A STRATEGY FOR THE USE OF FIELD INSTRUMENTATION IN WATER QUALITY MONITORING

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SUMMARY

The potential for cost saving by moving programmed monitoring from laboratories to field instruments was reviewed, together with wider aspects of the role of field measurements in Water Quality monitoring. Dissolved oxygen, pH, ammonia (and turbidity as an index of effluent quality) should be moved to field monitoring for cost saving reasons, to reduce sampling error caused by their high short term variability and to assist in pollution prevention by provision of real time data in the field. Ammonia will require more work to meet the monitoring performance requirements. This work comprises some 16% of the total monitoring workload and represents cost saving in the order of £0.45 million, part of which has already been achieved by Regional initiatives.

Implementation of the UWWTD will generate the need for a new type of instrumentation expertise in the specification and auditing the operation of automatic effluent samplers. Developments in self monitoring arising from implementation of IPC and possibly from the future environment Agency may give rise to more direct involvement in discharger's automatic monitoring systems, which will place more new demands on Regional instrumentation skills. These, plus the extra demands being imposed by Cyclops and hand held meters, indicate that the knowlege base of Regional instrument support should be widened and possibly the resource increased.

RECOMMENDATIONS

1 Hand Held Meters

Dissolved oxygen, pH, ammonia and turbidity should be monitored by hand held meters to save costs. Dissolved oxygen and pH monitoring can be moved to hand held meters now, but ammonia needs further work to meet all monitoring performance requirements. An implementation plan and timescale is proposed in this report.

2 Dissolved Oxygen, pH and Ammonia Sampling

These key river quality parameters have been shown to vary strongly seasonally and within a day, making spot sampling an inappropriate technique for detailed characterisation of water quality. Present river quality assessment schemes allow for this variability, but field instruments can facilitate a more frequent and more representative sampling strategy at low cost if required.

3 Pollution Prevention

The majority of effluent quality problems may well occur outside normal sampling hours. The use of Cyclops monitoring/sampling systems and hand held meters should be considered to broaden the sampling timeframe, increase the probability of detecting exceedances, and guide the selection of tripartite samples.

4 Urban Waste Water Treatment Directive

At present there is little basic understanding of whether and by what mechanisms the design and operational characteristics of automatic samplers affect monitored consent parameters. Sufficient knowlege and experience must be developed to facilitate provision of autosampler specification, evaluation and site audit activities arising from the UWWTD.

5 Permanent Monitoring Stations

There are strong cost saving benefits in using permanent monitors in certain situations. Examples in this report provide guidance on favourable applications. In certain instances it is advantageous to operate these systems on a multifunctional basis with Water Resources. Self monitoring implications of IPC and ENVAGE may increase the need for continuous monitoring expertise significantly by more direct involvement in dischargers' automatic monitoring systems; either by encouraging optimal use of instrumentation, control and automation or, where appropriate, by direct telemetry of monitoring information to the regulatory body. These developments may open a number of options for the NRA to better monitor and manage its rivers and estuaries.

6 Instrumentation Support Resource

The resource requirements of the four additional instrument areas identified in this report should be quantifed as follows:

(i) Cyclops support requirements have been identified by the National Centre;

(ii) hand held meter requirements are identified in this report;

(iii) autosampler resource requirements should be investigated by evaluation of commercially available instruments at the National Centre's evaluation facility;

(iv) self monitoring instrument-related needs will be determined when policy is sufficently developed.

CONTENTS

MAJOR FINDINGS

1 PROGRAMMED MONITORING

1.1 Dissolved oxygen, pH, ammonia, turbidity and a number of other associated determinands are amenable to field monitoring using hand held meters. They have marked diurnal variability, particularly dissolved oxygen, and field monitoring would allow a more flexible monitoring strategy for these highly variable parameters than is feasible with current spot sampling and laboratory analysis procedures.

1.2 Ammonia is a special case because its measurement limit of detection is close to GQA classification limits, and further work is necessary to ensure that GQA surveys will not be adversely affected by a change in measurement technique. It may be that presently available sensors will not reach acceptable performance criteria. If so, implementation will be delayed until new sensors of acceptable performance become available.

1.3 There are two options to carry out programmed monitoring by hand held meters: dissolved oxygen and pH only or these plus temperature, conductivity, ammonia and turbidity. Both approaches have their advantages; two parameter monitoring has a low risk and relatively easy implementation whereas six parameter monitoring has a higher cost saving potential and additional pollution prevention benefits, but higher risk because of ammonia measurement uncertainty. On balance the six parameter approach is recommended because of its greater payback potential and added benefits. Cost saving would be in the order of £454K pa (in practice many Regions are already part way along this route and have already achieved some of this saving).

1.4 An implementation programme for six parameter hand held meters is proposed, using the National Centre as a central resource for methods of operation, training and repair.

2 CONSENT MONITORING

2.1 Continuous monitoring information shows that the worst quality of sewage works effluent often occurs outside normal sampling hours; and conventional spot sampling is unlikely to detect the majority of consent exceedances. Cyclops portable monitor/loggers and, to a lesser extent, six parameter hand held meters are well placed to select the most relevant samples (including out-of-hours) for laboratory analysis when conditions justify a move beyond programmed consent monitoring.

2.2 Implementation of the UWWTD will generate the need for specification, evaluation and site audit of automatic samplers and their effects on consent determinands. In some instances the sampling of influents and the measurement of flow will also be required. There is at present little first hand knowlege within the NRA on these aspects of instrumentation and the appropriate expertise will have to be developed.

3 AUTOMATIC MONITORING DATA TREATMENT

3.1 Automatic river quality monitoring stations have strong cost justification in specific applications where they can initiate intervention or remedial action. Frequently, they are an economic alternative to highly expensive civil engineering solutions.

3.2 Water quality and water resources automatic monitoring is frequently carried out using the same equipment. Where different monitoring needs are able to be met by single systems there are advantages of economy of scale and merging of flow and chemical information which can lead to better interpretation of results.

3.3 Moves toward self monitoring arising from IPC and ENVAGE may lead to direct involvement in examining dischargers' own continuous monitoring data and systems, and possibly also in direct telemetry of monitoring information from the discharger to the regulator. These developments will require more in-house expertise in the processes that are being monitored and in importing and interpreting the monitoring data.

4 NEW DEVELOPMENTS

4.1 Water quality instrument developments have in the past undergone steady progress but are currently experiencing rapid changes as fundamentally new techniques such as immunoassay and thick film manufacture are being applied to sensor development. Trace organics and trace metals are now being brought into field measurement capability and disposable sensors with inbuilt quality assurance and calibration are being developed with the objective of providing field measurement with no operator skill or technician support requirement.

4.2 The instrument R&D programme is well focused on major items identified in this review; namely ammonia sensor development, investigation of BOD alternatives, documentation of quality systems and development of dispensable sensors. In addition, common instrumentation interests with HMIP and WRAs are being explored and European instrument standardisation initiatives are being supported.

5 INSTRUMENTATION HUMAN RESOURCES

5.1 In general Regions have minimal arrangements for instrument technical support. Cyclops and hand held meters place extra demand on Regional resources even though they will receive central support by the Instrumentation Centre. The UWWTD's requirement for autosampler expertise will place additional and technically different demands on technician resources, although it may be predominantly inspectorate rather than operative. Finally, self monitoring may bring a completely new instrument-related requirement; the need to electronically accept, interpret and audit dischargers' own automatic monitoring data. These additional requirements are as yet only partially scoped.

INTRODUCTION

The NRA's Strategy for Water Quality (1) sets out an innovative approach to monitoring as a key element in achieving its aims. The introduction of on-line continuous monitoring and held-held instruments were identified as part of the innovative approach, as was examination of the potential to transfer routine measurements from laboratories to field instruments.

Field instruments have been used for water quality monitoring for many years, and a number of individual initiatives have become nationally adopted. In general, however, they addressed areas such as pollution incident response and intermittent discharge monitoring; and the mainstream water quality monitoring programme remains a predominantly laboratory-served process. The purpose of this report is to review the possible applications for the use of field instruments in all water quality monitoring applications and make recommendations on optimal usage. Two areas have been omitted in this review, groundwater and marine monitoring, until their monitoring policy details have been finalised. Other than these exceptions, the statutory, general quality assessment and permissive monitoring areas have been examined together with the pollution incident response and general river quality management needs.

Instrumentation needs of the Urban Waste Water Treatment Directive have been examined, and the wider issue of future self monitoring instrument needs has been attempted. Both have significant, and new, implications on field instrumentation.

2 BACKGROUND

There are two basic approaches to making water quality measurements: the measuring instruments can be taken to the site or samples can be taken to a laboratory which houses the measuring instruments. In many instances, only one option is practicable. For instance temperature must be measured on site and a suite of pesticides can only be measured in a laboratory. Other determinands can be measured by either approach and the best selection is determined by cost, performance and data usage considerations. The present laboratory/field monitoring distribution has arisen predominantly from performance and usage considerations. It has been generally felt that data quality assurance needs are best met by laboratory techniques and field monitoring is restricted mainly to pollution incidents and river quality management where speed of response is the primary requirement.

In hardware terms, there are four groupings of field measurement techniques for water quality monitoring: permanently sited instruments; portable instruments; hand held meters; and test kits.

Permanently sited instruments are usually housed in brick or concrete enclosures and are linked by telemetry to control centres. There are approximately 100 in use within the NRA and many are supported by partially or fully bought-in services. A number of these systems are housed in trailers and can be moved from site to site.

A range of portable consent monitoring instruments have been developed within the NRA. They are small enough to be moved by two people and a van, and can be deployed more easily than trailer-based systems. They are fitted with telemetry linkage and automatic samplers. Essentially, they continually monitor a sample point and take a discrete sample for laboratory analysis when pre-set limits of the monitored determinand are exceeded.

Hand held meters that monitor a number of determinands simultaneously were developed by instrument manufacturers at the request of the NRA, but now have sales beyond the NRA alone. At the moment there is one "standard" instrument used by the NRA. Details of its procurement and performance are given in Appendix 1. Advantages of these instruments are that they can be used to investigate pollution problems in real time because of the immediacy of data feedback, and can be left unattended on automatic logging mode for several days if investigations demand it.

Test kits are available for a wide range of parameters. In general, they are less useful than hand held meters because they do not produce continual or logged data for investigational work, but they are the only route to measuring many determinands on site and are a valuable tool for pollution incident response.

It is worth noting that fundamentally new instruments are being developed and will bring many more determinands within the capability of field measurement. The two major types are immunoassay sensors for trace organics measurement and anodic stripping voltammetric sensors for trace metals measurement. Also, disposable solid state sensors will allow the traditional instrument parameters to be measured much more easily than present instruments. Some of these innovations are already in the marketplace, and independent assessment indicates that the water quality instrument capability situation will undergo a radical change over the next three to five years (19).

3 MONITORING BUSINESS NEEDS AND INSTRUMENT CAPABILITY

3.1 General Discussion

The NRA Specification of Laboratory Requirements (2) lists some five hundred combinations of determinands and purposes. To reduce this to a manageable number of target applications for instrument monitoring, a review of monitoring needs was combined with an initial screening out of these instances where instrument application is at present clearly technically impossible or financially impractical. This initial screening and review of business needs was carried out for the monitoring areas identified in the Introduction section, as detailed below.

3.2 Statutory Monitoring

The majority of this category is not amenable to instrument monitoring because the measurement processes require extraction and preconcentration steps in addition to sensing. Organic determinands at low concentrations can be ruled out on this basis. Equipment is being developed to measure low concentrations of many metals in the field but there is not yet sufficient information to review their potential. Instrument application to statutory monitoring is thus effectively limited to some general determinands, namely dissolved oxygen, pH, temperature, ammonia and turbidity. Determinands in the proposed Statutory Water Quality Objectives Fisheries Ecosystem

Classification are particularly amenable to instrument measurement. Limits of detection for the relevant parameters are as follows: dissolved oxygen 0.2 mg/l, total ammonia 0.025 mg/l, dissolved copper 0.5 μg/l and total zinc 3.0 μg/l. Accuracy and precision requirements are 10% each, giving a maximum total error requirement of 20%.

3.3 Consent Monitoring

The monitoring of effluents is complicated by the need for legal accountability and the requirement to take tripartite samples if the effluent is suspected of failure. BOD and suspended solids are the most common consented parameters for sewage treatment works and other dischargers of waste with a high organic load (they appear in 89% and 96% respectively of all NRA numeric consents). Ammonia is also a commonly used parameter (used in 20% of consents) and dissolved oxygen and temperature are also commonly used. Other determinands are involved for specific processes, and a major R&D project is investigating the potential of toxicity-based consents. These are particularly relevant to complex discharges where exact compositions of mixtures of chemicals may be unknown.

Generally accepted limits of detection for the major consented parameters of BOD, ammonia and suspended solids are 2.0 mg/l, 0.5 mg/l and 3.0 mg/l respectively.

All of the above determinands, except BOD, can be measured by instruments, but analysis of tripartite samples for enforcement purposes needs the supporting information on traceability and quality assurance that are presently only available from laboratory measurements. An additional requirement is the need to detect when a consent exceedence occurs. Work carried out in South Western Region illustrated the variable nature of consent parameter concentrations in sewage works effluent over twenty-four hour periods, and concluded that normal sampling hours are likely to coincide with best quality effluent discharge (3). Appendix 2 illustrates the variability of a sewage treatment works when monitored continually, together with information on the variation in sampling times. Similar findings were reported by Thames investigators (11).

3.4 General Quality Assessment

There is one GQA suite of determinands; BOD, dissolved oxygen and ammonia. Nutrients will be required in the future for a nutrient classification scheme. Performance criteria for BOD, ammonia and dissolved oxygen are similar to SWQO requirements in Section 3.2. The values of these determinands to define the lowest classification grade are, unfortunately, not sufficiently greater than analytical limits of detection to be confident that method interaction is excluded from measurements. Consequently, exceptional care should be taken to ensure that any replacement method (even one that complies with specified bias, precision and limit of detection criteria) does not induce an artificial shift in assessment data.

3.5 Permissive Monitoring

Permissive monitoring spans a wide range of purposes, and its size and structure is determined by the Regions. Guidelines are being developed to promote a nationally consistent approach and ensure best VFM. It is proposed that the size of permissive monitoring programmes should be controlled through budgetary constraints and reviewed by audit (4). The multiple uses of permissive monitoring preclude an overall summary of performance criteria requirements, but the GQA suite is particularly recommended for non-classified river sampling and operational investigations; and the same determinands are involved in many discharge impact assessments. In the absence of more definitive rules, the performance criteria required for GQA monitoring can be taken as applicable for these cases. Accepted analytical performance specifications are adequate for this use and the comments on additional protection to guard against step-changes in GQA data are not applicable.

3.6 Pollution Incident Response

Most instruments presently in use are employed in this category, and it was the principal reason for initiating development of six-parameter hand held instruments. The main requirement for this category is immediate feedback in the field to guide remedial action, rather than formal data quality needs. In 1992, oil and sewage pollution formed 26% each of the total pollution incidents, followed by farm pollution at 11% and chemicals pollution at 6% of the total (5). Thirty-one per cent of incidents could not be classified in one category, but solid wastes, foam, construction waste and vehicle washings were its major component parts. Hand held meters can provide all the monitoring data for some 30% of pollution incidents that require water quality analytical information.

3.7 River Quality Management

This category spans the uses to which fixed site instruments are put. These cover a wide range of uses such as protection of drinking water intakes (for which costs are recovered through Water Resources abstraction licences), monitoring eutrophication - prone stretches, modelling and direct control applications. The data quality requirements are a function of their end use but obviously, since they are wholly instrument generated, the quality of the instrument-generated data must be adequate for the purpose.

4 REVIEW OF IDENTIFIED DETERMINANDS

4.1 Dissolved Oxygen

This determinand is unusual in that the standard SCA method document acknowledges the acceptability of both laboratory and field instrument methods (6). Some Regions moved to the instrument method before the NRA was formed whereas others retain the laboratory method. Both methods are reviewed in detail in Appendix 3. In summary, the instrument method is more accurate because it is selective to oxygen whereas the laboratory titration method measures total oxidents/reductants including reduceable organic matter, but it is more liable to drift unless regularly recalibrated.

Dissolved oxygen is an extremely variable river quality parameter, and Appendix 4 shows a timeseries plot of its concentration over typical 24 hour period. It can be seen that the difference between the minimum value (the early hours of the morning) and the maximum (in the late afternoon) in summertime can be large enough to span several categories of classification. Ramifications for GQA analysis are illustrated by Appendix 5, a timeseries dissolved oxygen plot over one year for one sample point. It can be seen that short term (one day) variability is of the same order as the long term (one year) trend, ie most daily sampling timeframes in the June-September period experience approximately the same magnitude of variability as the mean change over the year. In fact, for many days the time at which the sample is taken determines whether it falls within one of four GQA categories A, B, C or D. In this situation a laboratory to instrument method change will have no discernable effect on the classification, but the time of sampling will. Statistical theory advises that once the analytical uncertainty is reduced to a third or less of the sampling uncertainty further reduction in the analytical uncertainty is of little importance (18); ie the route to better dissolved oxygen monitoring is to characterise its diurnal variability by more sampling rather than by more accurate analysis. It is for data clients to decide whether to minimise sampling interaction by moving to daily average values, but the capability to do so can be provided at low cost by instrumentation if required.

4.2 pH

This determinand is again unusual in that the SCA standard method is an instrument procedure based on the voltametric glass electrode, ie the same technique is used in laboratory and field instrumentation procedures. Provided that both are operated with comparable quality assurance there is no reason to assume that their data will not be of comparable quality.

pH is known to vary significantly within a day, particularly in rivers with high algal content as carbon dioxide is stripped from water by plant photosynthesis. It is also liable to change in transit from sampling point to the laboratory as carbon dioxide is desorbed from the sample. In fact, the standard SCA method recommends that pH should be measured in situ if high accuracy is required. As an illustration of the importance of pH in unionised ammonia calculation, in the pH range 8.7 to 9.5, a change of 0.2 pH units causes a 5% shift in calculated percentage ammonia. The time of sampling can therefore have a major effect on the accuracy of derived unionised ammonia measurement through pH diurnal variation.

4.3 BOD

Biochemical oxygen demand is an empirical bioassay of air-saturated aqueous samples, with allylthiourea added to restrict oxygen demand to organic oxidation only. Arguments for and against its use as a broad-scale indicator of pollution have continued since its introduction in 1912, but it is well established globally. It is not possible to transpose the analytical method to instrument use, consequently field monitoring initiatives have concentrated on developing surrogates that predict BOD to an acceptable accuracy or alternatives that give different estimates of oxygen demand. On-going R&D projects are investigating the potential for the use of BOD alternatives and surrogates. Results so far indicate COD to be the best alternative to BOD. Appendix 7 is a plot of BOD against COD for a number of sewage works effluents, with the uncertainty limits of BOD measurement superimposed on the plot. This indicates the extent to which the poor precision of BOD measurement tends to mask the extent of correlation with alternative parameters. On-going work also indicates that it may be possible to predict BOD accurately for sewage works effluents by a linear combination of turbidity and ammonia data, both of which are hand held meter measurements. Finally, hand held BOD sensors are under development that use respirometry or metabolic activity of immobilised bacteria as their sensing mechanisms.

The SCA standard method (7) states that the LOD for BOD measurement is unlikely to be better than 2 mg/l. Appendix 2 illustrates that the BOD from a sewage works effluent can vary strongly over 24 hour periods. Little information is available on the variability of BOD in river samples, other than the fact that high algal concentrations undermine its usefulness as a water quality index by increasing the dissolved oxygen content in rivers and effectively acting as "negative BOD" but, in contradiction, increasing measured BOD values by decomposition during the test. A further complication for GQA application is that the measurement method's limit of detection is approximately the same as the difference between classification grades and any replacement method could thus induce step-changes because of the unsoundness of the present method, even if its own limit of detection was of a comparable level.

4.4 Suspended Solids

Suspended solids is a gravimetric measurement and, as such, cannot be transposed to a field instrument technique. However, turbidity has been proposed as an alternative that can be supported by field instrumentation (8). On-going R&D investigations indicate that conventional nephelometric turbidity is, in fact, related more closely to BOD than to suspended solids; but forward scatter turbidity may give a closer relationship with suspended solids. Nevertheless, a report from South Western Region reviewed the relationship between nephelometric turbidity and suspended solids and concluded that they are sufficiently well correlated for it to continue as a consent monitoring parameter (9).

4.5 Metals

Metals are not routinely measured by field instruments, but the review of statutory requirements identified calcium, copper and zinc as important adjuncts for full field measurement capability of SWQO and GQA suites. Disposable metal sensors for use in hand held meters are being developed and the first two (for copper and lead) have recently been marketed (10). It is probable that the SWQO and GQA requirements with be met by this type of instrument within eighteen months.

4.6 Ammonia

The SCA reference method determines ionised and unionised ammonia as a total value, and calculates unionised ammonia from pH measurement and the appropriate equilibrium constant. Field instrument procedures measure ionised ammonia using selective ion electrodes, and calculate unionised and total ammonia values from pH and equilibrium constant information.

Selective ion electrodes in use now do not deliver limits of detection lower than 0.5 mg/l or total uncertainties lower than ± 1 mg/l; but more formalised quality assurance and calibration could reduce these limits. Nevertheless, it is improbable that they could reach the lowest SWQO or GQA requirements. In order to protect the continuity of GQA data, it is essential that an instrument-based method should not replace laboratory methods until it can be clearly demonstrated to reach an acceptable performance.

Continuous monitoring information shows that total ammonia can vary greatly within a day, although it is a less consistent and marked variation than that of dissolved oxygen. Appendix 6 is an example of within-day variation of ammonia in a river sample point. Also Appendix 2 illustrates the high within-day cyclic variability of ammonia in a sewage works effluent. Investigations by Thames Region indicated diurnal variation in sewage works effluent and changes in river flow as two major factors influencing the variability of ammonia in rivers. As mentioned previously, changes in pH within a day as carbon dioxide is used up in photosynthesis exacebates the variability of unionised ammonia by changing the ionised/unionised species ratio. Instrument monitoring of ammonia could thus improve the measurement of ammonia by reducing the within-day sampling variability but any advantage would be conditional on also achieving an acceptable limit of detection.

4.7 Toxicity

The R&D programme to investigate the need for toxicity-based consents is evaluating both laboratory based and field test methods. Another R&D project is funding the development of a hand-held toxicity meter based on disposable thin film sensors. If toxicity-based consents are adopted for complex effluents it is likely that field testing kits will be available for screening within two years.

5 REVIEW OF MONITORING OPTIONS

5.1 General Costing Considerations

Hand held meters are the only instruments where cost savings can be clearly quantified by their potential to replace laboratory analysis, because fixed and transportable instruments cannot cover the range of monitoring sites. The purchase of six parameter handheld meters was justified for pollution prevention reasons as well as monitoring cost saving, but individual dissolved oxygen and pH meters can be considered in terms of monitoring cost saving alone, with no added complication of non-cost benefits.

The National Laboratory Service has made substantial cost savings by moving to fewer, larger laboratories that operate more cost effectively by large scale automation techniques applied to large workloads. Work is generally organised into "suites" of determinands which can be measured together at a lower cost than if they were measure individually. The relationship between decreasing laboratory workloads and cost saving will therefore be a series of discrete steps as co-analysed determinands are removed, rather than a smooth curve. In the same way, the cost of field monitoring will increase in a series of discrete steps based on levels of support necessary to ensure acceptable quality.

An additional complication is that the workload pattern is changing. Specifically, Regions are reducing their GQA and permissive workload requirements and, clearly, this will reduce the work available for instrument monitoring.

5.2 Six Parameter Hand Held Meters Costing

5.2.1 Equipping Sampling Staff

This scenario assumes that 20 meters per Region will equip all sampling staff, that they will be fully supported by one technician (one technician will actually be under-employed on 20 instruments), and that data from the meters will be transformed to laboratory-style formats to be acceptable by clients data systems.

20 meters/Region = 160 total

Each one costs £3.4K and can be written off over 7 years.

Instrument cost = 160 x 3.4 ÷ 7 =	£77.7K
8 technicians at £40K each	£320.0K
Support and QA at £1K/meter	£160.0K
£10K/Region data treatment cost written off over 7 years	£11.0K
Total	£568.7K/year

This will enable sampling staff to measure statutory, GQA and some permissive work.

5.2.2 Equipping Sampling and Investigative Staff

This option assumes that 40 meters per Region would equip all samplers and relevant investigators, and enable the full statutory/consent/GQA/permissive range of monitoring to be addressed, together with pollution incident response. Other support services are the same as in the previous option.

Instrument cost = 320 x 3.4 ÷ 7	£155.0K
8 technicians at £40K each	£320.0K
Support and QA at £1K/meter	£320.0K
Data treatment cost	£11.0K
Total	£806.0K

5.3 Two Single Parameter Hand Held Meters Costing

This option considers equipping each Region with 40 dissolved oxygen and 40 pH meters to enable the full statutory/consent/GQA/permissive range of monitoring to be addressed, together with pollution incident response. It assumes that they can be supported by 0.5 FTE technician resource, and an allowance is made for data handling which may be more difficult than for the six parameter instruments because single parameter meters do not have inbuilt data logging (an allowance for data handling must be made because if the data are placed onto client registers via the laboratories the NLS will understandably make a charge for the service).

80 meters/Region = 640 total

Assume each one costs £0.5K and can be written off over 7 years.	
Instrument cost = 640 x 0.5 ÷ 7	£45.7K
8 technicians at £20K	£160.0K
Support and QA at £.25K/meter	£160.0K
Data treatment cost	£11.0K
Total	£376.7K

5.4 Laboratory Statutory Monitoring Costing

This option considers statutory, GQA and consent monitoring categories collectively because many samples have multiple reporting purposes and would complicate further breakdown into monitoring categories. Thames and Southern Regions showed very similar requirements; in the order of ten thousand dissolved oxygen, twenty-two thousand pH, twenty-two thousand unionised ammonia/total ammonia and one thousand turbidities each. If these were extrapolated to every Region's requirements and were assigned unit analytical costs of £2.00, £1.50, £3,00 and £1.00 respectively the total laboratory cost would be £0.96 million. There would also be additional laboratory costs for transcribing temperature and producing both saturation and concentration dissolved oxygen units, but these have been ignored.

An estimate of the work affected by single parameter instruments can be made by considering dissolved oxygen and pH costs alone. Using the above values this is equivalent to £0.42 million.

5.5 Laboratory Permissive Monitoring Costings

The permissive workload is tending to reduce as a result of ongoing client review. It is a good target for instrument applications because of its investigative nature, and it is important that instrument cost savings should not be overestimated by overestimating the eventual size of the permissive market sector.

Thames Region's permissive workload for 1994/95 will be some 20% of the total workload. Of this, 4,500 permissive samples require the GQA analytical suite plus TON, chloride and phosphate. These 4,500 samples represent 14% of the total workload. The former Northumbria's permissive workload that could be met by the GQA analytical suite plus TON, suspended solids and alkalinity was estimated to be 52% of the total permissive work or 11% of the total programmed workload.

These data suggest that, nationally, some 32,000 samples in the permissive workload need the GQA analytical suite plus some other determinands that can be measured in the field. If the other determinands are ignored (ie field measurement costs are assumed to equal laboratory costs) and the laboratory cost for a GQA suite is assumed to be £9.00, then the cost of this laboratory work will be some £0.27 million.

The dissolved oxygen and pH component of these costs is £0.11 million.

5.6 Laboratory Pollution Incident Monitoring Costs

This unplanned monitoring sector can only be quantified broadly. It was estimated that some 30% of incidents could be analysed by hand held meters and would require no other laboratory based measurements. From Thames and Southern Regions' Corporate Planning Submissions a national figure of 3,000 samples was estimated. As in the previous section, if a laboratory cost of £9.00 was assumed, the total cost for this work would be £0.03 million.

5.7 Costing Overview

Sections 5.3 to 5.5 estimated the costs of laboratory workloads as £0.96 million for statutory, £0.27 million for permissive and £0.03 million for unplanned pollution incident monitoring. Unit costs used to derive these values are best guesses for guidance until more accurate determinand costs are made available by the Laboratory Service.

An alternative "top down" approach was made to validate these estimated costs. The statutory/GQA/consent work that could be measured with hand held meters equates to some 0.7 million determinations, and permissive monitoring plus pollution incident monitoring represents around 0.2 million determinations. The total is therefore 0.9 million determinations, or approximately 16% of a total of 6 million determinands. If the laboratory service has a budget of 14.45 million, 16% of the workload would cost some £2.3 million if each determinand had the same costs. If, however, the Laboratory Service develop a differential costing to reflect relative difficulties in analysis, the hand held meter determinations would be on the lower side because of their ease of measurement. The Laboratory efficiency report (12) showed that the 6 million determinations were comprised of 3.9 million general, 1.2 million metals and 0.9 million organic measurements. Extreme differentials would have to be applied to these determinand categories in order to make the hand held meter workload equate to £1.2 million. As an illustration, if metals analysis were rated as twice the cost of general analyses and organics three times the cost of general determinations, a general determination would be half the cost of the overall mean cost for a determination. This would assign a value of £1.15 million to the hand held meter workload. In other words, the value of the work amenable to instrument monitoring can only be reduced from £2.3 million to £1.15 million if the general determinand costs are drastically reduced to one third of an organic analysis cost or one half of a metals anaysis cost.

There is no indication that the laboratory service will make such an adjustment, and this alternative costing approach suggests that a value of £1.26 million for the fraction of the laboratory workload that can be moved to hand held meters is probably an underestimate.

6 HAND HELD MONITORING OPTIONS

6.1 Statutory, Consent and GQA Monitoring by 6 Parameter Meter

Section 5.2.1 showed that sampling staff could be equipped with meters and full support facilities for £0.57 million per year. The laboratory costs from sections 5.2.3 and 5.2.4 for an equivalent service would be a minimum of £0.96 million, giving a cost saving of £0.39 million per year on moving to instrument monitoring.

The advantage of this option is that it could facilitate a more meaningful monitoring strategy for dissolved oxygen, ammonia and pH by reduction of the predominant source of error, short term variability of sample concentration. Its major disadvantages are the high risk that ammonia measurement will not meet the performance criteria, and the requirement for support staff.

6.2 Statutory Plus Permissive and Pollution Monitoring by 6 Parameter Meter

Section 5.2.2 costed the equipping of all sampling and investigative staff with meters and full support to be £0.816 million. Subsequent sections identified the equivalent statutory, GQA, permissive and pollution incident laboratory cost to total £1.26 million. The cost saving on moving to instrument monitoring would therefore be £0.45 million per year.

As with the previous option this selection has the advantage of supporting a more meaningful programme of monitoring for highly variable parameters. Moreover, it does enable the pollution prevention advantages of six parameter measurement in the field to be fully exploited; ie the ability to increase the intensity of consent monitoring at low cost, to extend investigations to 24 hour monitoring if required by use of unattended logging, better selection of samples for laboratory analysis and groundwater monitoring in situ by use of a flow cell (spot samples are likely to be changed by oxidation when they are brought to the surface). In addition, there may be a spot-checking audit role in the event of self-monitoring by dischargers. The principal disadvantage is again that ammonia measurement may not meet the performance criteria for the statutary part of the workload.

6.3 DO/pH Monitoring

The cost of equipping sampling and investigative staff with dissolved oxygen and pH meters was estimated to be £0.38 million, and the cost of statutory plus permissive monitoring that it would replace was in the order of £0.53 million, giving a cost saving of £0.15 million. Its strong advantage over the six parameter scenarios is that there is a very high probability of achieving the payback since ammonia and its associated performance reservations are avoided. Its disadvantages are that it brings little general pollution prevention benefit because ammonia, conductivity and turbidity are basic parameters for on-site pollution prevention guidance; and there is no single instrument with integral data logger to act as a platform for upward expansion if extra relevant sensors (such as BOD) become available in the future.

7 CONSENT MONITORING OPTIONS

The common consent monitoring determinands are reasonably well covered by the hand held meter. Ammonia is available, and R&D work to be reported in the near future is will outline the accuracy of prediction of suspended solids from turbidity, and effluent BOD from ammonia and turbidity.

Separate investigations by South Western (2) and Thames (11) water quality staff reached similar conclusions: that sewage effluents tend to vary in a systematic and predictable manner because of their influent diurnal variations, and the normal sampling hours of 9.00 to 16.00 coincide with the best quality of effluent ie peak concentrations tend to be outside normal sampling hours. The Thames report quotes an example of an effluent sample point where the 24 hour flow weighted composite ammonia value would be 3.2 mg/l, the daily 95 percentile 7.0 mg/l, but the typical spot sample taken in normal working time would be 0.5 mg/l. The South Western report concluded that operational biological treatment works were more prone to cyclically varying effluents, but activated sludge works tended to deliver worst quality effluents at weekends when the process was unattended. Although these investigations may not be representative of all sewage effluents, in fact works maintenance periods during normal working hours have also been identified as poor effluent periods, they do imply that random sampling over the 24-hour period would be the best approach. This suggests that the major use of instrumentation should be to extend the sampling window beyond normal working hours and present more relevant samples for laboratory analysis. At this stage, it would be difficult to bypass the tripartite sampling/laboratory analysis process by exclusively instrument-based monitoring but instrumentation can target tripartite sampling effectively.

The best instrument to do this is the Cyclops portable monitor/sampler, and 26 units are on order for distribution to every NRA area. Their main purpose is to detect and sample consent exceedances and it is unlikely that they will alter the laboratory workload significantly (costed as part of statutory monitoring). Hand held meters have a contributory role in that they can extend the sampling coverage in working time and overnight by unattended logging.

Implementation of the Urban Waste Water Treatment Directive will have a profound effect on the monitoring of discharges from treatment works. The NRA will continue a reduced spot sampling regime to enforce the Water Resources Act elements of the consent. The emphasis will be switched to self monitoring based on 24 hour composite samples, with audit by the NRA. This will be phased in from 1995 and it is important that the NRA is involved in the development of automatic samplers for use by industry that satisfy our our audit role. At some treatment works it will be necessary to develop automatic samplers that will operate on influent as well as effluent so that percentage reduction can be calculated. Also, there will be a requirement to measure effluent flow. The tasks of specification, evaluation and possibly on-site audit of these instruments will necessitate the acquisition of a range of new instrumentation expertise to address questions such as: will the pumping process degrade suspended solids, will nitrifying bacteria coat inner surfaces and reduce the ammonia concentration, will BOD be affected by the sample storage process.

The wider issue of self-monitoring by dischargers is still under discussion. The Environmental Protection Act is currently transferring control of prescribed processes to HMIP and the NRA are keen to encourage the increased use of instrumentation, control and automation in the running of these processes. It is also possible to specify that monitored information should be telemetered directly to the regulatory body, which may present opportunities for better monitoring and management of rivers and estuaries. However, a note of caution has been flagged by several reviewers of this report draft in that if dischargers move to continuous monitoring of their own effluents, either to respond to these automatic auditing techniques or for their own process improvement reasons, they may develop the capability to control their effluent just below the upper tier consent value. This could result in a higher loading placed on the river system than was planned for in the original consent setting.

8 RIVER QUALITY MANAGEMENT USING PERMANENT MONITORING STATIONS

If frequent and instant water quality information is required from a specific sample point the justification is not one of instrument versus laboratory measurement (laboratories are not competitive in this application); it is whether to do it at all.

The strongest cost benefit justifications lie with those instruments that are used to initiate corrective action if certain conditions are detected. This is best illustrated by a number of examples.

The Thames tideway monitoring system is comprised of a network of monitoring stations on the Thames estuary which supply dissolved oxygen and ammonia data to a control system at Reading. A problem discharge (typically a storm sewage overflow) is detected, its environmental effect on the estuary predicted and if necessary corrective measures are called up. These include reduction in drinking water abstraction to increase freshwater dilution, aeration of sewage effluents and direct injection of oxygen into the polluted river. Deployment of these measures cost some £3 million, and the capital cost of the automatic monitoring system approximately £0.25 million. The alternative option not involving automatic monitoring stations would have been construction of relief sewers costing several hundred million pounds, and the do nothing option would be high probability of several million fish deaths in the London tideway from storm sewage discharges. This actually happened in 1987.

The proposed Maidenhead Flood Alleviation Scheme has automatic water quality monitoring stations as a key component of its design. The potential risk is that low flows and high algal growths could give rise to high oxygen variability leading to large scale fish deaths. Automatic monitoring will enable management strategies such as flow adjustment, aeration or weed removal to be employed when necessary. The alternative to automatic monitoring would be a (prohibitively) expensive redesign of the channel.

A continuous monitoring station on the Great Stour in Kent ensures that water fed from the estuary to irrigate reclaimed marshland is controlled to a recommended salinity level for the protection of crops and animals.

A paper mill in the Medway estuary is subject to continuous monitoring of its effluent discharge. Data were used to calibrate a mathematical model to aid the setting of consent conditions, and to manage the estuary environment by appropriate effluent restrictions.

Trailer mounted systems are also commonly used to enable this intensive monitoring capability to be moved from location to location as cicumstances dictate.

9 SELECTION OF INSTRUMENT OPTIONS

9.1 General Discussion

Previous sections describe an overlapping range of instrument types ranging from permanently sited to trailer mounted, portable, portable consent monitoring, hand held multiparameter and single parameter, and test kits. In general selection is a matter of fitting options to individual circumstances. Many applications are long-standing commitments and their capabilities and resource requirements are well established. Two situations however, consent sampler/monitors and hand held meters, are different in that they address purposes previously outside the scope of instrumentation: automatic formal sampling and programmed monitoring. These are detailed below.

9.2 Consent Monitoring

All areas are being equipped with a Cyclops automatic formal sampling instrument. The Instrument Centre will provide training, maintenance and repair support for these instruments. It is probable that with this backup one such instrument per area can be operated with existing regional resources. If the numbers of instruments are to be increased further it may be more cost effective to move to Regional technical support.

9.3 Hand Held Meters

Options were detailed in section 6 in terms of cost saving, risk and additional benefits, and are summarised for convenience in the following table.

Summary of Hand Held Meter Options

attribute	2 parameter	6 parameter	6 parameter
scope of monitoring	statutory	statutory	all
instrument cost	£ 376k	£ 569k	£ 806
laboratory cost	£ 530k	£ 960k	£ 1260k
saving (lab - inst)	£ 154k	£ 391k	£ 454k
risk	low	high	medium high
added benefits	low	medium	high

Options are polarised between the low risk, low payback two parameter instrument scenario and the higher risk but higher payback six parameter instrument application for statutory and permissive monitoring. The third option, six parameter instrument measurement of statutory work only, can be discounted because it does not offer low risk or high payback benefits. The two leading options are fairly evenly balanced, but the non-cost advantages of enhanced pollution prevention are important and should be exploited fully, making the six parameter instrument the preferred selection.

10 MONITORING INSTRUMENT IMPLEMENTATION

10.1 General

The long-standing instrument applications are supported by in-house or bought-in technician resource, but in general the new areas of Cyclops consent monitors and six-parameter instruments are not. Regional feedback to the first draft of this report emphasised strongly that instrumentation has failed to take off in the past because of inadequate human resources to support them and the new applications could only be implemented successfully if new full-time technician posts were created. This was considered particularly important for hand held meters where quality assurance is required in addition to maintenance support.

10.2 Hand Held Meters, Current Status

The following table summarises the present position for hand held meters.

Hand Held Meter Status

REGION	NUMBER OF METERS	TECHNICIAN SUPPORT	QUALITY SYSTEM
South Western	28	partial	none
Southern	18	partial	implemented
Thames	45	full	implemented
Welsh	8	none	none
Anglian	10	partial	partial
Severn Trent	22	partial	partial
North West	8	none	none
N'umbria/Yorkshire	24	full	in progress

At present, only Thames Region is equipped to make full use of hand held meters.

10.3 Hand Held Meter Implementation and Timescales

Implementation can be divided into four areas; development of operating and quality assurance procedures, training staff in use of the instruments according to appropriate procedures, training technicians in maintenance and calibration support, and development of a procedure to automatically transfer data to archives. A practicable approach to implemenation would be to introduce the instruments for dissolved oxygen and pH initially using the National Centre to provide all instructions, training and repair support, then bring ammonia measurement on-stream when user confidence has built up and the National Centre has developed best operating procedures. Temperature and conductivity require minimal support and can be implemented at any convenient stage. Turbidity is also straightforward and only requires the national

Centre to develop a standardised calibration format. Individual activities and timescales for the National Centre's commitment to implementation of the exisiting instruments to this overall design are proposed in appendix 8.

This schedule should enable Regions to introduce the instruments for dissolved oxygen and pH monitoring measurement by September 1994, and for all parameters by March 1995. March 1995 will also be a convenient time to review progress nationally on implementation within regions, the effectiveness of National Centre support and the final performance of ammonia measurement. This will provide guidance to plan future purchases and technician support.

10.4 Hand Held Meter Quality Systems

A report from the evaluation facility (17) confirms that hand held meters can achieve acceptable performance for dissolved oxygen and pH, and characterises the instrument's stability over an extended period. A further evaluation of the performance of the modified ammonia probe is in progress. These data should be used in conjunction with a client specification to define optimal operating and calibrating procedures. A further evaluation should be carried out to determine a practical verification system to ensure that meter performance does not deteriorate in the field, and this should be incorporated in a basic quality assurance system.

11 RESEARCH AND DEVELOPMENT

Current R&D projects address the problems identified in the main body of this report, such as investigation of alternatives to BOD, development of a more accurate ammonia sensor and production of quality schemes for field instrumentation. In addition R&D initiatives are contributing to self-monitoring policy development, exploring common instrumentation issues for the organisations that will comprise the Environment Agency, and establishing an NRA presence in European monitoring instrument standardisation schemes. Individual projects are outlined below.

11.1 Review of Field Test Kits

Although this project primarily addresses the NRA's water quality business requirements it also scopes the needs of the waste regulatory bodies and HMIP. The WRAs are large users of test kits because of their need for immediate feedback on site, but determinands and concentration ranges are different from NRA uses. HMIP has closer analogy with NRA site test requirements, but as yet their field staff do not carry out site measurements.

11.2 Moored Marine Monitor

The NRA has a statutory duty to monitor out to the three mile limit and to investigate the effects of polluting discharges to the marine environment. The marine monitor will be a self contained moored water quality buoy capable of monitoring a number of physical and chemical determinands.

11.3 Field Measurement of Effluent BOD

Previous R&D showed that optical absorbence at 650 nm is closely correlated with the amount of BOD in sewage effluents. The mechanism of correlation is thought to be that most of the sewage effluent BOD is carried in colloidal particles. These particles are the main cause of 650 nm light attenuation. An R&D project to confirm this relationship and the production of a prototype, low cost, portable, BOD sensor is proposed.

11.4 Oil in Water

A review of equipment to measure the presence of oil in (and on) water and to monitor the amount of oil is being carried out. Liaison with dischargers with similar interests (eg British Steel) is included.

11.5 Trace Metals in the Marine Environment

The contractor has produced a disposable sensors using anodic stripping voltammetry to determine trace metals in the field. The R&D project will develop a bench top device using microelectrodes to determine trace metals in the Marine Environment. Phase I will develop electrodes to detect lead , copper, mercury, cadmium and zinc. The detection levels will be sub part per billion level. Phase II will look at arsenic, nickel and chromium. If successful, it will allow these analyses to be undertaken at sea and enable better sample targeting in high concentration gradients. The sensors may have a role in the moored marine monitor project.

11.6 Chemical Environmental Sensor Arrays

This is a link programme of the Department of Trade and Industry. The consortium involved are Unilever, Siemens, Southampton University, Drinking Water Inspectorate, National Rivers Authority and the Water Research Centre. The Authority has not put any money into the project but is involved as an advisor/potential end user. The first stage of the project is to produce a conductivity, temperature, reference, pH and dissolved oxygen sensor. Signal processing strategies will then be evolved to handle the signals produced. The second phase will look at the prototyping of trace metals, ammonia and chlorine sensors. The advantage fro the NRA will be disposable sensors for field use that need no skill to operate and are pre-calibrated and quality assured.

11.7 Inland Use of Airborne Remote Sensing

Archived marine sensing data will be evaluated to determine whether near infrared or ultaviolet spectra at organic material absorbance wavelengths will correlate with BOD and whether it can be used to monitor any other inland water quality parameters

11.8 Self-Monitoring Instrumentation

A business study is reviewing the implications of equipment (instrumentation and autosamplers) for self-monitoring and compliance auditing.

12 DATA TREATMENT CONSIDERATIONS

Analytical data are transferred from the laboratories to clients by electronic transfer from LIMS to client information systems. As yet there is no national standard, but each laboratory transmits its data in a format suitable for each Region. If a proportion of work is to be removed from laboratory to instrument measurement the users would expect it to be delivered in an identical format to the laboratory data. The best way to achieve this would be to develop a PC-based system which would receive data from hand held meter data loggers, reformat it to client requirements and transfer it to the users' data systems. A preliminary review by South Western staff estimated that the in-house cost of software development would be in the order of £10,000. A similar cost has been assumed for the other Regions in the preceding costing exercises.

Merging of laboratory and permanent instrument monitoring data are more complex. Technically, continuous monitoring data could be reformatted by a similar process to that described for hand held meters. In practice, the sampling frequencies are so disparate that the two data populations would not be harmonious. For example, dissolved oxygen monitored once every three weeks presents a very different picture to dissolved oxygen monitored continually at fifteen minute intervals. In many Regions multifunctional systems share the same monitoring and telemetry platforms for economy of scale, producing data on water quality, flow, rainfall, radar rain prediction. To date little emphasis has been placed on integration of of data. For example, flow and concentration data could easily be transformed to load, and selected hydrology information can enhance predictive models of water quality. parameter changes.

As mentioned in section 7 an expansion of self-monitoring by dischargers may result in the need to interpret dischargers' own continuous monitoring data of their influent and effluent flow and quality, either by direct telemetry or on-site inspection of the data and monitoring systems. It is unlikely that dischargers' instrument data would be in a suitable form to be compatible with in-house systems, and considerable IS and interpretive resource would be required. In some instances, there may be a requirement to develop automatic audit monitoring instruments for use by the regulator. This subject is being explored in an R&D project (11.8).

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16 G Smeaton, "DO Probe Winkles Winkler". Water and Sewage Works, August 1979.

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APPENDIX 1: PERFORMANCE OF THE GRANT/YSI 3800 HAND HELD METER

This instrument was selected by a process of specification and evaluation. The specification was prepared by Severn Trent Region and confirmed nationally. Basically, the performance required was ± 10% error (maximum) for each measured parameter. The evaluation was constructed to a third party, WRc, who used the NRA Nottingham Laboratory for most of the testing. Four instruments were selected for evaluation and the Grant YSI instrument performed the best and was selected for national purchase. In general, it met all the performance requirements other than for ammonia. Ten per cent error is difficult to achieve for ammonia analysis using laboratory techniques and, although the Grant YSI meter gave the best performance for ammonia analysis, it is probably beyond the capability of existing ammonia sensors to achieve less than 10% error. The performance of the Grant YSI meter during evaluation can be summarised as:

Temperature:	less than 10% error;
Dissolved oxygen:	11% error;
Turbidity:	less than 10% error;
pH:	less than 10% error;
Conductivity:	less than 10% error;
Ammonia:	greater than 10% error above 20 mg/l, ± 0.85 mg/l error over 0-2 mg/l range

These evaluation data were from tests that modelled field conditions (ie range of temperature, sample matrices, etc) but were not actual field performance data.

A subsequent test at South West Region gave the following performances:

pH:	5% error
Conductivity:	12% error
Dissolved oxygen:	11% error
Turbidity:	± 3.5 NTU

Similar tests at Thames and Wessex Regions confirmed this order of results but neither was formally reported.

An extended field test at the NRA Evaluation Site at Reading gave the following performance values:

Dissolved oxygen:	6% error
Temperature:	± 0.2°C
pH:	± 0.2 pH units
Conductivity:	± 38 μS
Turbidity:	± 3 NTU

In all, the available test data are reasonably consistent, and suggest that the instrument is capable of the following performance.

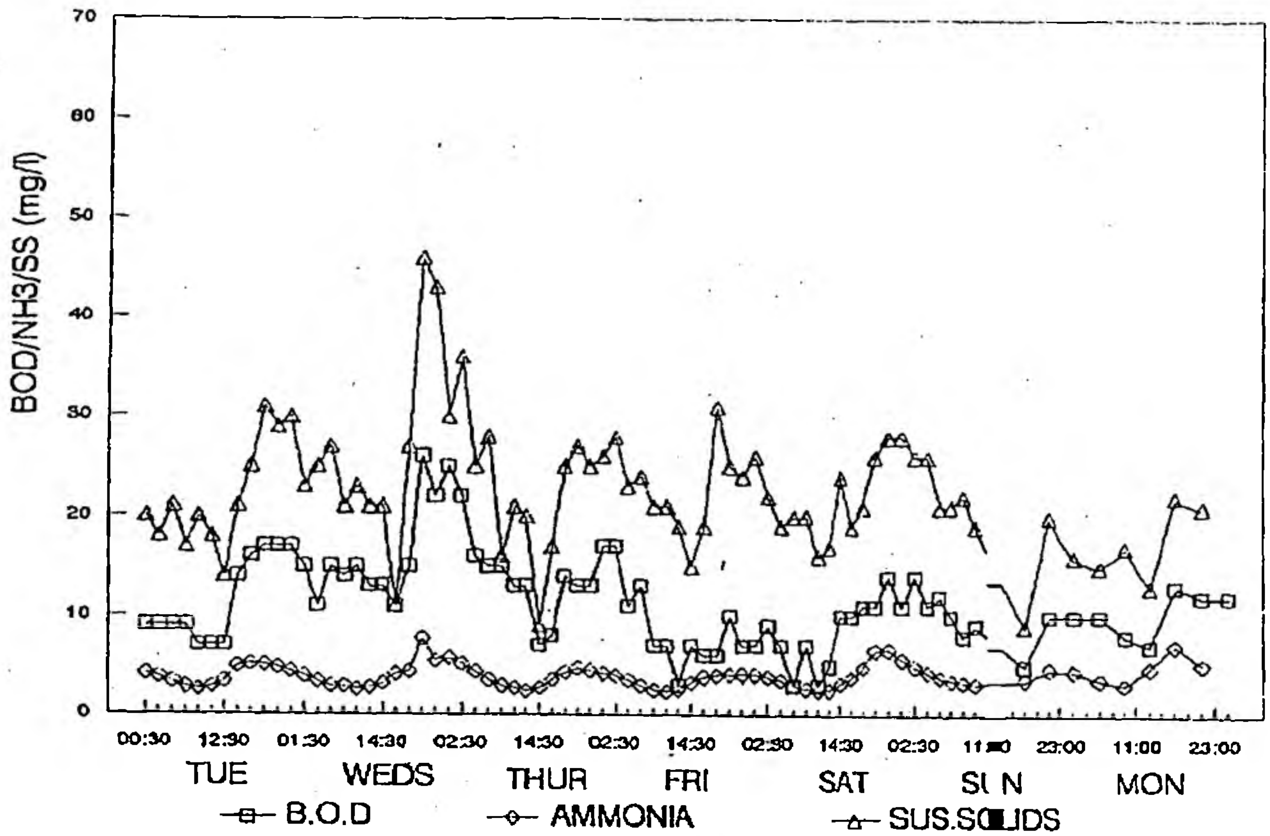
Temperature:	± 0.2°C
Conductivity:	± 12%
Dissolved oxygen:	± 0.2 units
Turbidity:	± 3 NTU
Ammonia:	± 1 mg/l

These data represent the quality of data that the instrument can deliver is operated with a suitable quality system. Present indications are that temperature and conductivity do not require regular calibration; they need only an initial verification against a standard to adjust any bias, and occasional cleaning of the sensor surfaces. Turbidity requires a monthly calibration. Ammonia and pH sensors require weekly calibrations. Dissolved oxygen needs a daily calibration, but this is a simple procedure which can be carried out by the operator.

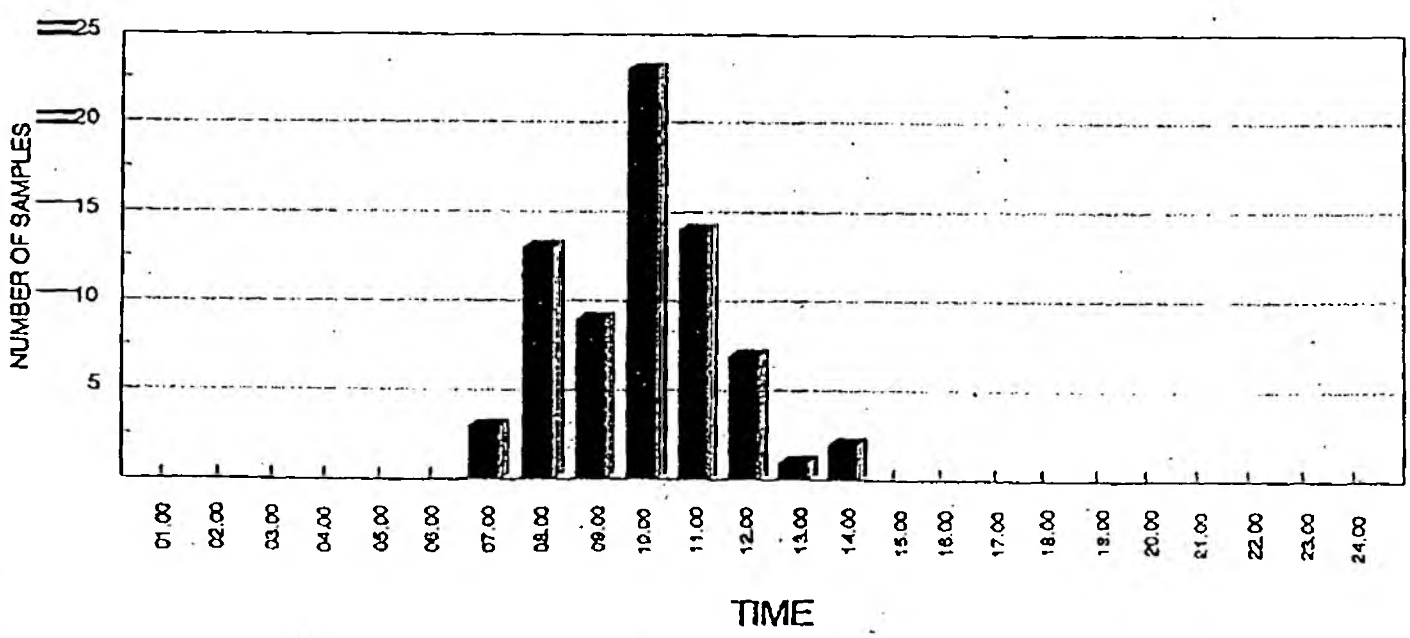
In summary, present indications are that the instruments would require weekly calibration and maintenance by an instrument technician in order to maintain optimal performance.

DEVIZES STW FINAL EFFLUENT ANALYSIS

26 FEB - 4 MAR 1991



DEVIZES STW DISTRIBUTION OF SAMPLES DURING DAY 1988-1990



APPENDIX 3: DISSOLVED OXYGEN ANALYSIS

The standard SCA method for dissolved oxygen analysis (6) describes two reference techniques, a titrimetric method and an electrical sensor method.

The titrimetric method is the Winkler procedure, in which oxygen is fixed in situ by manganous hydroxide freshly precipitated in the sample bottle. Subsequent laboratory procedures are addition of iodide and titration of liberated iodine with thiosulphate. The instrument method involves an amperometric cell separated from the sample by a gas-permeable membrane. Oxygen diffuses through the membrane into the cell, where it is reduced to hydroxide at the cathode.

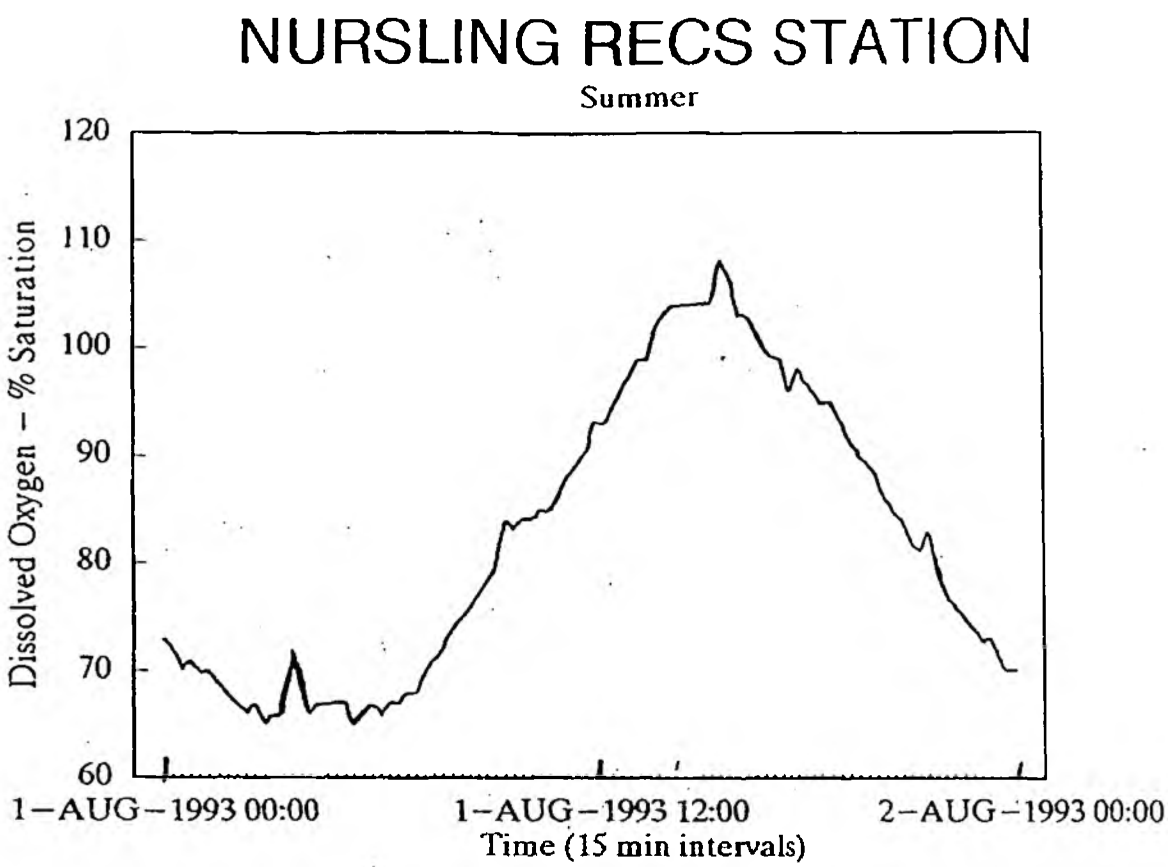
There is little to choose between the methods in performance terms. The SCA document quotes similar limit of detection, bias and precision data for both techniques. If anything, the sensor method is more accurate and the titration method more reliable. The titrimetric procedure is prone to interference from reducing or oxidising agents. The principal interferent is likely to be oxidisable organic matter (for example, sewage suspended solids) and the Winkler method becomes more erroneous for higher BOD samples. The electrochemical cell is liable to interference from permanent gases that can be reduced at the cathode, for example chlorine and nitric oxide, but these are less likely to be present in river and effluent samples than organic matter, the major Winkler interferent. On the other hand, the Winkler method uses primary standard solutions whereas the electrochemical sensor has an arbitrary response and must be calibrated. There is therefore a greater probability of systematic error with the sensor method unless it is operated under a good quality assurance scheme.

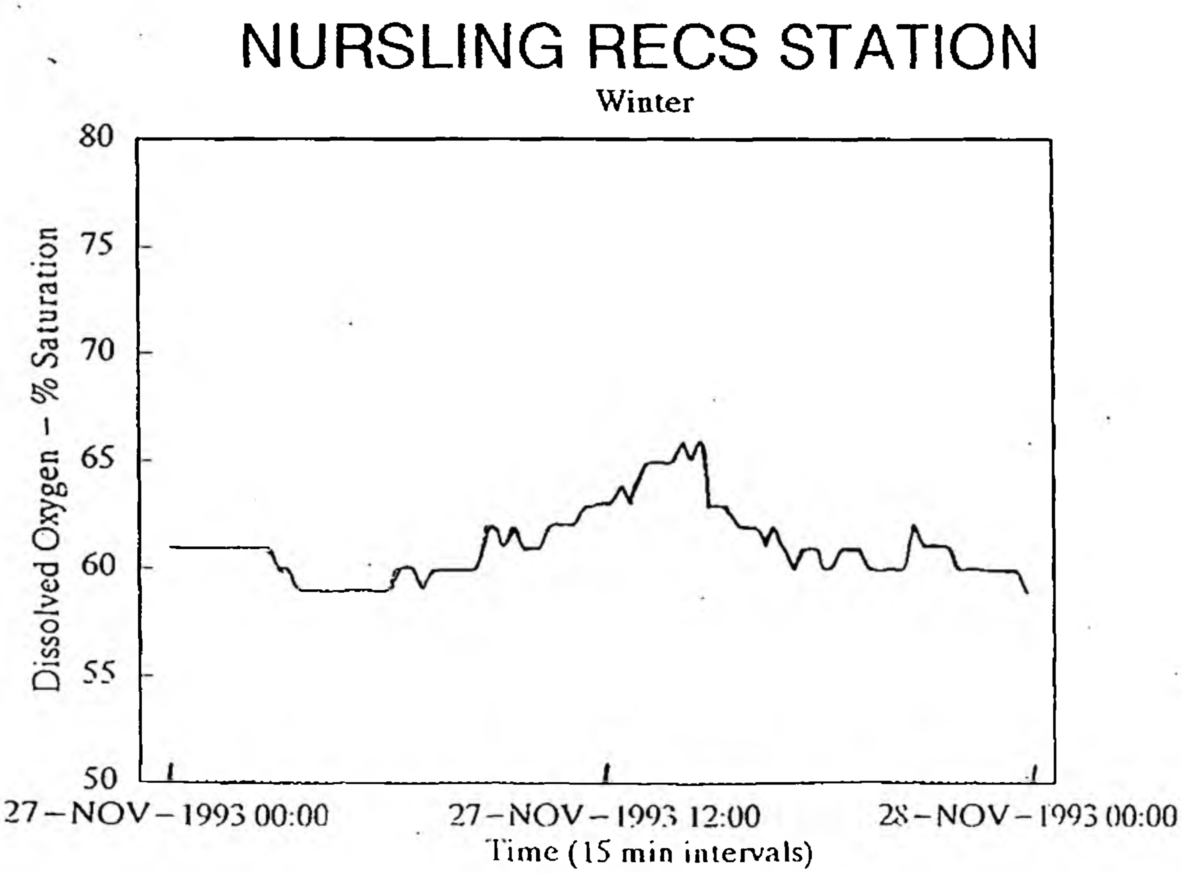
The current position is that some regions have stayed with the titration procedure whereas others have moved to the sensor method. Those that moved to the sensor technique may have carried out comparative testing at the time but no in-house NRA data are currently available to clarify the relative performances of the two techniques. Discussions with Thames Region established that an evaluation carried out before the NRA's formation showed the instrument method to be more accurate and of lower cost (3). However, discussions with South Western Region identified some reservations on the quality of instrument data and the desire for a more formalised quality system (14).

A WRc instrument evaluation of the Grant/YSI dissolved oxygen probe included testing the probe and the Winkler method with standard solutions of dissolved oxygen, obtained by saturating water with certified mixtures of nitrogen and oxygen (15). The mean total error for the sensor method was 2.5%, and the mean total error for the Winkler method was 6.6%. These data, indicating the sensor method to be the more accurate, are to be expected from a controlled evaluation where both methods are used with care.

A published comparison of the Winkler and sensor methods (16) concluded that the Winkler procedure was three times more labour intensive than the sensor method and was twice the cost of the sensor method. Again there are no in-house data to confirm these findings.

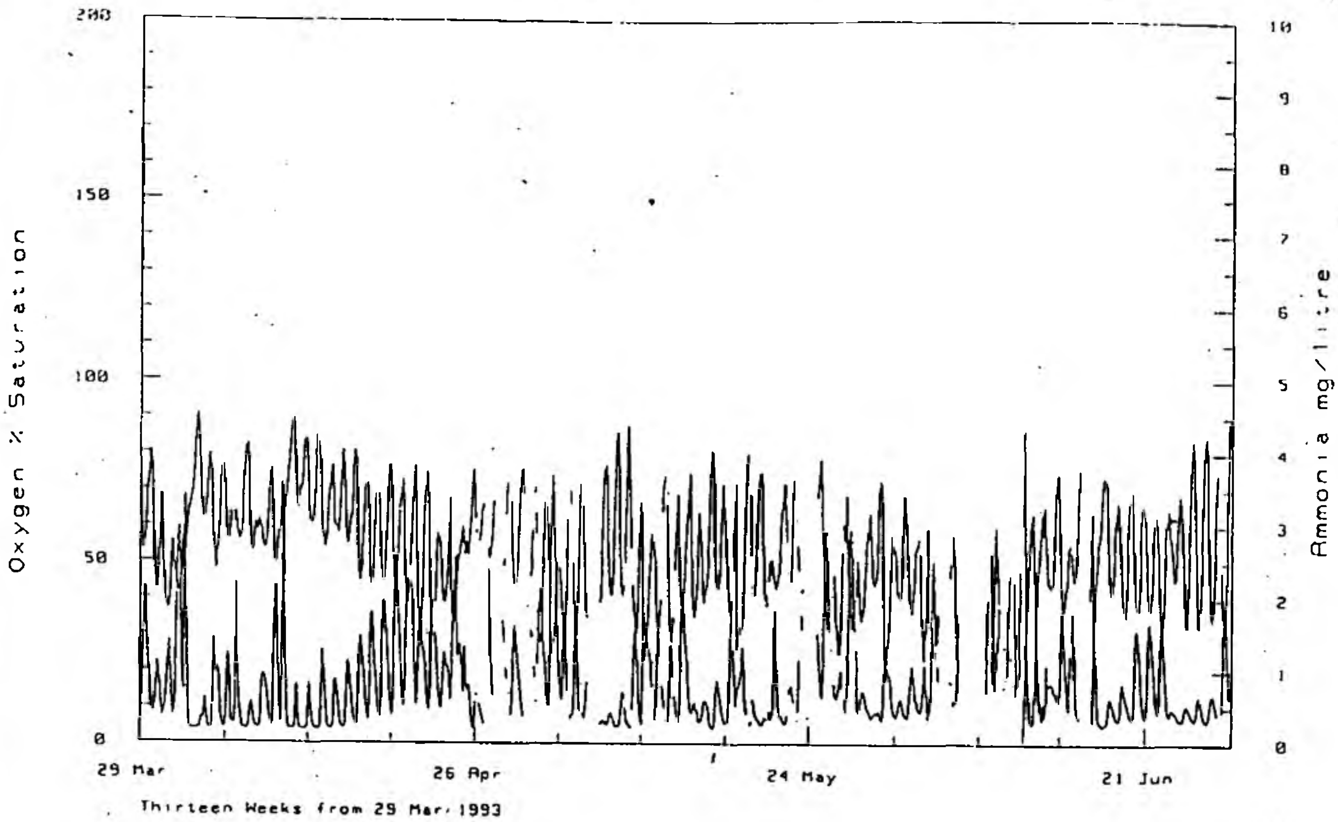
Appendix 4
Dissolved Oxygen Timeseries Plot



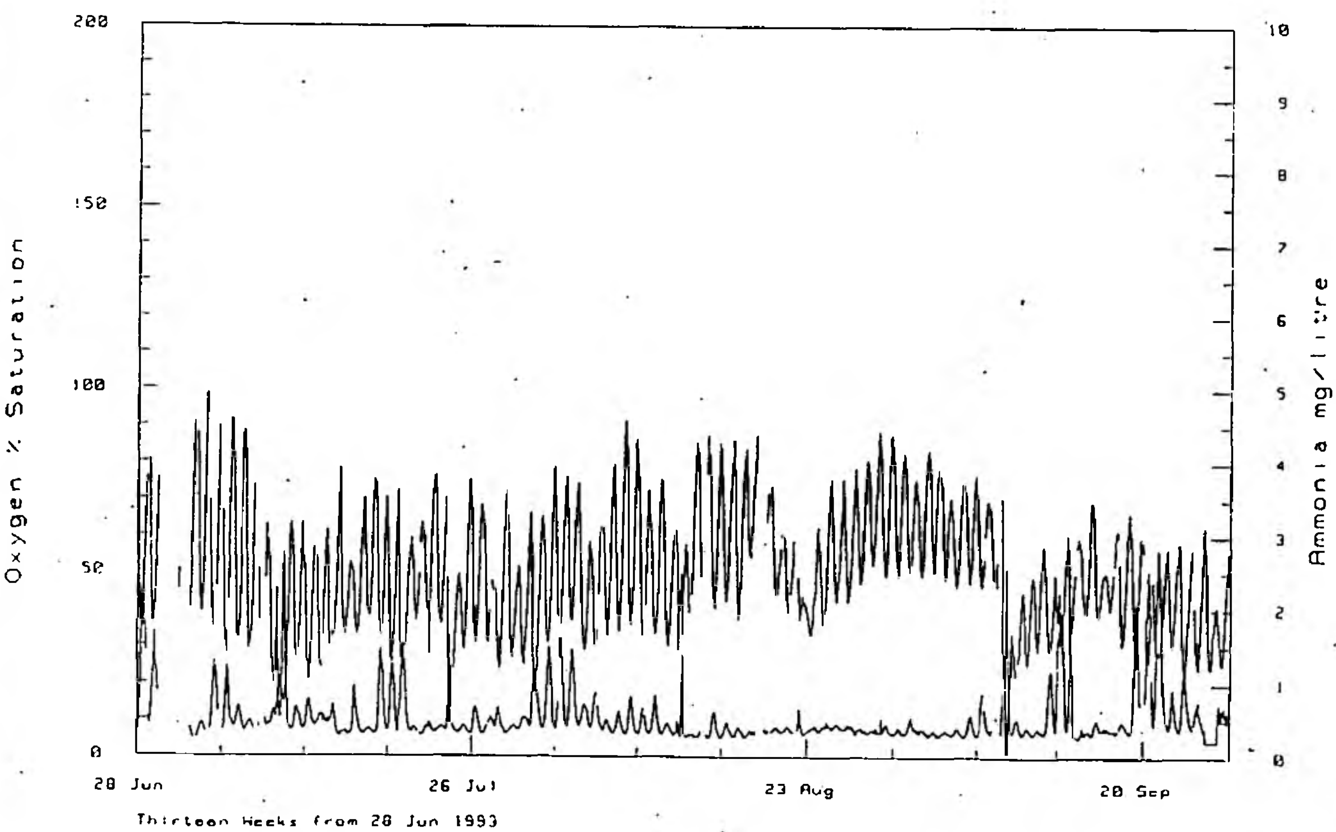


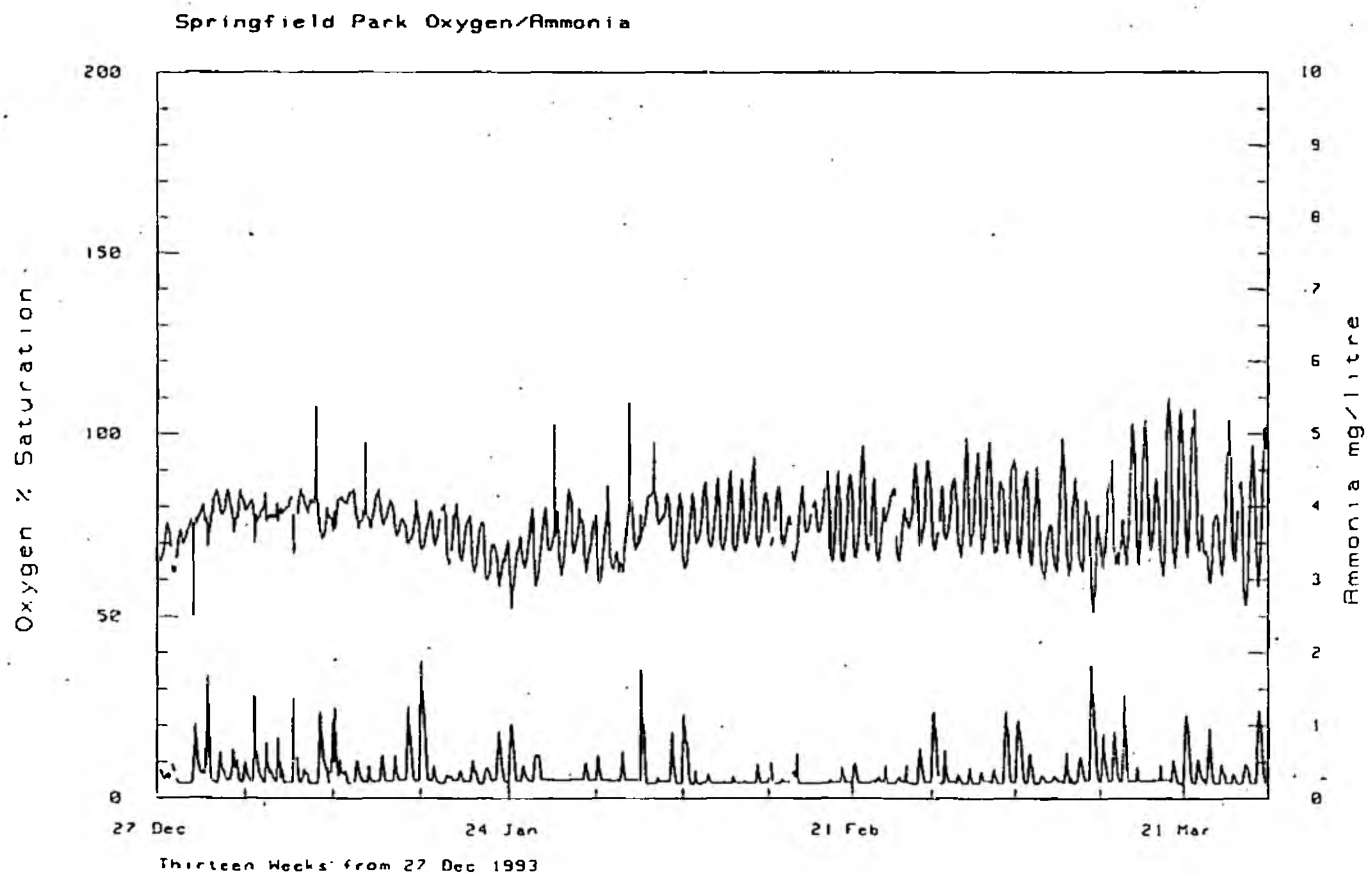
APPENDIX 5 - DISSOLVED OXYGEN CONTINUOUS MONITORING

Springfield Park Oxygen/Ammonia



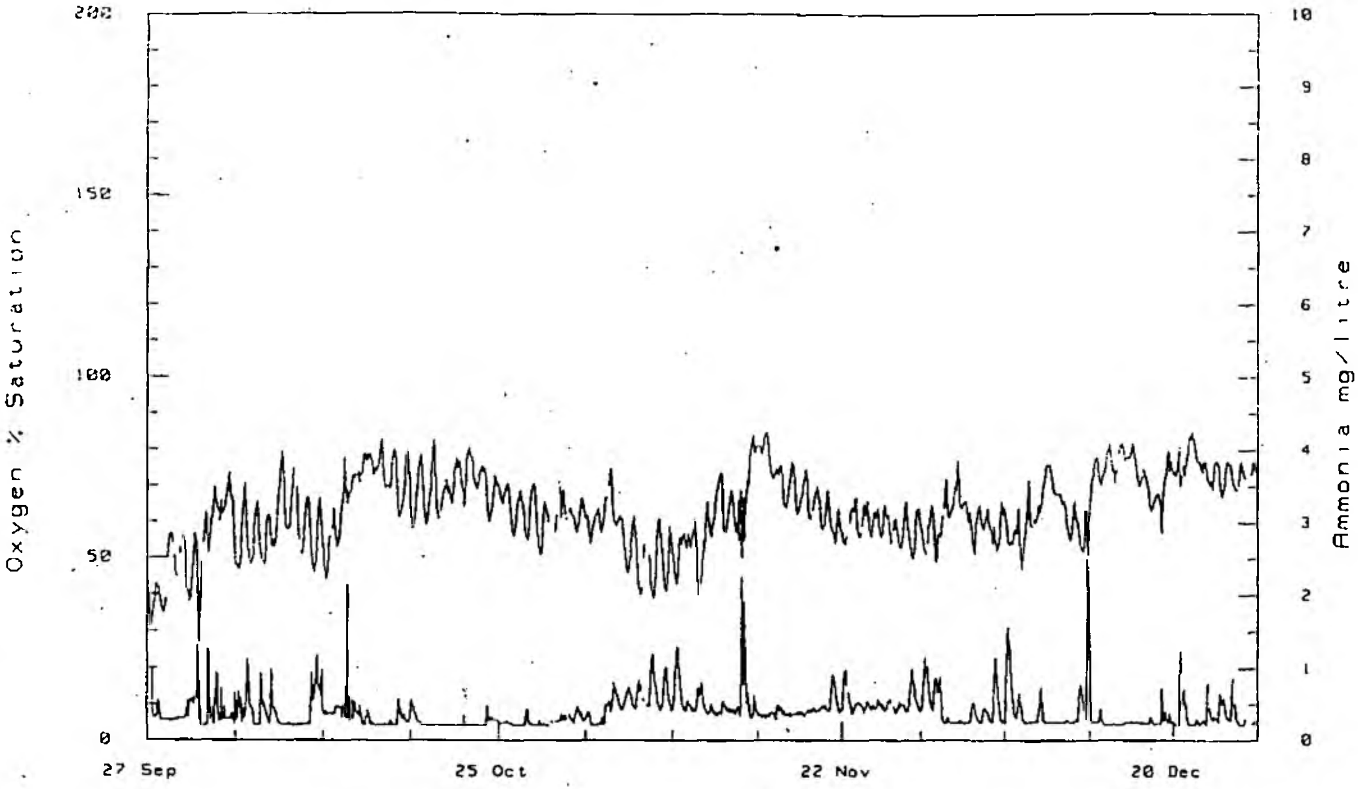
Springfield Park Oxygen/Ammonia





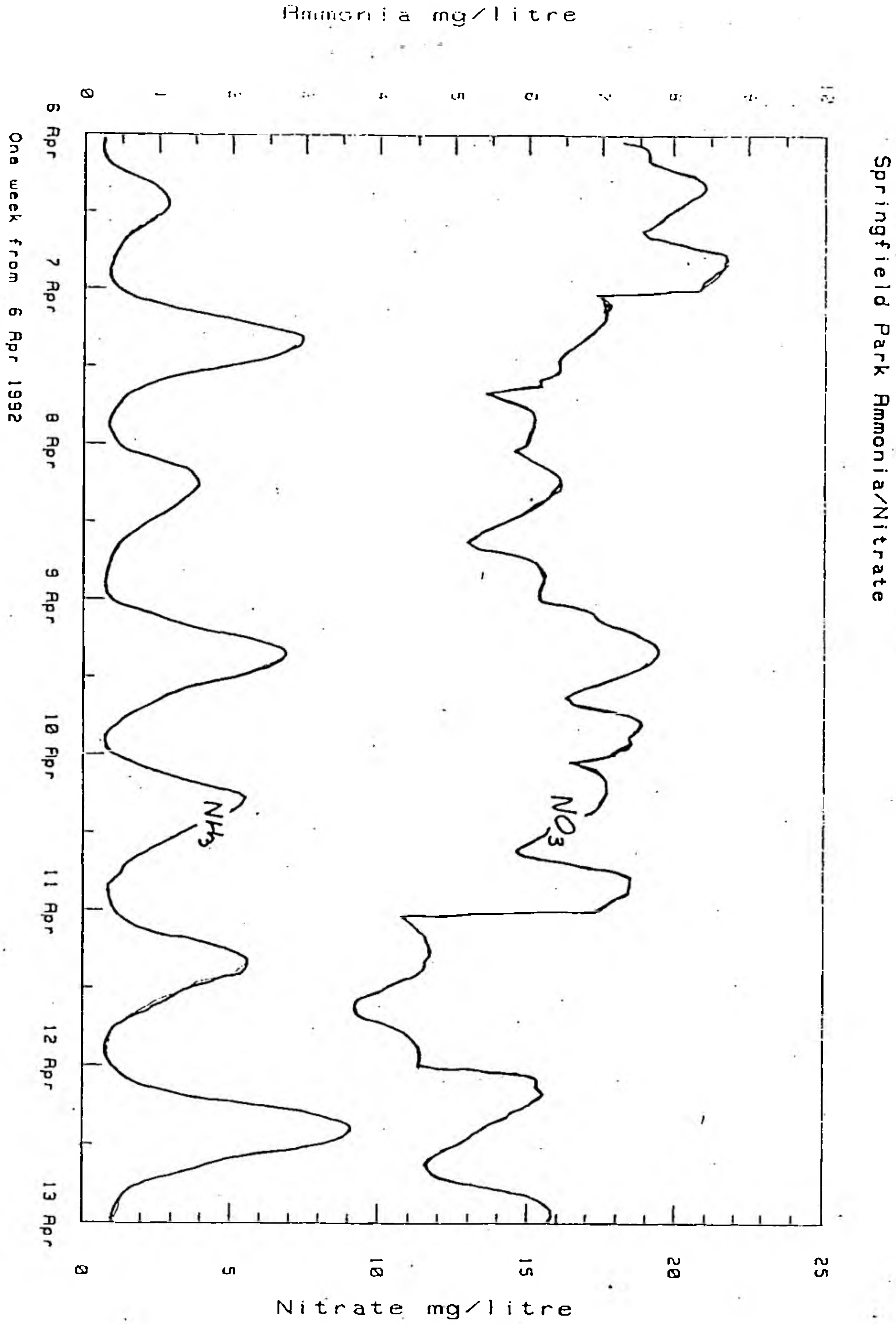
Springfield Park Oxygen/Ammonia
200
150
100
50
0
Oxygen % Saturation
10
9
8
7
6
5
4
3
2
1
0
Ammonia mg/litre
27 Dec
24 Jan
21 Feb
21 Mar
Thirteen Weeks from 27 Dec 1993

Springfield Park Oxygen/Ammonia

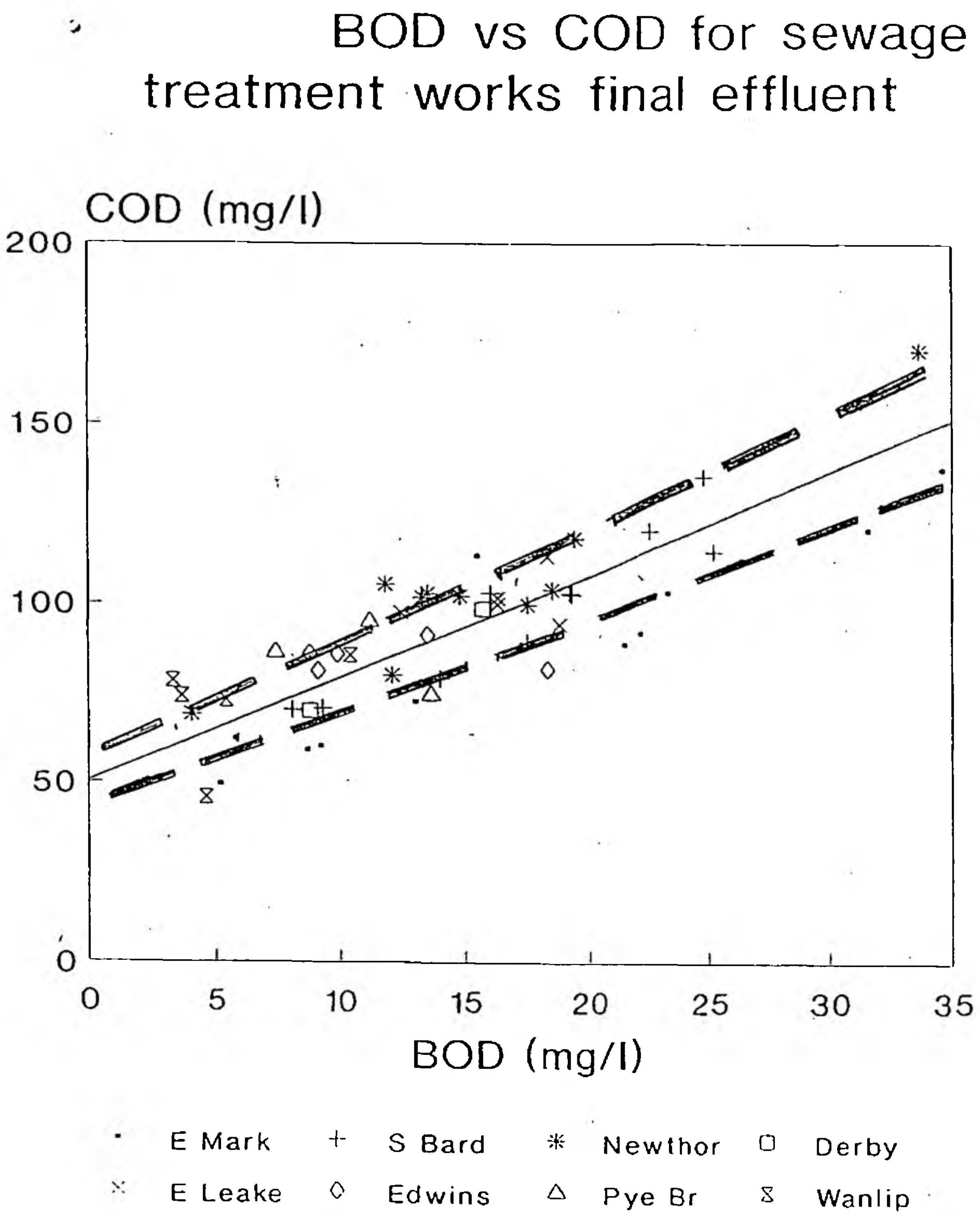


Thirteen Weeks from 27 Sep 1993

Appendix 6
Ammonia Timeseries Plot



Appendix 7
BOD/COD Relationship for Sewage Effluents



APPENDIX 8
HAND HELD METER IMPLEMENTATION PLAN

National Centre Commitment

Development of operating/QA procedures for:	
Dissolved oxygen	August 1994
pH	August 1994
Temperature	September 1994
Conductivity	September 1994
Turbidity	October 1994
Ammonia	January 1995
Training core Regional operators	July 1994
Training Regional maintenance technicians	August 1994
Provision of replacement/repair scheme	December 1994
Provision of troubleshooting helpline	July 1994
Development of data transfer to archives	March 1995

Regional Timescales

Training core operators at National Centre	July 1994
Training all operators	August 1994
Training maintenance technician	August 1994
Trial monitoring DO and pH	September 1994
Review monitoring	January 1995
Implement automatic data transfer	March 1995