# Environmental Quality Standards for Dissolved Oxygen

**WRc** plc

R&D Note 130

# ENVIRONMENTAL QUALITY STANDARDS FOR DISSOLVED OXYGEN

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This report is the result of work jointly funded by the national Rivers Authority and the Scotland and Northern Ireland Forum for Environmental Research.

# Dissemination status

Internal: Released to Regions

External: Restricted

#### Research contractor

This document was produced under R&D Contract 053 by:

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Tel: 0491 571531 Fax: 0491 579094

WRc Report Nº NR 24 15/1/4226

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The NRA's Project Leader for R&D Contract 053:

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ENVIRONMENTAL QUALITY STANDARDS FOR DISSOLVED OXYGEN

M J Stiff, N G Cartwright and R I Crane

#### SUMMARY

This report proposes environmental quality standards for dissolved exygen (DO) for the protection of the different uses of water. The standards have been derived from Laboratory and field data on the effects of deficiencies of dicsolved exygen in aquatic organisms taking into account its environmental chemistry. The standards proposed by other regulatory and advisory agencies are included in the report for reference. The standards proposed are given in Table 1 and the justification for the standards is provided in Section 4. Whereas the standards suggested for the different freshwater uses are based on a relatively large database, inadequate data are available for the derivation of separate standards for the protection of estuarine life.

The current standard analytical methods for dissolved oxygen are adequate in terms of sensitivity and limits of detection for monitoring compliance with the EQSs.

Report No PRS 2415-M, Apri! 1990 58 Pages, 7 Tables, 3 Appendices Project reference: 7.2.1a

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#### SECTION 1 - INTRODUCTION

Oxygen is essential for all life and although abnormally high levels can be harmful it is usually a deficiency of oxygen which gives rise to environmental problems. Thus oxygen is different from environmental contaminants in that Environmental Quality Standards (EQSS) will usually be concerned with minimum levels to be maintained and not maximum allowable levels.

This report examines the properties of oxygen, its behaviour in the environment, and the oxygen requirements of aquatic biota. Based on the data presented EQSs are suggested in Table 1.

SECTION 2 -OXYGEN IN THE ENVIRONMENT

#### 2.1 GENERAL CHEMISTRY

On the Earth oxygen forms about 21% by volume (23% by weight,  $1.1 \times 10^{18}$  kg) of the atmosphere, about 45% by weight of the rocks of the crust and 89% of water. In the atmosphere oxygen is mainly present as free molecules but in rocks and water it is mainly combined with other elements.

There are three natural isotopes of oxygen,  $^{160}$  (99.76%),  $^{170}$  (0.04%) and  $^{180}$  (0.20%).

The naturally stable form of pure oxygen is the diatomic molecule,  $0_2$ , which is a colourless gas with a boiling point of -182.96 °C at normal atmospheric pressure. In the upper atmosphere, at  $25\pm10$  km height, the triatomic molecular form (allotrope) ozone is present at up to 10 ppm but it also occurs in the lower atmosphere, particularly as a component of photochemical smogs. Ozone is thermodynamically unstable and reacts with many other components of the atmosphere which gives it an importance in atmospheric chemistry at both high and low altitudes.

Table 1 - Recommendations for EQSs for dissolved oxygen

Water 1	Use (See Note 1)	EQS	Units	Status	Notes
FRESHWA	TERS				
ai	Direct abstraction to potable supply Al treatment A2 treatment A3 treatment	7 0 5 0 3 0	% satn % satn % Satn	90P,G 90P,G 90P,g	
aii	Abstraction to a reservoir	-	-	-	
aiii	Food for human consumption		-	-	
aiv	Protection of freshwater life				
	- designated salmonid fisheries	9 9 7	mg/l mg/l mg/l	50P,I 50P,G MIN, G	
	<ul> <li>sensitive aquatic life (eg salmonids)</li> </ul>	9 5	mg/l mg/l	50P 95P	
	- designated cyprinid fisheries	7 8 5	mg/l mg/l mg/l	50P,I 50P,G MIN,G	
	<ul> <li>less sensitive aquatic life (eg cyprinids)</li> </ul>	5 2	mg/l mg/l	50P 95P	
av	Agricultural uses				
	<ul><li>irrigation of crops</li><li>livestock watering</li></ul>	-	-	<u>-</u>	
avi	Industrial uses		-	-	
SALINE	WATERS				
bi	Food for human consumption	-	-	-	
bii,	Protection of saltwater life				
biii	- designated shellfisheries	7 <b>60</b> 80	% satn % satn % satn	50P,I MIN, I 95P,G	

Table1 - continued

Water Use (See Note 1)	EQS	Units	Status	Notes
- saltwater life	5 2	mg/l mg/l	50P 95P	1 0 1 0
<ul> <li>sensitive saltwater life (eg fish nursery grounds)</li> </ul>	9 5	mg/l mg/l	50P 95P	1 0 1 0
- migratory fishery	5 3	mg/l mg/l	50P 95P	1 1 11
FRESH AND SALINE WATERS				
aix, Bathing and water contact sport	80-120	% satn	50P,G	12
ax, bvi Aesthetic acceptability	10	mg/l	95P	13

#### Notes

indicates insufficient data available for deriving a standard or a standard for this use, or a standard is not appropriate for this use

- indicates a guideline value in an EC Directive G
- Ι indicates a mandatory value in an EC Directive
- percentile
- concentration MIN minimum
- the numbering of each water use follows the system used in Gardiner and Mance (1984) EC Surface Water Directive (CEC 1975)
- 2
- see Section 4.2 3
- see Section 4.3
- EC Freshwater Fish Directive (CEC 1978; see Section 4.4.1) 5
- early life stages or particularly sensitive species may require higher DO levels (see Sections 4.4.1 and 4.4.2) 6
- see Section 4.7
- see Section 4.8
- EC Shellfish Water Directive (CEC 1979)
- see Section 4.5.2 10
- higher values may be required where fish have to traverse distances >10 km, or where high quality migratory fisheries are to be maintained 11 (see Section 4.5.1)
- EC Bathing Water Directive (CEC 1976) see Section 4.6 12
- 13

In the aquatic environment oxygen is present as dissolved, molecular oxygen (DO), as part of the water molecule and in various dissolved anions such as carbonate, nitrate, sulphate and phosphate. Some micro-organisms, such as anaerobic bacteria use these anions as their source of oxygen and some, the obligate anaerobes, may actually be poisoned by dissolved oxygen. However, most aquatic organisms are entirely dependent on molecular oxygen either dissolved in the water or obtained directly from the atmosphere.

The equilibrium, which exists between dissolved oxygen in water and the gas in the atmosphere, can be described by Henry's Law.

$$P = kX$$

where: P = partial pressure of oxygen in the atmosphere X = mole fraction of oxygen in water in equilibrium with airand k = Henry's Law constant for oxygen in water (in units of pressure) (4.75  $\times$  104 atm at 30 °C)

At low concentrations the moie fraction is directly related to the concentration and the Henry's Law relationship can therefore be expressed as (Sukatsch and Dziengel 1984).

$$c = P/H$$

where : c = saturation concentration of oxygen in water and H = Henry's Law constant expressed on a concentration basis (in units of pressure-volume/mass) (0.86 atm  $m^3/mol$  at 25 °C)

The value of the constant varies with temperature and with ionic strength (salt content, and thus salinity). Thus the solubility of oxygen decreases both with increasing temperature and with increasing salinity. The temperature and salinity dependence of oxygen solubility is discussed more fully in Section 2.4.2. Supersaturation of water with oxygen can occur, for instance in waters with high algal activity.

The terms "oxygen" and "dissolved oxygen" (DO) in this report refer to molecular oxygen,  $\circ_2$ .

#### 2.2 SOURCES AND SINKS

The atmosphere is the main reservoir of oxygen in the environment. Photosynthesis in plants using light and the catalyst chlorophyll to form new plant tissue from atmospheric carbon dioxide and water is the principal subsidiary source of oxygen and has the other vital function of maintaining the oxygen/carbon dioxide balance.

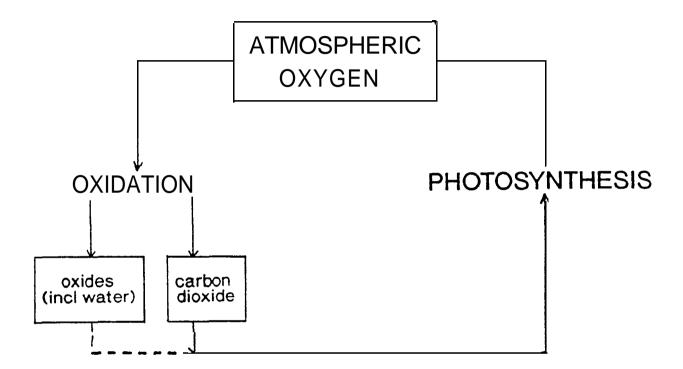
$$nCO_2$$
 t  $nH_2O \rightarrow (CHOH)$ , +  $nO_2$ 

The electrolysis of water as an industrial process contributes an insignificant quantity of oxygen to the environment.

The main input of oxygen to a river or lake is by "re-aeration" by diffusion of oxygen across the air-water interface. In an estuary the DO level will vary with the state of the tide. Water from the open sea can be expected to be well oxygenated, whereas the freshwater river inputs may be depleted by biological activity. In addition any biochemical oxygen demand (BOD) will have a greater effect at low tide because of the smaller volume of water. For example, the range of dissolved oxygen in the Yorkshire River Ouse in a tidal stretch at Blacktoft has been measured at 5 to 10% saturation at low tide and 65 to 75% saturation at the following high tide (data provided by NRA Yorkshire Region) .

Oxygen is consumed by a variety of natural and artificial processes all of which are oxidation processes including:

combustion other chemical oxidations biological oxidation respiration The oxygen cycle comprises depletion by oxidative processes and generation by photosynthesis.



# 2.3 ANALYSIS

# 2.3.1 Analytical requirements for EQS monitoring

WRC recommends (Gardiner and Wilson 1976, Cheeseman and Wilson 1076) the following accuracy requirements for the selection of an analytical method to monitor a quality standard of X concentration units:

- i) Bias of analytical results should not exceed X/20 or 10% of the measured value, whichever is the greater.
- ii) The total standard deviation of individual analytical results should not exceed X/40 or 5% of the measured value, whichever is greater

In summary, these requirements imply a target limit of detection of X/10. For example, this would mean that for a proposed EQS value of 1 mg/l, the detection limit should not exceed 0.1 mg/l, the total standard deviation of individual results should not exceed 0.025 mg/l or 5% (whichever is the greater) and the bias should not exceed 0.05 mg/l or 10% (whichever is the greater).

#### 2.3.2 Analytical techniques

Dissolved oxygen can be determined by chemical methods or electrometrically using oxygen electrodes. UK and other national and international standard methods make use of both kinds (DoE/NWC 1980, APHA-AWWA-WPCF 1985).

#### i) Chemical methods

The cormnoniy used method is that devised by Winkler after whom it is named. A number of modifications to the basic method have been devised which are applied according to the type of water being analysed and the interferences expected.

The method (DoE 1988) consists of the addition of manganese (II) sulphate solution to the test water immediately followed by the addition of strong alkaii. Manganese (II) hydroxide is precipitated and the oxygen present in the water rapidly oxidises an equivalent amount of the precipitated manganese (II) to higher oxidation states. Addition of iodide and acidification results in turn in the oxidation of iodide to iodine which is then determined by titration with a standard solution of thiosulphate using starch solution as indicator. The sequence of reactions can be represented, in a simplified form, by the following equations:

$$Mn^{2+} + 2 OH_{-} = Mn (OH)_{2}$$
 $O_{2} + 4 Mn (OH)_{2} = 4 MnO (OH) + 2 H_{2}O$ 
 $4 MnO (OH) + 1 I_{-} + 12 H_{+} = 2 I_{2} + 4 Mn^{2+} + 1 8 H_{2}O$ 

Thus one molecule of oxygen gives rise to two molecules of iodine.

Modifications to the method include:

- a) the azide modification which is applied to remove interference by nitrite which is the most common interference in, for example, waters subject to contamination by sewage effluents and biological activity
- b) the permanganate modification if ferrous iron salts are present
- c) the alum flocculation modification if high concentrations of suspended solids are present
- d) the copper sulphate-sulphamic acid flocculation modification if biological flocs such as activated sludge which have high oxygen uptake rates are present.

The azide modification is used almost universally for the analysis of surface waters. The reagent is a strong alkaline solution of sodium azide and sodium or potassium iodide. It provides the alkali for manganese precipitation and the iodide for the final iodine generation as well as azide which reduces nitrite to generate nitrous oxide and nitrogen. If not removed nitrite would interfere with the analysis by oxidising iodide to iodine and catalysing the reaction between iodide and atmospheric oxygen during the titration.

The required volumes of the manganese and iodide reagents are added carefully to the water under test in a glass bottle fitted with a ground glass stopper and filled to capacity. The stopper is replaced immediately ensuring that the bottle remains full without any free air-space. The contents of the bottle are completely mixed by repeated inversion of the bottle. The oxygen/manganese sulphate reaction effectively fixes the dissolved oxygen present enabling the acidification/iodometric titration step to be carried out at any time when convenient.

#### ii) Electrometric methods

The earliest electrometric DC determinations were performed by a polarographic method using the streaming mercury electrode or the rotating platinum electrode (DSIR 1959). The technique was difficult to use and was subject to considerable interference particularly by polluted waters and was fairly rapidly overtaken by the introduction of membrane electrodes (DSIR 1964).

In methods utilising membrane electrodes dissolved oxygen is determined directly. The DO electrode consists of two solid metal electrodes immersed in an electrolyte solution which is separated from the water under test by a plastic membrane, either polyethylene or PTFE, which is impervious to water but permeable to oxygen gas. Oxygen diffuses across the membrane barrier into the liquid electrolyte and is reduced at the cathode of the electrochemical cell.

Two variants of the DO probe are available, the polarographic and the galvanic.

Polarographic electrodes, eg the Clark electrode, consist of an inert metal (platinum or gold) cathode and a silver/silver chloride reference electrode as anode. The electrolyte is normally a potassium chloride solution. An electrical potential difference is maintained between the cathode and reference electrode such that oxygen is reduced at the cathode and this reaction produces a current. The magnitude of the current is limited by the rate of mass transfer of oxygen to the cathode and is in turn proportional to the concentration of oxygen in the water under test. The reactions are represented by the following equations:

cathode 
$$O_2 + 2 H_2O t 4e = 4 OH^-$$
 anode (silver)  $4 Ag i - 4 Cl = 4 AgCl t 4e$  overall  $O_2 t 4 Ag + 4 Cl + 2 H_2O = 4 AgCl t 4 OH^-$ 

Galvanic electrodes, eg the Mackereth electrode, consist of a perforated cylindrical silver cathode surrounding a lead anode immersed in an alkaline electrolyte, typically potassium hydroxide, which may be saturated with potassium hydrogen carbonate to eliminate any interference from carbon dioxide. Oxygen diffusing across the electrode membrane is reduced at the silver cathode and produces a current which, as in the polarographic method, is proportional to the DO concentration in the water under test. The reactions can be represented by the following equations:

```
cathode O_2 t 2 H<sub>2</sub>O t 4e = 4 OH<sup>-</sup> anode (lead) 2 Pb t 6 OH<sup>-</sup> = 2 PbO (OH) - + 2 H<sub>2</sub>O + 4e overall O_2 + 2 Pb + 2 OH<sup>-</sup> = 2 PbO (OH) -
```

Both types of electrode use up the oxygen in the water. Therefore for a steady reading to be obtained water must be kept flowing over the membrane of the electrode.

Both types of electrode have to be calibrated before use and this is usually done in terms of 100% and 0% DO saturation. solution can be prepared by bubbling air through clean water, giving an electrode response equivalent to 100% saturation. solution can be prepared by the addition of a reducing agent to clean water, which chemically reacts with any DO present. sulphite or metabisulphite are commonly used. The addition of an excess amount of reducing agent ensures that no re-oxygenation takes place during the subsequent measurement which is equivalent to the 0% saturation value. Commercial DO meters have provision for calibration at 0 and 100% saturation. Calibration should be carried out with the calibrant solutions at the same temperature as the body of water under test so that the saturation values are equivalent. Electrodes are available with built-in temperature compensation. Calibration in terms of concentration units is carried out with solutions whose DOs are also determined by the iodometric method. Calibration in the field can be carried out retrospectively with the addition of the manganese sulphate and alkaline-azide reagents to

fix the DO on the spot allowing acidification and the final titrimetric step to be performed in a laboratory when convenient.

Atmospheric oxygen can be determined using chemically modified field effect transistors (chemfets). These are solid state devices and in the case of oxygen the sensor is a modification of a fuel cell. However, these devices do not yet appear to be adaptable to the aqueous environment.

2.3.3 Sensitivity and limits of detection

The titrimetric method is capable of discriminating 0.1 to 0.4 mg/l and has been shown to have a limit of detection of 0.38 to 0.46 mg/l (DoE/NWC 1980). The electrode method has a sensitivity (1% full scale deflection) of 0.1 mg/l and has been shown to have a limit of detection of 0.25 to 0.43 mg/l. With both techniques, the precision is better than 0.1 mg/l even at DO levels of less than 0.5 mg/l.

- 2.4 ENVIRONMENTAL AND AQUEOUS CHEMISTRY
- 2.4.1 Expression of oxygen concentration

There are several ways of expressing the concentration of oxygen in water:

mass per unit volume  $\,$  eg 5 milligrams per iitre (mg/l) per cent saturation or per cent air saturation value eg 10% saturation (% ASV or %)

partial pressure or oxygen tension, p02 eg 76 mm Hg (0.1 atm.)

Mass per unit volume has the advantage of being a measure of the actual amount of oxygen available to the aquatic biota.

Expression as per cent saturation has the inherent disadvantage of being equivalent to different amounts of oxygen depending on temperature and salinity and, strictly, on atmospheric pressure because the saturation

concentration varies with these parameters. Measuring instruments have to be precalibrated and it is important to ensure that the calibrant solutions are at the same temperature and of the same salinity as the medium under test. Expression as partial pressure is virtually equivalent to per cent saturation and has the same disadvantages of temperature, salinity and atmospheric pressure dependence. Water saturated with oxygen under normal atmospheric conditions will have a  $p0_2$  of 0.21 atm.

# 2.4.2 Environmental oxygen equilibrium

The oxygen in the atmosphere and the dissolved oxygen in water exist in a state of dynamic equilibrium. There is a continuous interchange between the two phases across the phase boundary, the surface of the water. At steady state, with water and the atmosphere in equilibrium with regard to oxygen concentration, water is 100% saturated. Any departure from the equilibrium concentration gradient across the two phases will result in a net flow of oxygen across the phase boundary and the rate of transfer will be a function of that concentration gradient. Since, as a first approximation, the concentration of oxygen in the atmosphere can be taken to be constant, the most common effect is transfer of oxygen from the atmosphere to water if the water becomes depleted of oxygen because of the occurrence of oxygen-consuming processes.

The value of Henry's Law constant increases with temperature, from 2.55 x 10<sup>4</sup> atmosphere at 0 °C to 4.75 x 10<sup>4</sup> at 30 °C (Perry and Green 1984). However, the published values for the Henry's Law constant for the same conditions differ and this may account for the slight differences in reported dissolved oxygen solubilities. Table 2 gives a selection of DO saturation concentrations at different temperatures and salinities, based on data published by UNESCO, which are considered to be the best available (DOE 1988) .

Table 2  $\rightarrow$  Effect of temperature and salinity on saturated dissolved oxygen concentration (mq/1)

Temp °C	0	Salinit <sup>5</sup>	y (gram 10	s NaCl 15	per kiloo 20	gram wat 25	er) 30	35
0	14.6	14.2	13.7	13.3	12.9	12.4	12.0	11.5
5	12.8	12.4	12.0	11.7	11.3	10.9	10.5	10.2
10	11.3	11.0	10.7	10.3	10.0	9.7	9.4	9.0
15	10.1	9.8	9.5	9.3	9.0	8.7	8.4	8.2
20	9.1	8.9	8.6	8.4	8.1	7.9	7.6	7.4
25	8.3	8.0	7.8	7.6	7.4	7.2	7.0	6.8
30	7.6	7.4	7.2	7.0	6.8	6.6	6.4	6.2

The solubility of oxygen decreases as the concentration of dissolved salts increases. Sodium ions in particular are solvated in solution, each ion being surrounded by a shell of water molecules. This can then be regarded as reducing the effective amount of water present and accounts for the reduced solubility. In hard freshwaters the dominant cation is usually calcium which is solvated to a lesser degree than sodium. The solubility/salt content relationship will thus be different from that in seawater and data in DO/salinity tables are therefore not strictly applicable. However, most freshwaters have a mineral content of less than C.5 g/l and the difference between the solubility of oxygen in such waters and that in pure water is negligible.

The equilibrium concentration varies with changes in atmospheric pressure, but for the purposes of this report, the magnitude of these variations can be regarded as negligible.

2.4.3 Transfer of oxygen to and from the aquatic environment; re-aeration

Transfer of oxygen from the atmosphere to water occurs by diffusion. A body of water at rest can be regarded as being divided into a series of horizontal diffusion layers. Diffusion takes place across the air-water

interface and from layer to layer, through concentration gradients from high to low concentration.

Re-equilibration following any change in oxygen concentration or water condition (eg temperature) is limited by the rates of diffusion and the concentration gradients across the diffusion layers. The flux of oxygen is also a function of diffusion surface area which can be increased by surface agitation eg by wind, by flow over a waterfall, weir or stones, or by bubble aeration.

The rate of re-aeration by diffusion is directly proportional to the oxygen deficit, the difference between the saturation concentration and the instantaneous DO concentration, and can be expressed by the equation (APHA-AWWA-WPCF 1985)

$$dD/dt = -kaD/V$$

where : D = DO deficit concentration,

a = interfacial area,

V = volume of water

and k =the mass transfer coefficient

#### 2.4.4 Abiotic chemical reactions

Although oxidation reactions are common, eg combustion and corrosion, they usually take place only slowly at ambient temperature. One reaction which is fast enough to deplete DO in natural waters is the oxidation of ferrous iron  $(Fe^{2+})$  to ferric iron  $(Fe^{3+})$ .

$$2 \text{ Fe}^{2+} \text{ t } \frac{1}{2} 0_2 + 2 \text{ H}^+ \rightarrow 2 \text{ Fe}^{3+} + \text{H}_2 0 \qquad \text{E}^\circ = 0.46 \text{V}$$

Iron present in groundwaters is usually in the ferrous state as these waters tend to be de-oxygenated. Where groundwater infiltrates surface waters re-oxygenation of the water occurs and ferrous iron is oxidised to ferric iron which in turn precipitates as ferric hydroxide and leads

to a red discoloration at the infiltration site. Discoloration due to this reaction can also occur where mine drainage waters enter surface waters.

#### 2.4.5 Biological oxidation (biodegradation)

Micro-organisms play an important part in the cycling of organic matter in aquatic ecosystems. Under appropriate conditions they are able to break down almost all naturally-ocurring organic substances and many industrial chemicals into new cells, carbon dioxide, water and various inorganic substances. They are also involved in changing various inorganic compounds, eg fixing nitrogen, nitrification and denitrification. Since biodegradation processes are oxidative, complete biodegradation generally only occurs in the presence of oxygen. Under anaerobic conditions, although bound oxygen in the form of anions such as sulphate may still be available, conversions are slower and often incomplete. Accumulation of the products of incomplete degradation and/or non-degradable materials may lead to a reduction in the aesthetic quality of a water or the presence of materials toxic to aquatic organisms. On the other hand rapid biodegradation uses up dissolved oxygen, possibly at a rate faster than the natural re-aeration rate. This may be a problem especially during the summer months when micro-organisms are more active.

Oxygen uptake by micro-organisms varies with the substrate being utilised and with the fraction of the substrate which is converted to biomass, to mineral products (largely carbon dioxide and water) or to other organic metabolic by-products. As an illustration, the conversion of glucose ( $C_6H_{12}O_6$ , C:O=1:1) to biomass with a carbon to oxygen ratio 1:2.4 will require excess oxygen of about 1.9 g oxygen per gram of carbon. The conversion of glucose completely to carbon dioxide and water (6  $CO_2 + 6 H_2O$ , C:O=1:3) requires 2.7 g oxygen per g carbon.

Aerobic biodegradation overall obeys first order kinetics and the rate of oxygen removal can be expressed by the equation

$$dD/dt = kL$$

where: D = the DO deficit concentration,

L = BOD concentration

and  $k = the \ biodegradation \ rate \ constant, \ which \ is \ dependent \ on temperature$ 

The re-aeration and the biodegradability equations can be combined as  $f \circ l \ l \circ w \ s$ .

$$dD/dt = k_1 L - k_2 D$$

where:  $k_1$  is the biodegradation reaction rate constant and  $k_2$  is the re-aeration rate constant

Integration of this equation gives the Streeter - Phelps oxygen sag curve equation (Pfafflin and Ziegler 1976)

$$D = k_1 L_0 \qquad \frac{-k_1 t}{(e - e)} - k_2 t - b_0 e$$

$$(k_2 - k_1)$$

where:  $L_0$  = initial BOD concentration and  $D_0$  = initial DO deficit concentration

The biodegradation rate constant varies with the nature of the organic matter present, with values in the range 0.05 to 0.30 d-1 (DOE 1988). The re-aeration rate constant is unique to any particular body of water, being a function of many factors including depth, the state of the surface (degree of ripple), velocity and turbulence. Many empirical formulae have been developed, such as the Whipple equation which gives a simple approximation of re-aeration in streams:

$$k_2 = 21.62 \cdot U^{0.67/H1.68}$$

where: U is the stream velocity (m/s) and H is the stream depth (m) (Pfafflin and Ziegler 1976).

#### 2.4.6 Respiration

In small organisms (eq bacteria, algae, protozoa and some invertebrates) oxygen uptake is achieved by simple diffusion across the external membranes to the sites of oxidation. In larger organisms (greater than about 1 mm diameter) a specialised respiratory surface is necessary to increase the surface area available for diffusion (eg gills in fish and lungs in amphibians, reptiles, birds and mammals), and a transport system (eg blood) to carry the oxygen to the sites of oxidation. pigments (eq haemoglobin), which readily combine with oxygen Respiratory (eg 1 molecule of haemoglobin combines with 4 molecules of oxygen to form oxyhaemoglobin) at high oxygen tensions and just as readily release oxygen at low oxygen tensions, are commonly found in transport systems. Such pigments increase the amount of oxygen that can be carried by the blood and release it where it is needed. They have the added advantage of maintaining a low free dissolved oxygen concentration in the blood and therefore of maintaining the oxygen concentration gradient across the respiratory surface, promoting the continued diffusion of oxygen into the **blood**.

In both aquatic and terrestrial vertebrates, oxygen diffuses into the organism across an aqueous phase covering the respiratory surface. Although diffusion in air is rapid it is much less so in water and it is important that there is continued ventilation of the respiratory surface to maintain the diffusion potential. in fish a variety of pumping mechanisms have evolved to maintain an adequate flow of water across the gills. Ventilation rate and thus the volume of water flowing over the gills will increase when the dissolved oxygen levels in the surrounding water are low, and when the fish is in an active state and thus requires more oxygen to sustain metabolic activity (Alabaster and Lloyd 1980). Thus with progressively lower dissolved oxygen concentrations fish can maintain the uptake of oxygen. However, there will inevitably come a point where such compensatory mechanisms become ineffective and the fish will not be able to obtain enough oxygen to survive. Adaptation of fish to reduced levels of oxygen has also been reported (Doudoroff and Shumway 1970). This is achieved by an increase in erythrocyte numbers and haemoglobin content of the blood.

Although some organisms (anaerobic bacteria) can function entirely by anaerobic respiration, most organisms undergo anaerobic respiration for only part of their respiratory cycle, converting glucose to pyruvic acid by glycolysis. During periods of intense activity or in times of limited oxygen availability (eg in intertidal organisms when the tide is out) the anerobic phase of respiration can support the energy requirements of an organism for a limited period. The release of energy ahead of a sufficient oxygen supply is termed oxygen debt and results in the accumulation of metabolic by-products such as lactic acid in animals and ethanol and carbon dioxide in plants. These by-products produce fatigue in animal muscle and must subsequently be oxidised (Davis 1975).

In algae oxygen diffuses into the organism across the cell surface and in higher plants oxygen diffusion takes place through stomata (specialised openings in the surface of the leaves etc) into the interior where it becomes available for metabolic processes. Oxygen is, however, also available from photosynthesis with amounts surplus to requirements being released into the environment. This process can result in the supersaturation of water with oxygen especially during summer days when photosynthesis is at its peak, and during algal blooms (Seki et al 1980). In the absence of sufficient sunlight and during the night the rate of internal utilisation of oxygen exceeds the rate of oxygen production and the flow of oxygen is reversed. This is the major factor in the diurnal variation in dissolved oxygen concentrations of surface waters at certain times of the year.

### 2.4.7 Effects of eutrophication

The eutrophication of a body of water is brought about by the presence of nutrients, eg phosphate and nitrate, in excess amounts, stimulating

the growth of plants at a rate which cannot be healthily sustained. Over-production of algae and plants can result in depletion of the DO and the obscuring of the surface of the water thus limiting re-aeration and photosynthetic activity below the surface. Ultimately, when plant growth is no longer sustainable, bacterial growth, feeding on the dying plants, becomes the dominant process resulting in depletion of DO.

#### 2.4.8 Septicity

Septicity is the state where DO has become virtually depleted and aerobic activity has ceased. Anaerobic bacteria make use of oxygen in chemically bound states, for example in sulphate, nitrate and carbohydrate. Anaerobic bacteria have lower metabolic rates than aerobic bacteria. Anaerobic bacteria therefore predominate only under anosic conditions. They often reduce their substrates to odorous products; thus sulphate is reduced to hydrogen suiphide and the degradation of nitrogenous matter such as protein gives rise to aesthetically obnoxious putrefaction products, such as organic amines, including putrescine.

#### 2.5 RECORDED LEVELS OF DISSOLVED OXYGEN IN THE ACUATIC ENVIRONMENT

Data on dissoived oxygen concentrations in UK surface waters have been obtained from the NRA regions in England and Wales and from the River Purification Boards in Scotland. Because of the vast amount of data available, the collection of data for this study has concentrated on those rivers where DO levels are depleted for at least part of the time yet where fish populations and/or other biota survive. The data are summarised in Table 3.

The lowest 95%-ile values where biota of different sensitivities have been recorded provide an indication of their DO requirements. Absence of species cannot be used to derive oxygen requirements because other factors such as ammonia or pesticides may have an effect and the physical conditions may not be suitable for individual species. On the other hand, presence at least shows that a particular water quality is

0

Table 3 - Dissolved oxygen concentrations and biota recorded in **UK** rivers (Data supplied by NRA Regions and River Purification Boards)

D.		. 1 1	0				G : 1.1	
River Site		issolved	Oxygen saturatio	n*)	BMWP*** score	Fish	Species recorded Dominant	invertebrates
Site	min	max	mean	95** %ile	score	11311	Dominant	invertebrates
ANGLIAN NRA REGION								
Bucklesham Hill Ipswich intake	7.5	14.1	10.9	7.5				
Bure Saxthorpe Mill	7.4	12.8	10.4	8.4		salmonids		
Cam Hauxton Mill	6.5	13.6	9.9	7.5		cyprinids		
Eye Brook Caldecot t	6.4	14.1	10.6	7.8		salmonids		
Great Eau Withern Br	4.6	13.0	9.5	6.5		cyprinids		
Hog Dyke Rings tead	1.1	11.6	5.1	0.5				
Lothingland Hundred Kessingland	4.4	11.6	7.9	4.2		cyprinids		
Ouse Sharnbrook	3.5	19.8	9.9	6.4		cyprinids		

Table 3 - continued

River Site			Oxygen saturation mean	n*) 95** %ile	BMWP*** score	Fish	Species recorded Dominant invertebrates
Scarrow Beck Calthorpe	7.7	12.4	10.1	8.2		salmonids	
Slea <b>Bonemill</b> Br	3.8	15.6	11.1	6.9		salmonids	
Stiffkey Uighton Br	8.8	13.1	10.8	8.7		salmonids	
NORTH WEST NRA REGION							
Alt Altmouth	1.6	9.2	4.4	0.8	1 - 7		snails, tubificid worms
Ditton Brook <b>Halewood</b>	2.5	9.1	5.5	2.4	3		chironomids, tubificid worms
Glaze Brook L Uoolden	1.1	9.6	4.6	0.7	6-18		chironomids, <u>Asellus,</u> tubificid worms
<b>Gowy</b> Stanney	2.0	11.3	7.9	4.2	18-32		chironomids, water boatmen, tubificid worms
Irwell Salford <b>U</b>	2.8	12.1	7.9	4.2	9-15		chironomids, <u>Asellus</u> , leeches, naidid worms
Irk Red Bank	5.5	9.7	7.9	5.9	9-17		chironomids, <u>Asellus,</u> snails, tubificid worms

Table 3 - continued

River Site		issolved ( /1, or % max	Oxygen saturation mean	n*) 95** %ile	BMWP*** score	Fish	Species recorded Dominant invertebrates
Hersey Flixton	4.3	10.6	7.7	5.0	18-27	stickleback	chironomids, <u>Asellus,</u> <u>Gammarus,</u> leeches, naidid and tubificid worms
Howley	4.1	10.4	7.5	5.0	6-31	stickleback	chironomids, <u>Asellus,</u> snails, tubificid worms
Medlock Chester Rd	5.6	10.8	8.2	6.1	3		chironomids, naidid and tubificid worms
Sankey Brook A57 rd br	2.6	9.9	6.3	3.3	5-12		chironomids, <u>Asellus</u> , tubificid worms
Veaver Ch Minshull	4.1	11.3	7.8	4.5			chironomids, <u>Asellus</u> , tubificid worms
SEVERN TRENT NRA REG	GION						
sow Hilford	0.3	16.0	a.9	5.3	94-108	cyprinid, perch	mayflies, damselflies, caddisflies, Gammarus tigrinus
Tame Chetwynd Br	4.0	12.0	7.2	4.5	27-47		Asellus
Dove Monks Br	4.8	17.0	10.9	8.5	125	brook trout, grayling	mayflies, caddisflies

Table 3 - continued

River Site			Oxygen saturation mean	n*) <b>95**</b> %ile	BMWP*** score	Fish	Species recorded  Dominant invertebrates
Derwent Uilne	6.1	16.0	10.4	7.2	45-54		diverse fauna including crayfish
Soar Red Hill	4.9	16.0	10.4	7.6	82-96	cyprinid	diverse fauna <b>incl</b> mayflies, caddisflies,
Idle Bawtry	7.9	17.0	11.2	8.4	46-55	cyprinid	diverse fauna <b>incl</b> caddisfly, <u>Gammarus</u> pulex
Trent Yoxall Br Trent Br	4.8 7.6	14.5 12.0	9.6 10.0	6.2 8.1	75-95 72-76		mayflies, caddisflies, shrimps, crayfish damsel/dragonflies, crustacea, molluscs, beetles, leeches
Dunham(tidal)	7.8	18.0	11.3	8.1	3 6		molluscs, shrimps
Tern Atcham	7.2	13.0	9.8	7.9	60-109	cyprinid, pik	e, mayflies, caddisflies
Stour(Severn) Stourport	0.8	12.6	8.5	6.5	28-31	coarse	Gammarus, Asellus
Teme Powick	0.8	13.0	11.0	8.8	87-93		mayflies, caddisflies
Avon <b>Evesham</b>	1.2	15.0	10.7	8.7	40-45		mayflies, caddisflies

Table 3 - continued

River Site		Dissolved () /1, or % max	Oxygen saturation mean	ı*) 95** %ile	BMUP*** score	Fish	Species recorded Dominant invertebrates
Severn (non-tidal)							
Shelton	a.1	13.5	10.7	a.8	81-116		mayflies, caddisflies
Haw Br	7.2	14.0	10.6	8.1	50-55	cyprinid, p	
SOUTH WEST NRA REGION							
Otter B001	9.0	13.1	11.1	9.3	150		mayf lies, caddisf lies, chironomids (midge larvae), beetles
Am B017	a.2	12.0	10.1	a.1			
Tamar							
E002	7.4	12.2	9.7	7.7		salmonids	
E003	7.3	12.9	10.4	a.8		salmonids	
Cober							
A001	a.5	11.0	9.9	8.6	64	salmonids	stoneflies, mayflies, caddisflies, diptera
A002	a.7	11.5	10.0	a.5			(chironomids and others), beetles, limpet
West Looe							
coo3	9.1	12.8	10.8	9.3	104	salmonids	stoneflies, mayflies, caddisflies, diptera, beetles, G <u>ammarus</u> , mites
Tresillian							
D001	9.3	12.0	10.5	9.3	86		stoneflies, mayflies, caddisflies, diptera, beetles

River Site	D (mg/ min	issolved ( '1, or % max	Oxygen saturation mean	n*) 95** %ile	BMWP*** score	Fish	Species recorded Dominant invertebrates
D002	8.1	11.7	10.4	8.7	93	salmonids	mayflies, caddisflies, diptera, G <u>ammarus,</u> beetles
Par A002 A003	7.6 7.6	12.2 12.8	10.0 9.7	8.1 7.8	22 61		dragonflies, caddisflies, diptera, beetles dragonflies, caddisflies, diptera, beetles, worms
Carnon E002 E003	4.6 6.7	8.6 12.6	6.4 8.0	4.7 5.8			
Gannel A001 A003	8.6 8.6	11.7 11.0	<b>10.4</b> 9.9		43 58		mayflies, caddisflies, diptera, beetles stoneflies, mayflies, caddisflies, diptera, beetles, roundworms
Newlyn A012	8.7	12.2	10.4		9 0		stoneflies, mayflies, caddisflies, diptera, beetles, <u>Gammarus</u> , bivalves
THAMES NRA REGION							
Role	2.2	10.0	6.5	2.7			
Kenne t	7.4	12.8	9.9	7.9		coarse	
Coln	7.2	14.2	11.4	8.9		brown trou	t + coarse

Table 3 - continued

River Site		ssolved ( 1, or % max	Oxygen saturatior mean	1*) 95** %ile	BMWP*** score	Species recorded Fish Dominant invertebrates					
Thames Hannington Br Abingdon Weir	4.7 7.8	12.9 13.0	8.5 10.3	5.0 7.9		coarse (poor) coarse					
Evenlode	8.7	14.0	10.9	8.7		trout + coarse					
Ash*	53	115	85		84	trout + coarse					
Lee* u/s E Hyde STU Wa terhall	61 57	144 112	9 8 9 0		60 71	salmonid + coarse					
Mimram*	60	120	9 7		76	salmonid					
Rib*	6 9	98	86		129	salmonid					
Roding*	55	119	9 5		65	sea trout + coarse					
Stort*	70	9 9	87		9 6	coarse					
WELSH NRA REGION											
Clwyd St Asaph	6.5	14.0	10.2	7.6	93-141						
Dee Old Bangor	9.1	13.6	11.3	8.9	78-121						

Table 3 - continued

River Site	Dis (mg/] min	solved L, or % max	Oxygen saturatio mean	n*) <b>95**</b> %ile	BMUP*** score	Fish	Species	recorded Dominant	invertebrates	
Loughor Ynys Llwchr	8.0	13.1	10.7	8.5	122-170					
Rhymney M'stone-y-F	8.4	11.2	9.2	7.2	16-20					
Seiont Caernarfon	7.0	14.1	11.0	7.9	68-131					
Taff Blackweir	7.0	12.4	10.2	7.3	24-41					
Tawe Swansea	7.3	13.0	10.7	8.9	13-70					
Teify Llechryd	9.4	12.6	11.1	9.4	159-199					
Usk Llantrisant	9.9	13.0	11.2		90-111					
Wye Redbrook	7.8	12.6	10.5	8.6	102-134					
YORKSHIRE NRA REGION										
Aire Swillington d/s Knostrop Weir	1.4 6.2	12.5 11.6	7.1 8.6	2.5	8 8	coarse (v po			chaete worms chaete worms	

59 Bart 19 6-22 bin 600 50-21 50-22 1980 1 50 1 855 Day god 1 1991 5<sub>0</sub>00 ...

Table 3 - continued

River Site		ssolved 'l, or % max	Oxygen saturation mean	n*) <b>95**</b> %ile	BMWP*** score	Spe Fish	ecies recorded Dominant invertebrates
Calder							
u/s Coopers Br	5.9	12.8	9.5	7.0		coarse	
Stanley	3.9	13.1	8.6	5.3		coarse (v poor)	
Foss							
Strensall	4.5	13.7	9.3	4.8	9 6	coarse (poor)	midges, <u>Asellus,</u> leeches, cockles, water boatmen, <u>beetles</u>
West Beck							
Whinhill Weir	7.5	13.9	10.4	7.6	99-131	salmonid	mayflies, chironomids, <u>G. pulex, Asellus</u> , snails, oligochaete worms
u/s Wansford Br	5.6	11.8	9.9	7.3	141	salmonid (poor)	mayflies, diptera, <u>G. pulex</u> , <u>Asellus,</u> snails, mites, cockles
d/s Wansford Br	5.5	12.8	10.1	7.1		coarse (v poor)	
Corps Landing	3.6	10.6	7.3	3.7	1 3 0	coarse (poor)	mayflies, diptera, <u>Asellus,</u> snails, cockles leeches, mites
Wiske							
Kirby Wiske	4.6	13.7	9.3	4.4	68-80	coarse (poor)	alderflies, diptera, <u>Asellus,</u> cockles, beetles, leeches, oligochaete worms
CLYDE RIVER PURIFIC	ATION BOAR	lD					
Clyde							
Wolfclyde	10.8	11.7	11.2		1 3 0		
Bonnington	9.8	11.2	10.7		1 3 0		
Motherwell	6.8	13.2	10.2		7 0	salmonids	
Rutherglen	4.4	12.6	8.6		2 5		

Table 3 - continued

River Site	Dissolved Oxygen (mg/l, or % saturation*)				BHUP***	E2 -l-	Species	recorded		
	(mg min	max	mean	95** %ile	score	Fish		Dominant	invertebrates	
White Cart										
Holehouse	7.1	13.1	11.2		9 0					
Linn Park	6.4	13.8	10.6		45	trout	(possible)			
Pollokshaw	5.7	12.5	10.0		65		-			
Kelvin										
Springf ield	7.5	11.4	9.8		130					
2 0	3.6	10.8	8.3		85					
Balmuidy Botanic Gdns	11.0	11.1	11.1		9 0					
North Calder										
u/s Calder-										
cruix STU	8.4	13.1	10.6		105					
Carnbroe Br	4.4	11.4	8.5		15					
Bargeddie	6.0	12.0	9.5		20					
South Calder										
Bowhousebog	5.0	10.7	8.8		25					
Hurdostone	8.0	11.6	10.2		50					
Col tness	8.9	12.3	10.6		40					
Brigbraemill	6.7	12.0	9.7		15					
FORTH RIVER PURFICA	ATION BOAR	D								
Leven*										
Nat. Steel	85	109	9 5		64		mi	dges, Asell	lus, naidid and tubificid worms	
Balfour Br	88	107	9 5		63				lges, lumbriculid and tubificid	
— — — — — — — — — — — — — — — — — — —	- <del>-</del>						wor	•		
Lothrie	84	98	9 2		61				riculid and tubificid worms	

Table 3 - continued

River Site		issolved /1, or % max	Oxygen saturation*) mean 95**		Fish	Species recorded Dominant invertebrates
Ore* Balfour Mains Clunybridge Crosshill	7 0 7 9 8 6	104 99 91	8 8 8 9 8 8	2 7 4 9 8 6		mayflies, midges, <u>Asellus</u> mayflies, diptera caddisflies, mayflies, midges, <u>G. pulex</u>
Gairney Water	8 8	130	106	113		mayflies, midges
South Queich*	8 6	126	102	115		mayflies, midges, tubificid worms
North Queich*	7 9	104	9 3	129		mayflies, midges, tubificid worms
Devon*	9 3	103	9 7	106		stoneflies, mayflies, midges
Allan*	8 5	102	9 5	120		stoneflies, mayflies, caddisflies, beetles
Teith*	8 9	111	9 8	2 6		mayflies
Forth*	8 7	98	91	114		stoneflies, mayflies, leeches
Duchray*	8 3	9 7	9 3	60		stoneflies
Carron*						
Ironworks Br	7 9	9 4	8 9	84		diptera, <u>Asellus,</u> oligochaete worms
Denny	9 1	9 9	9 4	94		mayflies, midges, tubificid worms
Carron Br	8 7	9 7	9 2	116	salmon	stoneflies, mayflies, midges, beetles
Bonny*	68	9 2	8 2	5 4		mayflies, diptera, <u>Asellus</u>

W

Table 3 - continued

River Site		issolved /l, or % max	Oxygen saturation*) mean 95** %ile	BMWP*** score	Sp Fish	ecies recorded Dominant invertebrates
_						
Avon*						
Jinkaboot	8 6	129	100	5 3		mayflies, caddisflies, diptera, Asellus
Torpichen Br	7 9	105	8 8	2 5		mayflies, Asellus
Slamannan Br	7 3	109	8 5	6 3		mayflies, <u>G. pulex</u> , beetles
Logie*	6 4	8 6	7 7	21		mayflies, midges, <u>Asellus</u>
Barbauchlan*	7 8	9 5	8 4	5 9		mayflies, diptera, <u>G. pulex, Asellus</u>
Couston*	4 6	7 9	5 4	3 4		mayflies, diptera, <u>Asellus</u>
Almond*						
Cramond Br	7 9	97	8 9	3 7	stone loach	mayflies, midges
Kirkliston	8 1	101	8 9	7 8	minnow	mayflies, diptera, Asellus
Birdsmill	7 3	9 4	8 6	8 8	stone loach	mayflies, diptera, <u>Asellus, G. pulex,</u> leeches
Livingston	8 3	9 4	8 7	6 3		mayflies, caddisflies, diptera, Asellus
Blackburn	71	9 2	81	5 5		mayflies, diptera, lumbriculid worms
Cowhill	8 5	9 5	91	5 1		mayflies, lumbriculid worms
Linhouse Water*	8 4	9 2	8 9	111		stoneflies, mayflies, caddisflies, diptera <u>G. pulex</u> , beetles
Breich Water*	8 7	109	9 5	3 4		mayflies, diptera, mussels, oligochaete
Water of <b>Leith*</b>	8 2	93	8 8	7 4	bullhead	worms stoneflies, mayflies, diptera, mussels, snails
Esk*	8 9	100	9 4	5 3	flounder	stoneflies, mayflies, midges

Table 3 - continued

River Site		ssolved l, or % max	Oxygen saturatio mean	n*) 95** %ile	BMWP*** score	Fish		Species recorded Dominant invertebrates
North Esk* Ironmills	0.0	100	0.5		0.0			to fire morfling and disfling dintana
Tronmins	9 0	103	95		68			stoneflies, mayflies, caddisflies, diptera G. nulex. snails
Lasswade Br	67	95	88		76			mayflies, caddisflies, diptera, Asellus
Roslin	81	94	89		76			stoneflies, mayflies, diptera, <u>Asellus,</u> beetles
Carlops	8 9	9 4	9 2		104			stoneflies, mayflies, caddisflies, diptera, <u>G. pulex</u>
South Esk*								
Dalkei th	86	96	92		77	brown	trout	stoneflies, mayflies, diptera
Newbat tle	87	98	93		9 3			stoneflies, mayflies, diptera
Redside	87	9 5	9 3		105			stoneflies, mayflies, caddisflies, diptera, <u>G. pulex,</u> beetles
Gore water*	71	95	89		77			stoneflies, mayflies, caddisflies, diptera <u>G. pulex</u>
Tyne*								
Knowes	83	108	9 6		86			stoneflies, mayflies, caddisflies, diptera Asellus, beetles
West Hills	83	101	92		9 4			stoneflies, mayflies, caddisflies, diptera
Pencaitland	64	84	77		26			mayflies, Asellus
Crich ton	8 9	91	90		70	brown	trout	stoneflies, mayflies, caddisflies, diptera G. pulex, snails

Table 3 - continued

River Site		solved I, or <b>%</b> max	Oxygen saturation*) mean 95** %ile	Fish	Species recorded Dominant invertebrates
HIGHLAND RIVER PURIS	FICATION BO	OARD			
Thurso River* at tidal limit	67	154	9 6	salmonid	
Wick River* at tidal limit	59	109	88	salmonid	
Conon* Conon Br	6 2	107	94	salmonid	
Kyle of Sutherland* Shin	84	107	96	salmonid	
Beauly* Lovat Br	88	105	9 6	salmonid	
Carron* New Kelso	86	107	96	salmonid	
Findhorn* A96 bridge	88	111	95	salmonid	
Nairn* Nairn	88	110	96	salmonid	
Ness* Inverness	0.4	115	98	salmonid	

Table 3 - continued

River Site			Oxygen saturation mean	*) 95** %ile	BMWP*** score	Fish	Species recorded Dominant invertebrates
Lochy* AM station	68	110	9 7			salmonid	
TAY RIVER PURIFICATION	BOARD						
Eden Kemback	9.3	14.9	11.4	9.1	102	salmon	mayflies, caddisflies, diptera, <u>G. pulex,</u> <u>Asellus,</u> snails
Earn Forteviot	9.1	12.7	11.1	9.2	152	salmon	stoneflies, mayflies, caddisflies, diptera, <u>G. pulex,</u> mussels
Almond Almond bank	a.7	13.9	11.2	a.5	119	salmon	stoneflies, mayflies, caddisflies, midges, beetles
<b>Tay</b> Pi tnacree	9.9	13.4	11.4	9.9	138	salmon	stoneflies, mayflies, caddisflies, midges, beetles
Perth	9.0	13.2	11.8	10.1	130	salmon	may flies, caddisflies, midges, <u>G. pulex,</u> beetles, snails
Tummel Portnacraig	a.9	12.6	11.0	9.0	153	salmon	stoneflies, mayflies, caddisflies, midges, G. pulex
Ericht East Hill	9.2	13.5	12.2	10.3	96	salmon	stoneflies, mayflies, caddisflies, diptera, beetles

**∨** 

Table 3 - continued

River Site			Oxygen saturation mean	on*) <b>95**</b> <b>%il</b> e	BMUP*** score	Fish	Species recorded Dominant invertebrates
Isla U <b>Cardean</b>	9.6	13.7	11.5	9.4	156	salmon	stoneflies, mayflies, caddisflies, diptera, beetles, snails
Dighty Water Balmossie	9.3	14.2	12.0	10.1	3 9		diptera, worms
Lunan Water <b>Kirkton</b> Mill	9.0	12.9	11.7	9.9	7 2	salmon	mayflies, caddisflies, midges, <u>G. pulex,</u> beetles, snails
South Esk							
Stannochy Br	9.4	13.6	11.5	9.5	158	salmon	stoneflies, mayflies, caddisflies, midges, G. pulex, beetles, snails
Kinnairds M	7.3	13.6	11.3	9.0	127	salmon	stoneflies, mayflies, caddisflies, diptera, G. pulex, beetles
North Esk <b>Marykirk</b>	9.8	13.3	11.3	9.5	142	salmon	stoneflies, mayflies, midges, beetles

Notes

<sup>\*</sup> DO concentration given as % saturation \*\* 95%-ile values are calculated, as equal to (mean -  $1.645\sigma_{n-1}$ ), except where more than 50 data points are available. \*\*\* BMUP = Biological Monitoring Working Party

adequate for survival. Salmonids have been recorded at 95%-ile concentrations of 7 to 8 mg/l and coarse fish at 4.2 mg/l. Excellent biological quality (BMWP score >150) has been recorded at 95%-ile concentrations of 9 mg/l and very good (90-150) at as low as 3.7 mg/l. Data have been obtained from two continuous monitors which show the effects of photosynthesis referred to in Section 2.4.7 above. The Kegworth monitor on the River Soar recorded diurnal variations in DO of magnitude between 1 and 2 mg/l in August 1988 (data supplied by NRA Severn Trent- Region) . Wider variations of magnitude between 4 and 7 mg/l were recorded on the West Beck at Corps Landing in July of the same year, (data supplied by NRA Yorkshire Region).

SECTION 3 - ENVIRONMENTAL QUALITY CRITERIA RECOMMENDED FOR DISSOLVED OXYGEN BY OTHER BODIES

Standards for DO in freshwaters for the protection of fish have been suggested by the inter-governmental European Inland Fisheries Advisory Commission (EIFAC), and by the US Environmental Protection Agency. Guidelines for dissolved oxygen were also adopted by several UK River Purification Boards and former Water Authorities.

# 3.1 EIFAC CRITERIA

EIFAC (Alabaster and Lloyd 1980) have derived tentative minimum criteria for dissolved oxygen for the protection of freshwater fish (Table 4).

Table 4 - Tentative minimum sustained DO for maintaining the normal attributes of the life-cycle of fish under otherwise favourable conditions (Alabaster and Lloyd 1980)

Attribute DO	)(mg/l)
Survival of juveniles and adults for one day or longer	2
Fecundity, hatch of eggs, larval survival	ა 5
10 per cent reduction in hatched larval weight	7
Larval growth	5
Juvenile growth (could be reduced 20 per cent)	4
Growth of juvenile carp (Cyprinus carpio)	3
Cruising swimming speed (maximum sustainable speed	·
could be reduced 10 per cent)	5
Upstream migration of Pacific salmon (Oncorhvnchus spp)	
and Atlantic salmon (Salmo salar)	5
Upstream migration of American shad (Alosa sapidissima)	2
Schooling behaviour of American shad	5
Sheltering behaviour of walleye (Stizostedion vitreum vitreum)	) 6

For resident populations of moderately tolerant freshwater species, such as roach, the annual SO- and 95 %-ile DO values should be greater than 5 mg/l and 2 mg/l respectively, and for salmonids the corresponding values should be 9 mg/l and 5 mg/l respectively.

The vaiues are intended to be for general guidance only because there are circumstances where due consideration should be given to the seasonal and geographical variation of DO. For example, for adult migrant salmonids the SO- and 95%-ile values for periods of low water during the summer months in the region of an estuary where the DO is lowest should be 5 mg/l and 2 mg/l respectively but higher values are recommended if the estuary has an extensive deoxygenated zone (more than a few kilometres). Also, because the early life stages of fish are especially sensitive, the lower levels of DO should not occur when such life stages are present.

#### 3.2 US EPA CRITERIA

The US national criteria for ambient dissolved oxygen concentrations for the protection of freshwater aquatic life are presented in Table 5 (US EPA 1986).

Table 5 - US national water quality criteria for minimum ambient dissolved oxygen concentration

	Coldwater	Criteria	Warmwater	Criteria
	Early Life Stages <sup>1</sup>	Other Life Stages	Early Life Stages <sup>1</sup>	Other Life Stages
30 Day Mean	NA <sup>2</sup>	6.5	NA	5 . 5
7 Day Mean	<b>9.53</b> (6.5)	NA	6.0	NA
7 Day Mean Minimum	NA	5.0	NA	4.0
1 Day Minimum 4,5	8.03 (5.0)	4.0	5.0	3.0

# Notes

<sup>&</sup>lt;sup>1</sup> Includes all embryonic and larval stages and all juvenile forms to 30-days following hatching.

<sup>2</sup> NA (not applicable).

 $<sup>^3</sup>$  These are water column concentrations recommended to achieve the required intragravel water dissolved oxygen concentrations shown in parentheses. The 3 mg/l differential is discussed in the criteria document. For species that have early life stages exposed directly to the water column, the figures in parentheses apply.

<sup>&</sup>lt;sup>4</sup> For highly manipulatable discharges, further restrictions apply.

<sup>&</sup>lt;sup>5</sup> All minima should be considered as instantaneous concentrations to be achieved at all times.

The criteria for cold water fish are intended to apply to waters where one or more salmonid species are present and were chosen as representing conditions where there is a risk of only a slight impairment of fish productivity. The 1 day minimum values are to be considered as instantaneous concentrations which should be achieved at all times.

The coldwater minimum was set at 4 mg/l as many of the insect species common to salmonid habitats were more sensitive to low levels than the salmonids for which acutely lethal levels at or below 3 mg/l were determined.

It is stated that the criteria do not represent assured no-effect levels. If a slight risk is not acceptable then the values given in Table 6 should be used for assessing the oxygen required for the protection of the relevant life stages and species.

#### 3.3 UK WATER INDUSTRY GUIDELINES

Anglian Water Authority (1986) adopted criteria for DO for the protection of fisheries in its region. For salmonid-dominated fisheries not more than 5% of values (5%-ile) should be below 7 mg/l and 1% of values (1%-ile) below 6 mg/l. For cyprinid-dominated fisheries the corresponding values are 6 mg/l and 4 mg/l.

The Humber Estuary Committee (HEC) has set dissolved oxygen criteria of 40% saturation for the tidal rivers (those upstream of Trent Falls) and 55% saturation for the estuary itself. More recently the HEC has reviewed their EQS for dissolved oxygen. They concluded that a 5%-ile of 5 mg/l and an absolute minimum of 3 mg/l would allow migration to occur.

The Highlands River Purification Board, has set criteria for both freshwaters and marine waters which support salmonid fisheries. For freshwaters the DO should not fall below 7 mg/l or 80% saturation whichever is the lower. For marine waters the DO should not fall below 6 mg/l or 80% saturation whichever is the lower. The conclusions of Doudoroff and Warren (1965) are used to support these criteria, that

Table 6 - Minimum dissolved oxygen concentrations (mg/l) versus quantitative level of effect (US EPA 1986)

Salmonid waters 1. Embryo and Larval Stages 11\* (8) No production impairment Slight production impairment 9\* (6) = Moderate production impairment 8\* (5) 7\* (4) Severe production impairment = Limit to avoid acute mortality 6\* (3) Other Life Stages No production impairment 8 Slight production impairment = 6 Moderate production impairment 5 Severe production impairment Limit to avoid acute mortality 3 2. Non-salmonid waters Early Life Stages No production impairment Slight production impairment = 5.5 Moderate production impairment 5 Severe production impairment 4.5 Limit to avoid acute mortality Other Life Stages No production impairment 6 5 Slight production impairment 4 Moderate production impairment = 3.5 Severe production impairment Limit to avoid acute mortality 3. **Invertebrates** No production impairment 8 5 Some production impairment Acute mortality limit 4

<sup>\*</sup> These are water column concentrations recommended to achieve the required intragravel water dissolved oxygen concentrations shown in parentheses. (The 3 mg/l differential is discussed in the criteria document. )

even small reductions in DO cause reductions in swimming performance, growth and larval size (information supplied by Highlands RPB).

The Forth River Purification Board has set a depth-averaged minimum dissolved oxygen criterion of 4.0 mg/l for the upper Forth estuary to avoid salmonid smolt and grilse mortalities, which used to occur in late spring and summer. It is claimed that in practice this is a target 95%-ile of 4.5 mg/l (Elliott et al 1988) .

From a review of the DO concentrations and the passage of migratory fish in UK estuaries, Hugman <u>et al</u> (1984) suggested two standards: a guideline standard of 5 mg/l as a lower 95%-ile for the protection of a high quality migratory fishery; and 3 mg/l (95%-ile) to permit limited migration of salmonids through estuaries.

SECTION 4 - LIMITATIONS OF THE PRESENCE OF LOW DISSOLVED OXYGEN LEVELS
ON THE USES OF WATER

# 4.1 INTRODUCTION

For contaminants either exceedence of the toxic concentration, absorption by biota, or visual or other physiological perceptions (principally taste and odour) can interfere with the use of the water. Dissolved oxygen is different because it is its deficiency which causes effects or which is an indicator of problems.

DO is considered in relation to each of the principal uses of water listed by Gardiner and Mance (1984).

### 4.2 ABSTRACTION TO POTABLE SUPPLY

For waters used for human consumption the deficiency or even absence of DO has no direct consequences. Thus for water used for abstraction to potable supply an EQS is not strictly required. However, low levels of oxygen in the water may indicate potential pollution which may lead to impairment of the water quality, eg taste and odour problems. The

measurement of DO may therefore afford a rapid indication of potential water quality problems. In such circumstances any criterion should be set in terms of percentage saturation, not concentration, because of temperature effects. For example the saturation concentration of freshwater at 30 °C is only one half of that at 0 °C.

The EC Directive concerning the quality required of surface waters intended for the abstraction to drinking water in Member States (75/440 EEC) (CEC 1975) recognised the potential effect that a lack of dissolved oxygen can have on the quality of water abstracted for potable supply and has specified guide values (G) depending on the level of treatment applied, Table 1 (see Section 1) . For water taken into storage for later potable use the quality of the water abstracted from the reservoir is relevant rather than the inlet water quality. The effects of stratification on DO may become important.

If DO standards are considered necessary for waters used for abstraction for potable supplies then the current EC guidelines would seem acceptable given that there is a variable criterion depending on the degree of treatment to be afforded to waters of different qualities.

## 4.3 FOOD FOR HUMAN CONSUMPTION DERIVED FROM WATERS

The concentration of dissolved oxygen is not relevant to the use of waters for producing food for human consumption in the sense intended by this category. That is DOE has no effect on the safety of food for human consumption.

#### 4.4 PROTECTION OF FRESHWATER LIFE

The literature on the requirements of DO by freshwater biota is discussed in Appendix A and the data are summarised in Table Al. A major review was published by Doudoroff and Shumway (1970) which was extended by Alabaster and Lloyd (1980) and by Chapman (1986). These have been updated by additional studies published in the recent literature.

Studies have been carried out on a variety of species including warm-water species which are not found in UK or other European waters. Further, while laboratory studies carried out by one researcher or group of researchers may in themselves be consistent, there is no universally adopted common test protocol and thus the range of test regimes used varies widely. Nevertheless, with the large amount of data available it is possible to draw conclusions in many of the relevant areas.

# 4.4.1 Protection of freshwater fish

The different life stages of fish have distinct DO requirements and to safeguard fish populations DO concentrations must be adequate to protect the whole life cycle, from embryonic development through hatching, larval development and subsequent growth to the survival of mature fish and finally through to breeding to perpetuate the species. The embryonic and larval stages are the most susceptible to low DO concentrations with salmonids being somewhat more sensitive than cyprinids and other coarse fish. Salmonids require special consideration as they are more sensitive at the adult stage than most other species. In addition salmon are migratory fish spending most of their adult life in saltwater and only returning to freshwater to breed.

It is impossible to determine precisely the critical DO levels because most fish studies have been made in the laboratory where conditions rarely approach those occurring in nature. DO levels in the laboratory are usually constant, acclimation to low levels of DO is not often provided for and the test fish are given no chance to avoid the low DOs. Test fish have ready access to food and are not subject to the added stress of foraging nor the many other stresses which fish normally encounter in nature.

The absolute minimum DO for survival of any life stage is 2 mg/1, but this level will not permit the survival of a population as a whole. A minimum of 5 mg/1 appears to be necessary to protect the whole life cycle. Because of the different sensitivities of the various life stages it might be possible to lay down different standards according to the season and the species of fish present.

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Due consideration has to be given to the diurnal variations in oxygen concentration in water, especially in the summer, when assessing the oxygen present,

# a) Salmonids

The EC Freshwater Fish Directive (CEC 1978) lays down a mandatory (I) value of  $\geq 9$  mg  $0_2/1$  (expressed as 50% of samples) for the protection of salmonid fish and requires that when the concentration falls below 6 mg  $0_2/1$  the cause is to be investigated and appropriate measures must be adopted. The directive has also set a guideline (G) value of  $\geq 9$  mg  $0_2/1$  (expressed as 50% of samples) and of  $\geq 7$  mg  $0_2/1$  (expressed as 100% of samples). The provisions of the directive apply to designated salmonid fisheries.

Adult trout have been shown to be able to survive DO levels of between 2 and 3 mg/1 for up to 3 to 4 days under laboratory conditions (Alabaster et al 1979) but at concentrations of less than 5 mg/1 the swimming speeds of both salmon and trout are impaired (Davis et al 1963, Jones 1971 and Katz et al 1959, cited by Chapman 1986). This may have an effect on survival in the wild, because of the reduced ability to escape from predators or of implementing avoidance behaviour. In laboratory tests adult chinook and coho salmon commonly avoided regions having DOs of 3 mg/1 or less and occasionally avoided regions with DOs of 4.5 to 6 mg/1 (Whitmore et al 1960, cited by Chapman 1986).

Reductions in the growth rates of juvenile salmonids have been recorded at DOs of less than 6 mg/l with temperature having a significant effect. While a concentration of 5 mg/l had no effect at 13 °C, a 34% reduction in growth was observed at 20 °C. It has been suggested (Alabaster and Lloyd 1980 after Itazawa 1971) that the minimum DO which allows the maximum growth of rainbow trout is 4 to  $4.5 \, \text{mg/l}$ .

The earlier life stages are more susceptible to low DOs. Severe mortalities of embryos have been reported at 3 mg/l and less

(Siefert et al 1974), with a maximum survival of only 20% occurring below 6 mg/l compared with maximum survival rates of 62% above 6 mg/l. At approximately 3 mg/l hatching is delayed and the surviving larvae are underdeveloped although apparently still viable. The "no-effect" level for embryonic and larval survival and development seems to be approximately 6 mg/l.

The field data summarised in Table 3 indicate that a salmonid fishery can be sustained where the median dissolved oxygen concentration is 8.7 mg/l and the 95%-ile is 7.7. This corresponds to data supplied by Alabaster (1973, cited in Alabaster and Lloyd 1980) who reported healthy salmonid fisheries at a mean DO concentration of 8.7 mg/l and a 95%-ile of 4.8 mg/l. However, it is likely that lower concentrations could be tolerated by adults whereas early life stages might require higher DO levels.

Table 4, taken from Alabaster and Lloyd (1980), can be expanded to include other attributes of the life cycle of salmonid fish, as shown by Table 7.

The early life stages of salmonid fish require particular attention because eggs are laid in redds made in the gravel of the beds of streams and the interstitial DO may be up to 3 mg/l lower than that of the main body of water. Thus in the field a higher DO concentration is required in the water of a stream than may have been determined in laboratory tests.

Table 7 - Minimum sustained DO for maintaining the normal attributes of the life-cycle of fish without significant impairment

Attribute	DO (mg/l)		
	Salmonids		
Spawning		5	
Hatching, embryo survival	7*	6	
Hatched larval weight		7	
Larval growth	6 "	5	
Larval survival for a few hours		3	
Larval survival, longer term	6*	5	
Juvenile growth	6	5	
Juvenile survival for a few hours	3	3	
Juvenile survival, longer term	5		
Adult survival for a few hours	2		
Adult survival, longer term	4	3	
Physiological stress, juvenile		5	
Physiological stress, adult	5	4	
Swimming speed, juvenile	6		
Swimming speed, adult	5	3	
Behaviour, adult		6	
Estuarine migration, salmon smolts	5		

<sup>\*</sup> refers to DO requirements for the interstitial water of the gravel beds

## Note

The values were derived from the data given in Table Al in Appendix A except for estuarine migration which is derived from Table B1 in Appendix B.

Based on the available toxicity and field data a standard of  $\ge 9 \text{ mg/l}$  as median and  $\ge 5 \text{ mg/l}$  as 95%-ile should be adequate for the protection of salmonid fisheries. However, adults are likely to be able to survive for extended periods at lower levels, whereas early lifestages might require more stringent conditions.

# b) Non-salmonids

The EC Freshwater Fish Directive (CEC 1978) lays down a mandatory (I) value of  $\geq 7$  mg  $0_2/1$  (expressed as 50% of samples) for the protection of cyprinid fish and states that when the concentration falls below 4 mg  $0_2/1$  the cause is to be investigated and appropriate measures must be adopted. The directive has also set a guideline (G) value of  $\geq 8$  mg  $0_2/1$  (expressed as 50% of samples) and of  $\geq 5$  mg  $0_2/1$  (expressed as 100% of samples). The provisions of the directive apply to designated cyprinid fisheries.

Most tests on non-salmonids have been carried out in the USA on species native to that country. However, many of those species have been introduced to European waters (Wheeler 1983) and thus the data are at least in part relevant.

The range of lethal levels of DO reported for adult European non-salmonids is wide, 0.4 to 3 mg/l. The range of critical DO levels at which metabolic changes become apparent and which can be survived for only limited periods is also wide, between approximately 2 and 3.5 mg/l at 10 to 20 °C (Burton and Heath 1980 and Chapman 1986) . Adult carp increase gill pumping action at 4 and 6 mg/l at 10 °C and 20 °C, respectively (Beamish 1964, cited by Chapman 1986) .

Behavioural effects have been observed below 7 mg/l, initially manifested by alterations in schooling and then at lower concentrations, often at around 1 to 2 mg/l, by avoidance (Stott and Cross 1973, Chapman 1986).

The concentrations of DO at which the growth of juveniles becomes impaired in various species including pike, carp and perch is less than 3 mg/l (eg Carlson et al 1980) but in largemouth bass it is 4 to 6 mg/l (Brake 1972, cited by Chapman 1986).

The DO concentrations affecting the survival of embryos are species dependent and, as can be seen from Table Al, range from 6 mg/l in smallmouth bass and scale carp to about 2 mg/l in white and largemouth bass and pike (eg Siefert et al 1974). The effect of DO on the survival and adequate growth of larvae appears to follow the same species dependency, with concentrations below approximately 6 mg/l adversely affecting smallmouth bass and below 3 to 4 mg/l adversely affecting white bass. Minnow larvae appear to require 5 mg/l for survival, whereas pike larvae have survived at 4 mg/l (Alabaster and Lloyd 1980).

The field data given in Table 3 indicate that a coarse fishery can be sustained at mean and 95%-ile dissolved oxygen concentrations of 7.9 and 4.2 mg/l, respectively. However, it is likely that coarse fisheries could be maintained at lower dissolved oxygen concentrations as suggested by Alabaster (1973, cited in Alabaster and Lloyd 1980) who reported that based on field data, the oxygen requirements for the maintenance of a coarse fishery are median and 95%-ile concentrations of 3.7 and 2.1 mg/l, respectively. Nevertheless, higher DO concentrations will have to be maintained during periods when early life stages of sensitive fish species are present, Table 7 summarises the minimum DO requirements to maintain the normal attributes of the life cycle of fish without significant impairment derived from Appendix A.

Based on the available toxicity and field data a standard of 5 mg/l expressed as median and 2 mg/l expressed as 95%-ile should be adequate to protect coarse fisheries. However, where sensitive early life stages are present more stringent requirements will have to be met.

#### 4.4.2 Protection of other freshwater life

The maintenance of invertebrate communities is of twofold importance in contributing diversity which enhances the aesthetic value and as food for higher fauna such as fish.

Data on invertebrates largely relate to the larval or nymphal stages of six orders of insects. Within each order there can be a wide range of sensitivity to reduced DO, for example in stoneflies the critical DO has been reported to be from 4.8 to 7.3 mg/l depending on the species (Benedetto 1970, cited by Chapman 1986). The most resistant mayfly and alderfly species have survived for 12 hours at less than 1 mg/l (Surber and Bessey 1974, cited by Alabaster and Lloyd 1980). For longer exposures, the 30-day LC50 for mayflies and midges has been reported to be between 0.5 and 5 mg/l depending on the species (Nebeker 1972).

Based on the available data the dissolved oxygen requirements for the protection of salmonid and cyprinid fisheries should also be adequate for the protection of other aquatic life in those waters. However, some species, for example stoneflies, may be particularly sensitive and therefore more stringent EQSs may be required locally. The EIFAC criteria for the protection of moderately tolerant freshwater fish (median DO 5 mg/l; 95%-ile 2 mg/l) should be sufficient to maintain a healthy diversity of invertebrates, although not necessarily protecting the most sensitive species.

# 4.5 PROTECTION OF ESTUARINE LIFE

For estuarine waters two aspects need to be considered. First, the requirements for the survival of marine species whose entire life span is spent in estuarine waters and second, requirements for migratory fish which in the UK include Atlantic salmon, sea trout and eeis. The two salmonid species migrate from the open sea through estuarine waters to freshwaters to breed. Both the surviving adults and the new stock of juveniles subsequently migrate from the freshwaters back through the estuarine waters to the open sea. Therefore, protection of estuarine waters is required, where appropriate, to allow the migration of both juvenile and adult fish.

The available literature on the DO requirements of saltwater biota is discussed in Appendix B, and summarised in Table B1. The literature is much more limited than that for freshwaters.

# 4.5.1 Migratory fish

The DO requirements for the upstream passage of migratory fish is dependent on the distance to be traversed. Curran and Henderson (1988) estimated a DO requirement of 5 mg/l as median and 2 mg/l as 90%-ile concentration for the successful migration of adults through an 8 km long estuary although they felt that this was probably too stringent. These values compare with the median and 90%-ile concentrations of 3.8 and 2.2 mg/l, respectively, obtained by Alabaster and Gough (1986) for the successful passage of fish over a distance of 10 km. Surveying several UK estuaries Hugman et al 1984 concluded that estuaries which had median and 95%-ile dissolved oxygen concentrations above 8.2 mg/l and 4.4 mg/l, respectively, supported regular adult migration and in addition for these estuaries no deleterious effects have been reported.

However, to maintain salmonid fisheries the downstream migration of smolts must also be protected. Curran and Henderson (1988) have estimated a median DO threshold value for smolts migrating through an 8 km long estuary of 5 mg/l and a 90%-ile value of 3 mg/l. Eels seem to be much less sensitive to low DO concentrations with eels having been reported to be present at concentrations as low as 1 mg/l. Based on the available information the minimum acceptable median and 95%-ile values to allow migration of salmonid fish appear to be 5 mg/l and 3 mg/l respectively for a 10 km migratory path. Higher values might be required where the fish have to traverse longer distances. For the protection of high quality migratory fisheries a higher standard may be required such as the 5 mg/l as a 95%-ile suggested by Hugman et al (1984) and the Humber Estuary Committee.

# 4.5.2 Estuarine species

The EC Shellfish Water Directive (CEC 1979) lays down a mandatory (I) value of ≥70% oxygen saturation (expressed as average value) for the protection of shellfish. The directive also states that if an individual result indicates a value lower than 70% of saturation, the measurement must be repeated and concentrations below 60% of saturation are not allowed, unless there are no harmful consequences for the

development of shellfish colonies. In addition the directive suggests a guide value (G) of 80% saturation (expressed as 95%-ile). The directive is applicable to designated shellfish waters.

Few data are available on the effects of low dissolved oxygen concentrations on estuarine species, however, the data for UK species suggest a general minimum DO requirement of 3 to 5 mg/l. In the absence of adequate data it is proposed that the same standard derived for the protection of less sensitive coarse fisheries and other freshwater life (median DO concentration of 5 mg/l and 95%-ile of 2 mg/l) is also applied for the protection of estuarine fisheries and other estuarine life. Where more sensitive species are present (eg where there are important fish nursery grounds) more stringent standards of 9 mg/l (median) and 5 mg/l (95%-ile) should be applied (Alabaster 1973).

# 4.6 RECREATIONAL USE AND AESTHETIC CONSIDERATIONS

Although Gardiner and Mance (1984) put recreational use and aesthetic acceptability as separate categories, as regards dissolved oxygen the two are very much inter-related. Considering the environmental effects of depleted DO, recreational activities are likely to be carried on only where waters are aesthetically acceptable. Water-related recreation includes swimming, boating and fishing. Although a DO deficiency has no direct consequences for recreational use, it has significant implication because a deficiency in DO can cause aesthetic problems interfering with the use:

- Fish-kills and the consequent sight of dead fish.
- Odours of putrefaction and of hydrogen sulphide from anaerobic activity.
- Discoloration of water for example from the formation of black ferrous sulphide caused by anaerobic activity.
- A reduction in the diversity of flora and fauna.
- Suppression of natural aquatic self-purification.
- Foaming

The EC Bathing Water Directive (CEC 1976) contains a guide value (G) for dissolved oxygen of 80 to 120% saturation and it is likely that waters could not be used for bathing where the DO is insufficient to support fish life (median DO of 5 mg/l and 95% of 2 mg/l). However, for waters which are only used for basic recreation such as bird watching, boating and walking a minimum dissolved oxygen saturation of  $\geq 10\%$  expressed as 95%-ile to avoid anaerobic conditions should be maintained. The requirements for fishing are covered under Section 4.4 (Protection of Freshwater Life).

# 4.7 **AGRICULTURAL** USES

The concentration of dissolved oxygen is of no direct consequence for water used for irrigation of crops although it may indicate that the water is grossly polluted and might restrict its application for certain crops. The deficiency in oxygen of waters used for livestock watering can have indirect consequences as the quality of the water might be impaired owing to taste and odour which could lead to the animals refusing to drink.

Any criteria which may be considered necessary for waters used in agriculture can only be set on the advice of agricultural or horticultural specialists, but may well depend on the type of plant.

## 4.8 INDUSTRIAL USES

In the food processing industry water may come into contact with or become incorporated into the product and it is therefore suggested that waters used for this purpose meet the quality required for drinking water. Regulations for water quality in the food industry are currently being prepared by MAFF to fulfil the requirement of the EC Drinking Water Directive 80/778/EEC (CEC 1980). It is expected that special needs for other industrial uses will be met by treatment within the plant and no separate standard is proposed for this use.

#### SECTION 5 - CONCLUSIONS

The proposed environmental quality standards for dissolved oxygen for the different uses of water are presented in Table 1 (Section 1) and the justifications for the suggested values are given in Section 4.

Standards for DO have been set already by various other bodies, both regional, national and international. As might be expected given the length of time that DO has been the subject of attention by regulatory authorities and of study by researchers, the values proposed in Table 1 agree largely with previously set values although some refinement has been possible in one or two areas in the light of more recent findings.

Existing methods of analysis are adequate in terms of discrimination and limits of detection for the standards proposed. Monitoring tends to be carried out during normal working hours unless continuous monitoring is available. Daytime monitoring can lead to an over estimation of the actual mean and minimum dissolved oxygen concentration present, particularly in lowland rivers subject to large diurnal variation because of biological activity. As daytime monitoring excludes the period where DO levels are at their lowest, this must be a continuing cause for some concern.

The various tests carried out on the effects of reduced DO levels on the toxicity of a number of substances indicate that reductions in DO increase the sensitivity of aquatic species to toxicants.

## **ACKNOWLEDGEMENTS**

The authors would like to thank the NRA regions in England and Wales and River Purification Boards in Scotland who provided field data on DO concentrations, on fish and other biota, and other relevant information. In many cases the data provided were extensive and the staff concerned had put in considerable effort in providing the information.

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#### APPENDIX A

# DISSOLVED OXYGEN REQUIREMENTS OF FRESHWATER BIOTA

### Al INTRODUCTION

Two comprehensive reviews of the dissolved oxygen (DO) requirements of freshwater fish have been published in recent years, by Alabaster and Lloyd (1980) and by Chapman (1986). This Appendix draws on those two reviews for older material and reviews the more recent available literature on dissolved oxygen requirements. The results of the studies referred to in this Appendix are summarised in Table Al.

As far as can be determined all laboratory tests were conducted under flow-through conditions. The usual technique for producing water depleted in oxygen for test purposes is nitrogen stripping and either partially re-aerating the oxygen-depleted water or mixing it with air-saturated water to give the desired dissolved oxygen concentration.

#### A 2 INVERTEBRATES

Aquatic invertebrate species show a variety of respiration methods: some are gilled: some respire by oxygen diffusion over their whole body area; and others are air breathers. Therefore the requirements for dissolved oxygen can be quite different. Of those species which are DO-dependent, gilled species are said to be less sensitive to reduced DO concentrations than non-gilled species. Chapman (1986) pointed out that there may be differences between nature and laboratory tests for species whose natural habitats are fast flowing streams. He claimed that the relatively low flow rates at which laboratory tests are usually conducted may restrict the availability of DO to test animals.

# A2.1 Crustaceans

<u>Daphnia magna</u>, initially less than 48-hour old, were exposed to reduced DO concentrations for 26 days in a continuous flow recirculating system (Homer and Waller 1983). There was high survival (85%) at  $1.8 \, \text{mg/l}$  but reproduction was impaired at that level of DO and at  $2.8 \, \text{mg/l}$  the final weight of adults was reduced by 17%. No adverse effects were observed at  $3.7 \, \text{mg/l}$  and above.

The effects of variations in DO on the filtering rate of <u>Daphnia pulex</u> were studied by Kring and O'Brien (1976). On sudden exposure to DOs less than 3 mg/l the rate first decreased sharply but following prolonged exposure to low DO, including up to 15 days at 1.5 mg/l, the filtering rate increased progressively until eventually the organism was able to filter much more rapidly than at saturation DO. The authors related the increase directly to the increased production of haemoglobin at the low DO concentrations.

Chapman (1986) quoted the results of acute toxicity tests on five crustacean species. From Gaufin (1973), the 96 hour LC50 for Gammarus limnaeus was <3 mg/l. The 24 hour LC50s for the others (Sprague 1963) were, for Gammarus pseudolimnaeus, 2.2 mg/l, for G. fasciatus, 4.3 mg/l, for Asellus intermedius, 0.03 mg/l and for Hvalella azteca, 0.7 mg/l.

A study by Vobis (1972) of the rheotactic response (the response to the stimulus of flowing water) of three Gammarus species was cited by Alabaster and Lloyd (1980). Under laboratory conditions the maximum response was observed at a water velocity of 50 mm/s and at DOs of 2.7, 3.3 and 5.3 mg/l for G. pulex, G. roeseli and G. fossarum respectively.

# A2.2 Insects

The larvae of aquatic insects may utilise atmospheric oxygen directly or they may be dependent on dissolved oxygen. Nebeker (1972) included DO-dependent species in continuous-flow tests designed to determine the safe levels of DO for common insects of importance as fish-food organisms. The tests were designed to simulate the flow requirements of each of the various species. A midge, <u>Tanytarsus dissimilis</u> was the most tolerant of the test species with a 30-day LC50 of 0.6 mg/l at 18.5 °C. The equivalent values for the stonefly, <u>Pteronarcys dorsata</u>, and two mayflies, <u>Baetisca laurentina</u> and <u>Ephemera simulans</u>, all lay between 4.4 and 5.0 mg/l. <u>Tanytarsus dissimilis</u> was able to effect the transition from larva to adult successfully, and to reproduce, at 0.6 mg/l but the emergence of the two mayfly species was impaired at DO concentrations of 7.6 mg/l or less.

Alabaster and Lloyd (1980) cited earlier tests by Kamler (1971) in which sudden transfer to water at 26% saturation at 5.5 °C and 15.5 °C (3.3 and 2.6 mg/l respectively) was almost immediately fatal to the stonefly Perlodes intricata, which is found only in mountainous areas. On the other hand the mayfly Cloeon diuterum, which is widespread in Europe at low altitudes, was able to exhaust the DO in a closed vessel down to 0.02 mg/l. They also referred to the work of Surber and Bessey (1974) where the minimum DO in which some Trichoptera, Ephemeroptera, Plecoptera and Odonata species could survive for 12 hours after successive reductions in DO by 1 mg/l at 12 hour intervals was 3.5 to 2.5 mg/l, with the most resistant Ephemeroptera, Odonata and Megaloptera (ie Sialis spp) being able to survive below 1 mg/l.

The results of a number of other studies were reviewed by Chapman (19861. Although carried out at different temperatures and water flow rates, they nevertheless also demonstrated the wide range of sensitivities to dissolved oxygen. Some European species of aquatic insects were reported, after Jacob et al (1984), to have 2- to S-hour LC50s of less than 1 mg/l while for two mayfly (Ephemeroptera) and two caddisfly (Trichoptera) species the values were in excess of 7 mg/l. The 96 hour LC50 values for 20 species of North American insects determined by Gaufin (1973) are quoted as varying between 1.6 and 5.2 mg/l, with half the values in the range 3 to 4 mg/l. As DO concentration falls insect larvae (or nymphs) may have to take active measures to increase the efficiency of their uptake of oxygen. The

concentration at which this change of behaviour occurs is called the critical DO. Critical DOs vary widely between species. For six species of European mayfly (Ephemeroptera) nymphs the critical DOs ranged from 2.2 to 17 mg/l, for three of these species the critical DO was in excess of the air saturation value (Fox et al 1937). Critical DOs for four species of European stonefly (Plecoptera) ranged from 4.8 to 7.3 mg/l (Benedetto 1970). However, the studies by Fox et al (1937) were carried out with a static test system and the high critical values for DO probably reflect the unrealistic conditions of water flow, reducing the efficiency of oxygen uptake, as well as any inherent sensitivity to low DO levels.

## A3 FISH

The effects of reduced dissolved oxygen concentrations on salmonid species have been more widely studied than for other species of fish. The effects are different for different species of fish, for different life stages and for different life processes. The early life stages are the most vulnerable, particularly around the time of hatching.

## A3.1 Survival of adults

It is generally agreed that mature fish, both salmonid and non-salmonid, can survive for at least several days at DO concentrations of 3 mg/l and more and that lethal levels are usually much lower. Alabaster and Lloyd (1980) refer to the findings of a survey of East European literature provided by Lysak (pers communication) that the lethal levels for salmonid species lie between 0.95 and 3.4 mg/l and for non-salmonid species between 0.4 and 3.0 mg/l. Alabaster et al (1979) found that the 3-day LC50 for salmon smolts (Salmo salar) in freshwater was in the range 2.6 to 3.1 mg/l, and deduced that the median lethal threshold concentration for DO is close to 3.3 mg/l.

Oxygen-supersaturation resulting from photosynthetic activity is not, in general, likely to be lethal by itself. Gas bubble disease (GBD) normally occurs only when the sum of the partial pressures of both dissolved nitrogen and dissolved oxygen rises above atmospheric

pressure. EPA (1973) quoted various authors to conclude that GBD can occur in the early life stages of salmonids at total dissolved gas pressures of 1.1 to 1.2 atmospheres. Alabaster and Lloyd (1980) referred to information supplied by Lysak (pers communication) that embryonic development in a range of non-salmonid species is impaired at supersaturated DO concentrations of 34 to 41 mg/l but did not give a total gas concentration. They also referred to super-abundant DO as having been shown by Weatherley (1970) to improve the thermal resistance of goldfish-(Carassius auratus) with the effect reaching its maximum at a DO pressure equivalent to five atmospheres.

# A3.2 Reproduction and early life stages

Depleted DOs may have an effect on fecundity. Chapman (1986) referred to Brungs' (1971) study of a life cycle exposure of fathead minnows (Pimephales promelas). No spawning occurred at 1 mg/l, the number of eggs produced per female was reduced at 2 mg/l, but at higher concentrations spawning was unimpaired. Alabaster and Lloyd (1980) noted that ova of the pike (Esox lucius) have been fertilised in the absence of oxygen at temperatures between 0 and 30 °C. Siefert and Herman (1977) found that constant DO concentrations down to 2.5 mg/l had no effect on the spawning of black crappies (Promoxis nitromaculatus). They did not conduct tests at lower concentrations to show at what level there would be an effect.

Davis (1975) cited Alderdice et al (1958) that eggs of chum salmon (Oncorhynchus keta) display a respiratory dependence. At an early stage the DO requirement is about 1 mg/l whereas those about to hatch require about 7 mg/l. Susceptibility to mortality occurs when the circulatory system develops in the embryos. Notwithstanding the data of Alderice et al, Alabaster and Lloyd (19801 have concluded that most salmonids can hatch successfully at DOs of 2 to 3 mg/l even though hatching will have been delayed and the resulting larvae will be smaller than normal. They also report that some non-salmonid species can produce normal larvae at below 2 mg/l, but others, including sturgeon (Acipenser guldenstaedti), bream (Abramis brama), and pike (Esox lucius) may

require concentrations of greater than 4 to 5 mg/l before deformed larvae occur. Also referred to is a report by Niimann (1972) that the larvae of pollan (Coregonus lavaretus) \* hatched from eggs collected from Lake Constance in a year when the minimum DO was  $4.3\,\text{mg/l}$  had malformations which did not occur in other years when the DO was much higher.

The effects of reduced DO on the development and survival of early life stages of young mountain whitefish (Prosopium williamsoni), whitebass (Morone chrysops) , and smallmouth bass (Micropterus dolomieui) were studied by Siefert et al (1974). A DO of 6 mg/l did not affect the survival of young mountain whitefish at 4 °C and 7 °C although some impairment in development occurred. With DO in the range 3.8 to 5.3 mg/l survival to test end (193 days after fertilisation) at 4 °C was reduced from 82% to 89% down to 66% to 72%. At lower DO ranges (2.8 to 4.1 mg/l and below) less than 20% survived to the test end. 7 °C with DO concentrations of 2.4 to 3.8 mg/l few fish hatched and no hatchlings survived for more than 24 hours. Whitebass were less and DO concentrations down to 1.8 mg/l at 16 °C had little effect on hatching success although larval survival (from hatching to test end) was reduced to about 50% compared with 74% to 98% at concentrations of 3.4 mg/l and above. The survival of smallmouth bass embryos at 20 °C was reduced by 20% at a DO of about 4.4 mg/l. At 2.5 mg/l the hatch was successful but the larvae produced were too weak to swim up and all died, and at 1.2 mg/l there was total mortality before or during hatch.

The results of similar tests on four further species were reported by Siefert and Spoor (1974). They studied white sucker (<u>Catostomus</u> <u>commersoni</u>), coho salmon (<u>Oncorhvncus kisutch</u>), brook trout (<u>Salvelinus fontinalis</u>), and walleye (<u>Stizostedion vitreum vitreum</u>) at different

<sup>\*</sup> Quoted by Alabaster and Lloyd (1980). However, there is some confusion as to whether they are referring to the pollan (or vendace, Coregonus albula) or the powan (C. lavaretus).

temperatures. Only brook trout embryos could survive continuous exposure to DOs of about 1.5 mg/l and even then embryo mortality was 59% and no larvae survived to four months. At 2.3 mg/l, and  $8 \,^{\circ}\text{C}$ , high mortality occurred at the pre-feeding larval stage. At 2.9 mg/l and above larvae started feeding four days later than at higher concentrations and displayed a difference in behaviour, remaining near the surface after feeding. Hatching and development in walleyes was not affected at a DO of 4.8 mg/l at 17 °C, but at 3.4 mg/l the survival of larvae was severely impaired, only 14.5% survived after 20 days. At concentrations of 2.4 mg/l and below no larvae survived for more than 20 Coho salmon were the most sensitive and at 7 °C survival and development were impaired at any concentration less than air saturation (11.6 mg/l): at 2.8 mg/l survival to 4 months was reduced by 11%.

Spoor (1977) studied the oxygen requirements of the early stages of largemouth bass (Micropterus salmoides) in a flow-through test with the eggs contained in trays to simulate nests. At 20 °C, the sensitivity of embryos and larvae to reduced DO rose with time over the six-day period after hatching. There was little effect on development at DOs down to 2.5 mg/l, but at 2 mg/l considerable deformation of the lower jaw in larvae was evident and at 1 mg/l few larvae survived after three hours At 25 °C the effects of reduced DO were greater, with a concentration of 2.5 mg/l being lethal. Although at 20 °C development was unaffected at 2.5 mg/l and above, there were behavioural changes. At 3 mg/l at 20 °C and at 4 to 5 mg/l at 25 °C the normally quiescent yolk-sac larvae became active and swam vertically above the substrate. The author concluded that this could lead to considerable loss by predation and through displacement from the nest. The findings of this study are in general agreement with those of Dudley and Eipper (1975) that some embryos of largemouth bass were able to develop and hatch at DOS as low as 1.0, 1.1 and 1.3 mg/l at temperatures of 15 °C, 20 °C and 25 °C but that concentrations below 2.0, 2.1 and 2.8 mg/1, respectively, significantly reduced survival, particularly during the hatching period.

Eggs of scale carp (Cyprinis carpio communis) were exposed to various levels of DO from fertilisation to completion of hatching at 25 °C (Kaur

and Toor 1978). Both survival and hatching rate increased with increased DO. At 1.2 mg/l the hatch rate was negligible: at 3 mg/l it was 40% successful: at 6 mg/l it was 65%; and at 9 mg/l it was more than 90% successful.

The combined effects of DO and temperature on the development and survival of lake herring (Coregonus artedii) were studied by Brooke and Colby (1980). Eggs were incubated in a continuous flow system at four temperatures between 2 and 8 °C and at five DO concentrations between 1 and  $12\,\text{mg/l}$ . The water velocity, 4.8 mm/s, was such that the eggs were tumbled gently during the course of the tests. At 1 and 2 mg/l the newly hatched fry were significantly shorter and below 4 mg/l a large proportion were deformed.

In the study of fathead minnows (Pimephales promelas) by Brungs (1971) if spawning occurred (>1 mg/l DO) the percentage hatch (81 to 89%) was not affected when the embryos were exposed to the same DO as the parent fish. The mean larval survival after 30 days was 6% at 3 mg/l, 25% at 4 mg/l, and 66% at 5 mg/l.

The hatch rates of eggs of Atlantic salmon (Salmo salar) artificially placed in the natural substrate of acidic streams was studied by Lacroix (1985). With pH 4.5 to 5 and temperature <10 °C the DO of 6 mg/l (in interstitial water) was not a limiting factor. Interstitial DOs were about 1 to 2 mg/l lower than the DOs in the overlying water. In a near-neutral stream the hatching success rate fell progressively from 77% at a DO of 9.2 mg/l to 5.6% at 1.4 mg/l. In this stream interstitial DOs were up to 6 mg/l lower than in the main body of water due to the lower permeability of the gravel. Mean embryo survival at < 6 mg/l interstitial DO was only 16.2%.

Barns and Lam (1983) reared larvae of chum salmon (Oncorhynchus keta) in pilot-scale experimental channels to evaluate the effects of deteriorations in water quality brought about by the excretion of metabolic products during the course of the tests. Intragravel DO levels fell to between 6 and 7 mg/l and had no effect on survival

(lowest recorded survival was 96%), but length and weight of alevins were each reduced by approximately 2% compared to controls. importance of these size reductions appears to be overstated by the authors. The above findings on larval survival contrast with those of Coble (1961), as cited by Chapman (1986), where the survival of steelhead trout embryos (Salmo gairdneril from eggs artificially buried in the gravel of a stream ranged from 36 to 62% at intragravel DO levels greater than 6 mg/l and from 16 to 26% at less than 6 mg/l. Water flow rate was, however, also a factor governing survival rate. There are a number of factors which may contribute to the differences in the two sets of findings. Firstly, in the Barns and Lam experiment the DO surrounding the eggs may have been higher than the intragravel levels because the sample baskets occupied the full height of the water column, whilst in the other experiment DO levels around the eggs may have been lower because of silting of the egg sacks. Secondly Barns and Lam tested fish only as alevins, which may be less sensitive to DO than earlier embryo stages.

Chapman (1986) pointed out that determining the oxygen requirements of embryonic and larval stages which develop in gravel beds in streams is complicated by the differences between the DO in the gravel and the DO in the overlying water. Intragravei DO may often be 2 to 3 mg/l less than the DO in the main body of water. He aiso made the point, citing Siefert (1973) on the mortality of northern pike larvae (Esox lucius) at DOs of 2.9 and 3.4 mg/l at the time of onset of feeding, that the added stress of activity or increased oxygen requirement for that life stage could be the determining factor.

A reduction of DO may cause a delay in hatching. Chapman (1986) referred to the increase in the time taken from fertilisation to hatch at DO levels below 6 mg/l as the flow rate of water past salmonid eggs decreases and attributed it to the influence that the flow rate has on the supply of oxygen to the microenvironment surrounding each egg. In work already quoted, Siefert and Spoor (1974) and Siefert et al (1974) reported delays in hatching time in response to low DO levels. At 7 °C hatching of coho salmon (Oncorhyncus kisutch) was delayed by 5 days at

about 5 mg/l and by 10 days at about 2.8 mg/l. For walleyes (Stizostedion vitreum vitruem) incubated at 17 °C there was no delay in hatching at a DO concentration of 3.4 mg/l, but below 2.4 mg/l hatching was delayed. At 4 °C and a DO concentration of 3.8 to 5.3 mg/l time to hatching of mountain whitefish (Prosopium williamsoni) was 29 to 38 days longer than in controls.

Lake herring (Coreqonus artedii) were incubated at four temperatures and five DO concentrations (between 1 and 12 mg/l) (Brooke and Colby 1980). The time to hatch was independent of DO which is in contrast to the study by Brungs (1971) of fathead minnows which showed hatching time lengthening with decreasing DO from the normal 5 days to nearly 8 days.

## A3.3 Growth

Juveniles, less than one-year-old, of a number of species of sturgeon (<u>Acipenser spp</u>) were exposed to reduced DO at temperatures in the range 6 to 26 °C (Klyashtorin 1976). The threshold oxygen tension for mortality was 20 mm Hg at 6 °C (equivalent to 1.6 mg/l) and 36 mm Hg at 20 °C (1.9 mg/l). The critical oxygen tension, at which a reduced respiration rate became apparent was 36 mm Hg at 6 °C (2.8 mg/l) and 76 mm Hg at 20 °C (4.1 mg/l).

Oxygen requirements for the growth of young coho salmon (Oncorhvnchus kisutch) with mean initial weights of 5 to 7 g and sockeye salmon (O. nerka) with mean initial weights of approximately 15 g were studied by Brett and Blackburn (1981). At 15 °C the growth of both species was markedly effected at DOs less than 4 mg/l, with zero growth at about 2.5 mg/l.

An analysis by JRB Associates (1984) of data from more than thirty separate tests on the growth of juveniles of different species of salmonid fish carried out under a diverse range of test conditions was cited by Chapman (1986). For salmon and trout, DOs of 6, 5 and 4 mg/l respectively resulted in reductions in median growth rates of 4 to 9%, 11 to 17% and 21 to 29%. The data of Warren et al (1973) were cited as

showing that the greatest effects on the growth of juvenile salmon occurred at temperatures of between about 18 °C and 22 °C. With chinook salmon (Oncorhynchus tshawytscha) at a DO of 5 mg/l growth was unaffected at 13 °C but was reduced by 34% at around 20 °C. Chapman also referred to tests by Hutchins (1974) with coho salmon (0. kisutch) in which growth rates at 5 mg/l were affected to some extent by water flow rates, a velocity of 85 mm/s having no effect but a velocity of 200 mm/s resulting in a 15% reduction. These results are consistent with those of Brett and Blackburn (1981) who observed reduced growth in juvenile sockeye salmon (Oncorhvnchus nerka) at DOs of less than 4 mg/l. The findings of Adelman and Smith (1970), that the growth of juvenile northern pike was greatly decreased at DO concentrations of less than 3 mg/l are cited by Chapman (1986) and by Alabaster and Lloyd (1980). The latter also quote the work of Itazawa (1971) as indicating a minimum DO for the unimpaired feeding, food conversion and growth in rainbow trout (Oncorhynchus mykiss) of 4 to 4.5 mg/l at about 10.5 °C and in common carp (Cyprinus carpio) of 3 mg/l at 21.5 °C.

Chapman (1986) cited the work of Stewart et al (1967) who found that at 26 °C the growth of juvenile largemouth bass (Micropterus salmoides) was largely unaffected at a DO of 5.8 mg/l but was reduced by 14% at 5.4 mg/l DO and 20% at 5.1 mg/l DO and the study of Brake (1972) who observed impairment of growth in the same species of 17% at a DO of 5.8 mg/l at 26.7 °C and of 15% at 16.7 °C. As Stewart et al carried out their studies in the laboratory whereas Brake conducted his in artificial ponds, Chapman suggested that the ease of food capture under laboratory conditions might underestimate the effects of DO on growth in nature. The results of tests carried out by Andrews et al (1973) are also cited in which the rate of increase in weight of channel catfish fingerlings (Ictalurus punctatus), exposed for six weeks to a DO of 5 mg/l and fed to repletion, was reduced by 20% compared with fingerlings kept at 8 mg/l.

In studies on the growth of both juvenile channel catfish (<u>Ictalurus punctatus</u>) and yellow perch (<u>Perca flavescens</u>) Carlson <u>et al</u> (1980) found that the fish could withstand regular short-term exposures to DO

concentrations that would otherwise have an effect on growth. They compared the effects of diurnally fluctuating DO concentrations with constant DO concentrations. Tests were conducted at saturation DO and at four reduced levels between 6.5 and 2.0 mg/l, and for the reduced levels with regular diurnal fluctuations of  $\pm 1$  to  $\pm 1.5$  mg/l. The growth of channel catfish was not affected by constant DOs of 5.0 mg/l and above at a test temperature of 25 °C but growths were significantly reduced at 3.5 mg/l. Yellow perch, at a test temperature of 20 °C, were not affected at 3.4 mg/l and above, but at 2.1 mg/l the growth was significantly reduced. The maximum growth of the catfish exposed to fluctuating DO occurred within the diurnal ranges 3.6 to 6.2 and 5.2 to 7.1 mg/l. The growth of the perch was unaffected by a diurnally fluctuating DO in the range 1.4 to 3.8 mg/l.

Alabaster and Lloyd (1980) concluded that moderately wide diurnal variations of approximately 5 mg/l have little effect on the growth of salmonid alevins. However, they also refer to the findings of Dorfman and Whitworth (1969) that older brook trout (Salvelinus fontinalis) of 4 to 10 months, exposed to much wider DO fluctuations in the range 2.4 to 10.6 mg/l, did not grow as well as those exposed continuously to a DO of 10.6 mg/l and concluded that wide diurnal fluctuations with minima of 2 to 3 mg/l have almost the same effects as a continuous exposure to that level of DO.

# A3.4 Physiology and behaviour

In a study. of the influence of a number of factors, including DO concentration, on ventilation frequency Carlson (1984) found that brook trout (Salvelinus fontinalis) only displayed a ventilatory response at DO concentrations below 4.8 mg/l (approximately 50% DO saturation) at the test temperature of 11 °C, whereas bluegills (Lepomis macrochirus) responded at the higher concentration of 6.7 mg/l (approximately 70% DO saturation) at 22 °C.

Brett and Blackburn (1981) reported that young coho salmon (0. kisutch) and sockeye salmon (0. nerka) showed no signs of respiratory distress,

as judged by the condition of the giils after six week exposures to DO concentrations of 3 mg/l and more. There was evidence for an adaptive response to reduced DO from increased haematocrit levels (compressed cells in a centrifuged sample of whole blood) which would increase the oxygen-carrying capacity of blood as the availability of oxygen decreased. This appears to be the first step of the mechanism of acclimation to DO depletion as suggested by Lloyd and Swift (pers communication) quoted by Alabaster and Lloyd (1980). In rainbow trout that first step took about six hours and the second step, which involves an increase in blood volume, a further 16 hours. The fact that rainbow trout introduced into Lake Titicaca thrive even though the saturation oxygen concentration does not exceed 5 mg/l because of the altitude of the lake (Everett (1973) in Alabaster and Lloyd (1980)), is further evidence for the ability to adapt.

in experiments designed to simulate the oxygen sag or stratification which might occur sithin a few hours in a shallow, highly productive system as a result of decomposition and respiration Burton and Heath (1980) exposed rainbow trout (Oncorhynchus mykiss), bluegills (Lepomis macrochirus) and brown bullhead (Ictalurcs nebulosus) to a gradual rate of reduction in DO concentration. In rainbow trout anaerobic metabolism (as determined by a shift from pyruvic acid to lactic acid production) in resting fish increased as DO levels decreased below a threshold value which depended on the temperature during acclimation. At an acclimation temperature of i5 °C the threshold occurred at a DO tension of 84 mm Hg (5.5 mg/l) and at 5 °C at 75 mm Hg (6.2 mg/l). Although the authors refer to a lower threshold with acclimation at lower temperature in DO tension terms, the threshold is actually higher when expressed as concentration. This may indicate that oxygen tension is more important to physiological processes than DO concentration.

Anaerobic energy production is costly from the standpoint of metabolic energy and survival under such conditions is short. The DO thresholds for anaerobic metabolism in resting bluegill sunfish and brown bullhead were each considerably lower than those for rainbow trout. For bluegill the threshold for fish acclimated at 20 °C was 40 mm Hg (2.3 mg/l) and

at 5 °C was 10 mm Hg (0.8 mg/1). With brown bullhead the threshold at 20 °C was 20 mm Hg (1.2 mg/1) but at 5 °C this species did not metabolise anaerobically even at DO near zero. The authors postulated that these fish are able to survive extended periods of DO deficiency because they have low anaerobic thresholds, a good ability to take up oxygen at low DO and also, very importantly, a low resting energy demand.

Chapman (1986) gives details of three studies of the relationship between resting metabolic rate and reduced DO.

The critical oxygen concentrations (COCs) were as follows.

Largemouth bass : 2.8 mg/l (30 °C), < 2.6 mg/l (25 °C)

(Cech et al 1979) and < 2.3 mg/l (20 °C)

Brown bullheads (Grigg 1969): 4 mg/l

Carp (Beamish 1964) : 2.9 mg/l (20 °C) and 3.4 mg/l (10 °C)Goldfish (Beamish 1964) : 3.5 mg/l (20 °C) and 1.8 mg/l (10 °C)

Physiological responses in fish to depleted DO concentrations are, as might be expected, species-dependent and generally occur at higher concentrations as temperature increases.

A more critical evaluation of Beamish's (1964) data by Chapman (1986) suggests that the first sign of hypoxic stress is not a decrease in oxygen consumption but an increase, perhaps because of the metabolic cost of the increased pumping of water over the gills to compensate for the reduced DO. In carp (Cyprinus carpio) these increases occurred at 5.8 mg/l at  $20 \, ^{\circ}\text{C}$  and at  $4.2 \, ^{\circ}\text{mg/l}$  at  $10 \, ^{\circ}\text{C}$ . These figures, showing an increase in oxygen consumption at a lower DO at the lower temperature, contrast with the figures for critical oxygen concentration. It is not clear why this trend is reversed from the initial response (increase in oxygen consumption) to the second response (reduction in resting metabolic rate) .

Cech et al (1985) observed that mosquito fish (Gambusia affinis) resorted to air gulping at DO partial pressures of 65 torr (equivalent to about 3.7 mg/l) and less and this became essential below 20 torr (about 1.1 mg/l) at 20 °C. Hyperoxia (DO of 16 mg/l) led to increased respiratory metabolic activity at 25 °C and 30 °C. Hypoxia (40 torr, 2.8 mg/l) only produced significant reductions in respiratory metabolic activity at 10 °C and not at higher temperatures, while extreme hypoxia (<25 torr, 1.1 mg/l) produced significant depressions at 30 °C and 35 °C also.

The maintenance of swimming performance is important for survival, including effective foraging, evading predators and in migration. Alabaster and Lloyd (1980) noted that, although fish continue to swim at near-lethally low levels of DO, the maximum sustainable swimming speeds of salmonids normally decline with any reduction of DO below saturation. They quoted the experiments of Smith et al (1971), where adult migrant coho salmon (Oncorhvnchus kisutch) continued to swim at about 560 mm/s for an hour at a DO of 5 to 6.6 mg/l and for a further hour at 4.5 to 5 mg/l whereas fish exposed at 4 to 4.5 mg/l for the second hour became fatigued, and there was evidence of increased fatigue even at cruising speeds.

Four further studies of the effects of reduced DO on swimming ability were cited by Chapman (1986). He noted that impairment of swimming performance, as a consequence of low DO, occurred more readily at lower temperatures. From Davis et al (1963), the maximum sustained swimming speeds of juvenile coho salmon, normally in the range 300 to 450 mm/s, were quoted as being reduced by 8.4%, 12.7% and 19.9% respectively at DOs of 6, 5 and 4 mg/l with the effects being slightly more severe at 10 °C than at 20 °C, and from Jones (1971) that reductions of 30% and 43% in the maximum swimming speeds of rainbow trout occurred at DOs of 5.1 mg/l at 14 °C and 3.8 mg/l at 22 °C. Katz et al (1959) reported that at 20 °C coho and chinook salmon were able to swim for 24 hours at speeds about one tenth of maximum at DOs of 3 mg/l and above and that at 25 °C sustained swimming of largemouth bass (Micropterus salmoides) for 24 hours at 240 mm/s was unaffected at DOs above 2 mg/l, but that at

20 °C they were not able to swim for 24 hours at a DO of 2.8 mg/l nor at 5 mg/l at 5 °C. The fourth study quoted was that of Dahlberg et al (1968), also with largemouth bass, whose maximum swimming speed at about 25 °C was reduced only slightly at DOs between 3 and 4.5 mg/l, but significantly at DOs of less than 3 mg/l.

There appears to be some doubt as to whether avoidance of regions of low DO is at least in part deliberate or whether it is an incidental effect of increased activity when a zone of low DO is encountered. Davis (1975) speculated that avoidance of low DO is a result of higher activity with more random movement which continues until a region of higher DO is discovered. This hypothesis could be supported by the findings of Serns (1976) who released batches of rainbow trout (Salmo gairdneri) into both the epilimnion (DO 6.4 to 7.3 mg/1) and the hypolimnion (DO 3.5 to 5.0 mg/1) of a lake and recovered a few individuals which had migrated from both zones across the intervening 2 to 4 metres of the metalimnion where the DO concentration was only 0.5 to 0.7 mg/1.

Roach (Rutilus rutilus) were kept in a laboratory channel divided into a number of discrete areas which could be maintained at different DO concentrations at temperatures of 9 to 10 °C (Stott and Cross 1973). It was demonstrated that fish discriminated against areas where the DO was less than 1.2 mg/1, but not areas with 1.3 mg/1 and above. This discriminating level was reduced to about 0.8 mg/1 for fish previously acclimated to a DO of 3 mg/1. Avoidance behaviour also became apparent at a DO of 1.4 mg/1 when the carbon dioxide concentration was greater than 20 mg/1. Alabaster and Lloyd (1980) cited these results as suggesting deliberate avoidance and also referred to Brodde (1972) who reported that vendace (Coregonus albula), burbot (Lota lota) and ruffe (Acerina cernua) successfully avoided the anaerobic region which developed near the bottom of Lake Ivösjön at the end of the summer of 1969.

A study by Whitmore et al (1960), quoted by Chapman (1986), showed that both chinook and coho salmon and largemouth bass had a strong preference

for DO levels of 9 mg/l or above compared with 1.5 mg/l and a moderate preference compared with 3 mg/l whereas bluegills avoided 1.5 mg/l but not higher concentrations. A further study cited, Bishai (1962), showed an age-related response to low DO in young Atlantic salmon (Salmo salar) and brown trout (S. trutta). While larvae apparently could not detect low DO concentrations, fry of 6 to 16 weeks showed a definite avoidance of concentrations up to 4 mg/l and older fry showed avoidance of concentrations up to 3 mg/l.

Alabaster and Lloyd (1980) referred to changes in behaviour at reduced DO which could have effects on survival. They quote Moss and McFarland (1970) that schooling may be altered at DOs of 7 mg/l and less, and that in the American shad (Alosa sapidissima) this occurs at less than 4.5 mg/l. They further quote Scherer (1971) that the walleye (Stizostedion vitreum) normally remains quiet under cover out of direct sunlight but that this behaviour progressively changes with a lowering of DO, to abnormally active swimming in the open at 1 to 2 mg/l. This compares with the abnormal swimming behaviour reported for sac-larvae of largemouth bass at low DO, mentioned in Section 3.2 (Spoor 1977).

## A3.5 Field data

Summarising field observations, Alabaster and Lloyd (1980) conclude that good mixed fish fauna have been found in inland waters where DO levels were below 4 to 5 mg/l and even in polluted waters where DO had not exceeded 4 mg/l for a long time. They also note however (from a personal communication by McGregor Weir) that a heavy mortality of Atlantic salmon occurred in the River Don in Scotland in 1971 at DO levels of about 4 mg/l when minimum temperatures were 18 °C and maxima about 23 °C, consistent with laboratory data which indicate increased lethality at higher temperatures. Brooker et al (1977) recorded a massive mortality of Atlantic salmon in the River Wye in 1976 when maximum daily DOs fell over a period of about four days from 5 mg/l to 2 mg/l on the day that fish kills were first observed and subsequently to 0.5 mg/l the day after. Water temperatures were also high at the time of this event with minimum daily temperatures rising over the period

from 21 °C to 25 °C and maxima from 23 °C to 28 °C but irrespective of these temperatures, mortality could have been expected at those DO levels. The decrease in DO was attributed to the death and decay of the macrophyte Ranunculus fluitans.

Kills of both young and adult salmon and trout in Norwegian rivers where DO was depleted to between 0.9 and 5.0 mg/l due to pollution by silage liquors were reported by Bergheim et al (1978). Water temperatures ranged between 16 and 18.5 °C. The authors concluded that stocks of salmonids would be drastically reduced if DO were to fall below 50% saturation (4.5 to 5 mg/l) during the mowing period in successive years. Although the undiluted silage effluents contained upwards of 100 mg/l of ammonia there was reported to be a considerable uptake of inorganic nitrogen by sewage fungus in the rivers themselves which served to maintain the concentrations of ammonia at relatively low levels. Therefore the authors believed that depleted DO causing respiratory distress was the primary cause of mortality and ruled out the possibility of a substantial effect of ammonia toxicity.

A report by Alabaster (1973) on the occurrence of fisheries in the River Trent catchment was cited by Alabaster and Lloyd (1980). For trout fisheries the median and 95%-ile annual DO concentrations were greater than 8.7 and 4.8 mg/l respectively and for coarse fisheries the equivalent values were 3.7 and 2.1 mg/l.

Coble (1982) reported the presence of a number of non-salmonid species including northern pike (Esox lucius), yellow perch (Perca flavescens), black bullhead (Ictalurus melas) and white sucker (Catostomus commersoni) in stretches of the Wisconsin River, USA, where DOs ranged from 4.6 to 6.5 mg/l and where average daily temperatures were about 23 °C.

In addition to Coble (1982), Chapman (1986) cited the conclusions of Brinley's (1944) survey of the Ohio River basin that although fish were more abundant where DO was between 3 and 5 mg/l than at lower concentrations they nevertheless showed a tendency to sickness,

deformity and parasitisation. He concluded that while increases in DO above 5 mg/1 do not significantly improve non-salmonid fish populations, DOs below 5 mg/1 give rise to increasingly poorer population characteristics as concentrations decrease.

#### A4 CONCLUSIONS

Whereas dissolved oxygen in rivers and other inland waters may vary diurnally and almost certainly from day to day, especially where the water is subject to effluent discharge and algal activity, laboratory tests are usually carried out under constant conditions. Thus it is difficult to judge from such tests precisely what degree of variation in DO can be tolerated by fish or other biota on a short time basis, or what stress might be caused by continual variations.

The data given here clearly show the differences in the oxygen requirements of the different life stages of fish, with the early stages particularly vulnerable to reductions in DO. A distinction must be made between the requirements for the mere survival of fish for a limited period and for the maintenance of a stable population, which will include all stages of life from spawning to development to maturity and breeding.

Oxygen requirements of fish are also species dependent, with the salmonids generally less resistant to low DO than non-salmonids. However, that premise should not be taken uncritically because there are non-salmonid species which appear to be nearly as sensitive, particularly in the early life stages. The embryonic stage of salmonids is particularly vulnerable to reductions in DO because of the concentration differential between the main body of water and the interstitial water in the gravel bed in which the eggs are laid and develop. After swim-up the larvae may be no more vulnerable than those of other species whose eggs were laid in a more favourable environment. While the early stages of some species (eg largemouth bass, white sucker and white bass) are tolerant of reduced DO, others (eg channel catfish, walleye and smallmouth bass) are as sensitive as the salmonids. The

growth of juvenile fish can be severely affected at reduced DO and there appears to be little general difference between the tolerance of salmonids and many non-salmonid species.

Whereas mature fish can survive for at least limited periods at dissolved oxygen concentrations of about 3 mg/1, the growth of juveniles may be severely restricted at concentrations of 4 mg/1 and less and the development of earlier life stages often requires concentrations in excess of 6 mg/1.

Fish can adapt to depleted oxygen levels by increased ventilation and by metabolic changes. Again the concentrations at which these changes commence are species-dependent and wide ranging.

The oxygen requirements of invertebrates vary widely. While some more marginal conditions may not allow the survival of the most sensitive species, it appears that a good diversity should be possible under conditions which allow the survival of fish.

Table Al - Effects of reduced DO on freshvater species

Species Tel	mp DO Level C mg/1	Life stage	Effect	Ref
CRUSTACEANS				
Cladocera				
Daphnia magna 21±	1 1.8		reduced fecundity	12
D. magna 21±			impaired growth	12
$\overline{D}$ . magna $21_{\pm}$			no effect	12
Hyalella azteca	0.7		24 hr LC50	30
Amphipoda				
Gammarus pulex	2.7		max rheotactic response at 50 mm/s water velocity	34
G. roeseli	3.3		max rheotactic response at 50 mm/s water velocity	34
G. fossarum	5.3		max rheotactic response at 50 mm/s water velocity	34
G. limnaeus	< 3		96 hr LC50	47
G. pseudolimnaeus	2.2		24 hr LC50	30
G. fasciatus	4.3		24 hr LC50	30
Isopoda				
Asellus intermedius	0.03		24 hr LC50	30
INSECTS				
Ephemeroptera (mayflies)				
Cloeon dipterum	0.02		survivable	26
Baetisca laurentina 18	.5 5.0		30 day LC50	16
Ephemera simulans 18			30 day LC50	16
B. laurentina/E. simulans 18			impaired emergence	16
various ephemeroptera species			12 hour survival	32
most resistant species	< 1		12 hour survival	32
6 ephemeroptera spp nymph	2.2-17		critical DO (change in respiratory response)	46
2 ephemeroptera spp	<u>&gt;</u> 7		2 to 5 hour LC50	49

Table Al - continued

	omp DO Level mg/l	Life stage	Effect	Ref
INSECTS continued				
Odonata (dragonflies)				
various odonata species	2. 5-3. 5		12 hour survival	32
most resistant odonata speci			12 hour survival	32
Plecoptera (stoneflies)				
	5.5 3.3		lethal	27
	5.5 2.6		lethal	26
Pteronarcys dorsata	4.4 - 4.8		<b>30</b> day LC50	16
various plecoptera species	2. 5-3. 5		12 hour survival	32
4 plecoptera spp	4.8-7.3		critical DO (change in respiratory response)	38
Megaloptera				
Sialidae (alderflies)	. 1		10 1	4 9
<u>Sialis</u> spp	< 1		12 hour survival	4 9
Trichoptera (caddis flies)				
various trichoptera species	2. 5-3. 5		12 hour survival	32
2 trichoptera spp	> 7		2-5 hr LC50	49
Diptera				
Chironomidae (midges)				
	0.6		<b>30</b> day LC50	16
various chironomid species	2. 5-3. 5		12 hour survival	32

Table Al - continued

Species	Temp °C	DO Level mg/l	Life stage	Effect	Ref
FISH					
Salmonids					
Salmo salar (Atlantic salmon)	<pre>≤ 10 ≤ 10 ≤ 10 ≤ 10 ≤ 10 ≤ 10</pre>	7.6* < 6* > 6* 9.2* 1.4* < 4 < 3 3.3	embryo embryo embryo embryo embryo fry, 6-16 wks fry, 26 wks smolt	estimated DO level for 50% survival at mean pH 6.5 16% survival no effect on hatching, pH 4.5-5 77% hatching success, mean pH 6.5 5.6% hatching success, mean pH 6.5 avoidance avoidance median lethal threshold conc	15 15 15 15 15 39 39
Oncorhynchus keta (chum salmon)		1 7 6-7*	embryo embryo alevins	oxygen requirement of earliest stages oxygen requirement near hatching survival unimpaired	3 5 3 5 3
<pre>Oncorhynchus kisutch (coho salmon)</pre>	7 7 10, 20 15	5 2.8 4-6 <b>&lt; 4</b> 3 4.5-6 <b>&lt;</b> 4.5	embryo larvae juvenile juvenile adult adult adult	hatching delayed impaired survival 20-8% reduction in swimming speed reduced growth commonly avoided occasionally avoided increased tendency to fatigue	17 17 45 5 55 55 1
Oncorhynchus nerka (sockeye salmon)	15	< 4	juvenile	reduced growth	5

Table Al - continued

Species	Temp °C	DO Level mg/l	Life stage	Effect	Ref
Oncorhynchus tshawytscha					
(chinook salmon)	13	5	juvenile	no effect on growth	5 4
	20	5	juvenile	34% reduction in growth	5 4
		3 4.5-6	adult adult	commonly avoided occasionally avoided	54 54
		4.5-0	aduit	occasionany avoided	JŦ
Oncorhynchus mykiss					
(rainbow trout)	≈10.5	4-4.5	juvenile	min DO for max growth	25
	1 5 5	5.5 6.2	adult adult	threshold of anaerobic metabolism threshold of anaerobic metabolism	6 6
	14	5.1	adult	swimming speed reduced by 30%	51
	22	3.8	adult	swimming speed reduced by 43%	51
(steelhead trout)		< 6	embryo	16-20% survival	42
		> 6	embryo	36-62% survival	42
Salmo trutta					
(brown trout)		< 4	fry, 6-16 wks	avoidance	39
,		< 3	fry, 26 wks	avoidance	39
Salvelinus fontinalis					
(brook trout)	8	1.5	embryo	less than 50% survival	17
,	8	≥ 2.9	embryo	no increased mortality, but behavioural differences	17
	8	1.5	larvae	lethal over a 4 month period	17
		2.4-10.6,		impaired growth	2 4
	11	(die1 varia	ation) adult	increased ventilation	
	11	₹.0	aduit	increased ventifation	
Prosopium williamsoni					
(mountain whitefish)	4	3.8-5.3	embryo	hatching delayed,reduced survival	la
	4 7	3.8-4.1 2.4-3.8	embryo	severe mortality	la la
	I	2.4-3.0	embryo	reduced hatch and lethal to hatchlings within 24 hours	1a

Table Al - continued

Species	Temp °C	DO Level mg/1	Life stage	Effect	Ref
Coregonus artedii (lake herring)	2-8 2-8	1-2 < 4	embryo embryo	newly hatched fry significantly shorter large proportion of newly hatched fry deformed	56 56
Coregonus lavaretus (powan) <sup>1</sup>		4.3	larvae	deformations: field observation	28
Miscellaneous salmonids		4 ≥ 6 0.9-5.0 8.7 4.8 0.95-3.4	juvenile juvenile all stages adult	21-29% reduction in median growth rates insignificant effect on growth fish kills observed during silage cutting period medium annual DO for trout fisheries 95 percentile DO for trout fisheries range of lethal levels for salmonid fish from European literature	50 50 4 22 22
Non-salmonids					
Alosa sapidissima (American shad)		< 4.5	adult	schooling behaviour altered	27
Esox lucius (pike)	15-19	2 4 4-5 <b>&lt;</b> 3	embryo embryo/larvae larvae juvenile	hatch significantly reduced adequate for survival limits for undeformed larvae significant growth impairment	23 29 1 23
Rutilus rutilus (roach)	9-10	< 1.2	adult	avoidance	21

Table Al - continued

Species	Temp °C	DO Level mg/l	Life stage	Effect	Ref
Pimephales promelas					
(fathead minnow)		3, 4, 5	larvae	mean survival 6, 25, 66% after 30 days	41
			larvae	25% growth reduction	41
		≤ 2	adult	impaired spawning	41
		1	adult	cessation of spawning	41
Abramis brama (bream)		4-4.5	larvae	limits for undeformed larvae	1
Cyprinus carpio					
(carp)	25	6	embryo	reduced hatch	13
-	-21.5	3	j uveni le	min DO for max growth	25
	10	3.4	adult	critical DO (reduced metabolic rate)	37
	20	2.9	adult	critical DO	37
	10	< 4.2	adult	increased pumping	37
	20	< 5.8	adult	increased pumping	37
Cyprinis carpio communis	25	1.2	embryo	negligable hatch	13
(scale carp)	25	3	embryo	40% hatch success	13
(Scare carp)	25	6	embryo	65% hatch success	13
	25	9	embryo	> 90% hatch success	13
Carassius auratus					
(goldfish)	20	3.5	adult	critical DO (reduced metabolic rate)	37
	10	1.8	adult	critical DO	37
Gambusia affinis	20		عاديات	"ain gulaing" natad	10
(mosquitofish)	20	<u>≤</u> 3.7 <u>≤</u> 1.1	adult	"air gulping" noted	10
	20	<u>S</u> 1.1	adult	"air gulping" essential	10

Table Al - continued

Species	Temp °C	DO Level mg/l	Life stage	Effect	Ref
Catostomus commersoni (white sucker)		2	juvenile	no effects on survival	19
Pomoxis nitromaculatus (black crappie)	13-20	<u>≥</u> 2.5	adult	no adverse effects on spawning	19
Perca flavescens (yellow perch)	20 20	2.1 3.4	juvenile j uveni <b>le</b>	significant growth reduction no effect on growth	8 8
Stizostedion vitreum (walleye)	17 17 17	< 2.4 4-8 3-4 2-4 1-2	embryo embryo larvae larvae adult	hatching delayed hatching and survival unimpaired heavy mortality lethal abnormally active swimming in open water	17 17 17 17 17 33
Micropterus dolomieui (smallmouth bass)	20 20 20	1.2 4.4 2.5	embryo embryo larvae	total mortality reduced survival hatch successful but lethal to larvae	18 18 18
Microoterus salmoides (largemouth bass)	15-25 20 20 25 20 25 20 25	1-1.3 2-2.8 1 2 2.5 3 4-5 5-5.5	embryo embryo larvae larvae larvae sac-larvae sac-larvae juvenile	hatchable at 15-25 °C hatch significantly reduced heavy mortality over 3 hr exposure high proportion deformed lethal after 3 h abnormal swimming activity abnormal swimming activity 14-20% growth reduction	11 11 20 20 20 20 20 20 53

Table Al - continued

Species	Temp °C	DO Level mg/l	Life stage	Effect	Ref
Micropterus salmoides	continued				
	26	5.8	juvenile	growth largely unaffected	53
	17, 27	5.8	juvenile	15% and more growth reduction	40
	20	2.3	adult	critical DO (reduced metabolic rate)	43
	25	2.6	adult	critical DO	43
	30	2.8	adult	critical DO	43
	20	2.8	adult	stamina impaired	52
	25	< 2	adult	stamina impaired	52
	5	5.0	adult	stamina impaired	52
	25	< 3	adult	stamina impaired	44
		1.5	adult	definite avoidance	55
Morone chrysops					
(white bass)	16	1.8	embryo	little effect on hatch success	18
,	16	1.8	larvae	reduced survival	18
	16	3.2	larvae	inhibition of yolk-sac absorption	18
	16	<b>≥</b> 3.4	larvae	high survival	18
Lepomis macrochirus					
(bluegill sunfish)	22	6.7	adult	increased ventilation	7
, 8		1.5	adult	limit of avoidance	55
	20	2.3	adult	threshold for anaerobic metabolism	6
Ictalurus nebulosus					
(brown bullhead)		4	adult	critical DO for reduced metabolic rate	48
	20	<b>≃1.</b> 2	adult	threshold for anaerobic metabolism	6

Table Al - continued

Species	Temp °C	DO Level mg/l	Life stage	Effect	Ref
Ictalurus punctatus (channel catfish)	25 25	3-5 5 5	juvenile juvenile juvenile	reduction in growth no effect on growth reduced growth, when fed to repletion	8 8 36
Miscellaneous non-salmonids		3 0.4-3 5 3.7 2.1	juvenile/adult adult all stages	96h survival in general range of lethal levels from E European literature limit for healthy populations of fish in USA median DO for coarse fisheries 95%-ile DO for coarse fisheries	20 14 9 22 22

# Notes

<sup>\* -</sup> Interstitial water

Quoted by Alabaster and Lloyd (1980) but there is confusion about whether they are referring to the pollan (or vendace, <u>C. albula</u>) or the powan (<u>C. lavaretus</u>)

#### Notes for Table Al continued

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#### APPENDIXB

DISSOLVED OXYGEN REQUIREMENTS OF ESTUARIAL BIOTA INCLUDING MIGRATORY FISH

#### B1 INTRODUCTION

There are two aspects relevant to this report. First, the DO requirements for the survival of species whose entire life span is spent in marine or estuarine waters and second, the requirements for migratory Atlantic salmon (Salmo salar) and sea trout (Salmo trutta), for example, migrate from the open sea through estuarine waters to freshwaters to breed. Both the surviving adults and the new stock of smolts subsequently migrate from those freshwaters back through the estuary to the open sea. Eels (Anquilla anguilla), on the other hand, spawn in the western Atlantic and after three years the elvers migrate to fresh waters to complete their development. Adults make a further seawards migration to their spawning grounds. Protection of estuarine waters is required to avoid disruption of the essential migratory stage in the life cycle of these species.

The data for this Appendix are summarised in Table B1.

## B 2 INVERTEBRATES

<u>Penaeus</u> species (brown shrimp and white shrimp) were shown to be able to detect and avoid low DO in laboratory tests carried out at levels of 1, 1.5, 2, and 3 mg/l. Brown shrimp (<u>P. aztecus</u>) were more sensitive than the white species (<u>P. setiferus</u>) and showed quicker avoidance behaviour. Other behavioural responses included an initial increase in the general level of activity, rapid eye-stalk movements and flexing of antennal scales. The white shrimp also displayed abdominal flexures which were often followed by exhaustion (Renaud 1986).

The shrimp, <u>Crangon vulqaris</u>, has been shown to respire normally at approximately 1.5 mg/l DO (20% air saturation value, ASV) at 21 °C and 23 °/ $_{\circ\circ}$  salinity (Huddart and Arthur 1971). At the same temperature and salinity a DO of approximately 1.2 mg/l (15% ASV) enabled survival for 5 to 6 hours and below approximately 0.6 mg/l (7.5% ASV) 50% mortality occurred rapidly within less than 15 minutes. At 14 °C and 1.3 mg/l DO (15% ASV) 10% mortality was observed after 6 hours.

Henderson (1984) reported that the variation in the abundance of Naiadidae species, eg <u>Paranais littoralis</u>, immediately below the tidal weir of the River Clyde correlated very closely with the variation in DO, with pronounced reductions in abundance when DOs were less than about 20% ASV. Tubificid species, eg <u>Tubifex benedeni</u>, on the other hand were reported to be tolerant of low DO and relatively unaffected, although reduced salinity lowered their tolerance to low DO.

B3 FISH

### B3.1 Survival

It has been found that an increase in salinity can slightly increase the resistance of migratory fish to low dissolved oxygen concentrations.

Alabaster et al (1979) carried out tests involving prior acclimation to different conditions of salinity and DO to attempt to simulate the conditions that might be encountered by salmon smolts (Salmo salar) in passing seawards through an oxygen-depleted estuary, with a falling then rising DO and an increasing salinity. Fish were acclimated for varying periods up to ten days, either at high DO or at low DOs of about 3 mg/1, in fresh water or 30% sea water before being exposed to test conditions. The 3-day LC50 in both 30% and 80% seawater was about 2.5 mg/l compared with 3 mg/l in freshwater at temperatures ranging between 13 °C and 16 °C. It was also estimated, from the results of tests involving exposures of 100 and 1000 minutes (17 hours), that the median threshold concentration for survival in 30% and 80% seawater, after several days acclimation to low DO, was about 2.6 mg/l compared with 3.3 mg/l in

freshwater for temperatures between 13  $^{\circ}\text{C}$  and 16  $^{\circ}\text{C}$ . However, although lethal concentrations were reduced by only a few tenths of a milligram per litre, the period of survival in saline water could be increased by up to tenfold compared with freshwater.

In laboratory tests at 25 °C Wu and Woo (1984) studied the tolerance of the red grouper (Epinephelus akaara), a sluggish species, and of the black sea bream (Mylio macrocephalus), an active species, to DO No abnormal behaviour or mortality was observed at 2 mg/1 depletion. and above. However, blood oxygen partial pressure was markedly reduced in both species after exposure for 1 hour at 4 mg/l although it appeared that the bream was able to adapt to low DO either by increasing oxygen uptake or by reducing oxygen utilisation. A DO concentration of 1 mg/1 was lethal to red groupers within about two hours but no mortalities in black sea breams were recorded after seven hours and only 10% of the fish showed abnormal behaviour at that level. A DO of 0.5 mg/l was lethal to 50% of the breams in 100 minutes. Both species therefore have a high tolerance to low DO levels with the bream being the more tolerant of the two.

Alabaster and Lloyd (1980) cite Alabaster (1973) that information on the disappearance of fisheries from the Thames estuary at the turn of the century and the return of some species from the 1970s suggests that the presence of lamperns (Lampetra fluviatilis), flounders (Platichthys flesus) and smelts (Osmerus eperlanus), all euryhaline species, requires at least 30 to 50 % saturation. Twaite shad (Alosa fallax) had not returned at the time of Alabaster's examination of the information and he concluded that that species has a higher DO requirement.

Off the California coast upwelling can result in DO levels as low as 3 to 4 mg/l or even close to 1 mg/l in inshore waters but there have not been any reports of any deleterious effects on fish or phytoplankton. The **biomass** of fish in deeper waters off the Californian coast was not affected by DO levels of 4 to 5 mg/l (Thurston et al 1979).

Henderson and Hamilton (1986) carried out studies of the status of fish populations in the upper Clyde estuary. Fish were collected daily from the screens of an industriai water intake between November 1982 and November 1983. The data showed that sand-goby (Pomatoschistus minutus) apparently avoided the area when the DO was less than 50% saturation. Their presence was not observed between May and September 1983 when mean DOS ranged from 10 to 38%. Furthermore, their abundance in November of that year when the DO of the water column at the observation point was 4 to 5 mg/l was less than in November 1982 when DOs were 11 to 12 mg/l. Flounders (Platichthys flesus) were present at times when DOs were above 25% and eels (Anquilla anguilla) at all times even at DOs of about The presence of eels indicates only their ability to survive periods of DO at this level. Their abundances were variable throughout the period of the study and not related solely to DO levels. et al (1988) reported that flounder and eelpout (Zoarces viviparus) are resident in the upper Forth estuary where the DO level can fall below 4 mg/l in summertime.

## B3.2 Migration

Salmon have been recorded as passing, apparently successfully, upstream through a zone of 4.5 to 6.8 mg/1 DO in the estuary of the River Tyne in March to April (Alabaster and Lloyd 1980).

Britain in relation to the salmonid fisheries that were supported. All estuaries which maintained regular fisheries and where no deleterious effects had been reported had mean DO levels of more than 8.2 mg/l and 95%-ile DO levels of more than 4.4 mg/l. The estuaries to which salmon were beginning to return (Trent and Thames) and where occasional oxygen restrictions occurred (Usk and Ribble) had mean DOs above 6.4 mg/l and 95%-ile DOs above 3 mg/l. The Tyne estuary is stratified and, although the depth-averaged 95%-ile DO value was only 0.6 mg/l, fish could select a depth where the 95%-ile value was 2.5 mg/l. The River Leven, a tributary of the Clyde estuary supports a good salmon fishery. Like the Tyne, the Clyde estuary is also stratified and again it is suggested

that fish select depths of the stratified estuary at which the highest DOs occur. During the smolt run of 1980 a layer with mean DO of 7.3 mg/l and 95%-ile 4.6 mg/l was available compared with depth-averages of 6.5 and 2.8 mg/l respectively. Occasional smolt runs were reported in the Yorkshire Ouse system which had a DO lower than 2.5 mg/l.

Curran and Henderson (1988) have carried out studies of the return of salmon to the River Gryffe, another tributary of the Clyde estuary upstream of the Leven, and to the River Clyde itself. Salmon returned to the River Gryffe in 1978 but not in any numbers to the River Clyde itself until 1983. The Clyde River Purification Board has carried out surveys of water quality at intervals of between 2 and 4 weeks since 1965 and Curran and Henderson analysed the data in an attempt to explain the apparent 5-year time difference and to estimate the threshold levels required for the re-establishment of salmon fisheries.

The seaward migration of smolts through estuaries appears to be by passive drift during ebb tides and smolts may descend to a depth of 10 metres or more to optimise the seaward drift. It is estimated that in the Clyde estuary passage from the tidal weir in Glasgow to the mouth of the River Leven, below which the estuary rarely suffers DO depletion, can take up to 9 tidal cycles (about 4.5 days).

Smolts were able to migrate seawards from the River Gryffe in the years 1977 to 1981 when the DO 90%-ile concentrations at some depth or other at low water at the time of the smolt runs in April to June exceeded 2.5 mg/l over a 6 km length of the estuary downstream from the Gryffe confluence. In the same period, smolt could not reach the estuary from the Clyde where the equivalent 90%-ile concentrations were 1.9 mg/l. Curran and Henderson concluded that a 90%-ile DO of 1.9 mg/l over 6 km represents an impenetrable barrier to smolt migration. They estimated the 90%-ile threshold DO values for successful smolt migration to be 2 mg/l over lengths of between 1 and 4 km, 2.5 mg/l over 6 km and 3 mg/l over 8 km.

The 90%-ile threshold for upstream adult migration in the period August to October was estimated to be 1 to 2 mg/l but was judged to be irrelevant because it is known that adult salmon prefer upstream migration during periods of higher river flow, when estuarine water quality is improved. The 50%-ile threshold estimates are given as 4.3 to 5.3 mg/l.

Curran and Henderson's values can be compared with those derived by Alabaster and Gough (1986) who analysed data from the Thames estuary. In the period from July to September 1984 DOs were less than 5 mg/l for considerable distances in the estuary but salmon (Salmo salar) were nevertheless found in freshwater stretches of the river. Median water temperatures lay within the range 18 °C to 23 °C. From their analysis of the data the authors concluded that successful passage is possible over distances of 1, 10 and 30 km at median concentrations of 3.5, 3.8 and 4.3 mg/l and at 90%-iie values of 2.0, 2.2 and 2.8 mg/l, respectively.

Alabaster (1988) similarly examined data from the lower Willamette River, Oregon, USA relating to times when adult chinook salmon (Oncorhynchus tshawytscha) migrated upstream. The fish appeared to display a preference for DOs in excess of 3.5 mg/l. The DO requirements for passage were deduced from a comparison of the times when salmon runs would have been expected and the times when runs actually occurred and the DOs when those times most closely coincided. The values for distances of 0, 8 and 32 km were median DOs of 3.6, 4.4 and 6.4 mg/l and 95%-ile DOs of 2.6, 3.2 and 5.4 mg/l respectively at average water temperatures of between 18.4 °C to 20.3 °C. These values are somewhat higher than those derived for Atlantic salmon and could reflect either a species difference or a temperature effect.

Other studies have been concerned with the movement of tagged fish.

The Usk estuary is subject to an oxygen sag caused by the oxygen demand of sediments resuspended by the tides and DO levels can fall to 3 mg/l or less over several kilometres. Aprahamian et al (1988) released

salmon (Salmo salar) fitted with radio tags into the waters of the lower estuary and found that relatively fewer fish (about 29%) migrated upstream into the upper estuary when DOs were between 3.3 and 4.5 mg/l than when DOs were between 4.7 and 5.2 mg/l (about 46%). Priede et al (1988) released small numbers of salmon (Salmo salar) fitted with oxygen-sensing acoustic transmitters into the Ribble estuary each July for a number of years. The situation was complicated by various factors, not least that it was not certain that all the fish were Ribble The fish caught for tagging may have included fishes from other rivers which were merely exploring the Ribble estuary. However. the results indicated that DO concentrations below 50% saturation were avoided where possible. Water temperatures were in the range 15 °C to 22 °C and the water in the test stretch was described as of high salinity, and an avoidance limit of 3.5 to 4.5 mg/l can be inferred.

#### B4 CONCLUSIONS

From the small amount of data available on acute toxicity, migratory fish appear to be able to withstand slightly lower DO concentrations in saline waters when compared to freshwater. How significant this is likely to be in practice is not clear. For migratory species such as salmon, the oxygen requirements in estuarine waters are those required for survival during migration. Adult salmon can presumably exert a degree of choice in timing their migrations to freshwater, avoiding times when water quality is unfavourable. Smolts on the other hand may not have this choice since smolt migration is apparently largely passive drift with the tides. Thus one key barrier to the establishment of a salmon fishery appears to be an estuarine DO regime which would prevent successful smolt runs.

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INVERTEBRATES					
Annelids Naiadidae Paranais littoralis		from 10 to 0		progressive decline in abundance	7
Tubificidae Tubifex benedeni		n 1		continued survival	7
Crustaceans Penacidea Penaeus aztecus		e Vi		avoidance, behavioural response	10
(brown snrimp) Penaeus setiferus (white shrimp)		£ <b>&gt;</b> I		avoidance, behavioural response	10
Caridea Crangon vulgaris	21	1.5		adequate for respiration LC50 within 15 minutes	14 14
	14	1.2		survival for 5-6 hours 10% mortality after 6 hours	14 14

FISH Salmonids

Table **B1** - continued

Species	Temp °C	DO Level mg/l	Life stage	Effect	Ref
Salmo salar		2.5	smol t	3-day LC50 for acclimated fish, 30% and 80% seawater	5
(Atlantic salmon)		2.6	smol t	median threshhold concentration for survival in seawater	5
		2	smol t	threshold 90%-ile for l-4 km seaward migration	6
		2.5	smol t	threshold 90%-ile for 6 km seaward migration	6
		3	smol t	threshold 90%-ile for 8 km seaward migration	6
		4.5 - 6.8	adult	successful migratory passage	4
		2.5-3	adult	95%-ile concns allowing migratory passage	9
		> 4.4	adult	95%-ile concns in estuaries with regular fisheries	9
		4.3 - 5.3	adult	threshold 50%-ile for 1-8 km seaward migration	6
		1-2	adult	threshold 90%-ile for l-8 km upstream migration	6
	18-23	3.5-3.8	adult	threshold 50%-ile for l-10 km upstream migration	3
	18-23	4.3	adult	threshold 50%-ile for 30 km upstream migration	3
	18-23	2.0-2.2	adult	threshold 90%-ile for l-10 km upstream migration	3
	18-23	2.8	adult	threshold 90%-ile for 30 km upstream migration	3
Oncorhynchus tshawytscha	20-24	3.6	adult	threshold 50%-ile for any upstream migration	2
(chinook salmon)	20-24	4.4	adult	threshold 50%-ile for 8 km upstream migration	2
	20-24	6.4	adult	threshold 50%-ile for 32 km upstream migration	2
	20-24	2.6	adult	threshold 95%-ile for any upstream migration	2
	20-24	3.2	adult	threshold 95%-ile for 8 km upstream migration	2
	20-24	5.4	adult	threshold 95%-ile for 32 km upstream migration	2
Osmerus eperlanus (smelt)		3-5	all stages	critical DO for presence	1
Non-salmonids					
<u>Lampetra fluviatilis</u> (lampern)		3-5	all stages	critical DO for presence	

Table **B1** - continued

Species	Temp °C	DO Level	Life stage	Effect	Ref
Anguilla anguilla (eel)		1	all stages	presence recorded	8
Zoarces viviparus (eelpout)		5	all stages	presence recorded	13
Pomatoschistus minutus (sand-goby)		< 5	all stages	avoidance	8
Platichthys flesus (flounder)		3-5 > 3 ≥ 4	all stages all stages all stages	critical <b>DO</b> for presence presence recorded presence recorded	1 8 13
Epinephelus akaara (red grouper)	25 25	< 2 1	adult adult	abnormal behaviour lethal	12 <b>12</b>
Hylio macrocephalus (black sea bream)	25 25 25	< 2 1 0. 5	adult adult adult	abnormal behaviour survivable per 7 hrs, 10% displayed abnormal behaviour 100 minute LC50	1 2 1 2 1 2
Harine species in upwelling area		3-4 4-5	all stages all stages	no deleterious effects no effect on biomass yield	11 11

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#### APPENDIX c

### EFFECTS OF DISSOLVED OXYGEN CONCENTRATIONS ON THE TOXICITY OF POLLUTANTS

### Cl INTRODUCTION

Alabaster and Lloyd (1980) hypothesised that for fish at lowered DO concentrations the increase in the ventilation rate needed to make up the deficit of oxygen increases the amount of contaminant which comes into contact with the gill surface where it may then be absorbed. several common contaminants it has been suggested that the LC50 for fish at a DO of 5 mg/l would be about half that at a DO of 10 mg/l. supported by the observations of Davies (1987) in tests with the fungicide chlorothalonil. However, Hughes and Adeney (1977) and Tuurala and Soivio (1982) provide an alternative explanation derived from experiments on the toxicity of zinc and of dehydroabietic acid (said to be a toxicologically significant constituent of Kraft mill effluents) with rainbow trout. Both substances impaired oxygen uptake, according to Tuurala and Soivio, by causing circulatory vasoconstriction and increasing the oxygen diffusion distance. The impairment of the respiratory mechanism would in turn affect the ability of fish to respond to the additional stress caused by a lack of oxygen.

The literature contains a range of studies of the effects of reduced DO in the presence of a variety of chemicals. Tests with ammonia have been carried out because of its presence in sewage effluents and hence widespread occurrence in polluted waters. Other chemicals have been included in experiments either because of their presence in other particular situations or because they represent specific classes of priority pollutants.

The data for this Appendix are summarised in Table Cl.

# c2 AMMONIA AND CYANIDE

Downing and Merkens (1955) cited by Alabaster and Lloyd (1980) found that the survival time of several species of fish in lethal solutions of ammonia at a DO concentration of half saturation was only one third of that in well-aerated solutions, and the conclusions of Lloyd (1961) that the effect of low DO is greater with ammonia than with other contaminants. The picture is complicated by the fact that in field situations a decrease in DO is likely to be accompanied by an increase in carbon dioxide and an accompanying reduction in pH which reduces the toxicity of ammonia. (The toxic ammonia species is  $NH_3$ , which is increasingly converted to ammonium,  $NH_4+$ , with decreasing pH.)

Thurston et al (1981) found that the toxicity of unionised ammonia (NH $_3$ ) to rainbow trout (Oncorhynchus mvkiss) fingerlings, 4 to 6 months old, in freshwater increased by a factor of more than 2 (96-hour LC50 values at DOs of 8.6, 3.6 and 2.6 mg/l were 0.70, 0.48 and 0.32 mg/l, respectively) . The DO concentration of 2.6 mg/l was the limiting concentration for the survival of control fish in the absence of ammonia.

Alabaster and his co-workers have studied the toxicity of ammonia and cyanide to salmon smolts at different salinities, simulating the effects a combination of reduced DO and pollutants might have on seaward migration.

Alabaster et al (1979) tested the effect of dissolved oxygen and salinity on the toxicity of ammonia to smolts of Atlantic salmon (Salmo salar). In 30% seawater and in freshwater, the toxicity of unionised ammonia was increased on reducing the DO concentration. At 12 °C and at DOs near to air saturation value (9.6 mg/l for 30% seawater and 9.5 mg/l for freshwater) the 24-hr LC50 of unionised ammonia was 0.3 mg/l in 30% seawater and 0.15 mg/l in freshwater. At low DOs (3.1 mg/l in 30% seawater and 3.5 mg/l in freshwater) LC50s, were reduced to 0.12 mg/l and 0.09 mg/l, respectively. When fish were pre-acclimated to ammonia at concentrations just below the unacclimated LC50 values, their 24-hr

LC50s increased by between 38 and 79%, with LC50s being higher both in 30% seawater and at high DOs. However, no clear pattern emerged for the percentage increase with respect to the different test conditions. The authors suggested that the large increase in LC50 found with increase in salinity from fresh to 30% seawater may result from reduced osmotic stress. However, they felt that the value for full strength seawater might be similar to the values obtained for freshwater.

Alabaster et al (1983) studied the acute lethal toxicity of ammonia and cyanide and mixtures of the two compounds to smolts of Atlantic salmon (Salmo salar) at low concentrations of DO in the presence of 5% carbon dioxide. These conditions were similar to those that prevailed in the Tees estuary.

The LC50s for unionised ammonia in freshwater were 0.21~mg/l at a DO of about 9 mg/l and 0.07~mg/l at a DO of about 3 mg/l. In 30% seawater the LC50 values were higher at 0.25~and~0.16~mg/l, respectively but were reduced to 0.2~and~0.14~mg/l, when the salinity was increased to 80% seawater.

In both 30% and 80% seawater the 24-hour LC50s of cyanide were similar to those in freshwater, about 0.07 mg/l at a DO of 10 mg/l and 0.02 to 0.03 mg/l at a DO of 3.5 mg/l. Acclimation to a DO of 6 mg/l rather than to the test value of about 3.5 mg/l produced a 24% decrease in the LC50 value, that is, a small increase in sensitivity to cyanide.

The toxicity of mixtures was complex. At the high DO the 24 hr LC50s were higher than those expected from adding the individual values, by a factor of 1.25, whereas at the low DO the LC50s of the mixtures were lower than expected, by a factor of 0.64. In other words there is evidence for a small but significant antagonistic effect at low DO.

Alabaster and Lloyd (1980) cited the findings of Cairns and Scheier (1957a). Fluctuations in DO between 9 and 2 mg/l increased the toxicity of cyanide to bluegill sunfish (Lepomis macrochirus) compared

with fluctuations between 9 and 5 mg/l by a factor of 2.5 for the 96-hour LC50 in soft freshwater at 18 "C.

## c3 CARBON DIOXIDE

In animals used to well-oxygenated conditions, an increase in carbon dioxide concentration can interfere with the uptake of oxygen by blood. Organisms which habitually live in low DO conditions are relatively insensitive to carbon dioxide fluctuations. Alabaster and Lloyd (1980) suggested that while sudden exposure to moderately high concentrations of carbon dioxide can cause a normally toierable low DO to be rapidly fatal, under natural conditions acclimation to increasing carbon dioxide levels is likely to occur before the concomitant decreasing DO reaches a critical ievel. Under otherwise favourable conditions acutely lethal effects can probably be avoided by maintaining the DO above 3 mg/1.

## c 4 CHLORINE

Alabaster and Lloyd (1980) quoted results of the Department of Scientific and Industrial Research (1958) which showed that the median period of survival cf rainbow trout (Oncorhvnchus mykiss) in a given concentration of chlorine (added as sodium hypochlorite) was shorter at low concentrations of DO than at high concentrations. Fish in solutions of about 0.1 mgil of chlorine at pi-i 7.4 were killed in 80 minutes at 40% air saturation compared with 1000 minutes at 90% saturation. At pH 6.3 the survival times were 53 and 733 minutes respectively. The increased toxicity at the lower pH could be expected since the species HOC1, which increases in predominance with a decrease in pH, is the toxic form of chlorine. The authors, however, suggested that some of the chlorine had reacted with ammonia excreted by the fish to form chloramines which, although less toxic than chlorine, are more persistent.

### c5 HEAVYMETALS

It is generally accepted that the toxicity of heavy metals increases at reduced DOs. Alabaster and Lloyd (1980) cited the findings of Lloyd

(1960) that the 24-hour LC50 for zinc to unacclimated rainbow trout was reduced by about 30% when the DO was decreased from 100% (9.5 mg/l) to 40% (3.7 mg/l) saturation. However, after prior acclimation to the lower levels of DO the effect of reducing DO concentrations to 3.7 mg/l (the lowest concentration employed) was nullified, although survival times were slightly lower at the lowest DO. Similar reductions in LC50s at low DO were reported for copper (Lloyd et al 1961) and for cadmium (Calamari and Marchetti, pers communication). Alabaster and Lloyd (1980) contrasted these results with those of Voyer (1975) with mummichog (Fundulus heteroclitus) where the 24- and 96-hour LC50s for cadmium were not affected by reductions in DO down to 4 mg/l with acclimation times to reduced DO of less than two hours. the work of Cairns and Scheier (1957b) with bluegill sunfish (Lepomis macrochirus) who obtained a 96-hour LC50 for zinc of 8.0 mg/l when DO fluctuated between 9 and 5 mg/l compared with 4.9 mg/l when the variation in DO concentration was more severe, between 9 and 2 mg/1.

In the studies of Hughes and Adeney (1977), zinc at 40 mg/l caused marked increases in ventilatory and coughing frequency and a decrease in heart beat rate. The effects were less marked at 10 mg/l but were apparently sufficient to interfere with the mechanisms involved in the uptake of oxygen at the gills. The authors concluded that the responses of rainbow trout to hypoxia with addition of this level of zinc, although complex, indicated that the presence of zinc produced a significant reduction in the ability of the fish to respond to low DO levels in the water.

Neuhoff and Theede (1984) found that the toxic effects of low copper concentrations (30  $\mu g/1$ ) on the polychaete <u>Pectinaria koreni</u> in long term exposure tests were increased at reduced DO resulting in increased respiratory activity and a reduced life-span.

### C6 ORGANIC CHEMICALS

The 96-hour LC50 of the fungicide chlorothalonil (tetrachloroisophthalonitrile) to rainbow trout at 53% saturation was  $10.5~\mu\text{g}/1$ 

compared with 17.1  $\mu$ g/l at 80% saturation (Davies and White 1985). Exposure to the fungicide resulted in a considerable increase in ventilation frequency (Davies 1987). Since reduced DO has the same effect, this may explain how the toxicity of the fungicide can be exacerbated at low DOs.

Carlson (1987) studied the effects of DO concentrations on the toxicity of 1,2,4-trichlorobenzene (TCB) to fathead minnows (Pimephales promelas) at the embryo, larval and juvenile stages. Reduction of DO to 5.6 mg/l had little effect on survival or growth, but at 4.5 mg/l mean survival to 28 days after hatching fell by 88.5% and mean weight by 60.5% at TCB concentrations of 920  $\mu$ g/l. Little effect was observed at 500  $\mu$ g/l and below, and it was concluded that reduced DO can induce an increase in susceptibility when toxicant concentrations are near "effect levels".

Alabaster and Lloyd (1980) noted that low DO both increases the toxicity of monohydric phenols and shortens the response time of fish to them. Tests by Herbert (1962) (cited in Alabaster and Lloyd 1980) with rainbow trout which showed that a reduction in DO from 100 to 50% saturation reduced the estimated threshold LC50 (the concentration lethal after long-term exposure) of phenol by about 20%. Gupta <u>et al</u> (1983) found that the toxicities of phenol, dinitrophenol and pentachlorophenol to the fish, <u>Notopterus notopterus</u>, all increased with a reduction in DO.

In studies of the relationship between DO and the bioconcentration of hydrophobic chemicals by fish, Opperhuizen and Schrap (1987) could detect no influence of DO concentrations of between 2.5 and 8 mg/l on either the uptake or the elimination rates of a tetrachlorobiphenyl and a hexachlorobiphenyl by guppies (Poecilia reticulata). Since the ventilation volume is inversely proportional to DO, and since the uptake rate constants should therefore be expected to increase with decreasing DO concentration, they concluded that the rate of diffusion of this type of chemical inside the fish is more important to bioconcentration than the rate of diffusion across the gills. This conclusion is in contrast with the findings for uptake of methylmercury by rainbow trout at well below acutely toxic levels by Rodgers and Beamish (1981) who found that

the rate of uptake was linearly related to the product of oxygen consumption and methylmercury concentration.

## c7 INDIRECT EFFECTS INVOLVING OXYGEN

Chemicals can exert an effect on the DO regime for example by interfering with photosynthetic activity and thus with oxygen production.

Tucker (1987) reported marked reductions in photosynthetic activity in the presence of the weedkiller propanil

(N-(3,4-dichlorophenyl)) propanamide) at concentrations below 50  $\mu$ g/1.

Further, oxygen levels can affect the sorption, release or formation of toxic substances in the environment. Hammer et al (1988) found that low oxygen concentrations of 1.8 mg/l led to a significant increase in the release of mercury from a lake sediment and the subsequent bio-accumulation by an aquatic plant (Ceratophvllum demersum) and a clam (Anodonta grandis) in comparison with DO concentrations of about 7 mg/l. It was suggested that under hypoxic conditions methylation of inorganic mercury occurs producing methylmercury which is more easily taken up by the biota.

Nitrite affects the oxygen-carrying capacity of the blood in at least some species, by causing methaemoglobinaemia, and hence decreases the ability of the fish to withstand reductions in DO levels (Lewis and Morris 1986). Studies by Watenpaugh and Beitinger (1986) confirmed the findings of other investigators (eg Bowser et al 1983) that channel catfish (Ictalurus punctatus) rapidly develop methaemoglobinaemia if they are exposed to sub-lethal nitrite concentrations. The test concentrations of DO employed by Watenpaugh and Beitinger (1986) decreased from 0.85 to 0.65 mg/l during the test. At this level of DO, the fish were inactive to accommodate the degree of hypoxia, except for an increase in both opercular rate and stroke volume compared with those noted prior to the hypoxic exposure.

In the absence of nitrite 13% of the haemoglobin in the blood was converted to methaemoglobin which increased to 78.5% when the fish were exposed to 1.5 mg NO<sub>2</sub>-N/1. The corresponding resistance times (survival times) decreased from an average of 173 min for the control to 37.8 min for the 1.5 mg NO<sub>2</sub>-N/1 exposure group. Bowser et al (1983) reported a mean percent methaemoglobin concentration of 3.2 in channel catfish fingerlings which was independent of the dissolved oxygen concentration Exposure to 2 mg/l and 10 mg/l nitrite and a DO of 8.5 mg/l increased the mean percentage of methaemoglobin to 26.9% and 89.9% respectively over a 48 hour period. Mortality was observed to increase with increasing nitrite and decreasing DO concentrations. However. the addition of 30 mg/l Cl- prevented mortalities during the 120 hour experiment even at the highest nitrite concentration tested of 10 mg/l and with DO decreasing to 1.5 mg/1. A DO of 4 to 5 mg/1, which would normally be adequate for channel catfish, did not prevent deaths when fish were exposed to 'high' nitrite concentrations (≥2 mg/l NO<sub>2</sub>-). All fish which had died during the 120 hour experiment had methaemoglobin levels in excess of 50%.

### C 8 CONCLUSIONS

A reduction in DO may have a direct effect on the toxicity of a pollutant normally increasing its toxicity by increasing the ventilation rate of the organism thus passing more pollutant over the gills or the pollutant may impair the oxygen uptake. There are other circumstances where the DO regime may have an effect on the chemistry of a pollutant and affect its solubility and its uptake by aquatic organisms. Chemicals themselves may also influence the DO regime in natural waters by inhibiting or promoting photosynthetic production.

Table Cl - Effect of low dissolved oxygen on the toxicity of pollutants

Substance and species	DO Level mg/l	Life stage	Effect	Ref
Ammonia, un-ionised (NH <sub>3</sub> )				
Salmo salar freshwate (Atlantic salmon)	9.6 3.5 9.6 3.5 10 3.5	smolt smolt smolt smolt smolt	24h LC50 0.15 mg NH $_3$ /l (unacclimated fish) 24h LC50 0.09 mg NH $_3$ /l (unacclimated fish) 24h LC50 0.20 mg NH $_3$ /l (acclimated to sub-lethal levels of ammonia) 24h LC50 0.14 mg NH $_3$ /l (acclimated to sub-lethal levels of ammonia) 24h LC50 0.2 mg NH $_3$ /l (acclimated to sub-lethal levels of ammonia) 24h LC50 0.08 mg NH $_3$ /l	2 2 2 2 3 3
30% seawat	9.6 3.1 9.6 3.1 9	smolt smolt smolt smolt smolt	24h LC50 0.30 mg $NH_3/l$ (unacclimated fish) 24h LC50 0.12 mg $NH_3/l$ (unacclimated fish) 24h LC50 0.50 mg $NH_3/l$ (acclimated to sub-lethal levels of ammonia) 24h LC50 0.18 mg $NH_3/l$ (acclimated to sub-lethal levels of ammonia) 24h LC50 0.25 mg $NH_3/l$ 24h LC50 0.16 mg $NH_3/l$	2 2 2 2 3 3
80% seawat	ter 9 3.6	smolt smolt	24h LC50 0.20 mg NH <sub>3</sub> /l 24h LC50 0.14 mg NH <sub>3</sub> /l	3 3
Oncorhynchus mykiss freshwat (rainbow trout)	er 8.6 3.6 2.6	adult adult adult	96h LC50 0.70 mg NH <sub>3</sub> /l 96h LC50 0.48 mg NH <sub>3</sub> /l 96h LC50 0.32 mg NH <sub>3</sub> /l	10 10 10
Carbon dioxide				
Oncorhynchus mykiss (rainbow trout)	> 3	adult	avoids acute lethal effects	I

	Substances and species	DO Level mg/l	Life stage	Effect	Ref
	Chlorine, 0.1 mg Cl/l				
	Oncorhynchus mykiss (rainbow trout)	90% sat 40% sat 90% sat 40% sat	adult adult adult adult	pH7.4 median survival time 1000 minutes pH7.4 median survival time 80 minutes pH6.3 median survival time 700 minutes pH6.3 median survival time 53 minutes	7 7 7 7
	Chlorothalonil				
C1.	Oncorhynchus mykiss (rainbow trout)	80% sat 53% sat	adult adult	96h LC50 17.1 mg/l chlorothalonil 96h LC50 10.5 mg/l chlorothalonil	6 6
v	Cyanide				
	Salmo salar fres (Atlantic salmon)	shwater 10 3.5	smolt smol t	24h LC50 0.073 mg HCN/l 24h LC50 0.024 mg HCN/l	3 3
	30%, 80%	seawater 10 3.5	smolt smol t	24h LC50 0.07 mg HCN/l 24h LC50 0.03 mg HCN/l	3 3
	Metals				
	Copper				
	Oncorhynchus mykiss (rainbow trout)	3.7 (40% sat)	adult	48hr LC50 30% lower than at DO 9.5 mg/l (100% sat)	9
	Cadmium				
	Oncorhynchus mykiss (rainbow trout)	3.7 (40% sat)	adult	30% reduction in LC50 values at 4 to 40 days	14

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Table C1 - continued

Substances and species	DO Level mg/l	Life stage	Effect	Ref
Fundulus heteroclitus (mummichog)	4	adult	24h and 96h LC50s unaffected by reduction in DO	11
Zinc				
Oncorhynchus mykiss (rainbow trout)	3.7 (40% sa 3.7 (40% sa	(40% sat) adult (40% sat) adult	unacclimated, 24h LC50 30% lower than at DO 9.5 mg/l (100% sat) acclimated, 24h LC50 similar to value at DO 9.5 mg/l (100% sat)	13
Lepomis macrochirus (bluegill sunfish)	fluctuating max 9, min 5 max 9, min 2	adult adult	96h LC50 8.0 mg/l Zn 96h LC50 4.9 mg/l Zn	<b>4</b> 4
Phenols, monohydric				
Oncorhynchus mykiss (rainbow trout)	50% sat	adult	20% reduction in LC50	<b>ω</b>
1,2,4-Trichlorobenzene				
Pimephales promelas (fathead minnows)	5.6 4.5	early stages	no effect on survival at 920 µg TCB/l impaired survival and growth at 920 µg TCB/l	വവ
Nitrite				
<pre>Ictalurus punctatus (channel catfish)</pre>	4.5 fi	fingerlings	lethal when exposed to high nitrite concentrations $(2-10~\mathrm{mg/l})$	12

## Notes to Table Cl continued

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