coast we must consider the effect on estuaries and coastal waters as well as rivers.

Dissolved Oxygen Depletion of the Tarawera River

Presented by: M. PIPER

D. OGILVIE: It is most unusual for an oxygen sag to be observed so soon after discharge. This has been explained by a large concentration of bacteria on the pumice bed. Does oxygen depletion occur similarly after a river "flush" washing out the light pumice sediments and their attached bacteria?

PIPER: Flushing of the pumice does not occur since the flood conditions necessary for this would be abnormal for the Tarawera. However, after periods of very low organic loading the activity of the sediments is reduced. This is more a starving out than flushing out. With an increase in BOD the activity of sediments will increase over several days as the biofilm develops.

McBRIDE: We are dealing here with pumice hydrology. Over a 20-year record of river flows, the maximum flow is about 100 m^3/s while the minimum is about 20 m^3/s. In such a river, there is not much flushing by floods!

C. RICHMOND: (a) What is the total BOD load to the river, including the discharges from outfalls above Tasman?
(b) For what low flow value has Tasman set a target discharge of 8 t/d BOD to maintain DO above 5 mg/ℓ?

PIPER: (a) Above Tasman the combined effect of sewage, geothermal activity, and paper mill effluent is approximately 4 mg/ℓ BOD_5 in the river at 25 m^3/s. Tasman BOD_5 is normally 10–12 t/d but may range from 5–15 t/d. Our discharge limit is 14.2 t/d.
(b) We have assumed a low flow of 25 m^3/sec in setting a target BOD of 8 t/d for a river DO minimum of 5 mg/ℓ in midsummer.

A. ATTWOOD: To improve the low flow characteristics of the Tarawera at Kawerau is it desirable to install lake level control and use Lake Tarawera as a storage basin?

PIPER: From a river management viewpoint, yes a controlled river flow would be desirable. Lake Tarawera is a valuable 'untouched' lake and the lake itself would be the primary consideration. Level control is not likely to be acceptable in my opinion.

M. E. U. TAYLOR: Can you please tell us more about the relative effects of intermittent and continuous discharges?

PIPER: Bacteria appear to thrive best with a continuous supply of food. If the food supply is

intermittent then the extent of bacterial growth will be reduced. Intermittent discharge will restrict growth of some fixed bacteria and may be useful for control of sewage fungi. On the Tarawera River we have found that high BOD loading for short periods has a negligible impact on DO. Also, periods of low discharge can reduce the oxygen depletion which occurs for any given loading.

Tarawera River

Presented by: G. B. McBRIDE

R. H. S. McCOLL: At risk of making your latest model more complex do you consider a downstream distance coefficient should be applied to the benthic O_2 demand factor to allow for possible peak population of benthic organisms at some point downstream?

McBRIDE: Prescription of a variable benthic demand parameter has not been seriously contemplated at this stage. It could be considered when more data (such as reported by Dr Gillespie in his coming paper) are available.

P. A. GILLESPIE: A comment. I will be presenting some data later which shows that the peak in benthic O_2 consumption occurs shortly downstream from the Tasman outfall.

Investigation of the Mechanisms of Oxygen Depletion in the Tarawera River

Presented by: P. A. GILLESPIE

M. SPENCER: In doing your V_{max} determinations, did you measure the loss of radioactivity due to respiration, and if so, was there any significant trend in percent respiration down river?

GILLESPIE: The V_{max} determinations are based on assimilated ^{14}C-glucose only. We did not measure respired $^{14}CO_2$ but assumed a constant ratio. On a comparative basis I expect that any variations in this ratio would be minor relative to changes in activity.

H. MORGAN: Values for ATP concentration in sediments below the Tasman outfall seem low in relation to the high bacterial populations reported. Has the efficiency of recovery of ATP from these sediments been determined?

GILLESPIE: The method used for ATP extraction was the one described by Bulleid (1978). In marine sediments he reported an extraction efficiency of 95%. We have not determined the extraction efficiencies with pumice sediments but have only assumed them to be similar. The ATP concentration seems low in relation to activity measurements but not necessarily to bacterial numbers. Perhaps this is a measure of the efficiency of the pumice-associated flora, i.e., high activity — low biomass.

J. C. RUTHERFORD: You present figures for the oxygen uptake of sediments in units g/m^2 per day and for overlying water in g/m^3 per day. How can you compare these data?

GILLESPIE: You could of course convert my benthic oxygen consumption data to a g/m^3 per day basis by using the average depth, but a benthic demand in my opinion is most appropriately expressed on an areal basis. For a valid comparison of the two you are right; they should be expressed in the same units.

Dissolved Oxygen Levels and Waste Discharges: A Case Study of the Taylor–Opawa River, Blenheim

Presented by: R. O. CARR

R. H. S. McCOLL: Comment. Conductivity measurements should be used with caution to identify groundwater inputs because of their sensitivity to photosynthetic and respiratory activity by aquatic plants.

CARR: The comment is noted — with thanks.

M. SPENCER: Have you carried out a series of closely spaced gaugings along the Lower Opawa River to determine the extent of groundwater recharging?

CARR: We have tried to do so, but the extent of weed growth in this section of the river makes it a major task. We hope to have more success after the seasonal weed cutting, or during winter conditions.

Waipa River

Presented by: G. B. McBRIDE

K. CURRIE: The k_1 values reported for rivers (Discussion section) are an order of magnitude higher than those reported from in-bottle studies (e.g., Table 4 of Dr Marshall's presentation) emphasising the limitations of determining k_1 in the bottle.

McBRIDE: I agree that extrapolation of values of k_1 from laboratory bottle tests to rivers can be most misleading. These values of k_1 are even higher than values that may be inferred from a recent paper by Wright & McDonnell (1979). These authors established some correlations between k_1 and river rate of flow or wetted perimeter.

The "bottle" values of k_1 lead one to conclude that maximum DO sag would occur 3 days after waste discharge, and that appears to be borne out in large rivers overseas. Our data suggest that the rate of exertion of BOD increases for smaller rivers. In the previous paper maximum DO sag occurred after only 3 hours!

Incidentally, the value of k_1 for the Mataura River should be about 2 days^{-1}, since the reaeration formula used for the Mataura River (equation for k_2 in the Mataura River paper) is in fact to base 10, not to base e as it should be.

Reference

Wright, R. M.; McDonnell, A. J. 1979: In-stream deoxygenation rate prediction. *Proceedings of the American Society of Civil Engineers 105 (EE2):* 323–35.

SESSION VIII CASE HISTORIES—ESTUARIES

Wairoa River—Case history

C. E. WEST

Waitaki-N.Z. Refrigerating, Wairoa

W. S. WAKELIN

Morrison Cooper & Partners, Wellington

Within the last 10 years the water quality of the Wairoa River has taken on a special interest because of the applications for water rights by the local freezing works and the Wairoa Borough. The region of the river under study has been the final 10 km to the mouth of the estuary, most of which is influenced by the tide. Although oxygen depletion does not appear to have been an issue of major concern, the Wairoa River is an excellent example of an estuarine river and information is presented here which could form the basis for establishing future water use, or for developing models for river management.

Background

The Wairoa River is approximately 60 km long and flows in a southerly direction into Hawke Bay draining an area of hill country where sheep and cattle farming predominate as the main agricultural use. The Wairoa River is tidal up to a distance of some 10 km from the mouth and most of the interest in its water quality concerns the last 8 km which flows through the township of Wairoa. The river has several large bends within this region, has the Waiau tributary joining it at Frasertown and several smaller rivers towards the head reaches (Fig. 1).

Simons & Haigh (1977) have provided information on the Wairoa River which shows that it has a recorded maximum flow of 11440 m^3/s and makes it one of New Zealand's largest rivers under these conditions. The range of streamflows for low flow conditions in summer is 15 to 60 m^3/s. In the vicinity of Wairoa Township, at the SH2 Bridge, the river cross section is 814 m^2, with hydraulic radius 6.5 m.

The flow characteristics of the Wairoa River have been briefly discussed by Wakelin (1978) in relation to estuarine models of oxygen depletion and reaeration. The estuarine features of a saline wedge and flow reversal combine to complicate the modelling of oxygen depletion and recovery within the region of interest.

The major industry in the region which has the most obvious point source of effluent discharge is the Wairoa Freezing Works, although other point sources have contributed to the river pollution such as the dairy factory and numerous septic tank outflows. Morrison Cooper and Partners (1976) estimated that the freezing works has a discharge of 5000 m^3/day with a BOD loading 6560 kg. Because of the nature of the Wairoa River catchment area, run-off from the land is likely to be of considerable importance in the general river pollution and many of the river water analyses within the last 10 years have provided a measure of this background pollution.

Segmentation of the river for analysis

Figure 1 indicates the location of sampling points on the Wairoa River which have been variously referred to by researchers from the Wairoa Works and the Hawke's Bay Catchment Board (HBCB) in their internal reports. The significance of several of these sites is described in Table 1.

Table 1. Sample point locations

Distance from mouth (m)	Location Ref. No.	Designation	Comments
27000	12	Waiau Pt.	The river above this point would be characteristic of hill country farm and bush
16500	11		The river water quality would reflect the additional discharges from Frasertown
14000	10	Showgrounds	Assumed upper region of tidal influence
11000	9		First easy sampling point from SH2
8000	8		The upstream edge of Wairoa Township
6250	7	Ski-Club/ Lockwood	Recreational and swimming use of river
5300	6	SH2 Bridge	Boat ramp and major road

Table 1. Sample point locations *continued*

Distance from mouth (m)	Location Ref. No.	Designation	Comments
4400	5	Wairoa Freezing Works	Outfall into River
3850	4	Spooners	Residential area
2850	3		Sample points to assess the degree of mixing or ponding in the estuary
1650	2		
550	1		

Dissolved oxygen

From water analyses records supplied by West (1980) and Haigh (1980) there have been some 161 separate dissolved oxygen analyses on water samples taken from the Wairoa River since 1971. The information on the samples has unfortunately not all been relevant to the assessment of oxygen depletion in the river, as in many instances the measure of salinity and the records of temperature are missing. For several of the analyses, the major interest has been in the associated levels of total and faecal coliforms, ammoniacal nitrogen, sulphide, or salinity and the dissolved oxygen measurements were supportive only. There have been numerous other

Table 2 Dissolved oxygen levels at sample location No. 6 — Boat Ramp

Date	pH	Temp. °C	DO mg/ℓ	% Satn.	Salinity mg/ℓ	Coliforms /100 ml Total/Faecal	Comments
3/01/74	8.10	22	8.6	100	6930	700	No kill for 12 days
6/11/73	7.92	23	8.4	100	2830	900	Kill/1½ hrs before HT
6/10/71	6.90	16.4	..		24	90	No kill for 10 wks/LT
11/08/71	7.09	11.0	..		52	160	2 hrs before LT
21/03/72	6.81	18.0	..		2446	160	3 hrs after HT
25/02/72	7.31	22.0	..		4100	20	3 hrs after HT
13/01/72	7.31	22.0	..		1798	12	
26/10/76	7.89	15.0	9.9	98	..	1700/1100	LT/No kill
28/10/76	7.80	15.0	10.1	100	..	100/-	5 hrs after LT/No kill
27/10/76	7.80	15	10.2	100	..	800/500	3 hrs before HT/No kill
29/10/76	7.72	13	10.3	98	..	300/300	4 hrs after LT/No kill
1/11/76	7.84	16	10.1	100	..	3500/500	LT/No kill
2/11/76	7.9	13	10.4	99	..	500/500	LT/No kill
3/11/76	7.98	18	10.7	100	..	9200/9200	3 hrs after LT/No kill
4/11/76	7.90	14	10.4	100	..	5400/3500	2 hrs before LT/No kill
5/11/76	7.86	14	10.1	98	..	1700/1700	3 hrs before LT/No kill
8/11/76	7.93	16	9.9	100	..	300/-	1 hr before LT/No kill
9/11/76	7.89	16	10.2	100	..	1300/800	2 hrs before LT/kill
10/11/76	7.79	16	10.0	100	..	500/100	2½ hrs before LT/kill
11/11/76	7.98	16	10.1	100	..	300/100	3½ hrs before LT/kill
12/11/76	7.89	15	10.3	100	..	-/-	4 hrs after LT/kill
15/11/76	7.80	12	10.5	98	..	300/-	1½ hrs after LT/kill
16/11/76	7.80	15	10.5	100	..	500/100	6 hrs after LT/kill
1/12/76	7.8	15	9.4	96*	..	1300/1300	LT/kill
8/12/76	7.75	22	8.1	95*	..	9200/1100	1 hr before LT/kill
5/12/76	7.76	18	8.5	92*	..	300/-	1½ hrs after LT/kill
5/01/77	8.02	21	9.9	100	..	300/300	LT/kill
12/01/77	7.77	17	9.1	97*	..	16100/9200	3 hrs before LT/kill
19/01/77	7.70	21	8.4	98*	..	3500/2400	LT/kill
26/01/77	7.40	21	7.9	92*	..	16100/16100	2½ hrs after LT/kill
2/02/77	7.74	23	8.0	96*	..	1300/500	1½ hrs after LT/kill
9/02/77	7.78	20.0	7.9	90*	..	5400/2200	2½ hrs after LT/kill
16/02/77	7.68	24	8.2	98	..	9200/2200	1½ hrs after LT/kill
16/03/78	7.25	23	8.7	100	3000		1 hr after LT/surface
16/03/78	8.05	22	9.3	100	2900		1 hr after LT/surface
16/03/78	8.10	21.5	7.8	82	14700		1 hr after LT/bottom
16/03/78	8.20	22.0	9.2	100	14400		1 hr after LT/bottom
13/06/78	8.21	10.0	9.4	85	1500		surface 1½ hrs before HT
13/06/78		10.5	11.0	99	1700		2 m depth 1½ hrs before HT
13/06/78	8.4	10.8	11.8	100	2000		4 m depth 1½ hrs before HT
20/09/78	7.88	11	11.1	100	..	1700/1700	1½ hrs after HT/surface
20/09/78	7.88	11	11.8	100	..		1½ hrs after HT/3 m deep

* Assumes chloride levels of 2600 mg/ℓ

LT Low tide

HT High tide

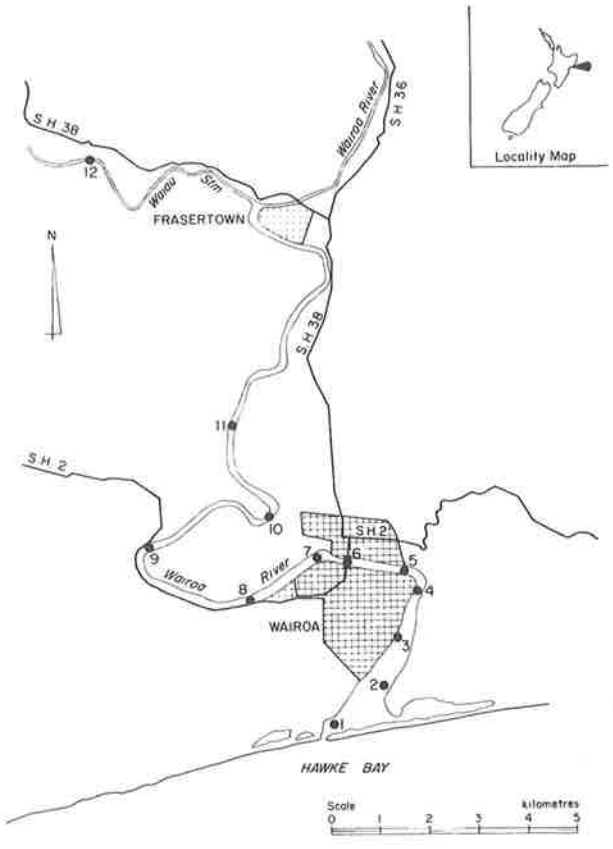

Fig. 1 Wairoa River location and key to sampling points.

analyses where the DO levels have not been recorded but there is useful information on pH, temperature, suspended solids, BOD and coliform levels, for samples taken at varying river conditions and throughout the year, which all combine to characterise the water quality of the Wairoa River.

An example of the information available relevant to dissolved oxygen is given in Table 2 for the sample Location No. 6 which is at the Boat Ramp region of the river near to the State Highway No. 2 Bridge.

Because of the interest in the effect that the discharge from the Freezing Works has on the water quality in the Wairoa River, the comments column in Table 2 indicates the operational status of the works. At this region of the river, the reverse flow at high tide takes the discharge up to and beyond the boat ramp region, and the water is visibly discoloured on those occasions.

The calculation of percentage oxygen saturation allows for the salinity of the water where this is known. The only sampling at known depths in the river were those by the HBCB in 1978 and their results are discussed later under Salinity Intrusion.

A similar series of analyses for the period 26 October 1976 to 16 February 1977 shown in Table 2 was carried out for the locations No. 4 (Spooners) and No. 7 (Lockwood) and provides an extensive record of the river conditions over a significant period of the year when low flow and high pollution levels are coincident.

From an analysis of the data available, the following comments are relevant to a discussion of dissolved oxygen levels at the region of the SH2 bridge.

(a) The river water temperature varies from 8.8 °C in winter to 26 °C at low flow summer conditions.

(b) The mean pH is 7.77 with standard deviation 0.33, variance 0.107.

(c) The dissolved oxygen depletion was greater than 10% on only one recorded occasion in the winter (13 June 1978) and this occurred in a surface sample only, but not in a sample taken deeper (2 m).

Generally the DO level is very high with many analyses recording values at saturation level.

(d) Salinity levels in the top one metre of water have a mean of 2600 mg/ℓ chloride with standard deviation 2000.

Salinity intrusion

An analysis of the water quality of the Wairoa River would not be complete without a measure of the salinity intrusion up the river. The significant work in this area has been in the gaugings carried out at the region of the SH2 bridge in 1975 by the HBCB, and in the analyses carried out in 1978 when sampling at various depths.

Gaugings

Information selected from the HBCB 1975 gaugings are tabulated in Tables 3, 4, and 5 and shown diagrammatically in Fig. 2. The tidal river flow is shown relative to the tidal period Ta in Fig. 2 (a). At two times in the tidal period Ta and Tb the point velocities are shown in Fig. 2 (b) and 2 (c). The intrusion of the lower saline water as a wedge flowing upstream on the incoming tide is characteristic of this type of estuarine river at low flow conditions.

Table 3. River tidal flow characteristic

Tidal Period	Downstream Flow m^3/s
0	0
0.1	2.3
0.2	2.9
0.3	2.9
0.4	2.6
0.5	1.6
0.6	0
0.7	−1.0
0.8	−1.1
0.9	−1.1
1.0	0

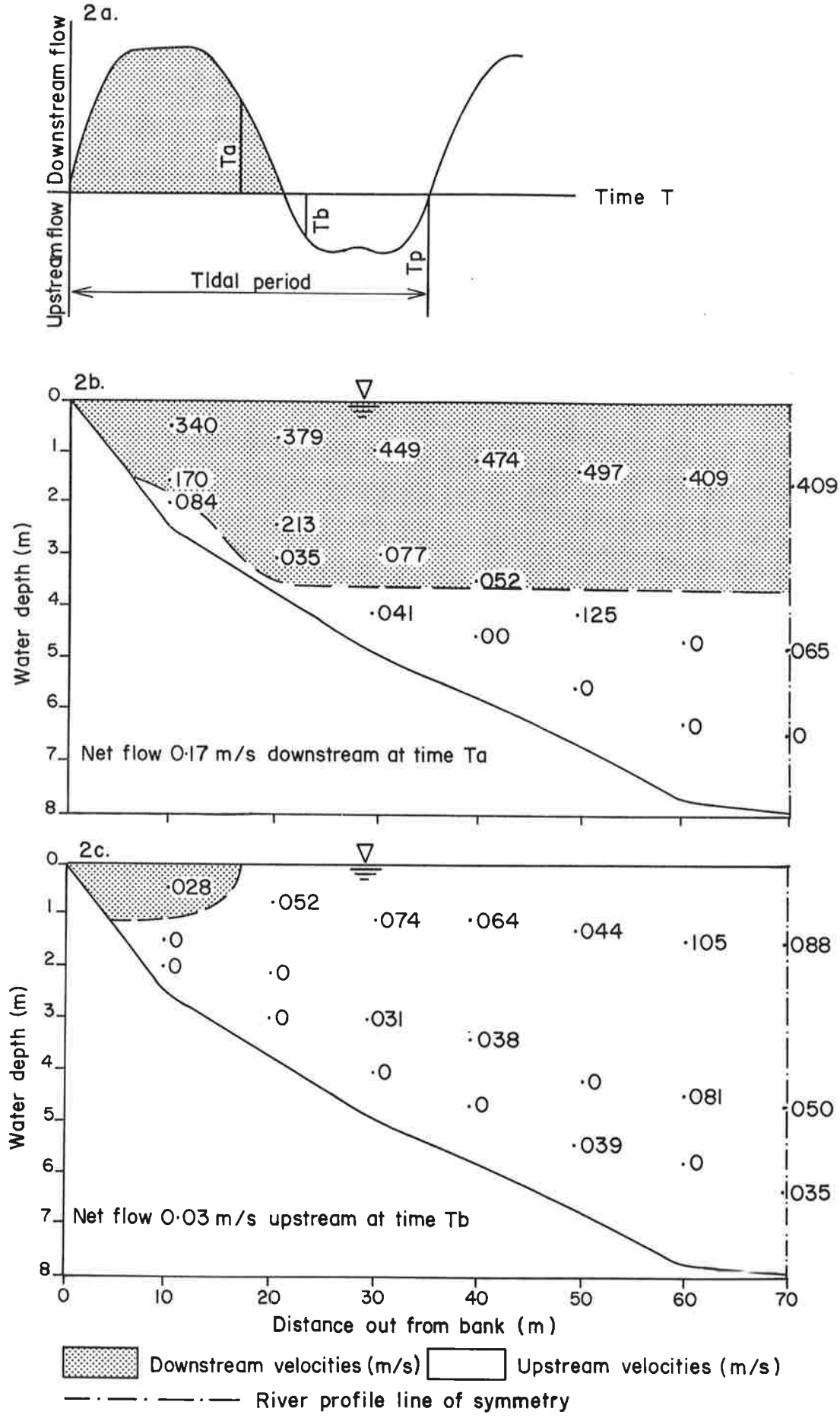

Fig. 2 Wairoa River gauging at SH2 Bridge for flow 60 m³/s.

Table 4. Point velocities at time Ta = 0.48 Tp

	Velocities (m/s)						
Distance out from bank (m)	10	20	30	40	50	60	70
Bottom depth (m)	2.6	3.9	5.0	5.9	6.7	7.7	8.0
Fractional depth							
0.2	0.34	0.379	0.449	0.474	0.497	0.409	0.409
0.6	0.17	0.213	0.077	0.052	−0.125	0	−0.065
0.8	−0.084	0.035	−0.041	0	0	0	0
Net downstream velocity 0.17 m/s							

Table 5. Point velocities at time Tb = 0.67 Tp

	Velocities (m/s)						
Distance out from bank (m)	10	20	30	40	50	60	70
Bottom depth (m)	2.6	3.9	5.0	5.9	6.7	7.7	8.0
Fractional depth							
0.2	0.028	−0.052	−0.074	−0.064	−0.044	−0.105	−0.088
0.6	0	0	−0.031	−0.038	0	−0.081	−0.05
0.8	0	0	0	0	−0.039	0	−0.035
Net upstream velocity 0.03 m/s							

Extent of Saline Intrusion

In a series of samplings carried out by the HBCB in 1978, the salinity level in the river was measured *in situ* at different depths for many of the locations noted in Fig. 1. The results of these analyses show that the saline intrusion is detectable up to Location 10 some 14 km from the mouth. The degree of separation of the saline and freshwater layers is shown by the record of salinity measurements given in Table 6.

Table 6. Salinity vs depth (Measurements taken 2 May 1978)

	Salinity (‰)							
Sample Location	2	4	5	6	7	8	9	10
Depth (m)								
0		4.2	3.5	3.0	0.3	1.5	..	
1				4.1	2.7	1.5	1.1	0.1
2	22	6.0		9.5	3.0	2.1	1.2	
		28.0						
3	25.5	29.5	14.0	17.5	5.5	2.8	1.5	0.05
4				24.5	−23.0	22.0	12.0	0.5
					24.5			
5			28.7	28.5		24.5	22.5	27.0
6							23.5	
7								

The graphical presentation of the results in Table 6 is shown in Fig. 3. For this figure, the interface is assumed to occur at the salinity level of 22‰ for ease of graphical representation.

Conclusion

The predominant interest in the water quality of the Wairoa River is its suitability as a recreational river within the Wairoa township. The major concern has been the level of coliform bacteria and not oxygen depletions, as the river appears to have a high level of dissolved oxygen at all times. The major single point effluent discharge, the Freezing Works, is within 4.4 km of the estuary mouth and the flushing action at low flow conditions is sufficient to pass the effluent out to sea within a 24-hour period. Real problems in oxygen depletion could exist if the bar at the estuary mouth was closed for a significant period.

Acknowledgements

The authors acknowledge the assistance of W. Haigh (HBCB) and Waitaki—New Zealand Refrigerating for granting permission to use their material.

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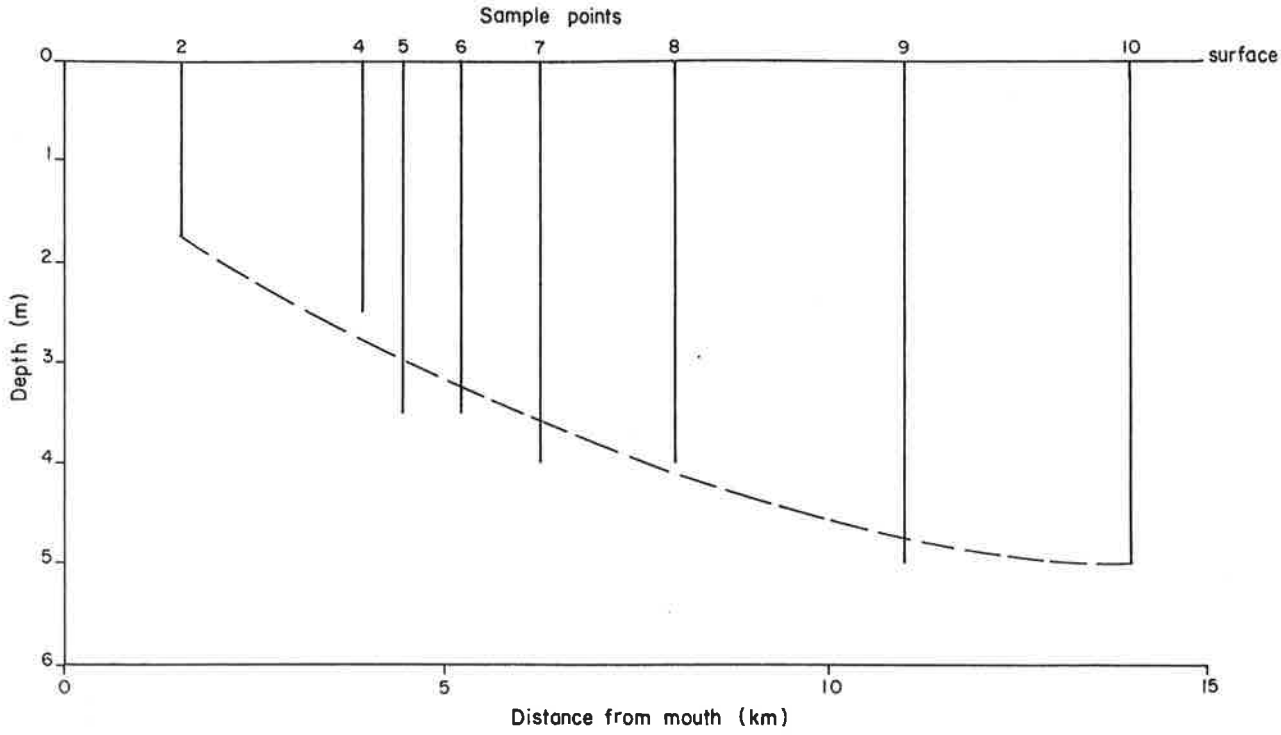

Fig. 3 Depth of saline/fresh water interface.

Case histories of some Northland estuaries

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In a survey at different seasons from January 1978 to September 1980, a broad analysis was carried out in four estuaries, of conditions relating to wastewater discharges and their effect on estuarine conditions, both with regard to dissolved oxygen and probable dispersion and dilution as identified by the examination of bottom sediments. Float testing tended to confirm the distances travelled and dispersion paths before reverse tidal effects resulted in local precipitation and decreased dilution levels as evidenced by sediment examination.

Introduction

Between January 1978 and September 1980, surveys were carried out by the Northland Catchment Commission and Regional Water Board of four estuaries in the Northland Region (Fig. 1). The parameters assessed were temperature, pH, salinity, conductivity, dissolved oxygen and total and faecal coliforms. Turbidity, in formazin units, was measured when this was considered relevant to the type of discharge and water usage in the area.

The surveys were directly related to the collection of data in respect of water rights to discharge waste water to natural water and the effects on the waters involved, with a view to the formulation of assimilative capacities for each waterway. This information would indicate the type of conditions which should be imposed on each such right to discharge, to ensure a minimum effect on the water quality.

The estuaries chosen for the investigations were:

(a) the Waikare Inlet and contributory rivers system;
(b) the Upper Whangarei Harbour;
(c) the Otamatea River;
(d) the Ngunguru River Estuary.

Waikare Inlet

The Waikare Inlet (Fig. 2) receives the flows from the Kawakawa River and its tributaries (one of which is the Waiharakeke Stream), with its outflow being via the Veronica Channel at Opua. This waterway system, comprising saline and non saline waters, is subjected to waste water discharges from a dairy factory and abattoir which discharge to the Waiharakeke Stream. Another source of discharge is the Kawakawa township's oxidation pond, with its outflow to the Kawakawa River. As oyster farming is carried out extensively in and around the Waikare Inlet, water quality is of prime importance.

The Waiharakeke to which the two major discharges are directed is subject to widely varying rates of flow, the lowest recorded being in 1973 with a flow of 80 ℓ/s. In an average year a mean average flow of 5000 ℓ/s can be expected.

The first detailed survey involving the measurement of DO, temperature, and conductivity was conducted by boat on 18 October 1979, so that actual fluctuations of the selected parameter levels could be recorded. The rate of stream flow at the launching site some 2 km upstream of the first known discharge point, that of the dairy factory, was approximately 6000 ℓ/s. Dissolved oxygen was 11.2 mg/ℓ, measured with a Yellow Springs DO meter and subsequently confirmed in the laboratory using the Winkler method. Temperature was 14 °C, conductivity was 100 Mho, total coliform/100 ml was 500 and faecal coliform/100 ml was 100.

These values remained fairly constant with no significant variation until the dairy factory discharge point was reached. A wastewater discharge consisting of whey and casein wash-water was taking place at the time and dissolved oxygen measured at a point 100 metres downstream from this discharge was 10.8 mg/ℓ, a drop of 0.4 mg/ℓ.

The temperature was unchanged at 14 °C but conductivity was up to 102 Mho. Total coliform/100 ml was 2000 and faecal coliforms/100 ml was 1200. The coliform increase, although significant, was more probably due to septic tank ground disposal fields in the area rather than the factory discharge. The stream bed and weed and willow growth in the area showed definite evidence of gross pollution with fungal growth and seaweed-like tendrils resulting from the whey and casein wash discharge from the dairy factory.

Samples of mud were taken for analysis in an endeavour to establish a relationship with regard to the degree of oxygen demand which could affect the stream and to assess the period of time over which this effect would be exerted if the factory discharge were to cease.

Three mud samples were taken at the outfall and at 50 metre intervals for a distance of 200 metres. Parallel water samples were also taken, and a very basic test was conducted as follows.

Each mud sample was weighed into a 1 gm conglomerate. The river water samples were aerated

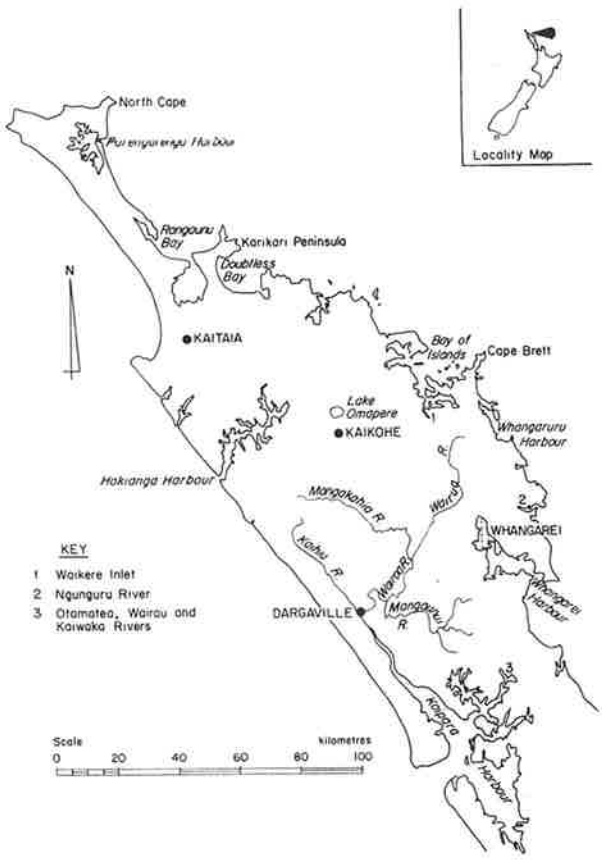

Fig. 1 Site map.

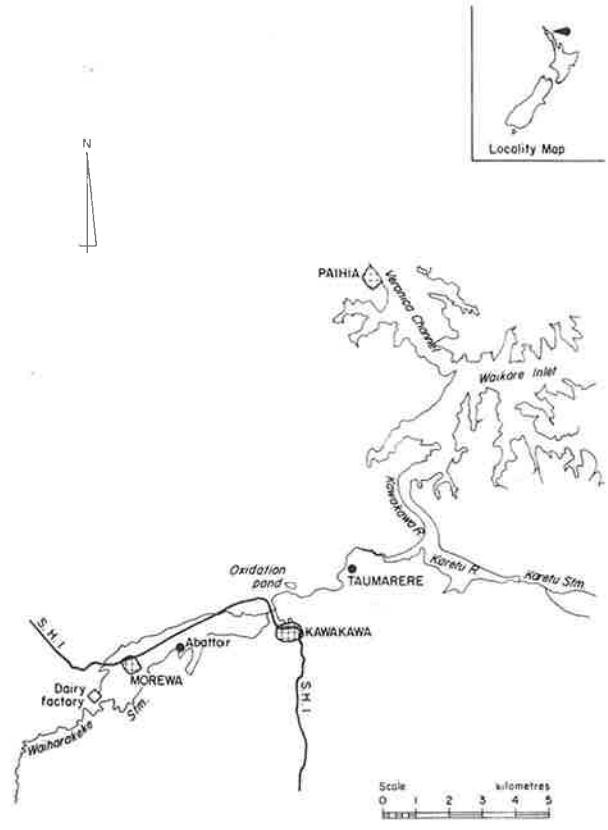

Fig. 2 Waikare Inlet and tributary rivers.

and the sediment samples introduced into BOD_5 bottles. Parallel samples using river water from each site were prepared and all samples were left in ambient conditions for 24 hours.

Oxygen depletion in the stream water samples averaged 0.6 mg/ℓ from a site 50 metres above the discharge point, 2.3 mg/ℓ 20 metres below the discharge and 4.2 mg/ℓ 200 metres downstream.

Oxygen depletion in the samples containing sedimentary material averaged 1.4 mg/ℓ at the control above the discharge, 4.2 mg/ℓ 20 metres below the discharge and 6.2 mg/ℓ 200 metres downstream.

Dissolved oxygen measured within the stream was 9.1 mg/ℓ at a temperature of 14.5 °C above the discharge, 8.3 mg/ℓ at 15 °C 20 metres downstream and 6.4 mg/ℓ at a temperature of 15 °C 200 metres downstream of the discharge point.

BOD_5 tests carried out using river water only showed the following pattern:

Upstream of discharge at control	0.4 mg/ℓ
20 m below discharge	3.8 mg/ℓ
200 m downstream	8.8 mg/ℓ

On first inspection these values would seem strange in the light of the expected increase in dilution as the distance from the discharge point increases, but the stream flow is interrupted by a series of pondings and low velocity areas with numerous eddies caused by willow trees and trapped debris, which allow the waste to accumulate in pockets of greater concentration than would be expected with an unencumbered channel flow.

Although these tests were rudimentary and the methods have several demonstrable flaws the indications were that the larger suspended solids contained in the wastewater, which exert a large proportion of immediate oxygen demand, were precipitating out of suspension. This appeared to occur at a progressive rate dependent on the stream characteristics, creating a long term resident demand for oxygen due to contamination of the sedimentary material.

Unfortunately the effect of the dairy factory discharge could not be traced for more than 2 km of stream flow because at about this distance the abattoir wastewater treatment system discharges to the river. Dissolved oxygen measured some 50 metres upstream from this discharge was 6.5 mg/ℓ and a BOD_5 figure of 6.0 mg/ℓ was recorded. The sediment sample recorded 2.8 mg/ℓ for the 24 hr test.

These results appeared to indicate that the demand for oxygen exerted by the dairy factory waste had reached a balance with the available oxygen to a point where reaeration could be expected to begin, but this could not be verified because of the abattoir discharges.

As the abattoir treatment system is effectively reducing the waste loading, it would be expected that a waterway with a minimum flow rate of 6000 ℓ/s, with average reaeration characteristics, would have an adequate oxygen content a short distance downstream from the discharge. However, this is not the case and an abattoir discharge of 8000 m^3 per

day, as provided for in the water right granted by the Northland Regional Water Board, does at times cause anaerobic conditions in the river.

Continuing the oxygen profile description, a sample taken from a site 50 metres downstream from the abattoir ponds outlet returned a dissolved oxygen figure of 6.5 mg/ℓ and a BOD_5 of 7.5 mg/ℓ. Some further 300 metres downstream a second discharge (from fellmongery waste treatment ponds) flows into the stream, which at this point is badly infested with willow growth — to such an extent that the next accessible sampling site is 500 metres further downstream. Dissolved oxygen at this site was 3.7 mg/ℓ. The last control point on the Waiharakeke is located at the Kawakawa railway bridge, where the dissolved oxygen measured 2.3 mg/ℓ. Weed growth, consisting largely of oxygen weed, is prolific — with nutrient levels at NH_3 0.20 mg/ℓ, NO_3 1.80 mg/ℓ and PO_4 0.25 mg/ℓ. Total coliform/100 ml was 46 600, with faecal coliforms/100 ml being 5050.

Because of swampy and willow infested conditions the first sampling site on the Kawakawa River is approximately 2.4 km downstream of the last Waiharakeke control and some 800 metres below the discharge from the Kawakawa township oxidation ponds. At this point dissolved oxygen measured 4.5 mg/ℓ at 20 °C with total coliforms/100 ml being 5250 and faecal coliforms/100 ml amounting to 550.

Eight samples were taken at regular intervals over the next 3.2 km. Dissolved oxygen levels remained fairly static reaching 6.2 mg/ℓ at the 3.2 km point with a total coliform count of 3100/100 ml and 100 faecal coliforms/100 ml, indicating a slow but progressive die off in this respect. The river at this point is tidal and fringed with areas of mangroves growing on the intertidal flats. No visual evidence of any detrimental effects attributable to the wastewater discharges was noted during the surveys of this tidal stretch of some 6.5 km, which ends at Opua situated at the head of the Waikare Inlet, the final control point of this particular investigation.

Ten samples were taken at regular intervals over the 6.5 km section for bacteriological determinations in order to record the die-off rate in relation to contact time and salinity. Although dilution does increase, the effect of this should not be great for a distance of some 4 km, when the river widens markedly before draining to a broad but relatively narrow-mouthed estuary.

The first sample was taken at the final control point from the previous section surveyed and similar results were recorded as follows:

> Temp 10 °C, DO 9.5, total coliform/100 ml 3800, faecal coliform/100 ml 380, salinity ‰ 0.

These levels were almost constant for the next two samples, with sample 3 taken approximately 1.5 km downstream and recording as follows:

> Temp 10 °C, DO 8.9 mg/ℓ, total coliform/100 ml 3500, faecal coliform/100 ml 340 and salinity ‰ 2.0.

As the salinity level rose coliform numbers dropped.

Sample 4 taken at a distance of 2.5 km showed:

> Temp 11 °C, DO 8.2 mg/ℓ, total coliforms/100 ml 1072, and faecal coliforms/100 ml 144 and salinity ‰ 9.

The next four samples showed that, neglecting dilution and time, the die off of faecal coliforms seemed to relate significantly to the percentage salinity recorded, while the total coliform numbers decreased at a similar but lesser rate:

Temp. °C	*DO mg/ℓ*	*Total coli. per 100 ml*	*Faecal coli. per 100 ml*	*Salinity ‰*
10°	9.5	3800	380	0
10°	9.2	3540	400	2
10°	8.9	3500	340	2
10.5°	8.2	1072	144	9
11°	8.3	1000	168	18
11°	8.3	1136	204	20
11.5°	8.0	1000	120	20
12°	7.9	940	16	25

Note: This section of the survey was carried out some 16 months after the preceding sections so that only a very broad relationship can be drawn with regard to the dissolved oxygen levels. At this stage the oxygen load imposed by the dairy factory discharge was very much reduced and largely confined to condenser cooling water and some timber washings. The main factory waste is now spray irrigated and the ash-carrying waste water from the tube blowing of coal fired boilers at the factory is now pumped to a three stage ponding system for treatment before discharge.

The oxygen demand from the wastewater discharges was detectable as far downstream as the junction between the Kawakawa River and the Waikare Inlet where the greater assimilative properties (due largely to dilution and in the case of the bacteriological profiles, the salinity) rendered more specific detection beyond the scope of our laboratory facilities.

Whangarei Harbour

The Whangarei Harbour (Fig. 3) is a drowned river valley estuary with the entrance restricted by a sandy spit. The upper harbour and Parua Bay are relatively infilled with only the channels containing water at low tide, leaving large areas of intertidal flats. The outer harbour is deeper with wider channels separated by large areas of shoal banks.

The input of fresh water is small and the salinity decreases in the upper harbour with little vertical variation. The Port Whangarei arm has the greatest variation in salinity because of the five rivers and streams which drain directly to it.

Tidal current velocities decrease gradually towards the upper harbour from the Darchs Point control to the Onerahi Yacht Club control but decrease rapidly beyond this point due to the diversion of flows into two upper harbour channels namely the Port Whangarei arm and the Portland reach. Residence times calculated by others using the fresh water fractions in the upper harbour range from 24 days in the winter to 120 days in the summer months.

A water quality monitoring survey of the Whangarei Harbour was commenced in 1976. Twelve

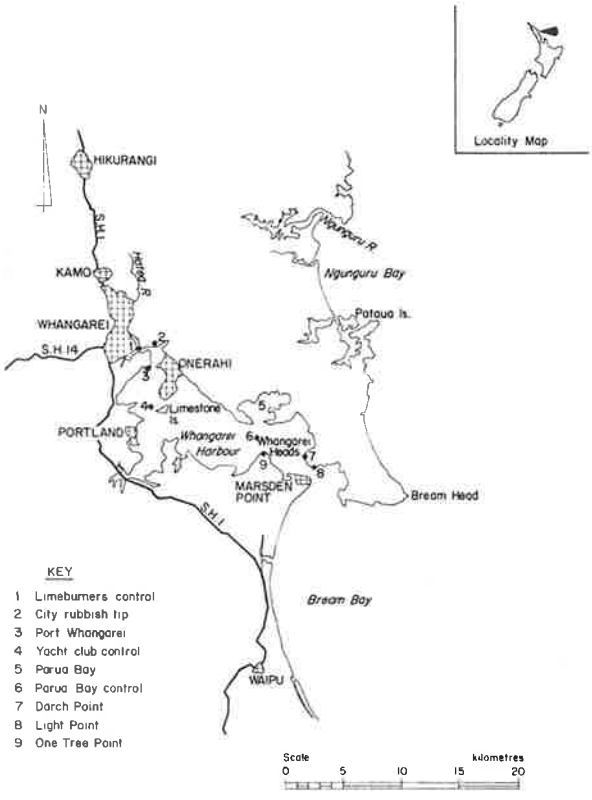

Fig. 3 Whangarei Harbour.

sites were selected on streams and beach frontages within the harbour catchment. The survey was continued, using the same sites, on a seasonal basis until February 1979. The partially saline sites from the Town Basin to Orams' Marina showed consistently high coliform counts throughout the series. At this point the Hatea River has drained an intensively farmed catchment as well as a section of the outer city area where sewage treatment is predominantly by means of individual septic tanks and ground disposal systems.

Approximately 1 km seaward from Orams' Marina, Limeburners Creek enters the upper harbour tending to form a broader reach which also receives the flow from the Awaroa River. The city rubbish disposal controlled landfill area at Pohe Island discharges stormwater runoff and tip leachate to the harbour near the confluence with the Awaroa River. The Whangarei City Corporation wastewater purification plant effluent is discharged at a point some 500 metres upstream within Limeburners Creek.

Results from the site situated near the centre of this reach showed high coliform counts for all tests taken during this series. With regard to dissolved oxygen or pH, the classified standard which is SC was not reached on several occasions. The sites from this point seawards showed a progressive reduction with respect to coliform numbers/100 ml with a steady rise in dissolved oxygen levels. The sites from the Onerahi Yacht Club seaward were of high quality (SB–SA) and well within the classified limits.

In order to obtain primary data with regard to all the parameters used in this series upon which to base profiles covering the harbour proper, five further tests were carried out. This testing was done at different states of the tide over a 30-day period at the site situated just seaward of the confluence of Limeburners Creek and the Port Whangarei arm of the upper harbour.

Three of these tests showed the dissolved oxygen levels as being below the 5 mg/ℓ required by the SC classification, ranging between 3 and 6.8 mg/ℓ (median values). Total coliforms/100 ml were recorded as 15 000 and faecal coliforms 3500/100 ml.

Although the City refuse tip contributes some degree of bacteriological pollution to the estuary at the mouth of the Awaroa River and thence to the harbour proper, the major source of pollutants has been localised as the discharge from the City wastewater purification plant.

Some 10–15 million litres of effluent is discharged from this plant daily and although the standard of operation is high the plant cannot (because of overloading) operate as originally designed. The average biological loading being transferred to upper harbour waters is of the order of 600 kg BOD_5 and 750 kg suspended solids daily.

In order to plot coliform transport and die off as well as dissolved oxygen recovery, together with an estimation of the average residence time within the Port Whangarei arm of the harbour, the original harbour survey was extended to encompass a further 12 km using the base figures previously established at the Limeburners Creek site with regard to dissolved oxygen, pH, salinity and total and faecal coliforms/100 ml. Monitoring was again carried out at all states of the tide and some estimation of currents and velocities were tabulated using floats dropped at intervals during the sampling trips.

As was the case in the shoreline series, total, and faecal coliform die-off appears to follow a consistent pattern in relation to salinity as well as distance travelled (time):

(a) Limeburners Creek Control
Total coliform/100 ml 15000
Faecal coliform/100 ml 3500
Dissolved Oxygen 3–5.8 mg/ℓ
Salinity 9.5–33 ‰

(b) Onerahi Yacht Club Control
Total coliform/100 ml 350
Faecal coliform/100 ml 46
Dissolved oxygen 6.9–7.3 mg/ℓ
Salinity 26–35 ‰
Distance from control (a) 5 km

(c) Parua Bay Entrance
Total coliform/100 ml 6
Faecal coliform/100 ml < 2
Dissolved Oxygen 7.0–7.9 mg/ℓ
Salinity 32–36 ‰
Distance from control (b) 12 km

The outer quality control site at Darchs Point some 5 km seaward from Parua Bay entrance has, since the harbour water quality monitoring programme was begun in 1976, consistently returned total and faecal coliform counts of < 2, dissolved oxygen 8.0–8.3 mg/ℓ and salinity 34–36 ‰.

At this stage no significant trend towards any water quality deterioration has been noted this far down harbour where shellfish is taken in large quantities from the as yet well stocked beds on the shoal banks.

Although time has not permitted any other than a brief examination thus far, three sediment samples taken from the Limeburners Creek control sampling point and from 1 km either side, have shown a markedly greater amount of organic matter when compared with similar grab samples taken from and near the Onerahi Yacht Club control site.

Samples were dried at 103 °C for 24 hours and weighed before digestion with 60 vol H_2O_2 for 4 hours then dried at 103 °C for a further 24-hour period, and re-weighed. No doubt this is a very rough method but it proved effective for some comparisons to be made.

Samples from the intertidal area opposite the Parua Bay control, when treated by the described method, showed less than 30 percent of the organic material measured at the Limeburners Creek control. These albeit rough determinations appear to indicate a similar transport pattern to the bacteriological profile previously described and, when time permits, will be repeated on succeeding surveys.

Summary

The lengthy residence time engendered by the present physical characteristics of the upper Whangarei Harbour undoubtedly causes retention of a large proportion of polluted water from several sources within the upper harbour reaches. Although this may be undesirable in some respects, the retention of this water is definitely acting as a buffer which allows bacteriological die-off to progress markedly before the more vulnerable harbour waters, presently relatively unaffected by pollution and extensively used for recreation, are irrevocably affected.

Although this does tend to allow more flexibility to the various wastewater dischargers with regard to water quality requirements, increasing discharge rates resulting from population and industrial growth, together with alteration of upper harbour patterns by dredging and reclamation, will eventually break through this tenuous barrier.

It is therefore essential that all contributing discharges be upgraded as soon as possible and that in-depth investigations be undertaken before any significant reclamations or alterations to the harbour prism are contemplated. These precautions should enable the harbour water quality to be kept in a state commensurate with every use of this valuable natural resource.

The Wairau, Otamatea and Kaiwaka Rivers

The Wairau River which drains an intensively farmed catchment of 26 km² enters the Otamatea River some 2 km downstream of the Maungaturoto township. The Otamatea River is in turn joined by the Kaiwaka River, a further 6 km downstream at Pt. Curtis. The Kaiwaka River drains a similarly farmed catchment of 32.5 km². From this confluence the Otamatea River continues for a further 16 km before flowing into the Kaipara Harbour proper near Batley (Fig. 4).

The Otamatea and Kaiwaka Rivers are similar in most respects with an average channel width at full tide of some 250 metres and low tidal channels of some 150–200 m in width. The upper intertidal areas on both sides of the rivers support a relatively narrow band of mature mangroves.

In the deeper parts of the channels near Point Curtis and the Ranganui railway bridge sediments consist of soft muds which are anaerobic immediately beneath the surface. Coarser sediments are found in pockets in the shallower waters near the banks of the rivers but generally muddy conditions prevail over most of the intertidal flats.

Both commercial and amateur fishing is carried out within the Otamatea and Kaiwaka Rivers, where flatfish and mullet are plentiful. Although several oyster leases exist in the upper Otamatea, none of these have yet been implemented.

A large dairy factory situated at Maungaturoto was granted (on 9 December 1977) a right to discharge wastewater, the expiry date of the right being 1982. Two discharges totalling some 440 m³/day consisting largely of condenser and stormwater are directed to the upper Wairau River and a third and major discharge of 2600 m³/day consisting of casein wash-water and other processing wastes is located some 600 m downstream of the Ranganui railway bridge on the Otamatea River.

A refuse tip operated by the Otamatea County Council is situated adjacent to the Wairau River some 2 km downstream of the dairy factory. While this tip is not contributing a great deal to the organic

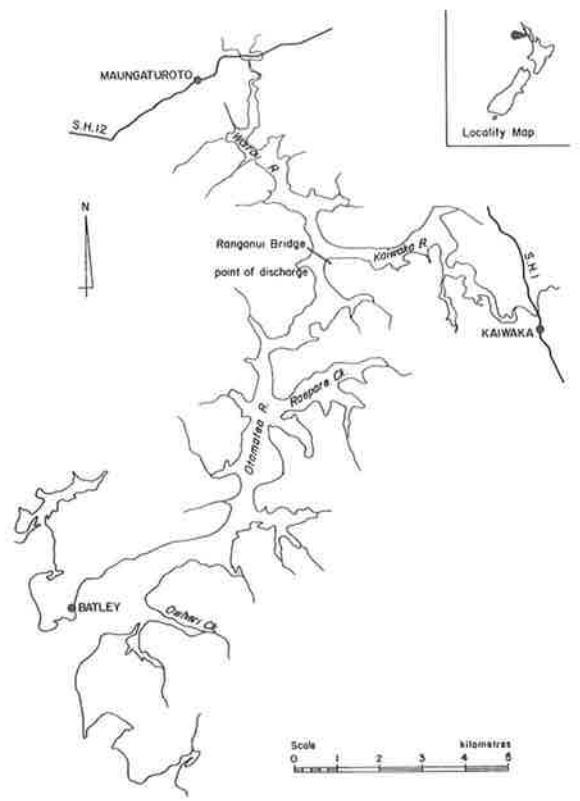

Fig. 4 Wairau-Otamatea-Kaiwaka Rivers.

loading presently exerted on the Wairau River its location leaves much to be desired.

From this point on the Wairau River for a distance of some 12 km on the Otamatea River the general configuration and channel cross sections are reasonably uniform. Current velocities at varying states of the tide show a similar uniformity with an average over the tide cycle of 1.7 km/hr on a falling tide and 0.9 km/hr on a rising tide.

The main dairy effluent, which consists largely of whey and casein fines, is pumped approximately 6.5 km through a PVC pipeline to a point some 600 metres downstream of the Ranganui railway bridge. The Otamatea River at this point is approximately 250 m wide. Mean water depth at the outfall is approximately 6 m with a minimum depth of 4 m on low spring tides and approximately 2 m on neap tides. The low tidal channel is approximately 200 m wide and the outfall has been located as near as possible to the deepest part.

Salinities vary, depending on river flows. The mean average discharge from the Wairau River is 620 ℓ/s with a 5-year drought flow of 13 ℓ/s and the mean average discharge from the Kaiwaka River is 780 ℓ/s with a 60 ℓ/s 5-year drought flow. During summer flow periods waters are highly saline with salinities in excess of 30 parts/1000, whereas in winter salinities are reduced to approximately 20 parts/1000 at high tide and may be less than 10 parts/1000 at low tide.

The waste discharge load per day to the Otamatea Rivers' complex is generally as follows:

Volume	2 600 m^3
Biochemical Oxygen Demand	35 000 kg
Total solids	58 000 kg
Suspended solids	1 500 kg
Lactose	40 500 kg
Phosphates	1 330 kg
pH range	4.5–5.5

After considering evidence presented on the various factors involved with this discharge, a condition limiting the discharge time to a period from 2 hours before high water to one half hour before the following low water was imposed in respect of the current water right.

Float tests conducted by Northland Regional Water Board staff during some of the 20 river survey trips carried out thus far indicate that a distinct eddy condition does exist at the confluence of the Kaiwaka and Otamatea Rivers. However, floats released over the 2 hours before high water at the point of discharge showed that the main tidal flow in this period was in the Kaiwaka River where the floats traversed approximately 2 km while in the Otamatea the distance travelled was 500 m.

Slack water (during which the minimum of wastewater dispersion with the receiving water can be expected) lasts from some 20–30 minutes before any significant current movement is noted until after another hour when the maximum tidal current velocity is reached.

Floats released at the point of discharge 1 hour after high water gave only indicative results which, broadly translated, showed that a maximum of 8 km would be traversed by the third 1-hour slug of waste with a commensurately diminished distance travelled by the continued discharge over the designated period. Although retention within the Otamatea and Kaiwaka Rivers has only been sketchily investigated it is probable that a time measured in weeks could be involved in summer conditions.

As a result of complaints from users of the Wairau, Otamatea, and Kaiwaka Rivers through the Ministry of Agriculture and Fisheries regarding water pollution and shoreline contamination in the summer of 1978, a more comprehensive survey to determine the general pattern of effect on the estuaries was initiated.

The initial testing series confirmed that with the low freshwater flows during the dry summer and with the high temperatures prevailing at the time, the estuarine waters were indeed badly polluted. Dissolved oxygen levels averaged 2.2 mg/ℓ and evidence of a major fish kill was noted over much of the upper Otamatea and lower Wairau rivers shoreline. Inspection of the 6 km pipeline through which the dairy factory wastes were discharged revealed several sections where leakage to the upper Wairau River had taken place. The discharge of casein wash-water from the factory was discontinued while repairs to the pipeline were effected. Further testing carried out in the estuary some 10 days later showed that while the wastewater discharge was reduced, dissolved oxygen levels had risen to an average of 6.8 mg/ℓ.

Although the water quality surveys to this date appeared to indicate that the pollution present in the waters of the Wairau, Otamatea and Kaiwaka Rivers was due to the dairy factory wastewater discharge, no real conclusion could be drawn because of the following factors.

(a) Pipeline failures had meant that the wastewater discharged was distributed over a wide area in the Wairau River instead of being directed to the designed discharge point in the Otamatea River.

(b) Because of equipment deficiencies such as inadequate storage capacity, pumping capacity etc., at the factory it was not possible to regulate the wastewater discharge to the recommended times.

To verify the conclusions reported to the Regional Water Board through the dairy company (upon which the conditions placed on the discharge right were largely based) it was necessary to carry out an intensive water quality monitoring programme on the Wairau, Otamatea and Kaiwaka Rivers for a further production season, during which all the stipulated discharge conditions could be met.

If the assumption that the conclusions reached in the report submitted on the dairy company's behalf were broadly correct there would be no further cause for concern and the estuarine environment would over a period resume a balance which would cope with the factory and other discharges while retaining a normal water quality.

Observations with regard to tidal movements, velocities and probable dilutions, together with related reactions noted in laboratory simulations (when the average waste was mixed with sea water at

several dilutions and salinity levels) did however give rise to some doubts.

In an endeavour to gauge a recovery rate and establish a basis upon which to assess the effects of the 1979–80 production season wastewater discharge on the water quality of the river complex, further sampling was carried out on 6 July 1979, when the factory had been out of production for some weeks. Samples were assessed for dissolved oxygen and sediment.

The average dissolved oxygen near and around the discharge site was 8.1 mg/ℓ, which is commensurate with levels recorded at Batley some 12 km seaward at a point thus far shown to be unaffected in this respect by the wastewater discharge.

Sediment samples taken from the three rivers at points usually affected by the waste discharges showed the following results after 5 days at ambient temperatures:

Otamatea River adjacent to the factory discharge point: O_2 depletion 4.0 mg/ℓ per gm sample

Kaiwaka River 500 metres upstream: O_2 depletion 3.4 mg/ℓ per gm sample

Wairau River 1 km upstream of Ranganui railway bridge: O_2 depletion 4.3 mg/ℓ per gm sample

Batley Control 12 km seaward of discharge point: O_2 depletion 1.2 mg/ℓ per gm sample

These results seem to be further indicative of the fact (which was noted during the elementary laboratory dispersion simulations), that some of the solid material contained in the wastewater discharge, which would normally remain in suspension, settles out when mixed with saline water. There is thus the possibility that a layer of this material (the thickness of which would presumably be largely dependent on river water velocities), is formed on top of, or intermingled with, the normal sediment material.

The testing programme was designed to monitor the river complex under the special conditions contained in the dairy factory water right. The project, commencing on 29 November 1979 (when the average dissolved oxygen was found to be 2.2 mg/ℓ), was to ascertain whether wastewater discharge conditions were being met during the 1979–80 production season.

Sediment samples showed no major change, with results averaging 3.2 mg/ℓ per gram sample of O_2 demand at the outfall and upriver sites, and 1.2 mg/ℓ per gram sample at Batley control. BOD_5 results from river water samples taken from the same sites averaged 1.6 mg/ℓ and at Batley control 0.8 mg/ℓ.

The programme was continued on a regular basis with eight sampling runs (one of which was in the company of factory staff and their advisers) being completed by 16 April 1980. The average dissolved oxygen level taken from all the tests was shown to be 4.3 mg/ℓ the highest value being 5.5 mg/ℓ and the lowest 1.8 mg/ℓ.

According to our general observations the overall effect of the wastewater discharge on the estuarine environment has been small in the short term but this could be due largely to the climatic conditions over the season. Should there have been a dry summer as was the case during the 1978–79 season, an entirely different pattern could have emerged.

A test carried out at Point Curtis on 15 July 1980 with the factory out of production for some weeks showed a dissolved oxygen level of 8.0 mg/ℓ, a figure commensurate with normal river conditions.

Results from the 1979–80 season have shown that, despite above average rainfall (in respect of duration rather than quantity) and lower temperatures, the wastewater discharged from the dairy factory has at times exerted an untenable demand on the receiving waters, notwithstanding strict adherence to all the special conditions imposed on the discharge.

The factors of residence time and high demand for oxygen exerted by the wastewater, combine to create a loading pattern beyond the immediate assimilative capacities of the receiving waters. It has been found that if the waste discharge ceases for approximately 72 hours, the dissolved oxygen resumes a normal level. Sedimentary loading, however, still seems to exert a demand which requires longer than the usual seasonal shutdown period of 2 months to be satisfied.

Experimental work has shown that should the biological load imposed by the wastewater be reduced by 50 percent, the river system could absorb this particular discharge without any undue immediate or long term effects, leaving some leeway for contingencies such as long dry summers etc.

In this water quality project the company involved is working in full co-operation with the Northland Regional Water Board staff.

The Ngunguru River Estuary

This estuary situated some 30 km north of Whangarei Heads (Fig. 5) is a drowned river valley infilled with marine sand. The waters of the estuary are largely unaffected by pollution and not as yet subjected to any trade waste discharge. The main loading presently imposed on the estuarine waters is that from domestic septic tank ground disposal systems with some contribution from surrounding farm land.

Surveys carried out to date have shown that although the drains and small streams which adjoin the populated areas along the estuary were badly polluted, bacteriological determinations from samples taken on the estuary proper show that these waters are as yet unspoiled. For this reason and because of the extensive recreational usage of this particular waterway, we have used results gained from oxygen and sediment sampling as a baseline for comparative purposes with the other described waterway systems.

The resident population at least doubles during the summer holiday season and this is reflected in the results to date from seasonal water quality monitoring surveys. It will no doubt be necessary for a sewage treatment system to be installed in the foreseeable future, which again makes this particular estuary a desirable subject for water quality monitoring. Data will then be available for plant design taking account of the estuary's ability to absorb biological loads without major effects.

During the surveys carried out since 1976 dissolved oxygen levels have been consistently of the order of

7.5–8.5 mg/ℓ, with good water quality standards (SB-SA). Sediment samples analysed according to our comparative method gave 5-day oxygen depletions averaging 1.0 mg/ℓ per gram sample. These results compare favourably with the outer control on the Otamatea River at Batley.

After several trials using different methods in an endeavour to determine oxygen demand from estuarine sediments the following method has been tentatively established for such determinations during the present ongoing surveys.

The procedure is an attempt to measure the probable oxygen depletion in estuarine waters, caused by microbiological activity in the sedimentary material. As such it does not attempt to measure the absolute oxygen depletion by simulating any given estuary environment, but rather to compare two or more sediments in a reproducible, artificial laboratory environment. The method is based on the logic of the 5-day BOD test, where oxygen depletion in a water sample charged with a known weight of sedimentary material is measured after incubation for 5 days at 20 °C in the dark.

Method

1. Samples of sediments are collected and kept in airtight plastic bags to reduce moisture loss.
2. (a) A 10.0 gm subsample is weighed into an evaporating dish and dried to a constant weight at 103 °C.
   (b) From this, the solid content is determined as a percentage.
3. A sample (usually 5.0 gms) taken from the original sample is then introduced into duplicate BOD bottles and dilution water containing 15% sea water is added. This is repeated for each sediment sample with duplicate blanks.
   Example:
   Initial weight of sediment = 10.0 gms
   Weight after drying = 5.9 gms
   $\therefore$ percent solid = 59%
   To obtain 5.0 gms solid from original sample
   $$= \frac{100}{59} \times 5.0$$
   $$= 8.4 \text{ gms}$$
   This weight of original sample is inoculated into a BOD bottle.
4. Determine the initial dissolved oxygen; incubate for 5 days at 20 °C and determine the final DO.
   The difference is the BOD_5 of the sediment when the correction for the blank is applied.

Notes

1. A small weight error is recognised as different sediments have differing salinity content. Samples could be washed in fresh water but this could possibly remove some important biological factor.
2. The dilution water is prepared by using sea water from the open sea with at least 30‰ salinity.
   Add distilled water until 15‰ is reached — use salinity meter.
3. Check BOD bottle volumes and adjust.
4. Shake incubating bottles at least twice daily.

This method was used for all the later determinations as the previously described methods showed wide discrepancies. Comparative results appear to show that the described procedure is less liable to such errors.

Sedimentary material from Ngunguru and Batley controls was mixed with sea water, which had been thoroughly mixed with casein wash-water at 1-2000 dilution. When comparative tests were undertaken, there was no mistaking the difference in casein wash-water-initiated oxygen depletion. Repeating this experiment using sewage effluent was not so conclusive but the effects were nevertheless identifiable. Further work over the next few years should see a continuing improvement in the water quality within these waterways and this to a large extent is due to the co-operation given the Regional Water Board staff by the different organisations involved in the described wastewater discharges.

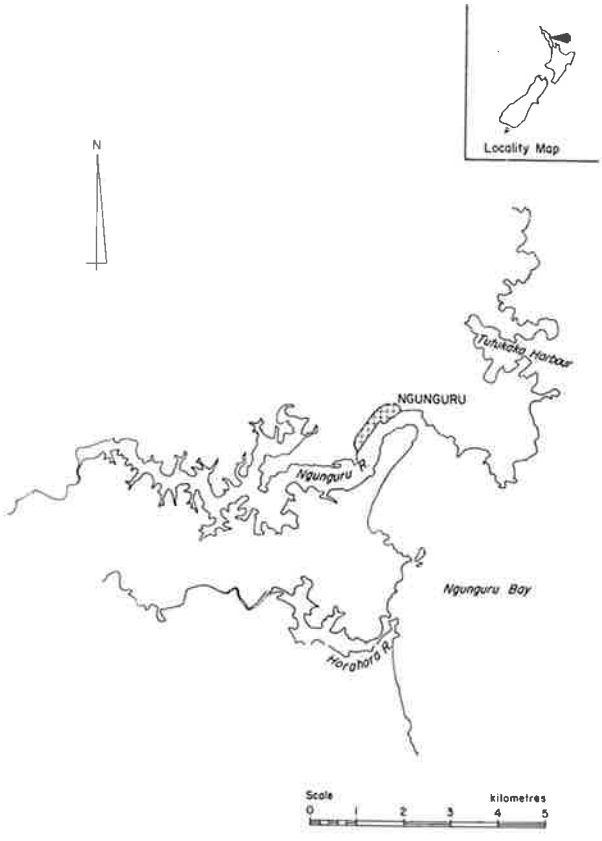

Fig. 5 Ngunguru River Estuary.

Acknowledgements

I wish to thank Mr P. Freeman for his able and innovative assistance during the sometimes trying boat trips and for his forebearance with my interference in his well organised laboratory.

An estuarine creek model — Upper Waitemata Harbour

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This paper outlines the application of a simulation method, the mixed segment approach, to an estuarine creek in the Upper Waitemata Harbour, Auckland. The water quality parameters BOD and DO are used as examples to illustrate the use of the model. Attention is drawn to the necessity for the accurate assessment of the model coefficients before confident conclusions are developed.

Introduction

This paper outlines the application of the mixed segment approach, a simulation method, to model the concentration of BOD and DO in the Lucas Creek sector of the Upper Waitemata Harbour.

The purpose of the paper is to indicate that a relatively simple model can be developed to facilitate approximate deductions on the water quality parameter profiles in an estuarine creek.

The results are limited to the prediction of parameter profiles for the quasi-steady state situation whereby it does not account for fluctuations within the tidal cycle. The mid-tide phase point is the case normally considered for engineering purposes.

Upper Waitemata Harbour study

The Upper Waitemata Harbour (Fig. 1) is the subject of an intensive study promoted by the Auckland Regional Water Board. The broad goals of the study are:

(a) to assess the present status and characteristics of the estuary and adjacent land;
(b) to predict the effect of urbanisation or other land use changes in the area.

The ability to address water quality problems and arrive at conclusions will enable informed planning decisions to be made.

The mixed segment model

This method is concerned with determining parameters such as BOD and DO at fixed locations along an estuarine creek. The predictions are limited to a particular tidal state, e.g., high tide, mid-tide, and the system is assumed to exhibit a cyclical variation with respect to time. That is, at a fixed point the parameter value is duplicated at successive identical states of the tide. The parameter varies, however, in its value over the intervening tidal period.

The calibration coefficients used in the model reflect the time averaging simulation perspective.

McDowell & O'Connor (1977) suggest that the mixed segment approach does produce acceptable engineering solutions, provided steep concentration gradients are not involved. It was applied with a high degree of success for the prediction of oxidised nitrogen, ammoniacal nitrogen and dissolved oxygen for the Thames Estuary (Downing 1971).

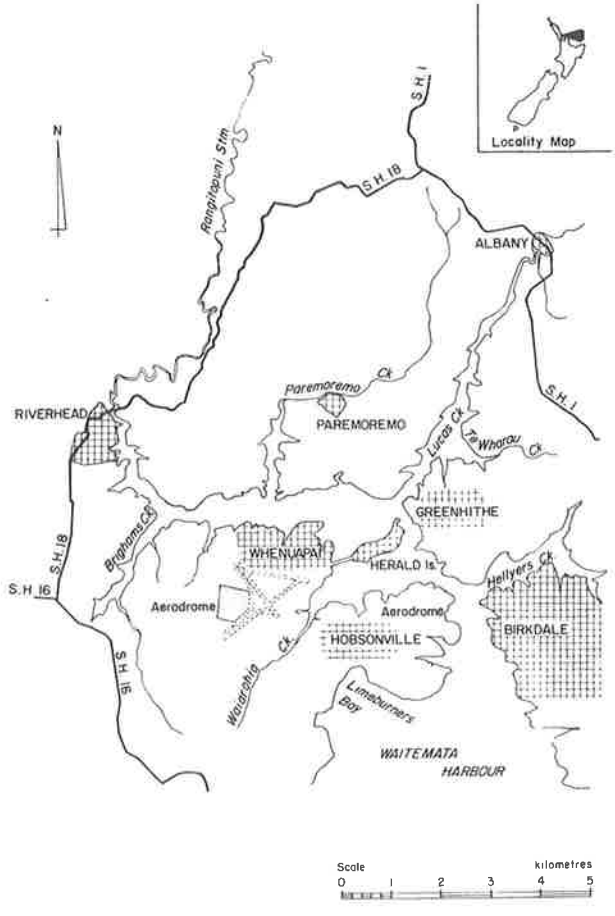


Fig. 1 The Upper Waitemata Harbour.

Theory

The estuary is divided into segments as depicted diagrammatically below.

Complete mixing is assumed in segments due to tidal action. The landward boundary of the first segment is selected where the flow is unidirectional and has approximately zero salinity. The seaward boundary of the last segment is sited at the entrance to the creek where the salinity remains approximately constant. *The model is one dimensional and each segment is characterised by a pollutant concentration, water quality parameter or salinity. This averaged value applies to the water volume in the segment.*

The mixing due to tidal action is simulated by proposing an exchange of fluid between adjacent segments. Freshwater inflows are assumed to be steady and directed into the appropriate segment. Continuity dictates the outflows as shown from each segment into the adjacent downstream segment.

Decay or production of substances can be included if required and applied to the appropriate segment or segments. Pollutant can be introduced into any segment.

The mass balance equations are written for each segment and the set of simultaneous algebraic equations yields the quasi-steady state concentrations.

The calibration of the mixing model revolves about the determination of the respective exchange volumes. It is convenient to express the exchange volumes in terms of the proportion of the upstream segment volume so that the results can be applied to cases where the segment volumes are different. This could be because of seasonal tidal fluctuations or simply the application of the scheme to another tidal phase. This is based on the assumption that the *percentage* volumes of water exchanged between segments is relatively constant.

In situations where the salinity profile is known, the data enables the direct computation of the exchange coefficients. Substitution of the coefficient values in the pollutant or water quality parameter mass balance equations enables the production of the relevant profiles.

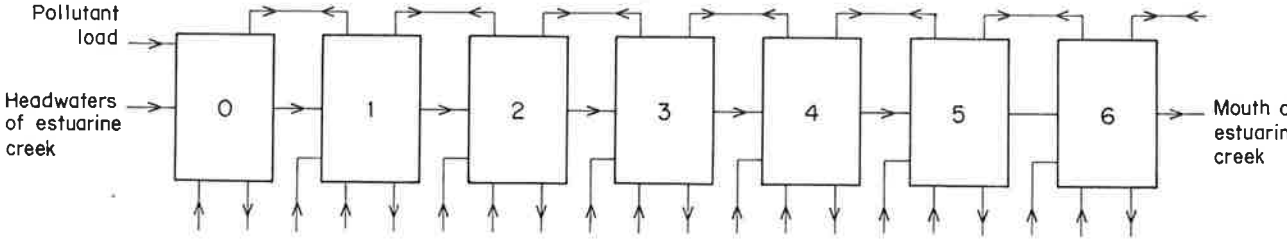
The calibration of the water quality modelling requires the determination of the appropriate BOD decay rate and reaeration coefficients.

Equations

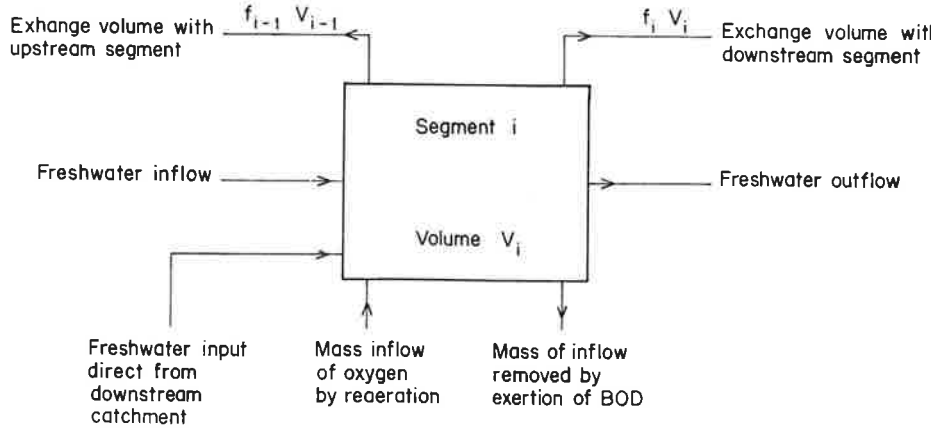
The mass balance equations for the salinity, BOD and DO can be set out. The salinity data enable the exchange coefficients to be computed. These coefficients are then substituted into the equations to solve for the BOD and DO concentrations in a two step procedure. The first step takes account of inputs, outflows and mixing but neglects decay and reaeration. The second step deals with these effects.

Application to Lucas Creek

Lucas Creek was divided into seven segments as indicated in Fig. 2. Two salinity profiles (longitudinal) were available for the calibration of the exchange coefficients (Fig. 3 and 4). These values are tabulated in Table 1, and the computed averages were used in the modelling of the BOD and DO. (Despite the differences, e.g., f_1 and f_4, salinity



SEGMENT SYSTEM



TYPICAL SEGMENT

predictions using both sets of coefficients yield resultant profiles with a maximum error of the order of 4%.)

Table 1. Exchange coefficients — Lucas Creek

Exchange Coefficient = (Exchange volume / Segment volume)	Field Data Set 11/12/78	Field Data Set 10/9/79	Average Value
f_0	0.77	1.60	1.2
f_1	1.17	0.76	1.0
f_2	0.39	0.57	0.5
f_3	0.34	0.36	0.35
f_4	0.83	0.29	0.56
f_5	0.34	0.35	0.34
f_6	0.87	0.99	0.93

Model results for Lucas Creek

Dilutions (Mixing)

The dilution of freshwater in the segments can be calculated as follows:

Freshwater fraction $f = \frac{S_o - S}{S_o}$, S = segment salinity

Dilution of freshwater $D = \frac{1}{f}$, S_o = harbour salinity

Table 2 indicates the computed dilutions for the high water of 10 September 1979 and the predicted dilutions for the three quarter and half tide cases.

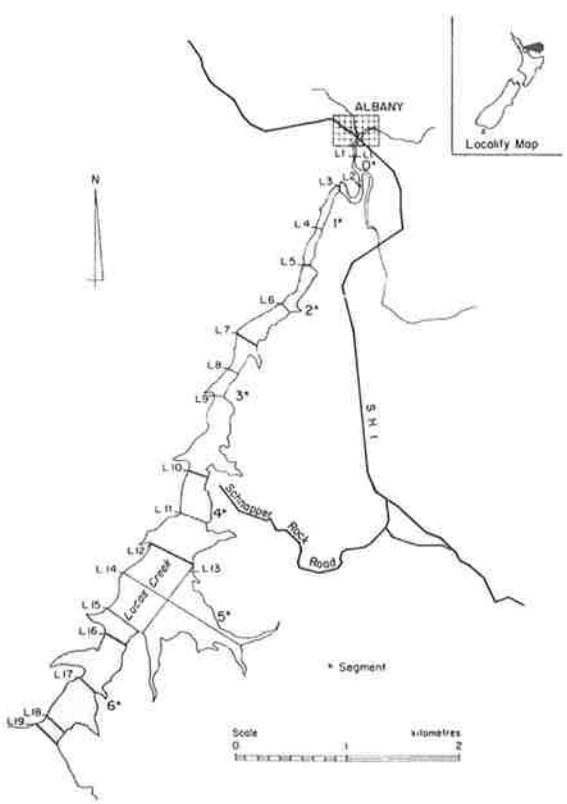


Fig. 2 Lucas Creek; cross-section locations.

Table 2. Dilutions — Lucas Creek

Segment	Distance from harbour (metres)	Dilutions Full tide	Dilutions ¾ tide	Dilutions ½ tide
1	5300	1.9	1.7	1.2
2	4500	2.6	2.3	1.4
3	3400	4.1	3.6	2.2
4	2300	7.9	6.9	4.0
5	1300	14.9	13.1	8.1
6	600	43.5	39.2	27.2

BOD profiles

The BOD is subject to exponential decay characterised by the rate constant k_1 ($\frac{dB}{dt} = -k_1 B$). The constant can range from 0.1 to 3.0 depending on the conditions. It is not uncommon for values of k_1 computed from laboratory tests to differ considerably from those computed by field tests. A representative set of k_1 values (0.1, 0.5, 1.0, 1.8) was therefore used to indicate the sensitivity of the resulting BOD profile to the value of the constant k_1 (base e, days^{-1}).

The boundary values of the BOD profile must also be specified. The harbour BOD background value was specified at 1.0, and the BOD in the freshwater input at the head of the creek was specified for three discrete values 5, 10, and 20.

The solution profiles for the mid-tide case are presented in Fig. 5.

Dissolved oxygen profiles

The DO is consumed at the same rate as the BOD decay, and is replenished by aeration at the water surface. The relevant constants are k_1 and k_2.

Dissolved Oxygen: Consumption rate
$= k_1 B : k_1$ (base e, days^{-1})

Dissolved Oxygen: Reaeration rate
$= k_2 (C_S - C) : k_2$ (base e, days^{-1})

where C_S is the saturation concentration of DO and C the *in situ* concentration.

In reality, the sediments will also significantly interfere with the DO levels and should be modelled for also.

For the DO predictions, both constants k_1 and k_2 must be known accurately and k_2 is known to be affected by wind and wave action. Further laboratory and field work could assist in estimating suitable values for k_2 and the coefficients appropriate to the oxygen exchange at the sediment interface.

Boundary values are again necessary, and for this study the following figures were used:

Harbour dissolved oxygen concentration 7.5 g/m^3
Dissolved oxygen saturation concentration 8.0 (~25 °C)
River input dissolved oxygen concentration 6.0 g/m^3

The solution profiles for the mid-tide cases are presented in Fig. 6 (reaeration coefficient used : 0.6, being a representative average from the literature. However the coefficient is found, (O'Connor & Dobbins 1958) to depend on velocity and depth.

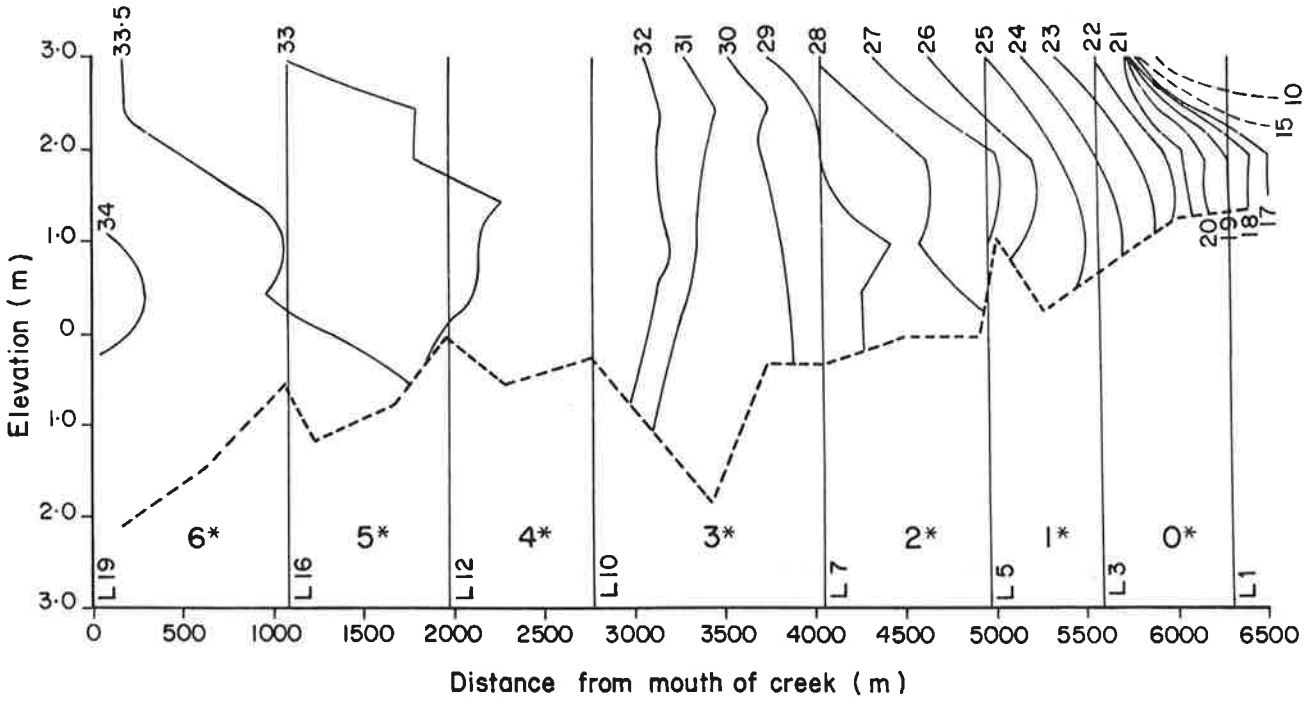


Fig. 3 Isohalines in Lucas Creek, 11 December 1978 (approx. High Tide).

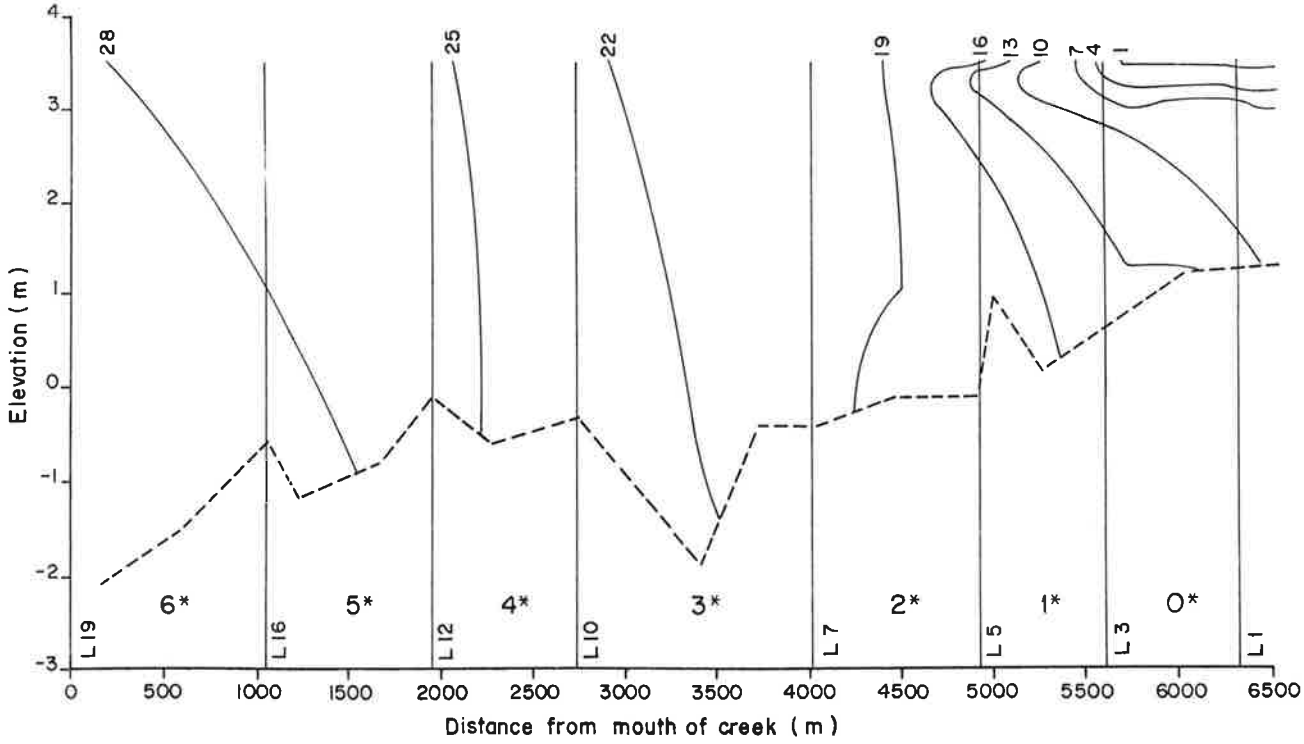


Fig. 4 Isohalines in Lucas Creek, 10 September 1979 (approx. High Tide).

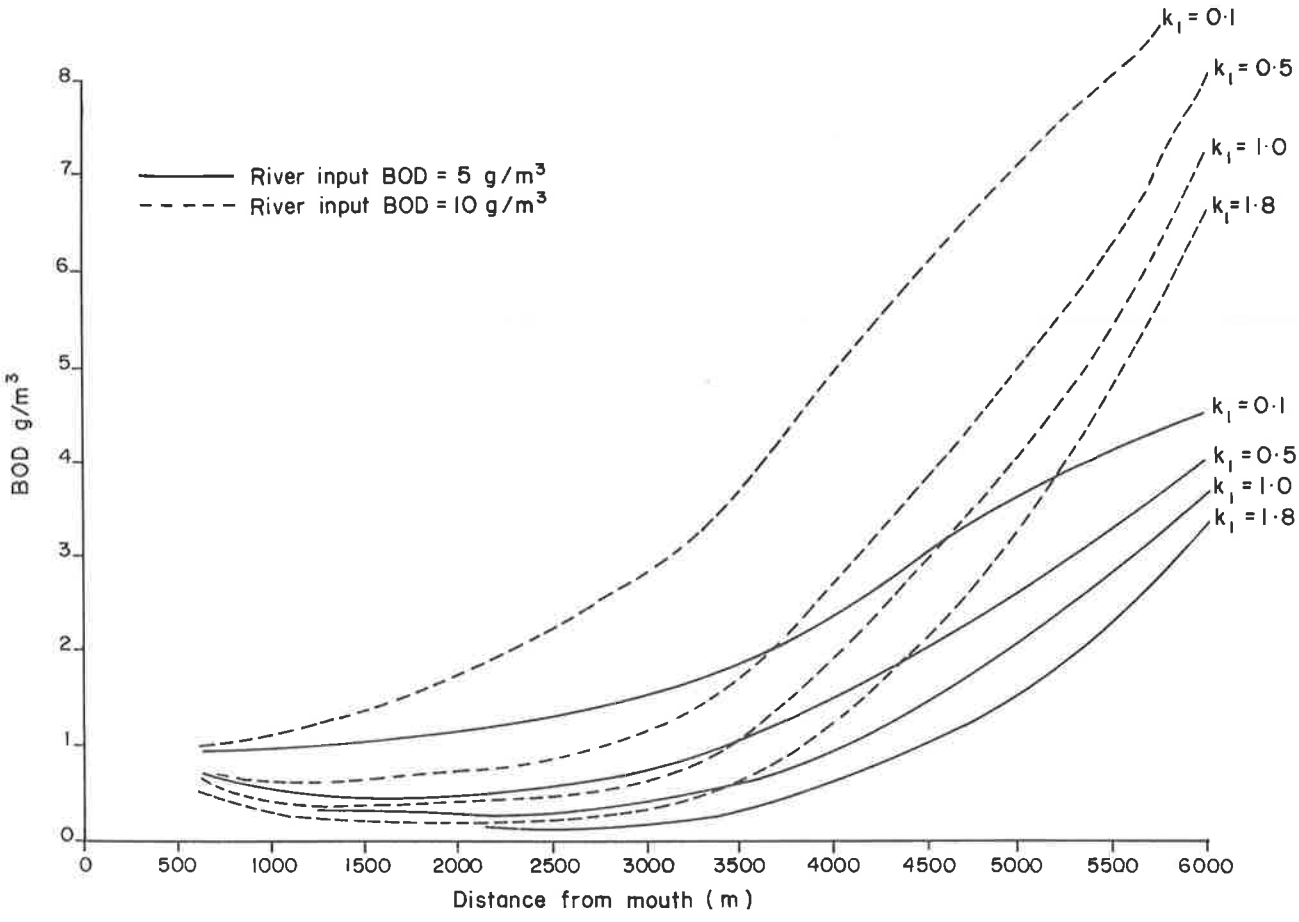


Fig. 5 BOD profiles—Mid Tide case (Harbour BOD assumed to be 1.0 g/m³).

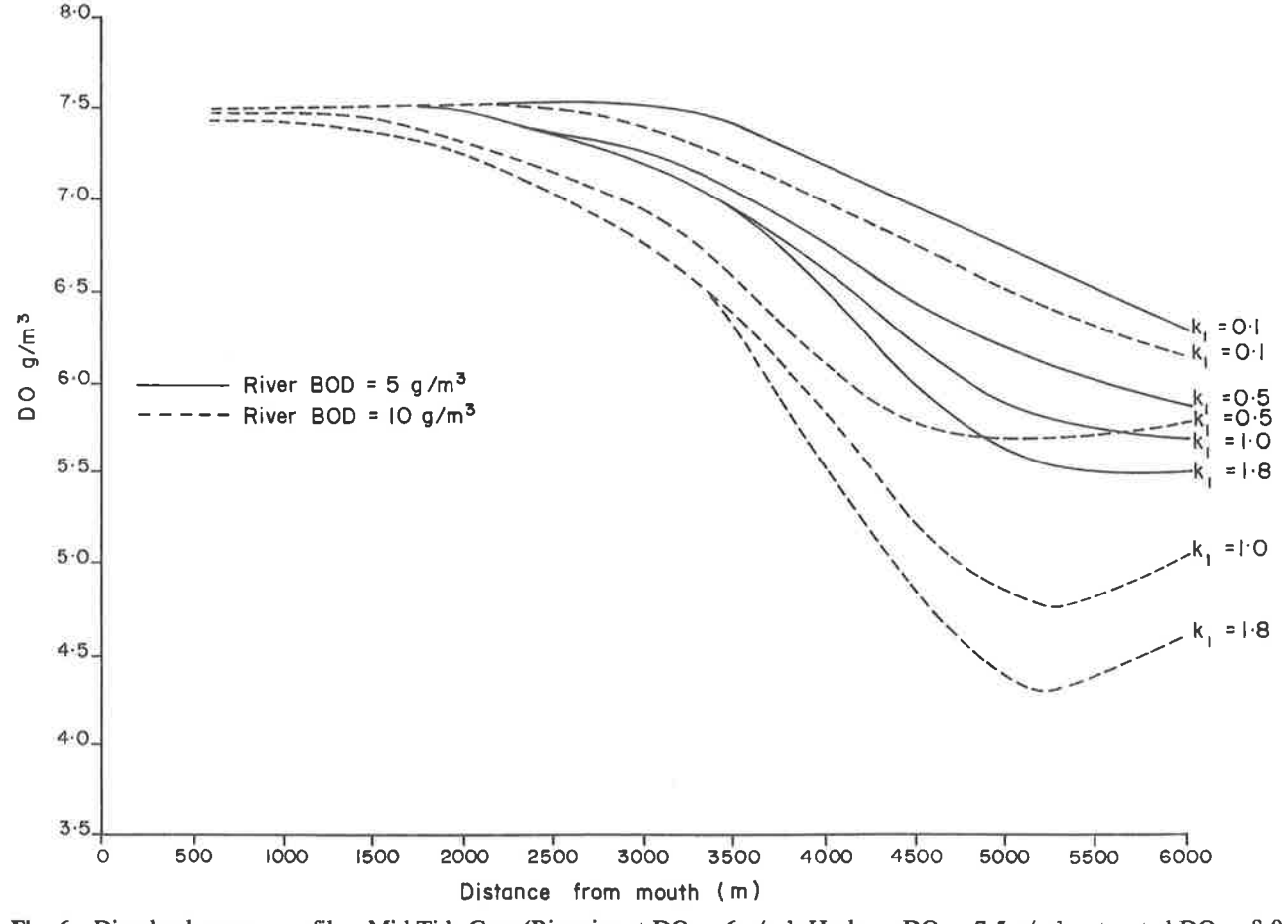


Fig. 6 Dissolved oxygen profile—Mid Tide Case (River input DO = 6 g/m³; Harbour DO = 7.5 g/m³; saturated DO = 8.0 g/m³).

Discussion of results

The dilution of freshwater input at the head of the creek is subject to a gradually increasing dilution up to the order of 4–8, to a point approximately 2200 metres from the junction of the creek with the harbour (cross section L12, Fig. 2). Harbourward of that point, the degree of dilution increases rapidly to the order of 25–45. The tidal excursion of the creek has been found to be approximately 3000 metres.

Without supporting field data as already outlined, only general observations can be made for the BOD and DO distributions.

For example, for a constant $k_1 = 1.0$, the BOD level is reduced from the river input level by a factor of 10 at the 3500 metre point. This point is approximately at cross section L9 where the estuary narrows significantly.

The DO profiles indicate low levels will only be a problem in the upstream section of the estuary for heavy BOD loadings and high decay rate characteristics.

Conclusions

From published literature it appears that the mixed segment approach to estuarine water quality modelling can provide solutions suitable for engineering purposes.

There are aspects of the scheme as applied which are capable of being refined. Two English researchers, Barret and Mollowney, (McDowell & O'Connor 1977) have extended the approach to deal with intertidal variations. The application of this refinement is to be investigated.

Before confident conclusions can be formulated, the following two steps must be pursued:

(a) the acquisition of accurate data for the coefficients k_1 and k_2 and those appropriate to the sediment's role in the dissolved oxygen balance;

(b) the comparison of model predictions with synoptic field profiles for BOD and DO.

Such data collection and comparisons would indicate the level of confidence to be assigned to this model or indicate aspects which require further development.

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DISCUSSION FOR SESSION VIII

Wairoa River — a case study

Presented by: W. S. WAKELIN

J. C. RUTHERFORD: Does the existence of a salt wedge in the Wairoa estuary increase the flushing rate and prevent dissolved oxygen depletion as in a fully mixed estuary?

WAKELIN: The presence of a salt wedge with the quite distinct boundary condition between the fresh water and the saline layer indicates that the effective river cross-section for the fresh water decreases towards the estuary mouth. It is therefore to be expected that the flushing rate is greater than for a fully mixed estuary. The dissolved oxygen depletion in the upper fresh water layer would therefore be less severe than for a fully mixed estuary as reaeration near the surface would be more effective; this beneficial effect would become more significant downstream of the point discharge as the freshwater depth is reduced.

G. B. McBRIDE: Do you think that the deoxygenation of the saline wedge is attributable to the discharge of organic wastes?

WAKELIN: The organic wastes discharged into the river could deplete the dissolved oxygen in the saline wedge through several mechanisms, namely, the solids that settle to the river bottom undergoing degradation; the increased suspended solids owing to coagulation effects at the saline/fresh water interface; and the diffusion of organic species from the freshwater to the saline wedge.

B. L. WILLIAMS: In the Wairoa River mouth region are there any other tracers, in addition to those measured, or any dye experiments conducted to assess the mixing characteristics?

WAKELIN: The authors are not aware of any dye measurements or other experiments with tracers to assess the mixing characteristics of the river. The measure of salinity is simple and applicable to any depth regardless of the level of suspended solids or substances likely to interfere with colorimetric measurements. However, it is appreciated that this has value essentially for determining the salt wedge profile only.

The blood colouration of the freezing works discharge can be an indication of the extent of the dispersion but apart from the obvious presence of the discharge at the near side of the river, there has been no attempt to quantify the dispersion by this method. Because water rights refer to the sampling of river water beyond the "mixing region" of a point source discharge, the measure of dispersion in estuarine rivers is important, and this matter should be the subject of further investigation.

M. E. U. TAYLOR: Have you looked at the condition of the sediments near the mouth of the river where coagulation of the effluent due to the high salt water pH is most likely?

WAKELIN: Sediments do occur where the salt water meets the works effluent and domestic sewage discharge, but the condition of the sediments has not been investigated.

A. G. BARNETT: (a) Dr Wakelin mentioned that a bar at the mouth of the river closed the estuary occasionally. Since this type of occurrence would presumably coincide with low river flows, this combination of events is likely to form a critical condition with reference to the worst case investigations of water pollution. Could Dr Wakelin be more specific about how commonly a bar does close the estuary?

(b) Presumably this study and possible subsequent modelling studies are directed towards assessing some change in the system. Is this to be an increase in production at the meat works or a modification of effluent treatment in connection with the current water right application?

WAKELIN: (a) There is really no straight answer here. Some years the bar is never closed yet at times it can happen at fairly frequent intervals. It can depend on:

(i) volume of water coming down the river;

(ii) movement of the sea water out in the bay causing pea shingle to bank up and block the river's exit. (A bitter southerly can come up and whip up the sea causing the shingle to block up the mouth. The sea bed in this vicinity is very, very unstable). So you can see the closing of the bar does not always mean a period of low rainfall.

When the bar is closed the whole estuary can become anaerobic because of the freezing works and domestic effluent discharges, and the estuary can smell really bad.

(b) The freezing works anticipates doubling the mutton/lamb kill and increasing the beef kill within the next few years with a proportionately increased effluent loading. Both the Wairoa Borough and the freezing works are required to meet substantially improved water rights for their respective discharges to the river from 1981 and this requires that the effluents be treated before discharge. It is in this context that the existing state of the river has been investigated so as to assess the effect of superimposed point source discharges.

Case histories of some Northland estuaries

Presented by: L. L. PARKER

M. E. U. TAYLOR: I note the anomaly in the BOD figures you give for river water in relation to the dairy factory discharge (section on Waikare Inlet). Can you tell us whether full precautions were taken to ensure that the samples were truly representative?

PARKER: The samples taken were as representative as possible in that samples were taken at five locations on the stream cross-section at each sampling station. These samples were mixed and used to measure the BOD_5 (three determinations for each station). The recorded results were the average of the three samples. I feel that the results represent the actual degradation pattern in the stream at the time of sampling.

Now that the dairy factory is no longer discharging waste to the stream a slow recovery is being recorded. Results will be checked over an extended period to endeavour to evaluate a recovery profile in this regard.

W. SILVESTER: In your paper (section on Wairau, Otamatea and Kaiwaka Rivers) you state that there are no significant effects of the dairy factories discharges on the estuarine environment. Yet as you show there are drastic effects on aquatic oxygen, which returns to normal after discharge ceases. Upon what evidence do you base your statement?

PARKER: As part of a necessarily very cursory effort, sediment samples were checked for predominant benthic marine life. In the analysis of samples only animals larger than 0.5 mm were considered. All samples were washed through sieves down to this mesh size. It was found that samples from the Ngunguru and Batley control compared favourably with samples taken from areas subjected to the transitionary low DO levels both in numbers and species.

A more detailed examination could reveal that the smaller marine life is affected, albeit temporarily, so that the statement could only be interpreted in the broadest of terms. A further study in this regard will be carried out in the factory off season.

Assistance in identification and interpretation by the Science Centre would be of great assistance in formulating more positive conclusions.

O. M. BORLASE: 1 Are the waters in question classified? If not, on what basis does the Commission set effluent standards?

2 How appropriate are the classification standards in the Water and Soil Conservation Act, as a basis for water quality management in your Commission's area?

PARKER: 1 Waikarakeke — Class D; Kawakawa — Class D; Waikare — Class A. Whangarei Harbour — Class A, B, D in designated areas. Otamatea — Not classified. W/R conditions are class B with regard to O_2 (6 mg/ℓ minimum).

2 The Water and Soil Conservation Act 1967 appears to be sufficient at the moment, i.e., if we can regulate the discharge qualities to attain these standards now, this will be a step forward. Further regulation and alteration of standards may then be needed.

The Northland Catchment Commission classifies its own waterways (for better or for worse) with due regard to all users of each waterway.

An estuarine creek model — Upper Waitemata Harbour

Presented by: B. L. WILLIAMS

C. W. HICKEY: I wonder whether it is biochemically sound to apply a single k_1 coefficient to an estuarine system which has a considerable salinity gradient. Do you think the salinity gradient would significantly affect the reaeration coefficient?

WILLIAMS: This study has used in a sense an arbitrary k value, however a range which is reasonable. I am not aware as yet of the relationship between the decay coefficient and salinity.

The salinity affects the DO saturation value significantly and I suspect the reaeration coefficient would not vary significantly due to salinity changes. However for detailed applications these factors must be explored further.

M. PIPER: Is diffusion a significant portion of that which you call 'mixing'?

WILLIAMS: Not in the strict sense, as longitudinal dispersion and trapping effects dominate. Here I take it you mean relatively small scale diffusion.

J. C. RUTHERFORD: In modelling an estuary the downstream boundary condition is very important. How do you specify this in the case of the Lucas Creek?

WILLIAMS: This study, to date, has included the calibration of mixing coefficients from field salinity data. Thus apart from specifying background conditions at the creek mouth (taken from field data) the boundary conditions are included. However, I concede that the tidal exchange mechanisms need to be more thoroughly investigated to tidy the boundary condition formulation.

M.E.U. TAYLOR: Dr Rutherford's question and your reply have me worried. My understanding was that one of the first objectives of the Upper Waitemata Harbour Catchment Study mathematical model would be to establish the residence times of the components of this multitributary system. Surely one of the early progress reports gave the residence time as about 10 days?

WILLIAMS: Yes that is correct using one or two of several approaches. Further resolution is required appropriate to the objectives of management interests.

G. B. McBRIDE: Could you get a situation where the evaporation of water from the estuary surface exceeds the fresh water inflow? Such a situation would then lead to a very long residence time.

WILLIAMS: This paper has not considered evaporation effects. However, it does appear that during intense dry periods this is a possibility. Considering the low summer flows (100 ℓ/s) and the large surface area of the creek, evaporation effects should be included.

W. S. WAKELIN: In your modelling of DO in Lucas Creek, what is the freshwater flow and BOD loading at the head of the creek in relation to the quantity of saline plus freshwater contained in segment 0 or 1? What evidence is there that within this segment the BOD will be mixed equally and not restricted to certain channels?

WILLIAMS: Freshwater flows in the headwater are in the range 0.1–0.4 m^3/s. Trial loadings of 20, 10, 5 g/m^3 have been used in this study. At full tide segment 0 and 1 volumes are 36,000 m^3 and 60,000 m^3 respectively. The low tide volumes are so small in this single channel creek that complete mixing is a reasonable assumption.

SESSION IX CASE HISTORIES—LAKES

Deoxygenation rates in twelve New Zealand lakes

J. C. RUTHERFORD

Hamilton Science Centre, MWD, Hamilton

The methods used to quantify oxygen depletion rates and the factors affecting DO concentrations in lakes are discussed. In an examination of data from 12 New Zealand lakes no simple relationship could be found between gross volumetric hypolimnion oxygen depletion (g/m^3 per day) or areal hypolimnion oxygen depletion (g/m^2 per day) and secchi disc clarity even when "corrections" were made for the effects of lake morphometry, in contrast to other studies in which such relationships did exist. Although in a lake "loading plots" can be used to estimate the impact of changing nutrient load on water clarity, this information cannot be extended using simple regression methods to give a reliable estimate of deoxygenation rate.

Introduction

Oxygen concentrations in lakes are important for several reasons. Firstly, they affect the types, numbers, distribution and growth rates of fish and other animals. Secondly, under anoxic conditions plant nutrients are released from the sediments and so DO concentrations can influence nutrient and algal concentrations. Thirdly, iron and manganese may be released from sediments under anoxic conditions and these affect its use for water supply.

Generally lakes with high quality are clear, have low concentrations of nutrients and algae, and are well aerated all year round, whereas lakes with low quality are turbid, have high concentrations of nutrients and algae and have a tendency to deoxygenate rapidly.

Three processes influence DO concentrations in lakes: mixing, atmospheric reaeration, and oxygen consumption. During winter most New Zealand lakes are isothermal, vertical mixing is rapid and DO concentrations are close to saturation. During summer, however, many lakes become thermally stratified: the surface layers (epilimnion) are warmed by the sun, become less dense than the bottom waters (hypolimnion) and vertical mixing is severely reduced.

The epilimnion remains in contact with the atmosphere and its DO levels usually remain high. The hypolimnion, however, often receives little replenishment of oxygen and as detritus is oxidised by bacteria, DO concentrations fall.

Quantifying oxygen depletion

The starting point for describing the oxygen status of a lake is a time-series of vertical profiles of water temperature and DO. The sampling interval needed to describe changes in DO concentration accurately varies from every 2–3 days in well mixed lakes such as Rotorua (which stratify intermittently for short periods and deoxygenate rapidly), to monthly in deep lakes such as Taupo, which stratify strongly and deoxygenate slowly.

Several parameters can be used to quantify oxygen depletion in lakes. We shall only consider parameters which describe conditions in the hypolimnion, where the most severe deoxygenation is likely to occur.

The net volumetric hypolimnion oxygen depletion rate (net VHOD in g/m^3 per day) is defined variously as the rate of change of hypolimnion oxygen concentration between the winter maximum, the onset of spring algal growth or the onset of thermal stratification (all measured when the lake is isothermal) and the minimum concentration measured in summer (or whenever the hypolimnion becomes virtually anoxic). Net VHOD measures the balance between oxygen consumption and replenishment and hence is a useful method for comparing lakes with similar mixing characteristics.

The gross volumetric hypolimnion oxygen depletion rate (gross VHOD in g/m^3 per day) is the rate of decrease of DO concentration in the hypolimnion of a stratified lake in which the water temperature has remained constant. Water temperature is a tracer which indicates when vertical mixing may have occurred and transported oxygen into the hypolimnion. In most lakes the gross VHOD exceeds the net VHOD, although in a lake with very strong stratification and hence poor vertical mixing they may be equal. One can expect the rates of oxygen replenishment to differ between lakes with different mixing characteristics. Consequently the gross VHOD appears to be a better parameter for

quantifying oxygen depletion rates than the net VHOD especially in lakes shallower than about 20 m.

Several limnologists have suggested that given two lakes with equal productivity but different depths, the deep lake should exhibit a lower volumetric oxygen depletion rate than the shallow lake, because the former has a larger volume in the hypolimnion to absorb the detritus produced in the epilimnion. This has led to the concept of areal hypolimnetic oxygen depletion rate (AHOD in g/m^{-2} per day) calculated by multiplying VHOD by the mean thickness of the hypolimnion.

Oxygen depletion and trophic state : a review

Hutchinson (1957) found that in deep, clear lakes net AHOD was proportional to the amount of organic matter (in g/m^2), but suggested that this relationship might not hold in lakes shallower than 20 m. Many limnologists took this to mean that oxygen depletion was determined solely by the rate of supply of organic matter to the hypolimnion which in turn bore a simple relationship to the biomass and productivity in the epilimnion. This led to the concept that AHOD was a useful indicator of trophic state, and several people have investigated the relationship between AHOD and other indicators of trophic state. Thus Lasenby (1975) proposed an inverse relationship between AHOD and secchi disc clarity based on a study of 14 oligotrophic and mesotrophic lakes in Ontario. This led Rast & Lee (1978) to derive a relationship between AHOD and total phosphorus concentration for thirty North American lakes and in a similar study Welch & Perkins (1979) related AHOD to phosphorus loading divided by lake flushing rate.

Data published by McColl (1972) indicates that the ranking of seven Rotorua lakes based on net VHOD agrees with the ranking based on clarity, alkalinity, chlorophyll, nutrient, iron, and manganese concentrations but the ranking based on net AHOD does not. Using data from three Rotorua lakes, Fish (1970) also found that the ranking based on net VHOD agreed with his subjective ranking but the ranking based on net AHOD did not. The finding in these New Zealand lakes that AHOD is not a good indicator of trophic state conflicts with the concepts described above. However, net VHOD and AHOD may underestimate actual oxygen consumption in a shallow lake if mixing replenishes oxygen in the hypolimnion, making a comparison between a shallow and a deep lake tenuous. Also a deep clear lake with low chlorophyll and nutrient concentrations may be equally productive on an areal basis as a turbid shallow lake with high chlorophyll and nutrient concentrations (Talling 1965) in which case Hutchinson would argue they should have comparable AHODs.

Recent work by Cornell & Rigler (1979) and Charlton (1980) indicate that AHOD depends not only on the productivity of the lake (and hence the rate of supply of organic matter to the hypolimnion) but also on the water temperature (which affects the rate of breakdown of organic matter) and the thickness of the hypolimnion. Apparently in a deep lake, organic matter is more likely to be completely oxidised before reaching the sediments and being buried.

Mitchell & Burns (1979) found that oxygen depletion rates in Lakes Hayes and Johnson (both eutrophic warm-monomictic New Zealand lakes) were highest at the onset of thermal stratification in early summer. Presumably the initial concentration of organic matter in the hypolimnion and/or the rate of supply from the epilimnion is highest at the onset of stratification.

Lake morphometry is advanced as a factor influencing oxygen depletion rates. A study in Lake Rotorua (Matthews 1979) demonstrated that the accumulation rate of sediment was very low in shallow water and increased with increasing depth. Presumably turbulence generated by currents and breaking waves prevents detritus from settling in shallow water and effectively concentrates it in the deeper part of the lake. Thus a lake with a large area of shallows may experience a higher than expected deoxygenation rate in its deeper regions.

To summarise: Oxygen depletion in the hypolimnion may occur as a result of bacterial metabolism either in the water column or in the sediments. In the water column the rate depends on the concentration of organic matter (which in turn depends on the initial concentration at the onset of stratification, the rate of loss to the sediments and the rate of replenishment from the epilimnion) and the rate of bacterial breakdown which is highly temperature dependent. In the sediments metabolic activity is often reduced by low rates of diffusion of oxygen and other compounds and especially in shallow eutrophic lakes a considerable amount of organic matter may be buried and hence not exert an oxygen demand on the overlying waters.

Oxygen depletion in some NZ lakes

Methods

Vertical profiles of temperature and DO were collated for 12 New Zealand lakes (refer to Fig. 2 for sources of data) and gross oxygen depletion rates calculated as follows: The data were scanned for pairs of profiles satisfying the following criteria:

(i) the lake was stratified on the earlier sampling date;
(ii) the average temperature in the hypolimnion did not differ by more than 0.20 °C between sampling dates;
(iii) the average DO concentration exceeded zero on each sampling date;
(iv) where DO concentration gradients were steep, only DO values at depths sampled on each date were used to calculate the hypolimnion average DO.

Gross VHOD was calculated as the difference in mean DO concentration divided by the time interval and the gross AHOD by multiplying VHOD by the mean thickness of the hypolimnion (i.e., the volume below the average depth of maximum temperature gradient divided by the area at the depth of

maximum temperature gradient) (see Fig. 1). Where several estimates of VHOD and AHOD were obtained for any lake the arithmetic average was calculated.

A new method was developed to correct AHOD estimates for the influence of lake morphometry, based on the observed dependence of settling rate on depth (Matthews 1979). The method is described in Appendix 1.

The only determinand available for all of the lakes which provided a measure of lake trophic status was secchi disc depth. This may not be a severe restriction in view of overseas experience which indicates that determinands such as nutrient and chlorophyll concentrations are closely correlated with secchi disc depth over a wide range of lake types.

Water clarity is known to vary inversely with algal concentration. As a first approximation it may be assumed that

$$SD \propto \frac{1}{C} \quad (1)$$

where SD = secchi disc clarity (m) and C = algal biomass concentration (g/m³). Rearranging and multiplying both sides by the mean depth gives an estimate of biomass

$$A \propto \frac{d}{SD} \quad (2)$$

where A = biomass (g/m²) and d = mean depth (m). Thus the ratio $\frac{d}{SD}$ provides a crude estimate of the amount of organic matter in the hypolimnion at the onset of stratification and possibly also of the rate of supply of organic matter to the hypolimnion later in the year.

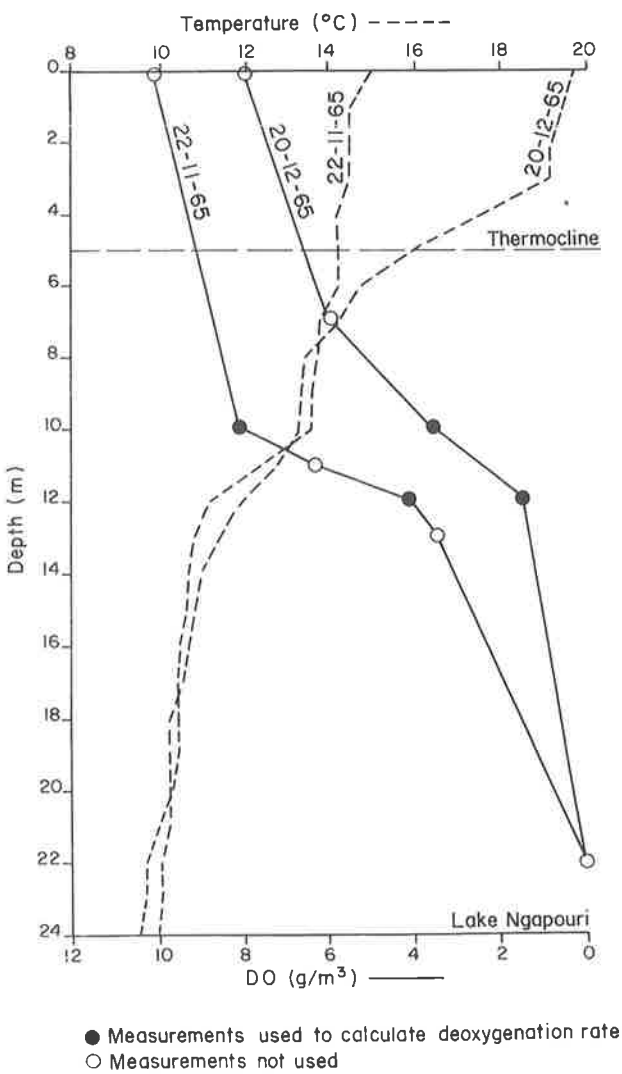

Fig. 1 Example of data used to estimate hypolimnion deoxygenation rate.

Results and discussion

The estimates of gross VHOD and AHOD obtained have a high uncertainty (guessed to be ± 50% of the mean) which arises because:

(i) usually no more than 2 or 3 DO measurements were made in the hypolimnion on any sampling date;
(ii) the thickness of the hypolimnion usually changed between sampling dates;
(iii) the thermocline is often difficult to locate objectively;
(iv) with the resources available it was not feasible to calculate average hypolimnion DO concentrations weighted in proportion to the volume of the lake at the depth of sampling as is recommended (Lasenby 1975);
(v) the available data were too sparse to allow depletion rates to be estimated by regressing hypolimnion DO concentrations against time as is recommended (Lasenby 1975).

Within each lake there was considerable variability in gross VHOD and AHOD. The standard deviation averaged 40% of the mean and ranged between 10 and 80%. No pattern in the variation could be discerned such as that seen by Mitchell & Burns (1979) in Lakes Hayes and Johnson where deoxygenation rates were highest immediately after the onset of stratification.

The variance of secchi disc depth in each lake averaged about 20% of the mean.

Figure 2 indicates that there is a weak inverse correlation between gross VHOD and secchi disc clarity. Lake Rotorua has a surprisingly high rate of deoxygenation when compared to lakes of similar clarity. Two factors may account for this difference. Firstly, Rotorua stratifies intermittently for short periods of time whereas the other lakes remain stratified for several months during summer. This favours an algal population dominated by diatoms which sink rapidly when the lake stratifies and also appears to favour a high productivity (Talling 1965; Fee 1980). Secondly, Rotorua has a summer hypolimnion temperature of 18–21 °C compared with 6–13 °C in the other lakes. Thus bacterial respiration rates may be twice as high in Rotorua as in the other lakes.

Figure 3 indicates the presence of only a very weak inverse correlation between gross AHOD and secchi disc clarity. The lakes with low clarity have highly variable deoxygenation rates. When the "correction" is made for lake morphometry the variability of AHOD is decreased markedly but the correlation with clarity is not noticeably improved.

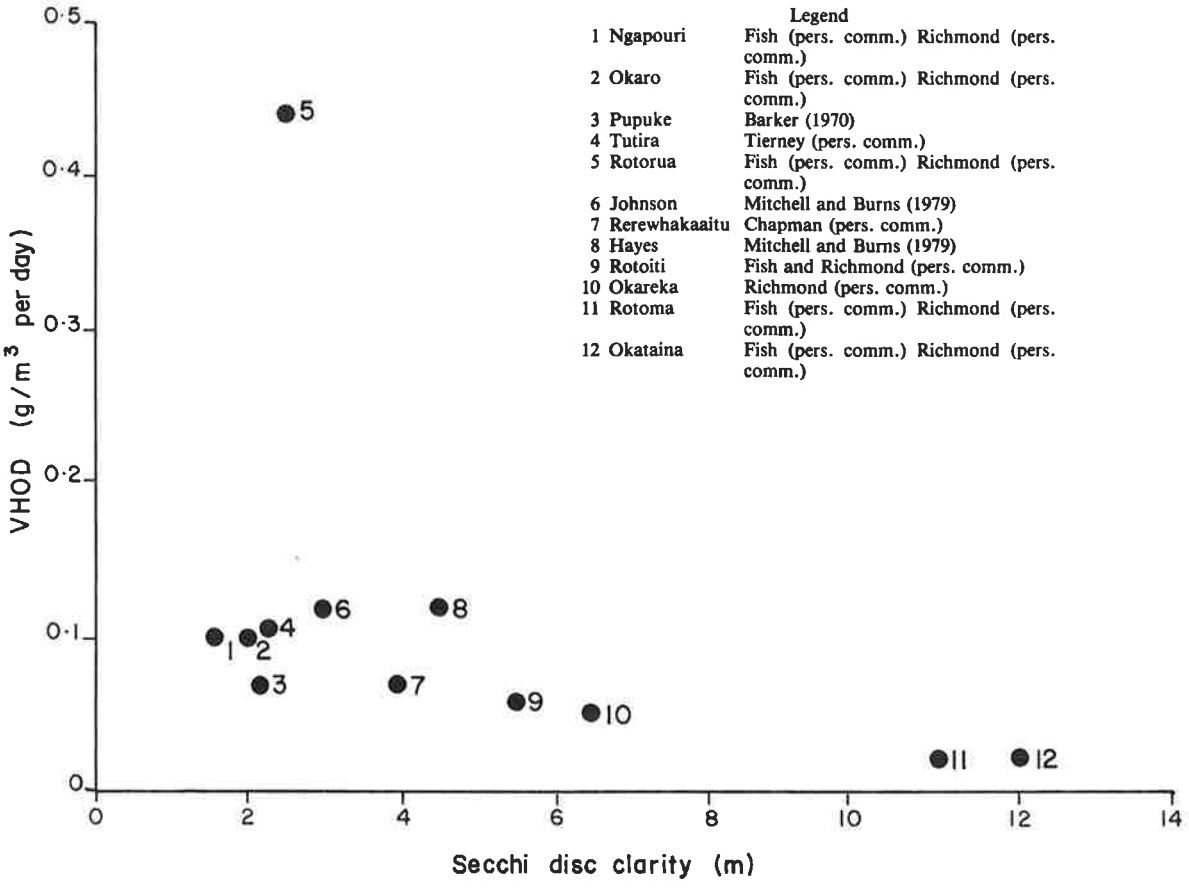

Fig. 2 Gross VHOD versus Secchi disc clarity.

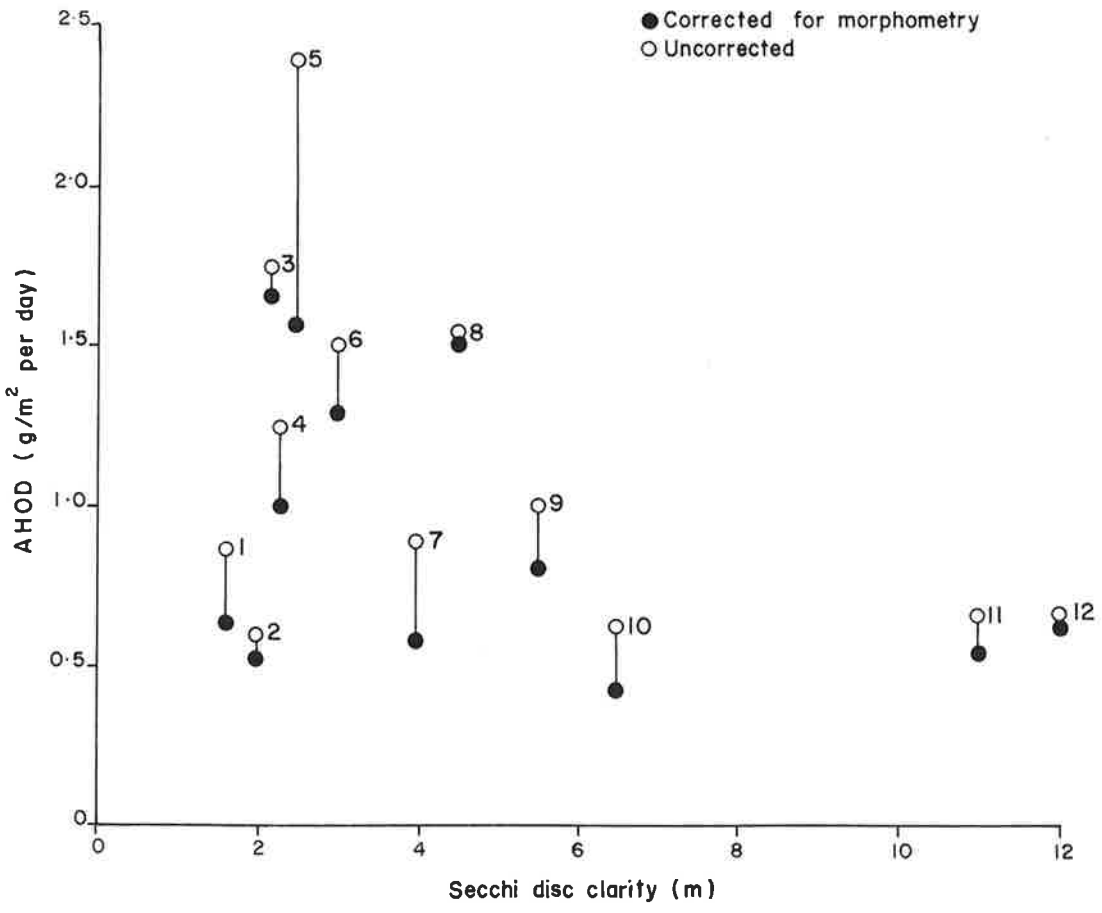

Fig. 3 Gross AHOD versus Secchi disc clarity (for legend see Fig. 2).

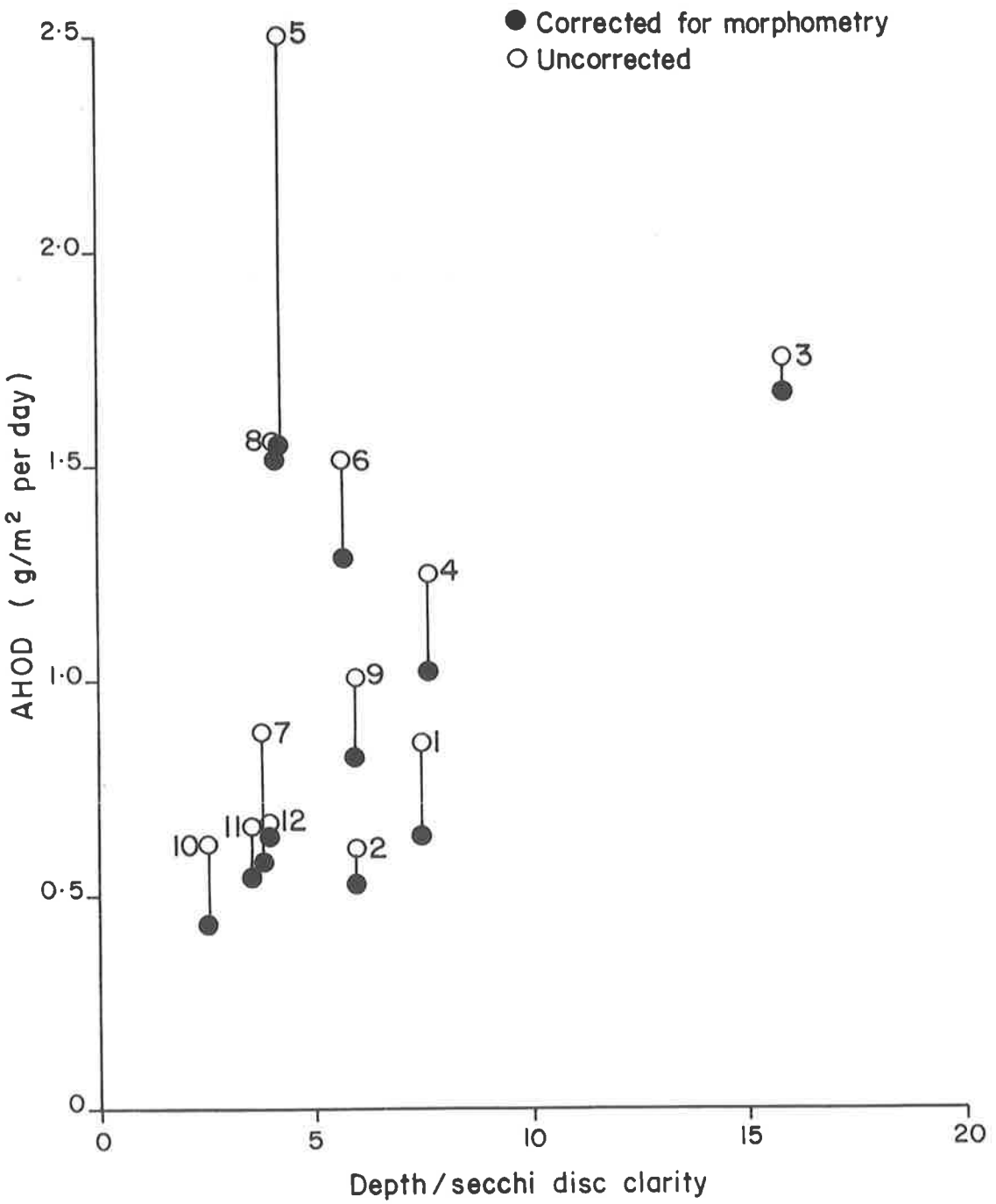

Fig. 4 Gross AHOD versus depth/Secchi disc clarity (for legend see Fig. 2).

Figure 4 indicates a weak positive correlation between gross AHOD (both "raw" and "corrected") and the ratio of depth to secchi disc clarity (an indicator of productivity as discussed above). The variability between lakes of similar estimated productivity is still quite high.

The implications of these findings for management are as follows. In lakes where few data are available, "loading plots" can be used to estimate the impact of changing nutrient load on the concentrations of nutrient and chlorophyll, and secchi disc clarity (Rast & Lee 1978). Such plots appear to give fairly accurate predictions over a wide range of lakes. This study indicates, however, that predictions of secchi disc clarity cannot be extended using simple regression techniques to give a reliable estimate of deoxygenation rate over a wide range of lakes.

In a particular lake where extensive data are available it may be possible to establish simple relationships between nutrient load, nutrient concentration, secchi disc clarity and deoxygenation rate.

Future effort at predicting deoxygenation rates should be based on measurements of rates of production in the epilimnion, the rates of sinking of seston into the hypolimnion, the rates of breakdown of organic matter in the hypolimnion and sediments, and mixing between the epilimnion and hypolimnion.

Conclusions

There is not a simple quantitative relationship between the deoxygenation rate expressed either in volumetric or areal terms and secchi disc clarity in the data presented here for 12 New Zealand lakes.

Nutrient "loading plots" and simple linear regression relationships between deoxygenation rate and clarity are unlikely to give reliable predictions of deoxygenation rates over a wide range of lakes.

Acknowledgements

G. R. Fish, C. J. Richmond, L. Tierney, and M. A. Chapman kindly made available unpublished data. R. H. S. McColl made valuable comments on the relationship between deoxygenation rate and trophic state. R. D. Pridmore and C. W. Hickey commented on several aspects of the problem. W. Vant and R. A. Hoare suggested changes to the manuscript.

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Appendix

The effect of lake morphometry on oxygen depletion

Assume that trophic state is determined by

$$\frac{F_t}{A_t} \tag{1}$$

where F_t = total detritus sedimentation, g/d; and A_t = lake surface area, m². Also assume that

$$V_h O_h \propto F_h \tag{2}$$

where F_h = detritus sedimentation into the hypolimnion, g/d; V_h = hypolimnion volume; and O_h = oxygen depletion rate in the hypolimnion, g/m³ per day. Now

$$F_t = \iint_{A_t} CUdA \tag{3}$$

$$F_h = \iint_{A_h} CUdA \tag{4}$$

where C = detritus concentration in the epilimnion, g/m³; U = net sedimentation velocity, m/d; and A_h = area at the depth of the thermocline.

From (2)

$$V_h O_h \propto F_t \frac{A_h}{\iint_{A_t} CUdA} \tag{5}$$

whence

$$\frac{F_t}{A_t} \propto \frac{V_h O_h}{A_t} \frac{A_t}{\iint_{A_h} DUdA} \tag{6}$$

Compare the RHS with

$$\frac{V_h O_h}{A_h} \tag{7}$$

which is the AHOD in g/m² per day suggested by Hutchinson (1957) as an indicator of trophic state.

Equation (1) can be simplified if C is assumed constant (i.e. the epilimnion is well mixed) and if U and A are known as functions of depth.

$$\frac{F_t}{A_t} \propto \frac{V_h O_h}{A_t} \frac{\int_o^h u(y) \frac{\partial A}{\partial y} dy}{\int_o^t u(y) \frac{\partial A}{\partial y} dy} \tag{8}$$

where u(y) = net sedimentation velocity in a part of the lake whose depth is y; $\frac{\partial A}{\partial y}$ is the rate of change of lake surface area with depth at depth y; h = total depth; and t = depth of the thermocline both measured upwards from the maximum depth.

The integrals in equation (8) can be evaluated numerically or the lake bathymetry and sinking rate simplified so that they can be evaluated analytically. For the 12 New Zealand lakes studied here numerical methods were employed.

Matthews' (1979) data on sedimentation rate in Lake Rotorua were used to estimate the net sedimentation velocity/depth relationship shown in Fig. 5 assuming an average detritus concentration of between 0.5 and 1.0 g/m³.

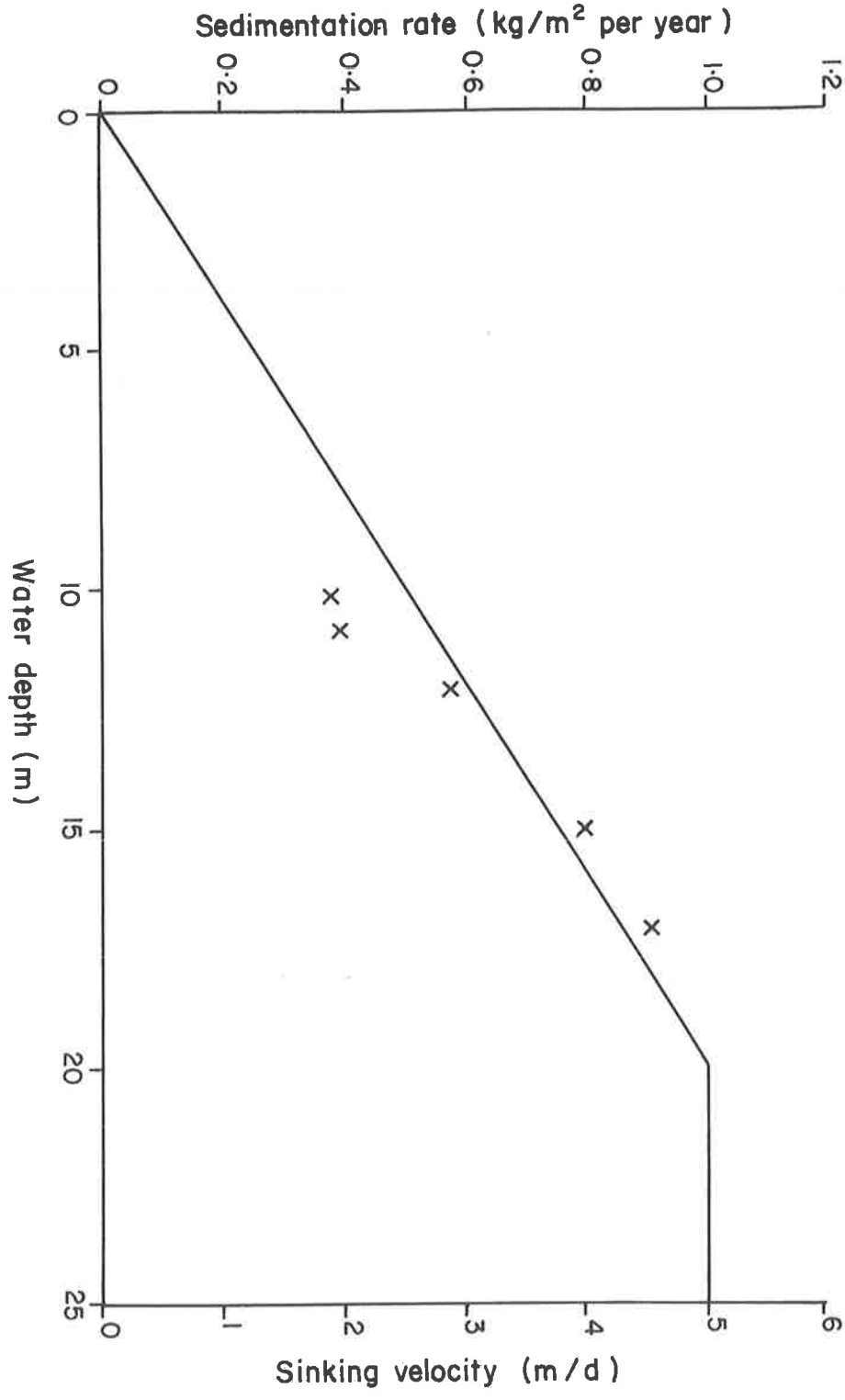

Fig. 5 Effect of water depth on net detritus sedimentation rate. (Sedimentation rate after Matthews (1979); Derived sinking rate (see Appendix)).

DISCUSSION FOR SESSION IX

Deoxygenation in twelve New Zealand lakes

Presented by: J. C. RUTHERFORD

C. RICHMOND: Have you attempted to apply Lasenby's depth weighted corrections to the depletion rates calculated?

RUTHERFORD: No.

C. RICHMOND: Given that bathymetric information is available for all the lakes mentioned I also think that use of Lasenby's depth weighted corrections would improve the relationship.

RUTHERFORD: I agree, Lasenby's method sounds attractive but it is not immediately apparent to me that this refinement would make a dramatic improvement. I also wonder whether in view of the shortcomings of the available data the refinement is justifiable in this case.

C. RICHMOND: A comment. You mentioned in your paper that you have made no correction for temperature. I think that if you did there would be a closer relationship between secchi disc clarity and DO depletion rate.

Epilogue

At the close of this Seminar a written set of six items was put to participants, for which written responses were sought on whether the existing information is adequate for management and whether research is headed in appropriate directions. Eleven responses were received. These items, and a short summary of responses, were:

Development of DO Criteria for Natural Waters. Several expressed the view that little information is available for, and more research is desirable on, the DO requirements of native fishes and invertebrates.

Ease and Precision of DO Measurement. This was considered satisfactory.

Measurement of Biologically Assimilable Material and Characterisation of Wastes. There was some thought that existing information is not yet adequate, but that research was starting to look promising.

Development of Measurement Techniques which Model the Rates of Natural Oxygen Uptake Processes. A comment was that information available for rivers was just adequate, but that there exists a big gap for lakes. Research seemed to be considered appropriate.

Development of Mathematical Modelling Techniques.

(a) Choice of Model Considerable comment was received on this point, including:

- DO models are generally useful, especially where there are, or are foreseen to be, DO depletion problems due to specific inputs of organic material;
- more information is needed on the choice of model for lakes, estuaries and coasts;
- specialist guidance is still needed, but models to be used by regional water boards should be as simple as possible;
- there should be DO models for supersaturation and loss of excess oxygen, river impoundment by hydro-electric installations, and river regime modification by channelisation.

(b) Verification of Model This seems to have been considered to be well covered.

(c) Measurement of Coefficients needed for Model Existing information on methods for prediction of coefficients, especially for situations presently unaffected by inputs of organic material, was considered inadequate in several responses.

Any Other Matters. A proposed handbook by Centre staff, of simple methods of prediction of river DO was welcomed in several responses. Another urged that more consideration be given to the effect of land management practices on water quality in general. Generally the Seminar appeared to have been well received.

In comments made during and after the Seminar it appears that the original objectives of assessing the state-of-the-art and examining appropriate directions for future research was quite well attained. Thanks are due to participants who all helped make the Seminar a success, especially to authors of the papers and to participants who responded to the questionnaire.

G. B. McBride
Seminar Organiser.

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Name	Affiliation*
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*Abbreviations

ARA — Auckland Regional Authority
DSIR — Department of Scientific & Industrial Research
MAF — Ministry of Agriculture & Fisheries
MIRINZ — Meat Industry Research Institute of New Zealand (Inc.)
MWD — Ministry of Works & Development
NZDRI — New Zealand Dairy Research Institute
WVA — Waikato Valley Authority

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