

Project 402

Interim Report R&D Project 402

Possible replacements for the Biochemical
Oxygen Demand (BOD) test and
suspended solids as measures of effluent
and water quality

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**POSSIBLE REPLACEMENTS FOR THE BIOCHEMICAL OXYGEN DEMAND (BOD)
TEST AND SUSPENDED SOLIDS AS MEASURES OF EFFLUENT AND WATER
QUALITY**

K Clark, S Comber and A M Gunn

**Research Contractor:
WRc plc
Henley Road Medmenham
PO Box 16 Marlow
Buckinghamshire SL7 2HD**

**National Rivers Authority
Rivers House Waterside Drive
Almondsbury Bristol BS12 4UD**

NRA Interim Report 402/6/HO

National Rivers Authority
Rivers House
Waterside Drive
Almondsbury
BRISTOL
BS12 4UD

Tel: 0454 624400

Fax: 0454 624409

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WRc plc
Henley Road Medmenham
PO Box 16 Marlow
Buckinghamshire
SL7 2HD

Tel: 0491 571531

Fax: 0491 579094

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NRA Project Leader

The NRA's Project Leader for R&D Contract 402:

T Long - Head Office

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SUMMARY

This report covers progress on R&D Project 402 for the period December 1992 to March 1993, assessing possible replacements for biochemical oxygen demand (BOD) and suspended solids as measures of effluent and water quality.

A limited assessment of archive data for sewage treatment works effluents has revealed a good correlation between BOD and COD, with little evidence of site-specificity. A much poorer relationship existed between BOD and TOC, but this may have been influenced by poor solids handling capability of the TOC instrument employed in the study.

A more comprehensive NRA laboratory evaluation of possible alternative determinands has now been initiated. This covers a range of rivers, sewage effluents and industrial effluents. TOC data are being obtained using four different instruments, two with good solids handling capability. Other determinands include BOD, COD, ammonia, suspended solids and turbidity.

Results from a WRc study of the relationships between BOD, uv/visible spectrophotometry and fluorescence, have indicated that fluorescence measurements are of limited use in predicting BOD for river and effluent samples. However, a very good correlation between BOD and spectrophotometric data has been demonstrated for sewage effluents. This has been found to be more dependent on light attenuation by fine suspended particulates than on true absorption by dissolved phase species.

Lastly, an assessment of the likely impact of a move away from BOD and suspended solids on water quality models has been undertaken. In some respects, there would be advantages here in changing from BOD to a more direct chemical measure of available organic carbon. However, any such change would inevitably have considerable cost implications in terms of redesign and recoding of models. The same would also hold for a change from suspended solids to turbidity measurements.

1. INTRODUCTION

In Interim Report R&D 402/2/HO (Parr 1992) possible replacements for biochemical oxygen demand (BOD) and suspended solids as measures of effluent and water quality were reviewed.

From this, it was recommended that the use of total organic carbon (TOC), chemical oxygen demand (COD), total oxygen demand (TOD) and respirometry should all be investigated as possible replacements for BOD as broad scale pollution indicators. Turbidity was identified as a possible replacement for suspended solids, although it was suggested that further investigation of the effect of the angle of light scattering/detection should first be undertaken.

This report describes subsequent progress in the period December 1992 to June 1993. A limited examination of historical NRA data covering relationships between BOD, COD, TOC and suspended solids has been undertaken. A work programme for laboratory assessment of possible alternative determinands has been set up and is now in progress at NRA Nottingham laboratory. At WRc, in collaboration with NRA Fobney laboratory, the relationships between BOD and uv/visible spectrophotometry, and between BOD and fluorescence, have been investigated. Finally, the implications of a possible change in determinands on water quality modelling have been addressed.

2. ASSESSMENT OF HISTORICAL NRA DATA

Relationships between BOD and COD or TOC have been examined many times in the past and it is well known that reasonably good correlations can be obtained on a site-specific basis for many effluents. However, it is also frequently pointed out that such relationships can break down if attempts are made to apply them on an across-site basis.

As part of the background information for the NRA Policy Group on Discharge Consents, a detailed evaluation was carried out for a series of sewage works effluents by NRA Severn Trent Region Nottingham laboratory. This data was never formally reported and has therefore been made available for the present study.

Samples were obtained from eight sewage treatment works within Severn Trent Region, on up to 12 occasions during 1989 and 1990. For every sample 12 replicate determinations of BOD, COD and TOC were made. Suspended solids was also determined in duplicate.

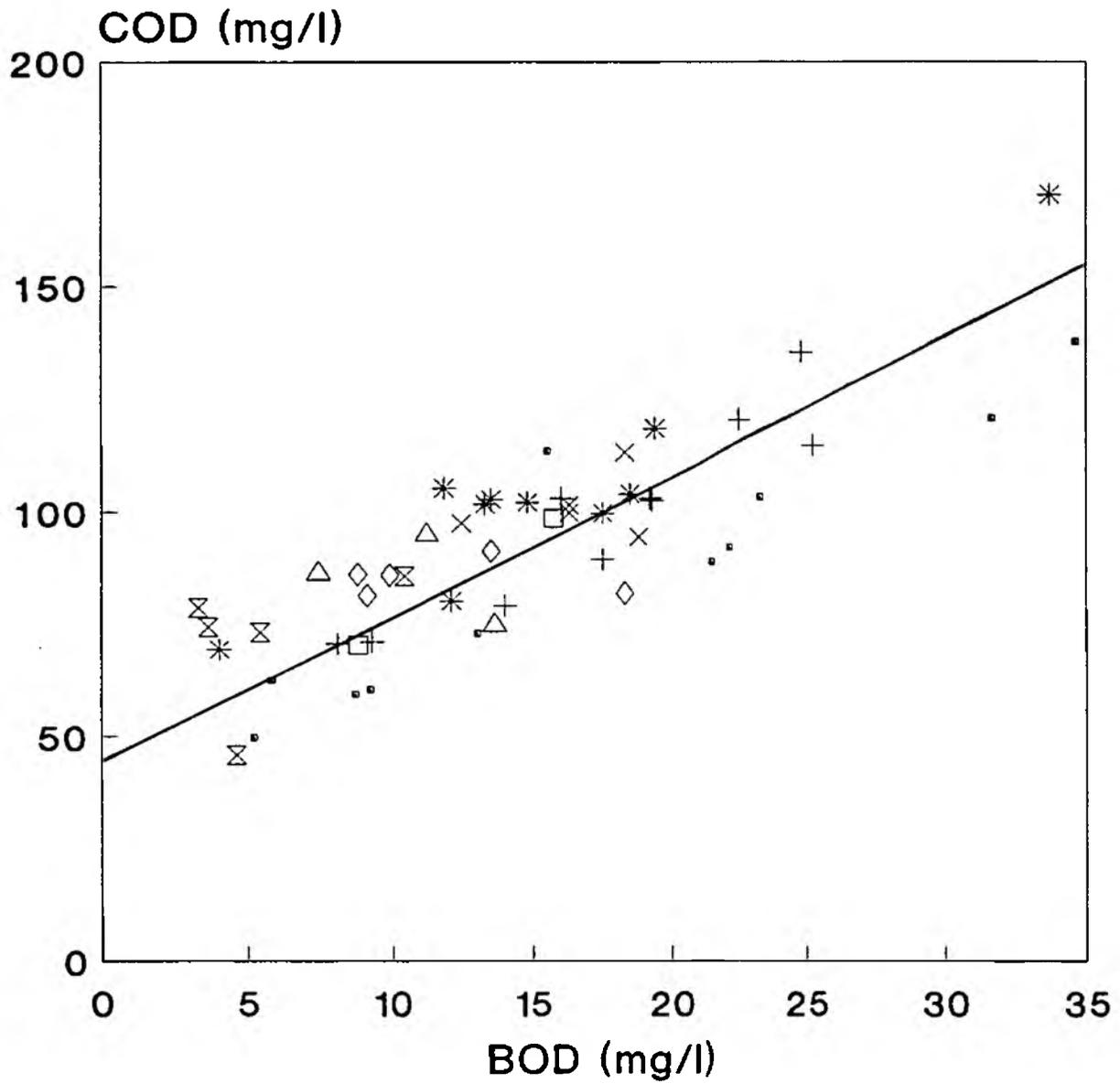
The degree of correlation between the four determinands, irrespective of sampling site is shown in Table 2.1. It can be seen that the strongest relationship occurs between BOD and COD ($r=0.82$) Furthermore, Figure 2.1 indicates that there is no major site-to-site variability in the relationship.

The relationship between BOD and TOC was much weaker ($r=0.57$) as illustrated in Figure 2.2. An important factor here is the fact that the TOC determinations were carried out on an instrument (Dorhmann DC80) with poor solids handling capability and samples were therefore filtered prior to analysis. The poor correlation may thus be a reflection of the fact that much of the BOD load in sewage effluents can be associated with particulate material. Support for this is provided by the significant correlation ($r=0.62$, Figure 2.3) between BOD and suspended solids and the, not surprisingly, poor relationship between this filtered 'TOC' and suspended solids ($r=0.26$).

For further work it is obviously important to include TOC determinations that are closer to true totals, including the solids contribution. This is being addressed in the NRA laboratory evaluation discussed in Section 3.

Table 2.1 Correlation coefficients for four determinands on sewage treatment works effluents

	BOD	COD	TOC	SS
BOD	1.000	0.823	0.574	0.619
COD		1.000	0.797	0.525
TOC			1.000	0.264
SS				1.000



▪ E Mark	+ S Bard	* Newthor	□ Derby
× E Leake	◇ Edwins	△ Pye Br	⊗ Wanlip

Figure 2.1 COD vs BOD for sewage treatment works final effluent

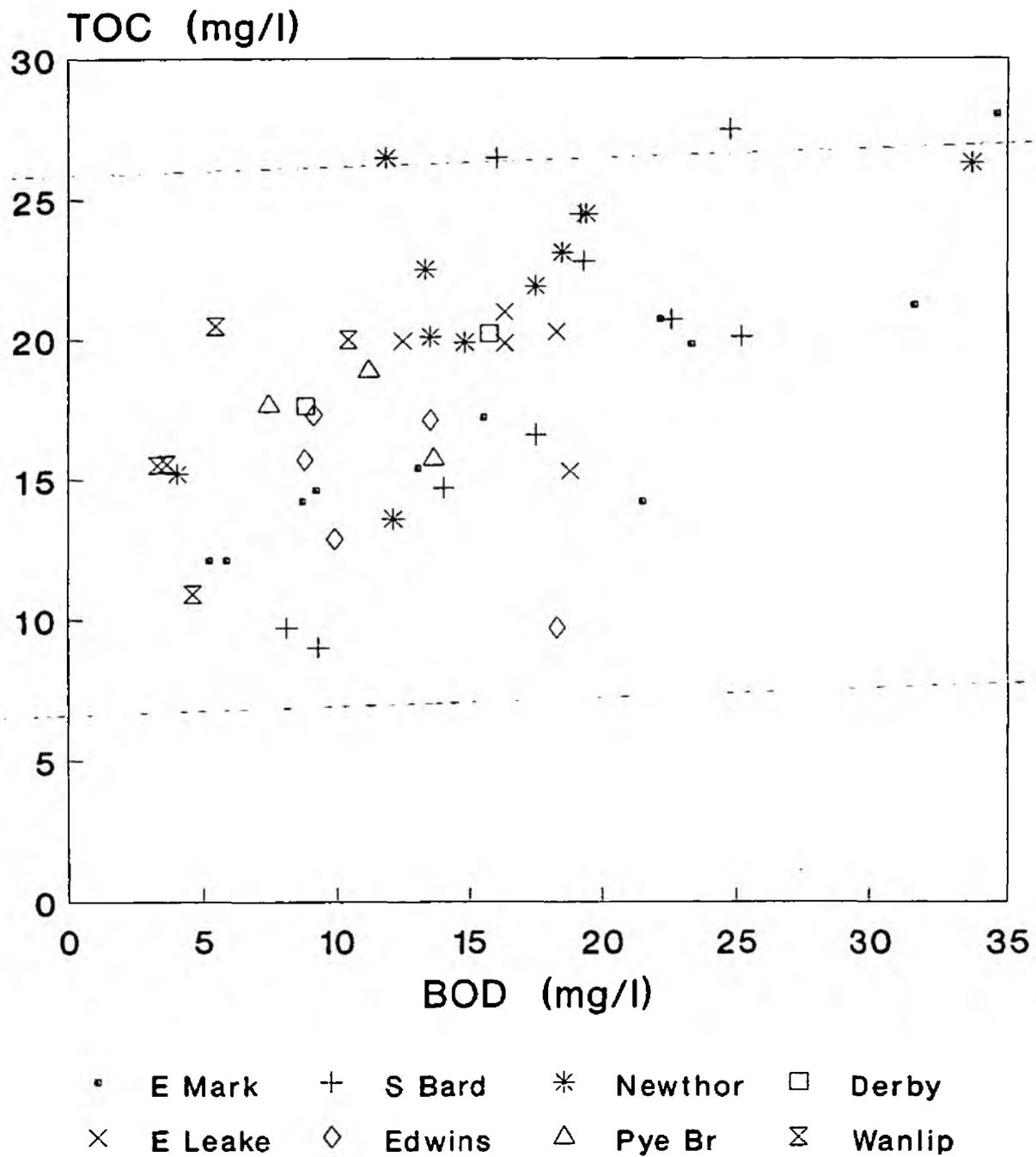


Figure 2.2 TOC vs BOD for sewage treatment works final effluent

3. NRA LABORATORY EVALUATION OF ALTERNATIVES TO BOD AND SUSPENDED SOLIDS

It is clearly advisable that the relationship between the existing consenting parameters and possible alternative determinands should be established over an extended period for a wide range of sample types. This phase of the project is now underway, with analyses being undertaken at the NRA Nottingham laboratory.

Initially, effort on BOD alternatives is being concentrated on COD and TOC determined on a range of different instruments with different operating principles. Other possible techniques, including respirometry and total oxygen demand (TOD), are presently being evaluated in the parallel R&D Project 427.

The full range of determinands now included in the scheme at Nottingham comprises:

BOD
TOC (Dorhmann DC190)
TOC (Astro)
TOC (Dorhmann DC80)
TOC (Skalar)
COD
Turbidity - NTU
Suspended solids
Ammonia

An important factor in the selection of the Nottingham laboratory for the investigation was the availability of the four different TOC instruments. Their principles of operation are summarised in Table 3.1.

The Dorhmann DC80 and Skalar instruments are not ideally suited to handling suspended particulate material. They suffer from clogging problems due to e.g. narrow bore injection valve or sampling arm tubing. For this reason samples are routinely filtered (GF/C) prior to presentation to these instruments. The determinand is therefore better described as dissolved organic carbon (DOC). The more modern Dorhmann DC90 and Astro 2001 instruments are both better equipped to handle suspended particulates. They have wider bore sampling/injection systems and the facility to stir samples loaded on the autosampler trays prior to introduction to the instrument. This agitation is achieved immediately prior to sampling on the Dorhmann, while on the Astro there is a short delay leading to the possibility of some settling. On the other hand, the Astro takes much larger sample volumes and therefore may in this respect be more representative in its sampling of solid material.

The aim has been to set the evaluation up to cover a fixed set of sample sites over an extended period, with samples at each site being taken, as far as practical, on a weekly basis. Ten river sites, ten sewage effluents and eight industrial effluents have been selected. In order to improve the range of industrial effluent types included, two of these are being sampled from outside the Severn Trent NRA Region.

Table 3.1 TOC instrument operating conditions

Instrument	Sample introduction	Means of digestion	Solids handling
Dorhmann DC190	Discrete	High temperature (up to 900 °C) catalytic oxidation	Good
Astro 2000	Discrete	Elevated temperature (up to 90 °C) uv/persulphate digestion	Good
Skalar	Continuous flow	Elevated temperature uv/persulphate digestion	Poor
Dorhmann DC80	Discrete	Low temperature uv/persulphate digestion	Poor

On arrival at the laboratory, duplicate analyses are performed on the samples for each of the determinands of interest. Further information on the precision of the different methods is also being obtained by examination of data from the Nottingham laboratory's routine Analytical Quality Control scheme. This includes five replicate analyses on a wide range of samples.

The evaluation has now been in progress for approximately three months. However, due to initial difficulties resulting from the extensive additional sampling required by NRA staff, available data are at present too limited to warrant extensive discussion. Nevertheless, it is already evident that relatively large differences in 'TOC' results can occur between the different instruments for certain samples. In the longer term, it is intended to establish the influence of solids sampling and oxidation technique on these differences, and on the relationship with BOD.

4. ASSESSMENT OF FLUORESCENCE AND UV/VIS SPECTROPHOTOMETRIC TECHNIQUES AS BOD SURROGATES

4.1 Background

One option under consideration has been the use of a simple spectrophotometric or fluorimetric determination as a broad-scale pollution indicator, particularly for sewage treatment works effluents. However, as the most appropriate operating conditions for such a procedure were not known, it was not immediately incorporated in the NRA laboratory evaluation scheme. Rather, a preliminary evaluation was carried out by WRc, in collaboration with Thames NRA Fobney Laboratory.

Samples were collected on ten separate occasions over a two month period. On each occasion approximately ten sewage work effluents, ten river samples and five industrial effluents were taken. These were selected at random from the laboratory intake on the day. On arrival at WRc, all investigations were completed within the day on which BOD analysis commenced.

Routinely, samples were allowed to settle for approximately 15 minutes and the supernatant decanted for use in the investigations. However, for a proportion of samples an aliquot was also prefiltered to 0.4 μm .

4.2 Fluorescence

The use of fluorescence measurements for assessment of the organic load of effluents has received considerably less attention than uv absorbance. Bari and Farooq (1985), however, have reported a reasonable correlation between fluorescence values and COD for a range of sewage effluents and mixed raw sewage/sewage effluents. Fluorescence has also been used as a predictor of organic carbon content of natural waters (Smart *et al.* 1976, Chen *et al.* 1993). One reason for inclusion of fluorescence in the present evaluation was that measurements are less influenced by sample turbidity than are absorbance data.

Readings were obtained on a Perkin-Elmer LS5 fluorimeter. Initial investigations demonstrated that the majority of samples exhibited a peak in their emission spectra centred around 430 nm. Routine measurements were therefore made with a fixed emission wavelength of 430 nm. Two excitation wavelengths, 250 nm and 350 nm, were employed.

Figure 4.1 shows results for unfiltered samples, for both excitation wavelengths, plotted against BOD. There proved, at best, to be only a very weak relationship between the two determinands. Indeed, for river waters there was a complete absence of correlation.

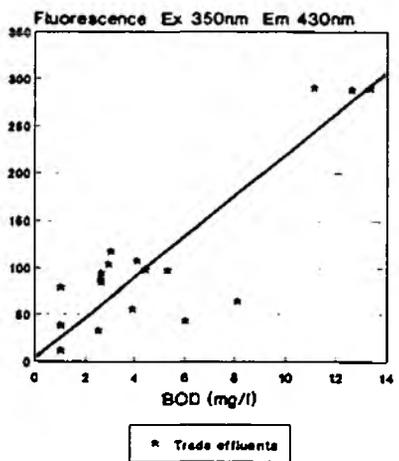
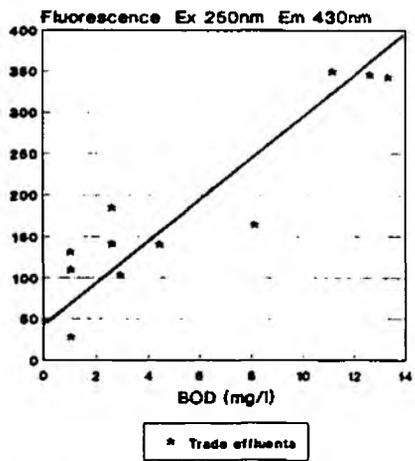
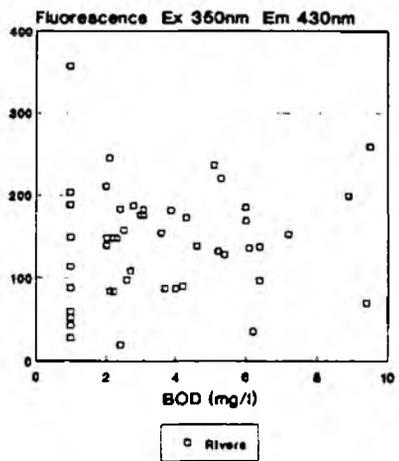
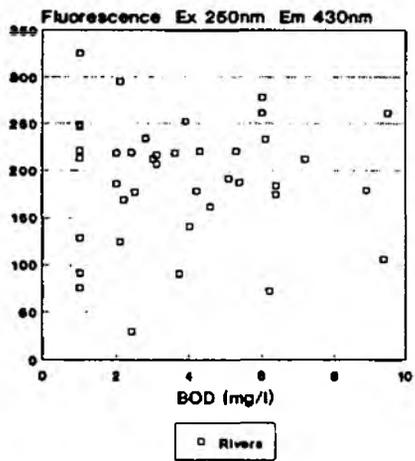
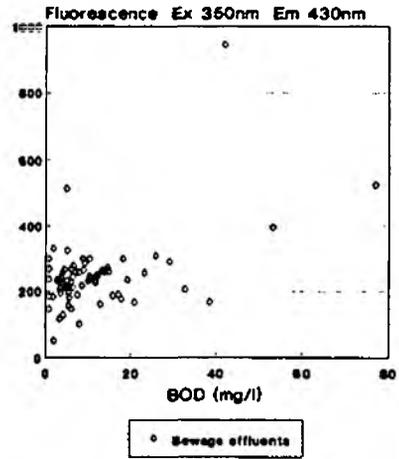
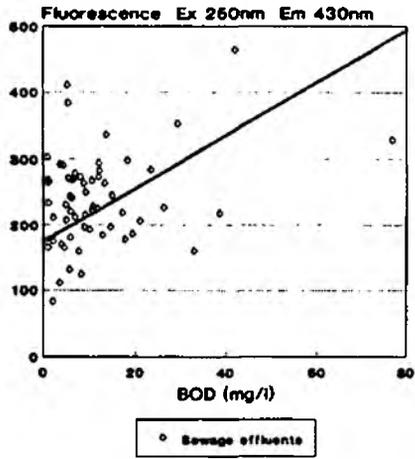


Figure 4.1 Fluorescence vs BOD for different sample types

4.3 UV/visible spectrophotometry

Data were obtained on a Pye Unicam SP8-400 uv/vis spectrophotometer, using a 2 cm pathlength cell. Spectra were scanned between 230 nm and 650 nm.

Results for sewage effluents demonstrated a strong positive correlation with BOD at all wavelengths. However, in general the correlation improved with increasing wavelength, as illustrated in Table 4.1 and Figure 4.2.

Table 4.1 Linear regression of absorbance against BOD for sewage treatment works effluents

Wavelength	Correlation coefficient	Intercept	Slope	%variance accounted
250	0.78	0.356	0.028	60.3
350	0.80	0.080	0.012	63.2
400	0.85	0.032	0.009	71.6
650	0.91	0.000	0.004	82.4

It must be borne in mind that absorbances measured in this way on unfiltered samples represent a combination of true absorbance of dissolved phase species in the sample and light attenuation by slowly settleable or non-settleable fine suspended particulate material. As a proportion of the total absorbance, the light attenuation effect increases in importance with increasing wavelength. This therefore suggested that light attenuation by particulates might be of greater importance than dissolved phase absorbance in accounting for the observed correlations.

To test this, a proportion of samples were filtered to 0.4 μm and their absorbances remeasured across the wavelength range. From Table 4.2 it can be seen that absorbance versus BOD correlations were very much poorer for these filtered samples than for their unfiltered counterparts. Although statistically significant, the relationship remained weak, even in the uv wavelength range. However, when the differences in absorbance between unfiltered and filtered samples were calculated and plotted against BOD, highly significant and essentially constant regression coefficients were obtained across the entire wavelength range tested (see Table 4.2).

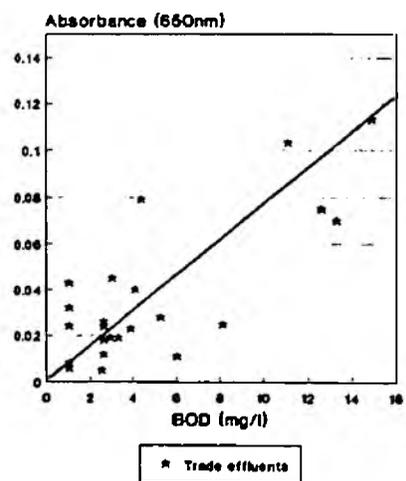
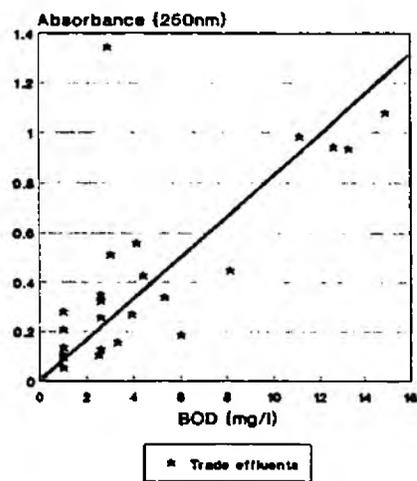
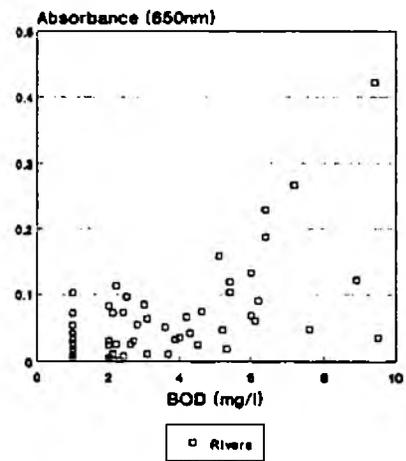
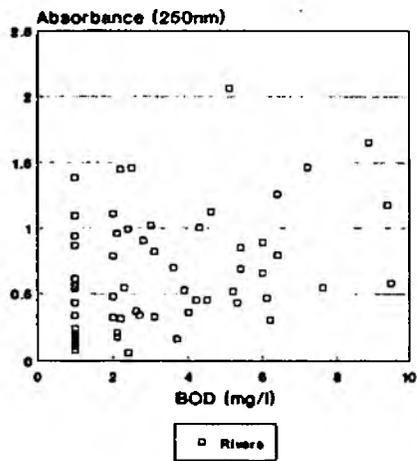
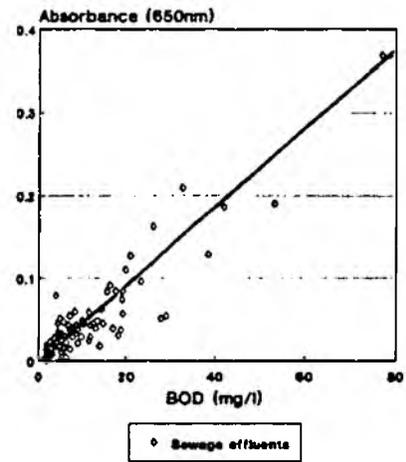
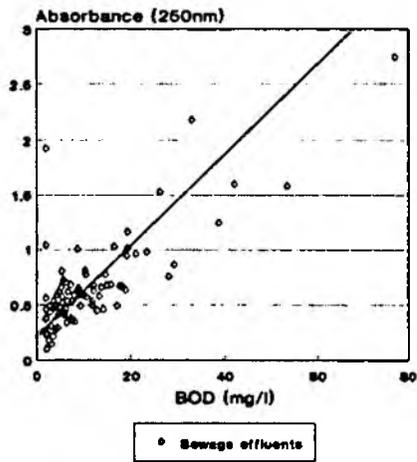


Figure 4.2 Absorbance vs BOD for different sample types

Table 4.2 Comparisons of absorbance/BOD regression data for unfiltered and filtered sewage effluent samples

UNFILTERED ABSORBANCES

Wavelength	Correlation coefficient	Intercept	Slope	%variance accounted
250	0.65	0.375	0.027	40.7
350	0.65	0.084	0.012	40.6
400	0.69	0.036	0.009	45.7
650	0.69	0.006	0.003	51.5

FILTERED ABSORBANCES

Wavelength	Correlation coefficient	Intercept	Slope	%variance accounted
250	0.44	0.388	0.0118	16.8
350	0.34	0.096	0.0031	9.1
400	0.33	0.045	0.0017	8.9
650	0.29	0.010	0.0003	6.9

(UNFILTERED - FILTERED) ABSORBANCES

Wavelength	Correlation coefficient	Intercept	Slope	%variance accounted
250	0.75	-0.01	0.0155	55.1
350	0.75	-0.01	0.0087	55.6
400	0.75	-0.01	0.0071	55.6
650	0.71	0.00	0.0031	49.6

This confirmed that light attenuation by non-filterable material was responsible for much of the observed absorbance/BOD relationship. On the other hand, the observed correlation between suspended solids and BOD for the full data set was relatively poor, as shown in Figure 4.3. Thus, it would appear that the fine, non-settling or slowly settling particulates which result in light attenuation carry much of the BOD load, while larger, lower surface area, fast settling particles may be of lesser importance.

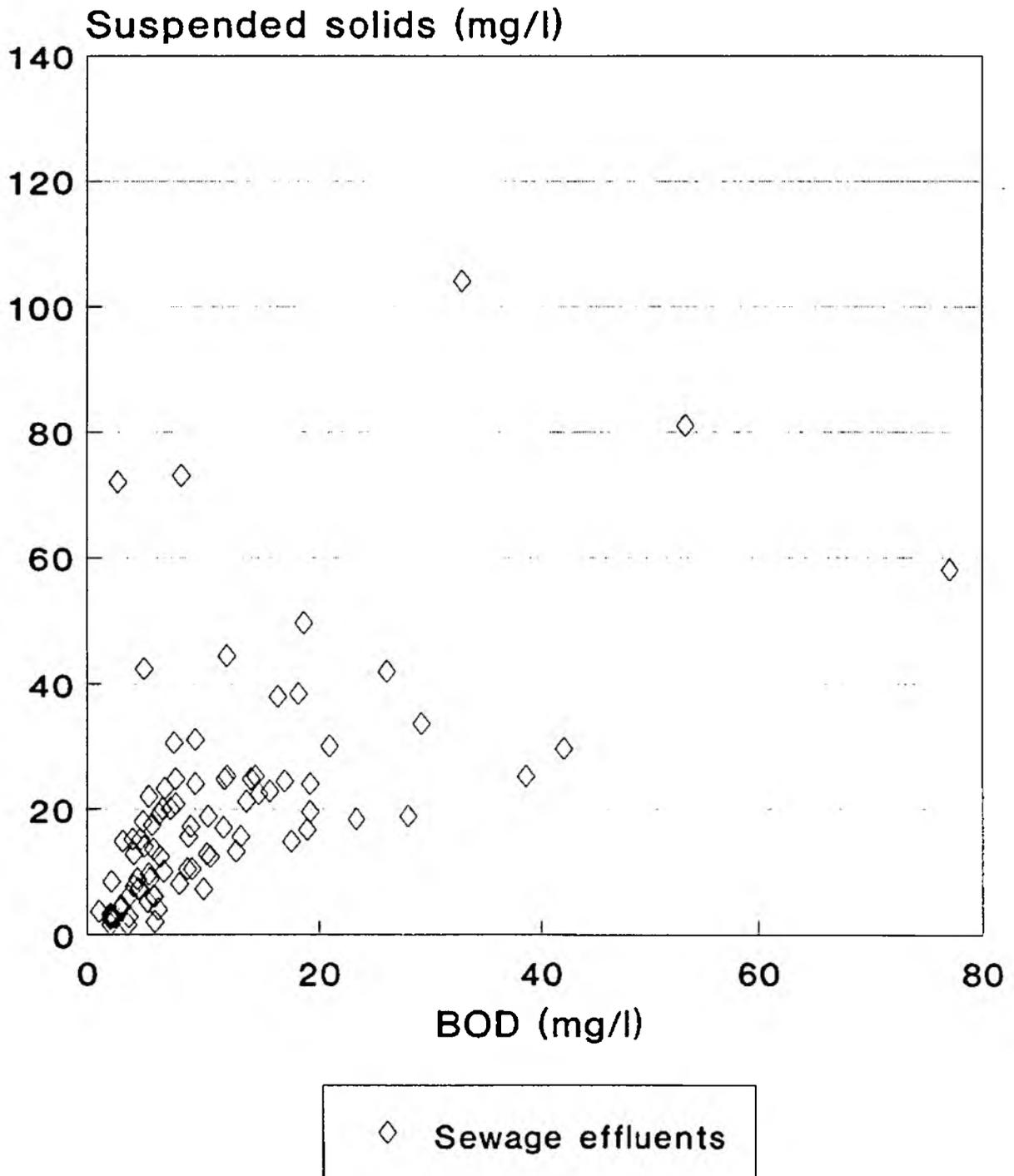


Figure 4.3 Suspended solids vs BOD for sewage effluents

Returning to Figure 4.2, the correlation between absorbances and BOD for randomly selected river water samples can be seen to be relatively weak. Again, as shown in Table 4.3, the correlation tends to improve with increasing wavelength. Variable degrees of absorption from non-biodegradable or slowly degradable organic material in different rivers is likely to be an important factor here. At 250 nm, a wavelength at which dissolved natural organics absorb strongly, filtered river waters demonstrated (Table 4.3) a complete absence of correlation between absorbance and BOD. Although less marked than for sewage effluents, the influence of light attenuation by fine suspended matter is again evident (e.g. $r=0.66$ for relationship between BOD and (unfiltered-filtered) absorbances at 650 nm). Overall, the findings suggest that some site-specificity would be necessary if a useful riverine BOD predictor were to be developed on this basis.

Table 4.3 Absorbance/BOD correlation coefficients for river waters

Wavelength	Correlation coefficient		
	Based on unfiltered absorbances	Based on filtered absorbances	Based on (unfiltered - filtered) absorbances
250	0.38	-0.06	0.47
350	0.44	0.20	0.48
400	0.56	0.32	0.58
650	0.64	0.28	0.66

The same would certainly be the case for industrial effluents, given the wide variety in both the nature and degradeability of their organic contents. Oddly, the randomly selected effluents studied here demonstrated reasonable absorbance/BOD relationships (Figure 4.2). Correlation coefficients of 0.72 and 0.79 were obtained at 250 nm and 650 nm, respectively, for unfiltered samples. However, the number of samples was limited and it would not be expected that this would be maintained on a wider range of effluent types.

5. IMPACT OF ALTERNATIVES ON WATER QUALITY MODELLING

5.1 Current Modelling practice

A wide range of water quality models is presently used by the NRA for varied purposes, including consent setting, river estuary or coastal water quality management and catchment management. Similar models are also used by the water utilities and industrial dischargers. The complexity of the water quality chemistry represented in different models varies with the use for which the model is designed. For example, a model used to predict sedimentation patterns is unlikely to be concerned with BOD, and a quick simple model used to set BOD consents may not use suspended solids.

However the models have all been developed to use the water quality parameters currently measured. Thus models use BOD and suspended solids (amongst other parameters such as ammonia) to characterise the quality of effluents entering a given system. The model predictions of water quality in the system are output in terms of BOD and suspended solids (and other parameters). These can then be used or compared with measured values of BOD and suspended solids from surveys of the system in a calibration or validation exercise.

Water quality models need measurements of BOD and suspended solids from several types of water: sewage effluent and industrial effluent for inputs to a model, fresh water from rivers or lakes for inputs to the model or for calibration purposes and possibly saline water for calibration purposes in the case of a coastal or estuarine model. Thus reliable, consistent values are required over a wide range of concentrations and sample conditions.

Water quality models are based on conservation of mass. The inputs to and abstractions from a system of each modelled substance, and the chemical and physical processes simulated govern the predicted masses or concentrations of each modelled substance. The treatment of BOD and suspended solids differs in a water quality model. Suspended solids is a direct physical (chemical) quantity - so many mg l^{-1} of solids. It is predicted directly by the model. BOD however is an indirect parameter - so many mg l^{-1} of oxygen used up by micro-organisms over the course of the test. BOD is an indirect measure of the amount of organic material which is readily degraded, thus depleting oxygen. Water quality models convert BOD values into an equivalent organic carbon concentration using measured or estimated decay rates. The model then predicts the fate of the organic carbon through the system, before re-converting this to BOD for output to the user. Therefore it may seem that a more direct measurement of organic carbon would be suitable for water quality models.

5.2 Impact of alternatives to suspended solids

Turbidity has been suggested as a suitable replacement for suspended solids, for some if not all applications. There are acknowledged difficulties of a turbidity value being dependent upon the choice of instrument and the sample conditions. However a

turbidimeter can be incorporated into a continuous monitor of water quality (Hatton 1992).

The major impact on water quality modelling of replacing suspended solids by turbidity results from turbidity being an indirect measure of the suspended solids content of a sample. A model will require the turbidity value to be converted to suspended solids, either within the model as for BOD at present, or during the preparation of data for the model. The predicted suspended solids concentrations within the system would then need to be converted to turbidity values for comparison with observed turbidities or the required water quality standards.

Therefore, from a water quality modelling viewpoint, it is vital that reliable relationships between turbidity measurements and suspended solids concentrations are derived. Such relationships are being investigated as part of this project. Existing models will require amendments and additional computer code to convert turbidity to suspended solids. These amendments may be quite complex if a simple relationship between a measure of turbidity and suspended solids cannot be identified. Additional data may then be required by models to derive the suspended solids values. These amendments will evidently have cost implications, the size of which will depend on the complexity of the turbidity - suspended solids relationship which is used.

5.3 Impact of alternatives to BOD

As described briefly in Section 5.1, BOD values (mg O₂/l) supplied to a model are converted to a substance usually referred to as organic carbon. A conservation of mass equation can then be written and solved for this organic carbon. However this organic carbon, since it is derived from BOD, only represents that fraction readily available for degradation by micro-organisms. (It also reflects any distortion of the BOD value from action of toxins or presence of slowly degrading compounds.)

Among suggested alternatives for BOD, which are undergoing further investigation, are TOC (total organic carbon), COD (chemical oxygen demand), TOD (total oxygen demand) and respirometry. The first three of these are chemical parameters. The last measures a biological response.

Respirometry, while widely used in treatment plant process control, is unsuitable for on-line monitoring of waters of low carbon content (Parr 1992). Thus respirometer readings would not be available for calibrating a model, nor for providing input values for relatively low carbon content effluents.

For use by a water quality model, each of the first three alternatives shares the problem of identifying what fraction of the measured value represents readily degradable matter, which will exert an oxygen demand within the lake, river or coastal environment. The fraction seems, on existing evidence, to be likely to be site or effluent specific (Parr 1992). Water quality models are often used in saline waters: the COD analysis is affected by chlorides. TOD and COD share the possibility of including oxygen demand exerted by inorganics as well as organic compounds.

A water quality model will require inputs of this available organic carbon, or methods of converting input data to organic carbon. Procedures for converting the chosen BOD alternative determinands to organic carbon as used by the model will therefore be needed. In order to be readily incorporated into water quality models these procedures must be simple, ideally of similar simplicity to the exponential decay rule presently used to link BOD and organic carbon.

Since existing models already use organic carbon data in their calculations, it would not seem worthwhile to use a necessarily simplistic relationship to convert the chosen alternative determinand data to BOD figures and then to reconvert within the model. However, establishment of the relationships between BOD and the alternative determinand(s) may reasonably constitute part of the process of deriving rules for defining organic carbon inputs to the model.

The impact on water quality models will therefore be caused by replacing the conversion of BOD to available organic carbon, with a yet to be fully identified method of conversion of the alternative chemical parameter to readily degradable organic carbon. This is likely to involve significant effort in re-design and re-coding of existing models, both on the part of chemists in deriving the model and on the part of modellers. If it is found that the relationship between the chosen alternative and the readily degradable organic carbon is effluent or site specific, then there will be additional site specific data requirements for the models. This additional data may be less burdensome for the simpler types of model. However the use of a new parameter which reflects better the longer term polluting effect of an effluent, could help improve the internal model representation of the degradation processes.

5.4. Other considerations

There are other impacts on water quality modelling apart from the technical issues of changing the substances on which the model works. These include the question of comparability: how to compare the goodness of predictions of, or the calibration against, say TOC, with those of and against BOD? Also, there are likely to be problems associated with the introduction of inconsistent data sets, i.e. water quality records which change from BOD to TOC or from suspended solids to turbidity, part way through the period to be modelled. There has been major investment by both the NRA and model houses in the existing water quality models. The changed parameters will require further major investment.

6. CONCLUSIONS AND FUTURE WORK

1. An examination of NRA archive data has demonstrated a very good correlation between BOD and COD for sewage treatment works effluents, with site-specificity not being a major factor in the relationship. The relationship between TOC and BOD for the same effluent set was very much weaker. However, this may simply have reflected the fact that the instrumentation employed was not capable of handling suspended particulates, on which much of the BOD load can be carried.
- 2. It is therefore important that TOC data should be obtained on instrumentation with good solids handling capability. This is now being addressed in an extended-term laboratory evaluation at NRA Nottingham. This evaluation will also provide information on the performance of instruments with different oxidation procedures: high temperature catalytic; and uv/persulphate.
3. Investigations of the relationships between BOD and uv/visible spectrophotometry, and between BOD and fluorescence, have demonstrated a good correlation between BOD and spectrophotometric data for a range of randomly selected sewage works effluents. With further work, a possibility here is the development of an on-line system capable of triggering a sample collector on occasions where there is a likelihood of consent exceedance.
4. The operation of existing water quality models involves conversion of BOD values into available organic carbon concentrations on the basis of simple decay rate rules. The fate of organic carbon is then predicted, before reconvertng to output BOD values. In principle, a change to a more direct chemical measurement of available organic carbon would therefore in some ways be desirable. However, whatever alternative to BOD is adopted, a simple rule for conversion to readily degradable organic carbon, as used by the models, will be required. The overall process is likely to require considerable effort in redesign and recoding of models. Furthermore, if a decision was taken to replace suspended solids with the purely empirical turbidity measurement, then for modelling purposes it would be essential to derive well-defined relationships between the two determinands. Again, depending on the complexity and possible site-specificity of these relationships, there are important cost implications here.
5. Effort on the project will now be directed towards assessment of data from the NRA laboratory evaluation of alternative determinands. The possibility of extending the scope of this study to include further alternatives, e.g. respirometry, will be considered once smooth running of the full sampling/analysis scheme is established. The likely impact of a change in determinands on other aspects of NRA work, including consent setting, will also be addressed.

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