EFFLUENT STANDARDS FOR RECLAIMING INDUSTRIAL RIVERS

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ABSTRACT

In industrial areas the waste water from the high concentration of population and heavy industry can cause overload of relatively small rivers. Uniform emission standards for the discharges are inappropriate even in these areas as variations in river flows would make a uniform standard too relaxed or too stringent, according to circumstances, at different points. The problem of fixing river quality standards which would allow fish to repopulate the industrial rivers in Yorkshire and then of applying them to produce appropriate standards for effluents has been examined by a group from the Yorkshire Water Authority. Provisional river water quality standards are recommended in different forms and the bases for these are discussed and comparisons made with the field measurements of river water qualities and the presence of fish. The standards are suggested as mean or median or 95 percentiles as appropriate and also in some cases as maxima which should not recur more often than a critical period if fisheries are to be self sustaining. Methods for applying them to the many effluent discharges in the industrial areas of Yorkshire are also discussed.

KEYWORDS

River Water Quality Standards, Fish Toxicity, Effluent Discharge Conditions, Storm Sewage Overflows, Consent Conditions

INTRODUCTION

The Yorkshire Water Authority area contains a population of 4.5 M and of this about 3.2 M is concentrated in the industrial areas of West Yorkshire and South Yorkshire/North Derbyshire. The average population density in these areas is about 1,000/km² even including the sparsely populated areas in the Pennine Hills. In addition the basic industries of wool textile dyeing and scouring and steel and coal including coal carbonisation add to the considerable load on to the river system which, up to the present, the sewerage and sewage treatment systems have been unable to treat to an adequate standard. The coal carbonising effluents, which have tended to discharge direct to the rivers, in particular have imposed an unacceptable load on the rivers which are relatively small and in dry weather the natural flow is much less than the flow of effluents.
As well as the degradable organic matter which can deplete the oxygen concentration chemicals such as ammonia, which are toxic to fish from both the sewage effluents and coal carbonising wastes, cyanide, phenols and metals are present so that fish are generally absent except in the headwaters above the major discharges. If the rivers are to be cleaned up economically it was necessary to decide which pollutants were critically causing the absence of fish and what concentrations could be tolerated in a good fishery. It was also necessary to determine how such river standards could be translated into the effluent standards required to bring about the improvements in the most economic way.

It was with this brief that a working group from the Southern Division and Head Office of the Authority was set up and this was later expanded to include other Divisions and sub groups dealing with water quality and mathematical modelling were formed. This paper is based on the work of these groups.

**WATER QUALITY CRITERIA**

It is the policy of the Yorkshire Water Authority to upgrade, as possible, all the presently unsatisfactory rivers to comply with Class II of the National Water Council's classification scheme. Whilst this would not be restoring them to the 1A or 1B class which is the natural state, and indeed the present state, of most of the rivers of Yorkshire, it would allow the presence of coarse fish and would thus produce a major improvement without the excessive expenditure involved in treating effluents to a standard approximating to the natural river water quality.

The processes by which toxic agents act to prevent the presence of fish in rivers are imperfectly understood and it is not clear whether the ultimately critical conditions are those which affect adult fish by preventing spawning or by stimulating avoidance reactions or whether lethality to fish fry, or adult fish is critical. Whatever the general reason for absence of fish it is clear that rivers can be non toxic for the major part of the year and still not contain a satisfactory fish population. That this is so is not really surprising as it is known that it may take a few years for a fishery to recover from a fish kill resulting from toxic conditions which have persisted for only a matter of a few hours.

As the conditions which govern the presence of fish are not precisely known, recourse is usually had to a comparison of the mean, median or 95 percentile concentrations of substances with the presence or absence of fish when setting river quality standards. Additivity of the toxicity of different substances may be taken into account by limiting the sum of the fractional 48 hour LC₅₀ in the Trent Research Programme (Garland and Hart, 1971) or by setting standards such that the concentrations are generally below the level at which the toxicity becomes additive. This may be about 20% of the median lethal threshold concentration for many poisons though this may not apply to all poisons and mixtures of some may show synergistic effects whereas other poisons have antagonistic effects on each other.

This empirical approach was adopted by the group; the standards proposed being devised by reference to the literature taking cognisance of conditions in Yorkshire, where appropriate, and of the need to avoid unacceptable additive effects. The standards are given in Table I and were intended to be, and must be regarded as, provisional and subject to amendment in the light of better information resulting from experience of their use. They are necessarily based on simplifications of the available toxicity information to make them generally applicable and make possible the development of mathematical models for planning the most economic methods of reclaiming the rivers. As this process of reclaim also entails improving the visual amenity of the rivers standards relevant to appearance as well as to fish toxicity are also included.
### TABLE I  Summary of Tentative Standards for a Class II River 
**Supporting a Good Fishery**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Support</th>
<th>Acceptance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.O.D.</td>
<td>less than</td>
<td>7 mg/l arithmetic mean</td>
</tr>
<tr>
<td>Dissolved Oxygen</td>
<td>greater than</td>
<td>40% (5%ile), min. 3.0 mg/l</td>
</tr>
<tr>
<td>Suspended Solids</td>
<td>less than</td>
<td>25 mg/l median</td>
</tr>
<tr>
<td>Unionised ammonia as N</td>
<td>&quot;</td>
<td>0.04 mg/l 95%ile, 0.2 mg/l max.</td>
</tr>
<tr>
<td>Nitrite as N</td>
<td>&quot;</td>
<td>1 - 2 mg/l 95%ile dependent upon chloride conc.</td>
</tr>
<tr>
<td>Iron (dissolved)</td>
<td>&quot;</td>
<td>1 mg/l 95%ile</td>
</tr>
<tr>
<td>Total cyanide, including complex cyanides as CN</td>
<td>&quot;</td>
<td>0.02 mg/l 95%ile, 0.1 mg/l max.</td>
</tr>
<tr>
<td>Phenols (lower alkyl only) as C₆H₅OH</td>
<td>&quot;</td>
<td>1 mg/l 95%ile</td>
</tr>
<tr>
<td>Mercury (downstream of Chlor-alkali works)</td>
<td>&quot;</td>
<td>1 μg/l as annual arithmetic mean</td>
</tr>
<tr>
<td>Cadmium (dissolved)*</td>
<td>&quot;</td>
<td>0.0015 mg/l arithmetic mean</td>
</tr>
<tr>
<td>Chromium (dissolved)*</td>
<td>&quot;</td>
<td>0.05 mg/l arithmetic mean</td>
</tr>
<tr>
<td>Copper (dissolved)*</td>
<td>&quot;</td>
<td>0.04 mg/l arithmetic mean</td>
</tr>
<tr>
<td>Lead (dissolved)*</td>
<td>&quot;</td>
<td>0.05 mg/l arithmetic mean</td>
</tr>
<tr>
<td>Nickel (dissolved)*</td>
<td>&quot;</td>
<td>0.13 mg/l arithmetic mean</td>
</tr>
<tr>
<td>Zinc (dissolved)*</td>
<td>&quot;</td>
<td>0.4 mg/l arithmetic mean</td>
</tr>
<tr>
<td>pH</td>
<td>&quot;</td>
<td>Between 6 and 9 for 95% of time, max. 9.5 (in the absence of pollutants seriously affected by pH)</td>
</tr>
<tr>
<td>Temperature</td>
<td>&quot;</td>
<td>28°C max.</td>
</tr>
</tbody>
</table>

*More stringent standards are required in water softer than 300 mg/l hardness*
As can be seen from the Table, the standards are generally given as mean or median or 95 percentile figures and this presentation is suited to the river monitoring programme in use which involves the taking of spot samples at regular intervals. The choice whether the average or the 95 percentile is the more significant depends on the nature of the pollutant under consideration. For poisons such as ammonia which are quick acting at their lethal threshold concentration the 95 percentile can be expected to be more relevant but for those such as cadmium which are slow acting at their lethal threshold, possibly because of accumulation effects, the total exposure is more relevant and the median concentration will give a more precise indication of this. The median concentration is also probably the best indication of the effect of pollutants which have an impact on the visual amenity of a river though clearly also extremely noxious events may only occur very rarely but still have an impact on the public conscious.

The 95 percentile standards are proposed as a means of ensuring that the distribution of concentrations is such that high concentrations detrimental to fish occur at an acceptably low frequency. It is possible that this objective may not always be achieved and attainment of the 95 percentile standard will not guarantee the absence of an atypical distribution including toxic conditions which are sufficiently frequent to prevent the development of a viable fishery. Certain proposed standards, therefore, include maximum figures which if complied with, should make sure that toxic conditions do not occur.

The bases on which the proposed standards have been devised are described briefly below.

**DERIVATION OF STANDARDS**

**B.O.D.**

The National Water Council standard for a Class II river is a 95 percentile of 9 mg/l which, it is suggested, relates to an annual arithmetic mean B.O.D. of 5 mg/l. However, in parts of the industrial rivers in Yorkshire there are indications that the B.O.D. could be tolerated at an annual arithmetic mean of about 7 mg/l before critical D.O. levels are reached and, bearing in mind the self purification which will occur along the length of the rivers, there appears to be some scope for relaxation of the National Water Council standard in certain reaches. However, there are indications that the Yorkshire rivers may have to achieve a 5 mg/l average standard in low flow conditions at their tidal limits if the Dissolved Oxygen level in the Humber estuary is to be satisfactory.

Though the B.O.D. test was developed to provide a means of testing the probable effect of an effluent on the D.O. in a watercourse, it also gives an indication of the biodegradable organic matter present. As there is merit in minimising the concentration of this material in a stream from the visual amenity point of view the sub group recommend that the arithmetic mean B.O.D. should not be allowed to rise above 7 mg/l and preferably, where it is economically possible, the National Water Council guideline of 5 mg/l should be aimed for.

**Dissolved Oxygen (D.O.)**

The standard that 95% of the results should exceed 40% saturation is the standard recommended by the National Water Council for tolerant coarse fish. Whilst there is evidence that fish survive at dissolved oxygen concentrations below 3 mg/l their activity is impaired and this is, therefore, suggested as the minimum figure
which should be allowed. Also, the effects of other poisons can be enhanced in low dissolved oxygen. For example, at 50% D.O. the toxicity of ammonia is increased by about a third as compared to the toxicity at 100% saturation D.O. Clearly some allowance for this effect should be made when setting standards in practice.

Suspended Solids

The standard of a median of 25 mg/l is suggested as an improvement on the draft E.E.C. Directive standard of a mean of 25 mg/l excluding flood conditions. This latter standard is difficult to apply in the absence of a definition of flood conditions and knowledge of river conditions leads to the judgement that a river appears visually acceptable if the median suspended solids is not significantly greater than 25 mg/l. The standards should also be satisfactory for fish viability even if the suspended matter normally consists of angular mineral particles which can be harmful to fish. Exceptional local circumstances could require more stringent standards for suspended solids; for example, if settlement of solids upstream of a weir leads to anaerobic conditions in the substrate and depletion of oxygen in the river.

Ammonia

The ammonia standard is based on unionised, rather than total, ammonia as this is much more toxic than the ionic form. However, this leads to some difficulties in application of the standard as unionised ammonia is not determined directly but is calculated from the total ammonia, pH and temperature of the water. The method of overcoming these difficulties is referred to later.

The standard proposed is a 95 percentile of 0.04 mg/l as N and is approximately double the European Inland Fishery Advisory Committee's (E.I.F.A.C.) no effect standard for all fish of 0.021 mg/l as N (Alabaster and Lloyd, 1980) but is about 20% of the median lethal threshold. The higher figure has been chosen as there is evidence that it allows the development of an adequate fishery and even this figure could lead to quite stringent effluent standards in the low dilutions available in the industrial areas of Yorkshire.

The maximum standard is 0.2 mg/l as N also proposed for ammonia is similar to the median lethal threshold concentration and this exerts its effect over about 24 hours (Solberg and Cooper, 1983). The standard thus refers to this period of time and it may be possible to exceed it for shorter periods without causing undue harm to the fishery. On the other hand if this concentration recurs at an excessive frequency the quality of the fishery may be expected to be poor and if the dissolved oxygen were low and other toxic agents were present in concentrations greater than 20% of their median lethal threshold concentration it is probable that no fish would be able to survive.

Nitrite

The information in the literature on this is somewhat contradictory and coarse fish appear to be less sensitive than salmonids. Monovalent cations and hardness may reduce the toxicity (Russel, Thurston and Emerson, 1981). The standards quoted refer to chloride concentrations of 60 and 240 mg/l respectively and calcium concentrations of 40 and 80 mg/l respectively. The toxicity of nitrite also increases as pH is decreased but this is not taken into account in the standards.
Iron

The presence of iron in drainage waters from active and abandoned mines is a serious problem in Yorkshire. The major effect is the precipitation as ochre deposits on stream beds which can persist for several kilometers and which, as well as being unsightly, lead to impoverishment of aquatic life and impairment of fish growth and breeding. The iron can also react with organic chemicals in effluents which, whilst it prevents precipitation of ochre and ameliorates the impoverishment of aquatic life, does have the disadvantage that unsightly turbidity is produced in the water.

It may also be that as the iron which is initially dissolved starts to precipitate there is transient toxicity which reduces as the particle size increases. The effects of iron are thus complex and it appears that there is scope for useful research to quantify the effects more precisely. In the meantime it was considered that 95 percentile dissolved iron of 1 mg l\(^{-1}\), based on the E.P.A. standard (Train, 1979) was the best available standard.

Cyanide

Complex cyanides, particularly ferrocyanide, can be rapidly decomposed in sunlight to give free HCN. The standard is based on a median lethal threshold to roach as 0.1 mg l\(^{-1}\), which may exert its effects in 3 to 5 days. It is also based on the assumption that 100% dissociation of ferrocyanides occurs in strong sunlight and thus may prove to be over-stringent. The 95 percentile standard has been set in order to avoid addition of its effects to those of ammonia, the principal toxic agent in most industrial rivers of Yorkshire. As with the ammonia standard the maximum cyanide value of 0.1 mg l\(^{-1}\) should not be allowed to recur at an excessive frequency.

Phenols

The standards are based on work using pure phenol in which the median lethal threshold concentration was assessed as 10 mg l\(^{-1}\) (Solbé and Cooper, 1983). However, the most practical analysis method is that using amino antipyrène which, in common with other methods, gives poor recovery with certain substituted phenols. To allow for this a maximum of 5 mg l\(^{-1}\) for phenols is proposed but where higher phenols, chloro and nitro phenols and 2 - 5 xylenol are known to be present separate standards are required to allow for their high and differing toxicities.

As phenol at its median lethal threshold concentration can exert its toxic effect in only seven hours (Solbé and Cooper, 1983) it is important that an adequate safety margin is maintained. The 95 percentile standard of 1 mg l\(^{-1}\) is 20% of the median lethal threshold concentration and is in agreement with the E.I.P.A.C. recommendation, of a maximum of 2 mg l\(^{-1}\), when the 50% allowance for poor recovery in the analytical test is made.

Mercury

The standard of 1 mg l\(^{-1}\) is that required by a European Commission directive and the groups did not consider whether any changes to this were desirable.
Metals (Cd, Cr, Cu, Pb, Ni, Zn)

The standards for the metals Cd, Pb, Ni and Zn were derived for well aerated borehole water low in organic content with 300 mg/l hardness as CaCO₃.

A hardness of 300 mg/l is typical of the industrial rivers but allowance for increased toxicity has to be made if it should be lower than this. As the toxicity of Cu is reduced in waters containing organic matter the standard for this metal was derived assuming the rivers contain plenty of humic material derived from sewage effluent. The toxicity of Cr is little affected by hardness but the hexavalent state is more toxic than the trivalent and, as little is known about the relative proportions of the two states, the standard assumes that it is all present in the hexavalent form to provide a basis for judging whether further work is necessary to establish whether Cr is present in toxic concentrations in Yorkshire rivers.

The standards are quoted as mean concentrations because the time of effect at the median lethal threshold concentration is very long so that the average conditions can be expected to have more relevance than the peak concentrations as these are unlikely in practice to persist for sufficient time to have an acutely toxic effect. In the case of Cu the time of effect for the median lethal threshold concentration is about 20 weeks but for Cd this is about 40 weeks (Solbø and Cooper, 1983).

Whilst the standards are quoted for dissolved metals the long time of effect indicates that they could be cumulative poisons and a poisoning effect could perhaps also result from ingestion with food as well as from solution. Whether this is important is, however, not known.

APPLICATION OF STANDARDS

The provisional standards above are intended to provide a guideline for the relative importance of the differing toxic effects which prevent the presence of fish in the industrial rivers and having produced these an assessment of the water quality at various river sampling points was undertaken to determine what improvements might be necessary. The relevant results for the 5 years 1976 – 1981 are shown in Table II and it can be seen that in general low dissolved oxygen and high unionised ammonias are the factors which may be critically preventing the presence of fish, though in some rivers (those which contain coal carbonising effluents) cyanides and phenols may also be of importance.

There is some doubt about the possible effects of metals as total, rather than dissolved metals have been determined, however, in general it seems unlikely that there will be sufficient metal in solution to cause problems.

The water quality in relation to the presence or absence of fish is considered briefly below.

1. River Calder at North Dene

The river at this point contains few fish but this may be due to its physical nature. However the sampling point is a short distance downstream of a large discharge and incomplete mixing may also be a factor.

2. River Calder at Cooper Bridge

This point is some miles downstream from North Dene and as the water quality would, in general, indicate supports a good fishery. As the cadmium concentration is
TABLE II  Comparison of Water Quality, in the 5 years 1976-1981 at Various Sampling Stations, 
(All results as mgl-¹ except as otherwise stated)

<table>
<thead>
<tr>
<th></th>
<th>Sampling Station</th>
<th>Proposed Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>B.O.D.</td>
<td>5.4</td>
<td>3.2</td>
</tr>
<tr>
<td>D.O. % sat</td>
<td>71</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>3.4</td>
<td>0.6*</td>
</tr>
<tr>
<td>S.S.</td>
<td>9.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Unionised NH₃</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Nitrite</td>
<td>0.12</td>
<td>0.03</td>
</tr>
<tr>
<td>Total CN</td>
<td>0.3</td>
<td>0.55</td>
</tr>
<tr>
<td>Phenols</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Diss. Fe</td>
<td>0.6</td>
<td>1.2*</td>
</tr>
<tr>
<td>Diss. Cd</td>
<td>0.005*</td>
<td>0.002*</td>
</tr>
<tr>
<td>Diss. Cr</td>
<td>0.007</td>
<td>0.03*</td>
</tr>
<tr>
<td>Diss. Cu</td>
<td>0.02</td>
<td>0.09</td>
</tr>
<tr>
<td>Diss. Pb</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Diss. Ni</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Diss. Zn</td>
<td>0.05</td>
<td>0.10</td>
</tr>
<tr>
<td>pH</td>
<td>6.6</td>
<td>6.7</td>
</tr>
<tr>
<td>Temp. °C</td>
<td>7.4</td>
<td>7.3</td>
</tr>
</tbody>
</table>

* indicates sub standard result
+ indicates borderline result
‡ indicates that total metal determined not dissolved metal

Sampling Stations

1. River Calder at North Dene Bridge
2. River Calder at Cooper Bridge
3. River Aire at Calverley Bridge
4. River Aire at Leeds Bridge
5. River Aire at Casteford Weir
6. River Dearne at Storrs Mill Bridge
7. River Dearne at Pastures Bridge
8. River Rother at Woodhouse Mill
9. River Don at Hadfield's Weir
higher than the standard there is some doubt whether this standard might prove to be unnecessarily stringent.

3. River Aire at Calverley Bridge

As the low dissolved oxygens indicate there are few fish at this point though the situation should improve as extensions to the Bradford sewage works are commissioned.

4. River Aire at Leeds Bridge

The results indicate some recovery of the river but there are still few fish present.

5. River Aire at Castleford Weir

Further discharges of sewage effluent cause a decrease in the dissolved oxygen and an increase in unionised ammonia so that there are no fish present.

6. River Dearne at Storr's Mill Bridge

There are no fish in the river at this point and the major reasons appear to be high ammonia and cyanide from a coal carbonising effluent though sewage effluents make some contribution to the high ammonia.

7. River Dearne at Pastures Bridge

Dilution with clean water from a tributary causes some improvement to the river at this point though this was offset by a discharge of pre treated coal carbonising effluent. Initially the coal carbonised effluent was discharged direct, but throughout most of the period it was discharged to a sewage works causing some overload of the works but a net improvement to the river. The discharge ceased in 1980 causing a further improvement to the river and in 1982 fish were beginning to establish themselves in this reach.

8. River Rother at Woodhouse Mill

As the results indicate the Rother is the most polluted river in the Yorkshire Water Authority area. The main pollutants are ammonia from sewage effluents and coal carbonising effluents and also cyanide and phenol from the latter. However, despite the relatively high B.O.D. the dissolved oxygen regime appears satisfactory.

9. River Don at Hadfield's Weir

This river at this point in the centre of Sheffield appears to be perhaps the most unpolluted of those under consideration, but it contains few fish. The only parameter which is subject to some doubt is the 95 percentile total cyanide concentration but as the 0.02 mg/l standard is probably over-stringent this is unlikely to be the explanation. Also it is known that in a canalised section of river further downstream, but which has essentially similar river water quality, a good fish population is beginning to be established.

It seems probable that intermittent discharges from the inadequate Sheffield sewerage system are responsible and if this is so it casts doubt on the use of 95 percentiles for the assessment of water quality. This is referred to later.
APPLICATION TO EFFLUENT STANDARDS

From the above assessment it is evident that the major problems in the Yorkshire industrial rivers are the periodic lack of dissolved oxygen and high concentrations of ammonia.

To determine with certainty the causes of the periodic low dissolved oxygen level and the measures needed to correct them would require an extensive experimental and modelling programme, particularly as one likely cause would be discharge of anaerobic sewage from the operation of storm overflows. Settlement and re-suspension of organic solids also affect the dissolved oxygen regime so that the interactions involved are complex. The group, therefore, decided that detailed consideration of the ammonia problem, as this is a soluble substance, was more likely to show quicker rewards. Until such time as detailed consideration could be given to the dissolved oxygen problem, progress in cleaning up the rivers could be maintained using the B.O.D. results as a basis for estimating the improvements necessary.

Several steps are involved in translating the proposed river water unionised ammonia standard into the effluent consent conditions required to achieve that standard. Firstly, the unionised ammonia concentration is dependant on the pH and temperature of the river water according to the equation:

\[ \text{NH}_3 = \frac{T_n}{1 + 10^x} \]

where \( x = \frac{1}{0.09912 + 0.00036T} - \text{pH} \)

and \( \text{NH}_3 = \text{unionised ammonia concentration (mg/l as N)} \)

\( T_n = \text{total ammonia concentration (mg/l as N)} \)

\( T = \text{temperature (°C)} \)

This equation amalgamates the dissociation equation with an equation describing the temperature dependance of the dissociation constant and it shows that the unionised ammonia is dependant on the river water temperature and pH as well as on the total ammonia discharged by effluents. In order to determine the total ammonia which can be discharged it was, therefore, necessary to convert the suggested 95 percentile unionised N standard into a total ammonia standard taking account of the variations in pH and temperature which occur. This has been done (Lai, 1982) using the Monte Carlo simulation technique described by Warn and Brew (1980) for predicting the distributions of concentrations of pollutants in watercourses which result from variations in flows and concentrations of discharges.

In the technique random numbers from the distributions of the parameters as measured at the river sampling points are inserted in equation (1) and an iterative adjustment of the values is made until the 95 percentile total ammonia corresponding to the 95 percentile unionised ammonia standard is determined. Any correlations between parameters are taken into account and this procedure has been used for sampling stations on three different rivers and the 95 percentile standards corresponding to the 0.04 mg/l standard for unionised ammonia calculated.

These calculations gave 95 percentile standards of 3.0, 3.9 and 8.6 mg/l total ammonia for the three rivers Rother, Dearne and Don respectively. The high figure for the Don is accounted for by its lower pH, and to some extent, temperature, regime as it rises in peaty moorlands but pH's and temperatures for the Rother and
Dearne are similar and the difference in standards for these rivers was somewhat surprising. However, it has been found that in contrast to the Dearne, the Rother shows a correlation between temperature and total ammonia and that if it is assumed that there is no correlation then about half the difference between the standards is removed. The reason for the correlation appears to be that high temperatures and total ammonias both coincide with low river flows in the Rother, where little ammonia is oxidised before discharge but that, in the Dearne, where most of the ammonia is oxidised, this effect is offset by the greater oxidation of ammonia which is obtained from sewage treatment plants in higher temperature conditions. It thus appears likely that, as the Rother is cleaned up and the ammonia oxidised, the required total ammonia standard will be somewhat less stringent than that presently predicted.

Having set the ammonia standard it is necessary to determine the effluent standards which are required to achieve that standard. This has been done for one river reach where there are a number of discharges on the basis that, to be even handed, each discharge should have the same consent condition and that the river quality required should only be achieved at the end of the reach. The method employed was again to use the Monte Carlo simulation but this time applied to the simple mass balance equation for each discharge progressively down the length of the reach. By undertaking this iteratively a uniform 95 percentile ammonia concentration was obtained for each discharge which gave the required 95 percentile river standard (Holmes, 1981). In this case it is of interest that the standard chosen for the end of the reach, of 5.2 mg l\(^{-1}\) total ammonia, gave a 95 percentile, and thus the consent condition, of 15 mg l\(^{-1}\) for each discharge. This standard should be readily achievable though, whether it will result in satisfactory conditions in the river can only be proved by experience, and it should be noted that fixing consent conditions on a uniform basis, even for short reaches of rivers, does not necessarily achieve the desirable most economic way of cleaning up the rivers. Some trade off between the consent conditions for different discharges to take advantage of any economies of scale is necessary to obtain this. However, to apply it to short reaches only will be much more economic than applying uniform conditions over an entire river basin where the dilutions of clean water available for discharges vary by several hundred fold.

FUTURE DEVELOPMENT OF STANDARDS

The above sets out procedures for applying standards which are expressed traditionally as either 95 percentiles or averages for substances which are in solution and behave conservatively. Clearly some development is required to amalgamate these with procedures for taking account of the solid phase, re-aeration and self purification reactions which occur in practice. However, before undertaking this it seems worthwhile to consider the extent to which 95 percentile standards are a sufficient description of the necessary river water quality.

As referred to above the data for the River Don at Hadfield's weir in the centre of Sheffield indicate that the river water quality is very good and yet it supports few fish. However, it is known that the sewers in Sheffield are inadequate and that they discharge prematurely though it has been calculated that, on average, such discharges only occur for about 3.5% of the time.

Clearly discharges which occur for this brief period may have little effect on the measured 95 percentiles but the observed quality of the fishery suggests that these, or some other intermittent discharge, are adversely affecting fish. The 95 percentiles thus have their limitations as indicators of the water quality necessary to support fish life and it is to be expected that such standards are only valid when they refer to situations in which the distributions of concentrations follow
a generally occurring pattern. If this is not the case and concentrations above the limit occur more frequently than usual the development of a good fishery could be prevented.

One way of making some allowance for this possibility would be to set standards in terms of, say, 99 percentiles and despite the difficulties in accurately estimating such figures this could be worthwhile as it would enable better account to be taken of the effects of storm discharges when improvements to a river system are planned. This could be done by using the Monte Carlo simulation technique to the mass balance equation developed by Aspinwall (1981) knowing the distributions of sewage and river flows. In its simplest form, when there is no pollution upstream of the overflow, this model can be expressed as the equation:

\[ Y = \frac{X}{n} \cdot \frac{n - m}{p + (n - m)} \] (2)

where \( Y \) = concentration of pollutant downstream of the overflow
\( X \) = concentration in the dry weather sewage
\( n \) = sewage flow as multiple of dry weather flow
\( m \) = overflow setting as multiple of sewage dry weather flow
\( p \) = river flow as multiple of sewage dry weather flow

The model predicts that the pollution level in a river caused by storm overflows rapidly reaches a maximum as the storm sewage flow increases but that then there is a steady decrease in concentration with further increases in flow due to the increasing dilution effect.

The above gives a possible way of planning more cost effective improvements in a river basin but it does not fully describe the water quality factors which limit the presence of fish in rivers. The sub groups discussed this aspect and came to the conclusion that probably the most relevant factor was the frequency with which unsatisfactory conditions recur. Clearly if the interval between toxic events is sufficiently long then a self sustaining fishery can develop irrespective of the damage caused at each event. The simplest way of using this approach would be to consider the return period of lethal concentrations but it should be noted that this is not necessarily the governing factor as lower concentrations which inhibit breeding or cause other effects may occur at a sufficient frequency to cause deterioration in a fishery.

Another difficulty in this approach is the determination of the return period which is critical for a viable fishery. Clearly this cannot be less than one year for fish kills at this frequency would prevent them breeding. At the other extreme a once in ten year return frequency would allow several generations of fish to co-exist and, whilst this may be desirable, it may not be essential for a good fishery as fish kills have been noted at greater frequencies in some fisheries without apparent detriment. It seems probable that the required return period is between those extremes and that it may be related to the time for different species to reach maturity which, for example, is 2 years for dace, 3 - 4 years for roach and 5 - 6 years for chub.

Another difficulty in developing this approach is that it is not just the concentration of toxic agent which is important, the length of time over which it persists also affects lethality. For example in the case of unionised ammonia a concentration of 0.2 mg l\(^{-1}\) which persists for 24 hours is just as toxic as one of
0.4 mg/l which lasts for about 3 hours. The probability that any concentration determined in a spot sample will persist for any given period of time would, therefore, need estimating. Development of the mathematical technique for taking this time dependence into account could well, however, eventually lead to it being possible to more reliably apply water quality criteria determined in the laboratory to the river conditions which occur in practice.

SUMMARY AND CONCLUSIONS

1. Provisional river water quality standards for commonly occurring toxic compounds are recommended which should enable self sustaining coarse fisheries to be established in industrial rivers.

2. Standards are also suggested which would improve the visual amenity of industrial rivers. These include a mean B.O.D. no greater than 7 mg/l and a suspended solids of about 25 mg/l maximum expressed as a median to avoid the difficulties of interpretation of means which include the high suspended solids concentrations in flood conditions.

3. The toxic substance standards are expressed either as means or 95 percentiles for compounds which have a long or short time of effect respectively at their median lethal threshold concentration.

4. These standards when tested against the river water qualities observed at various sampling points on Yorkshire rivers give a broad indication of the presence or absence of fish, but they are not fully reliable in that some apparently satisfactory river reaches do not support a satisfactory fish population.

5. A possible reason for this is that the intermittent discharges from storm sewage overflows are inadequately catered for in the standards. A procedure for overcoming this by applying the Monte Carlo simulation to a storm overflow mass balance equation is described.

6. The Monte Carlo simulation technique is also recommended for converting un-ionised ammonia standards to the total ammonia standards required for each sampling point when the pH and temperature variations found at those points are taken into account. Due to differing pH and temperature regimes the total ammonia standards differ widely.

7. This same technique has also been used to fix consent conditions for multiple effluent discharges in one river reach on an even handed basis. This should only be applied to short reaches to avoid too wide a variation in dilution and thus unnecessarily stringent standards.

8. Consideration of the results achieved has suggested that a more precise way of specifying water quality criteria would be as toxic events which are not to recur at a frequency which would prevent fish from breeding. This return period is probably between one and ten years but there are difficulties in applying the mathematically well developed percentile standard approach to this as the time of persistence of various concentrations needs to be taken into account.

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