MONITORING OF RIVERS AND EFFLUENTS

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A particular tribute is also made to all the staff who have been responsible for establishing and maintaining the automatic quality monitoring stations.

1. SUMMARY

The present system of chemical sampling of rivers and effluent relies mainly on the taking of spot samples at a predetermined frequency. Results from these samples form a common data base which is used for many purposes such as compliance assessment, trend detection and mathematical modelling.

This report provides evidence obtained from automatic monitoring systems to show that the data obtained from chemical spot samples is not representative of the total time period. This is mainly due to the time-dependent variations in quality that occur throughout the day and with season of the year. However, it is recognised that it is not possible to establish automatic monitors everywhere, and that spot sampling must continue. In the current programme, spot samples are taken at regular intervals throughout the year. This report shows that this method does not achieve the objectives of the monitoring programme and suggests that more emphasis should be placed on sampling at times of low river flow, and at the times of day when the quality of rivers and effluent is least good. The use of special surveys to further our understanding of the complexities of quality processes is also recommended.

2. INTRODUCTION

The taking of spot samples of rivers and effluent has long been an established part of the monitoring programme for pollution control management.

In many cases it is automatically considered that the need for better and more comprehensive data can be satisfied by extending the spot sampling programme and that all different objectives can be met from a common data base derived from spot sampling results. The programme usually requires a set number of samples to be taken at regular intervals throughout the year. This, then, assumes that each is representative of the time period between the samples.

Over the years much knowledge has been acquired with regard to quality variations that occur in rivers and effluents and, more recently, data from automatic quality monitoring stations have provided a comprehensive picture of the complexity of the quality data. The automatic quality monitoring stations provide a representation of the "total population" of quality.

By analysing this data, and comparing it to spot samples taken at the same site, an assessment can be made of how well spot samples represent reality, and an indication of the limitations of spot sampling can be obtained.

This report looks at the data derived from continuous monitoring of effluents and rivers, compares these with spot sample results, considers the objectives of the monitoring programme, and proposes a way forward.

3. SAMPLING OF SEWAGE EFFLUENTS

Many sewage effluents have wide variations in quality that do not occur in a random fashion but are clearly systematic and predictable. Figure 1 shows a plot of effluent ammonia concentration obtained from an automatic recorder at the Hogsmill Valley STW. This pattern is fairly typical of many sewage works and reflects the different retention times in the aeration lanes due to diurnal flow patterns of incoming sewage.

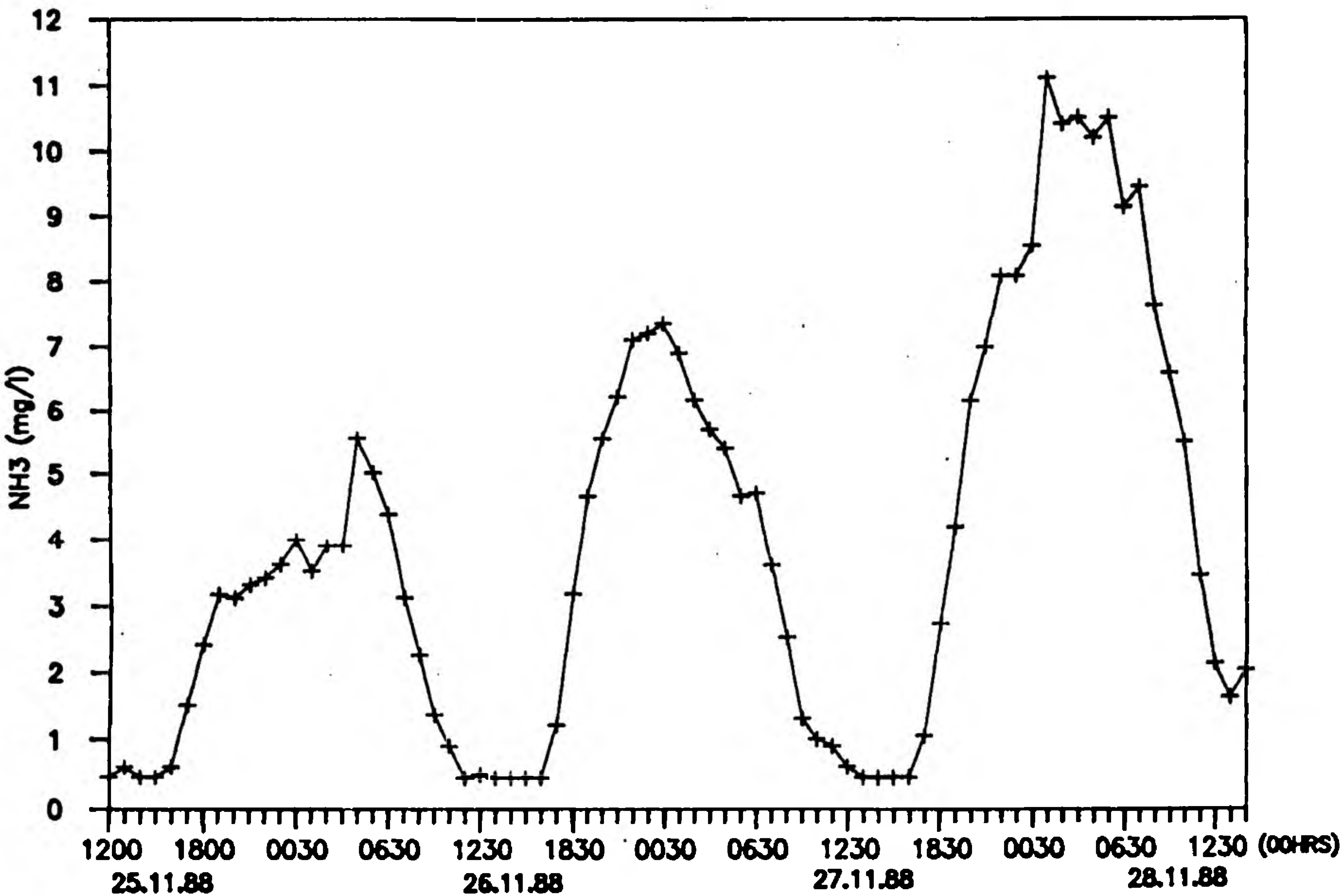
The quality variations are of great significance since between the times of 09.00 and 16.00 (normal sample window) ammonia concentrations are very low (less than 1 mgl^{-1}). Peak concentrations of between 5 and 11 times this value occur outside the sample window.

The following values summarise one day's ammonia concentrations and it may be observed that the spot sample does not give a good representation of quality for the day.

Spot sample (sample window)	0.5 mgl^{-1}
24 hour flow weighted composite	3.2 mgl^{-1}
Daily range	0.5 - 7.5 mgl^{-1}
Daily mean	3.3 mgl^{-1}
Daily median	3.5 mgl^{-1}
Daily 95%ile	7.0 mgl^{-1}

Figure 1

DIURNAL AMMONIA CONCENTRATIONS – HOGSMILL VALLEY STW EFFLUENT
25.11.88 – 28.11.88



4. SAMPLING OF RIVERS

An analysis of river automatic monitoring station data shows that variations in quality are not random and occur as a result of:

a) variations in quality of effluents (as described in previous section)
b) changes in river flow
c) sunshine and plant activity
d) temperature

The following figures are examples from the monitoring stations to demonstrate the variations that occur in D.O. and NH_3 concentrations and to highlight some of the problems that these variations pose to the sampling scheme.

Figure 2.

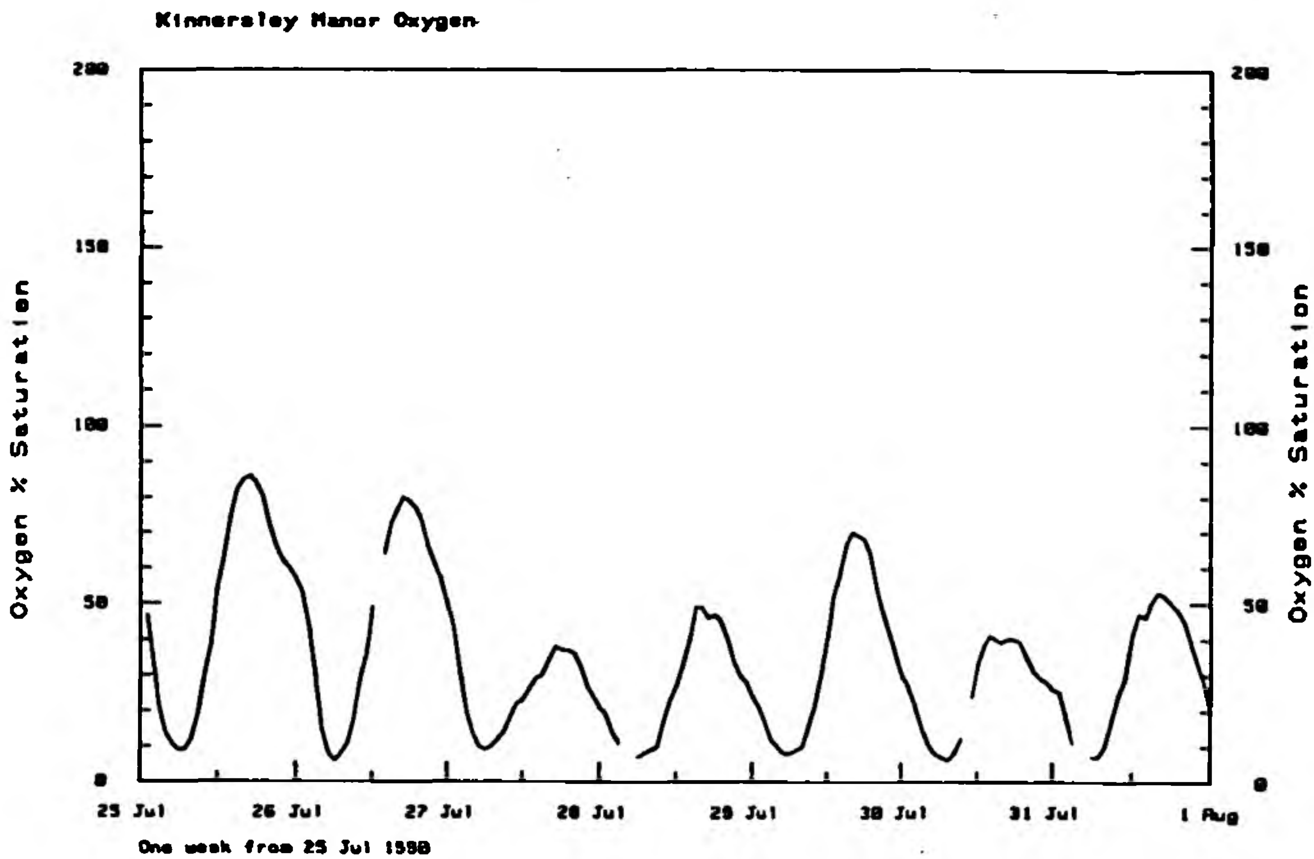


Figure 2 shows a fairly typical diel variation in D.O. from the Kinnersley Monitoring Station. In terms of obtaining information on quality and compliance wih standards, the time of sampling is crucial. Samples taken before midday would normally be below 40% (class 3) and those taken in the afternoon would be above 40% (class 2). Minimum D.O. is less than 20%.

The steepness of rise of the curve could result in a 10.00 hours sample of 20% saturation and 15.00 hours sample of 70%. The effect of low sunshine days can also be observed (July 27th) when the river is likely to be below 40% saturation for the whole day.

Figure 3.

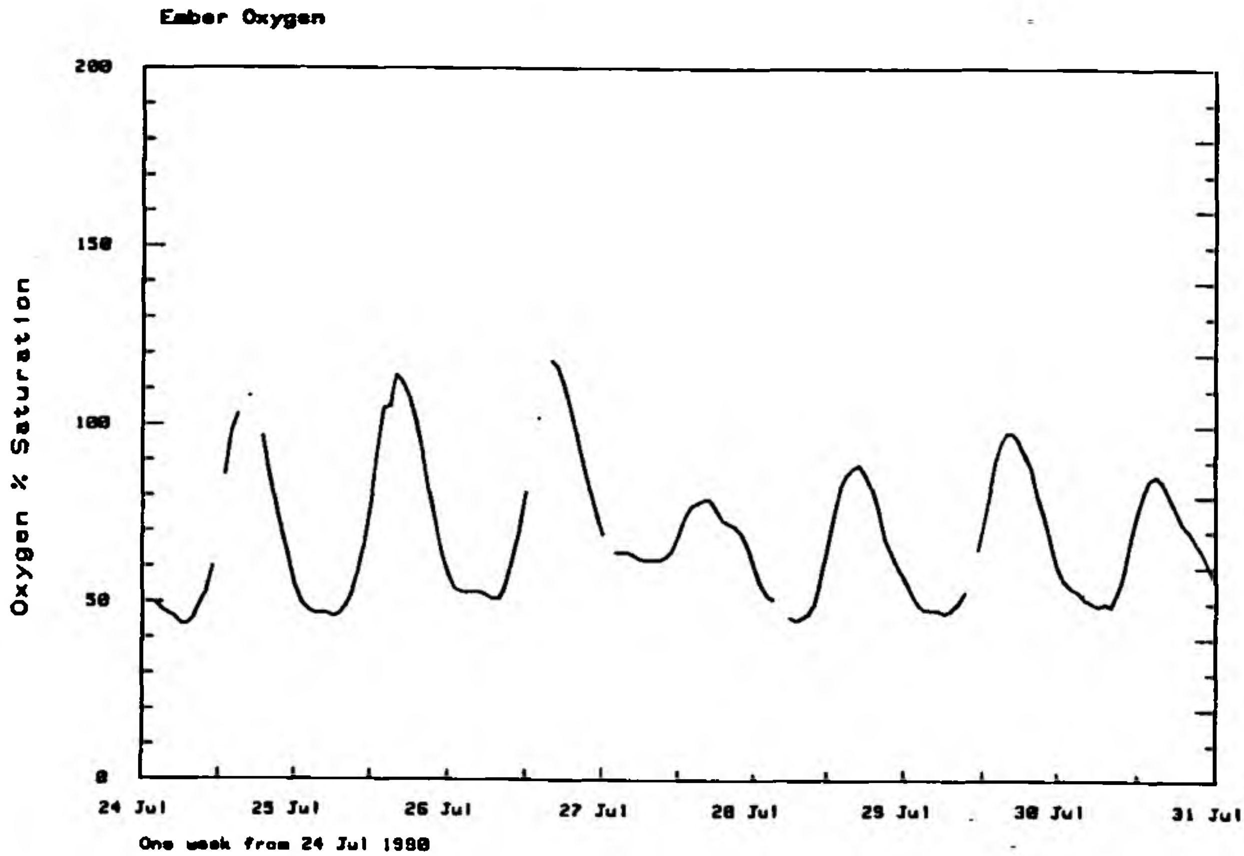


Figure 3 shows a similar pattern for a different monitoring station on the River Ember. The steepness of rise in D.O. is again significant and the change in pattern for the dull and cloudy day of July 27th is clearly observed.

Figure 4.

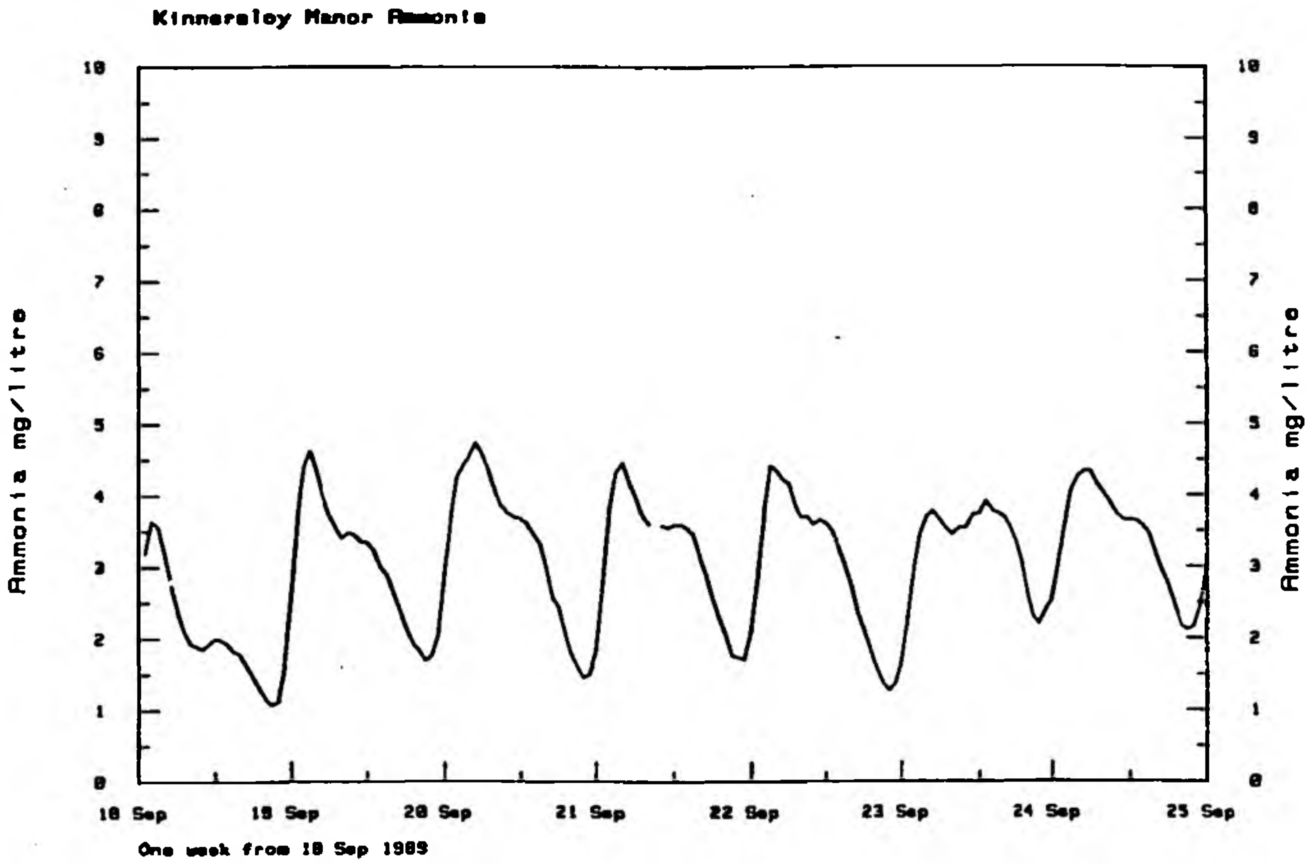


Figure 4 shows the diel variation in ammonia at Kinnersley Monitoring Station. These variations reflect the daily effluent quality fluctuations from the upstream sewage treatment works. In terms of assessing river quality and compliance, the time of sampling is critical. Samples taken before about 15.00 hours will be above 2.3 mgl^{-1} (class 2B) and samples taken after this time will be below 2.3 mgl^{-1} (class 2A).

Figure 5

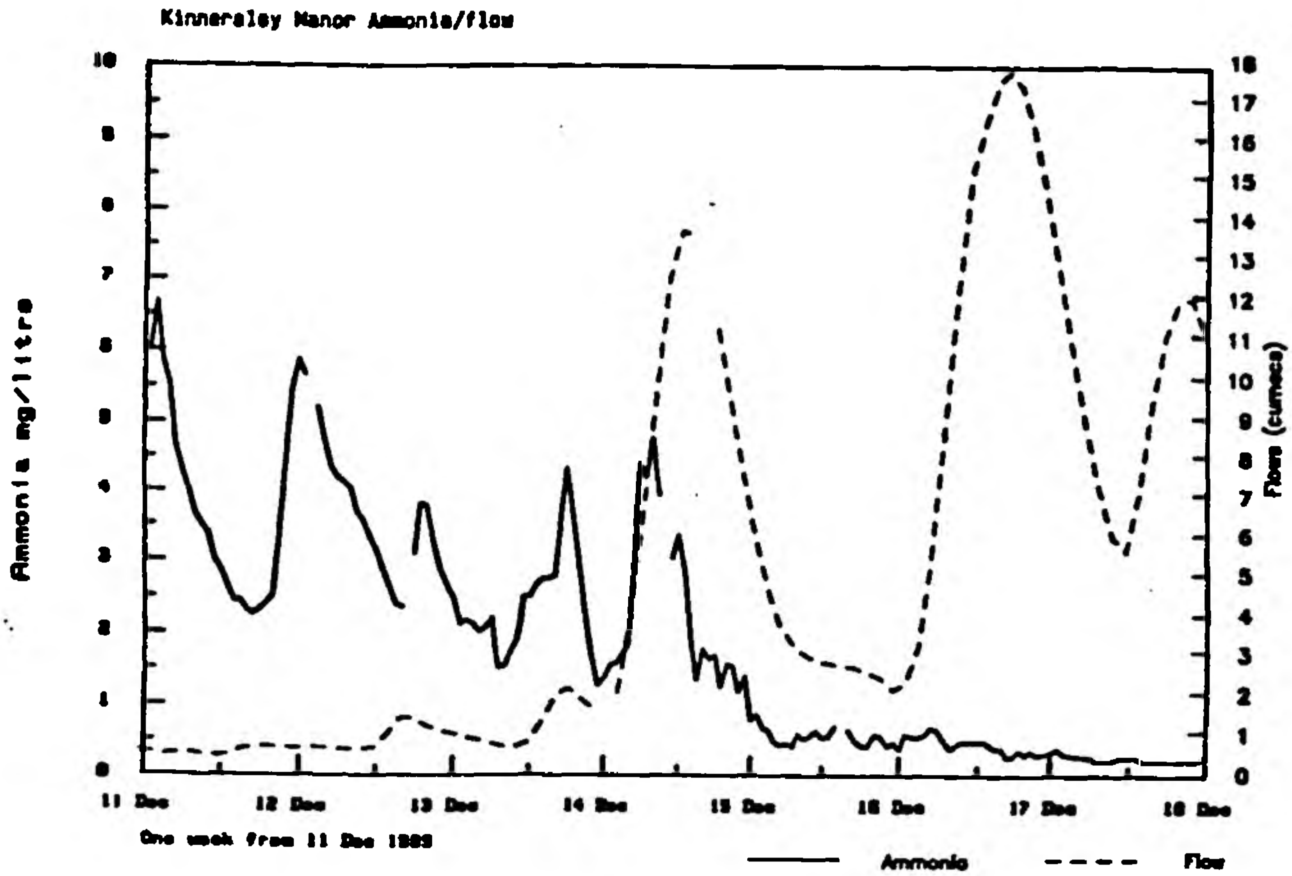


Figure 5 shows the effect on ammonia concentrations caused by a rapid increase in flow of the river from the afternoon of December 14.

Figure 6

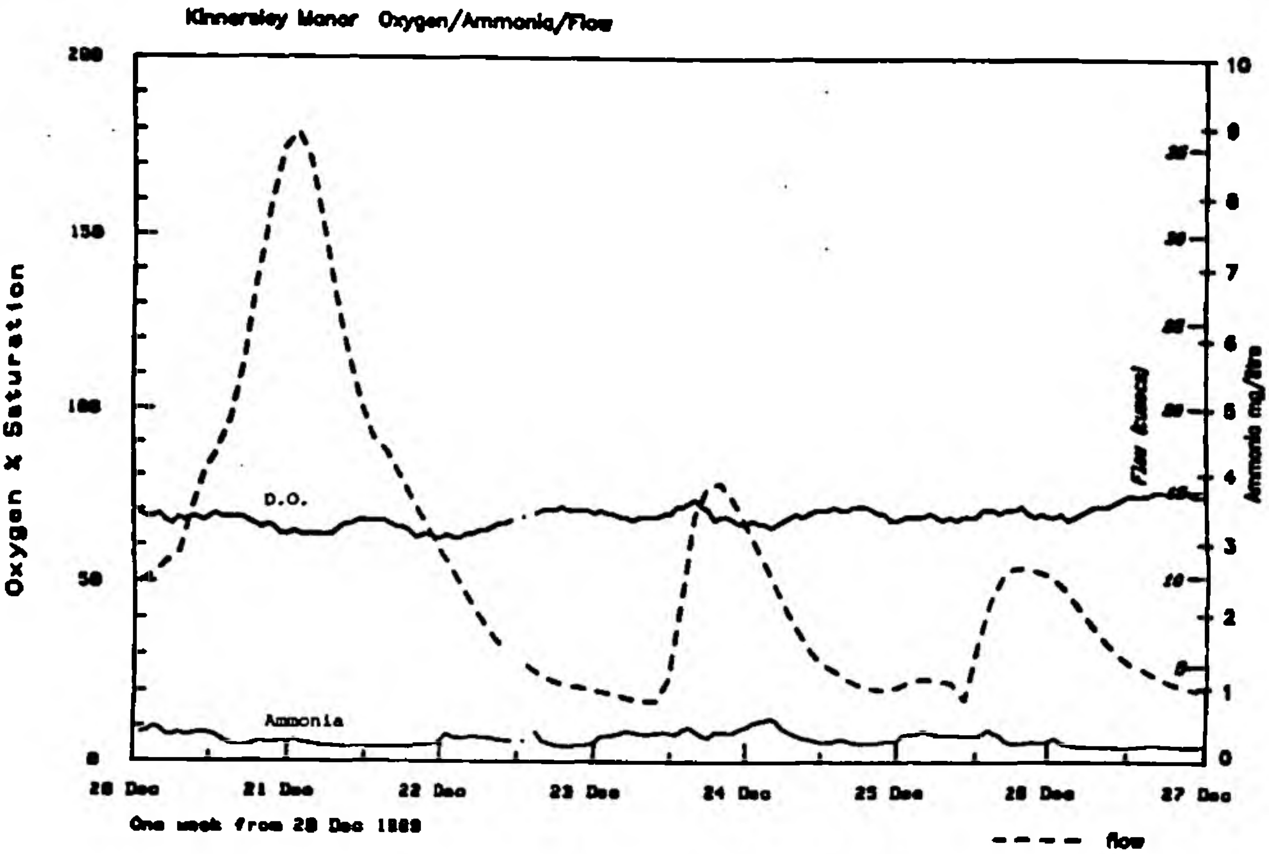


Figure 6 is an example of the condition of the river under high flow conditions where levels of D.O. and NH_3 reflect the benefits caused by dilution and diel patterns are scarcely noticeable.

5. SIGNIFICANCE OF QUALITY VARIATIONS

Many of the examples given in the previous section have been taken from the Kinnersley Manor Monitoring Station. Other stations show similar patterns and most special surveys that have been carried out at different times, demonstrate that diel quality variations are the norm rather than the exception, particularly where there is a large proportion of sewage effluent in the river.

In the context of the present sampling programme and existing data base, these quality variations are extremely significant. For example, a spot sample for D.O. may vary by up to 50% sat. depending on the time of day when it is taken. This could affect whether a standard is met or exceeded and doubts must be expressed as to the reliability of assessing compliance by this method. Similarly, detecting trends by use of data derived from spot samples can lead to errors since a change in time of day for sampling could appear to be a change in river quality.

The examples given in the previous section demonstrate some of the problems that can occur when attempts are made to interpret data obtained from spot sampling. It is useful to consider further some of these implications in the context of the objectives of a monitoring programme.

a) Compliance Assessment

Most river standards are expressed as 95 (or 5) percentiles. If samples are not taken at the times of day when peak values occur then no true measure of compliance can be made unless the standards against which compliance is being assessed also relate to the normal sampling window. Most of our river quality standards do not specify a time of day, although there is some thought in the Water Industry that relationships between uses and standards have been developed from data collected during the normal sampling window. However, recent work by WRC on Environmental Quality Standards for Dissolved Oxygen (1990) conclude that:

> "Monitoring tends to be carried out during normal working hours.... Daytime monitoring can lead to an overestimation of the actual mean and minimum dissolved oxygen concentration present, particularly in lowland

rivers..... As daytime monitoring excludes the period where D.O. levels are at their lowest, this must be a continuing cause for some concern."

No amount of extra sampling in the "daytime window" will ever detect failures that occur regularly outside of this window. The comment by WRC supports the need to use AQMS data where it exists to assess compliance against river quality standards.

b) Detection of trends

Samples taken at different times of the day cannot be compared, (unless diel variation is minimal), neither can samples taken under different flow conditions, nor those taken under different conditions of sunshine during the summer months (because of the effects of photosynthesis). If, as is presently the case, all of these samples are jumbled together and comparisons are made between different years it is likely that false trend detection may occur. This may be due to more samples being taken at one particular time of day for one year or more samples taken by chance on dull days or high flow days. Careful analysis of data is required, but this often leads to inadequate data sets for an assessment to be made.

c) Assessment of effect of an effluent on a river

Because of diel variation in effluent quality, this requires identifying the point(s) in the river and the time of day when the maximum effect is exerted. This must then be related to the variation in quality of the effluent and the time of travel in the river, which will vary depending on the flow. Spot samples are unlikely to cover these variations, so special 24 hour surveys for a few days at different flow regimes are really required to establish the relationships.

d) Comparision of different sampling points in the river

Great care is needed if any sense is to be made of the data derived from different points in a river system to observe, for example, how a river changes in quality over the course of its length. Samples taken at the same time of day will be necessary to compare D.O. values but samples taken at different times of day - to coincide with time of travel peaks - will be necessary to compare ammonia concentrations. In addition, D.O. values will have an element of both sunshine and effluent effects and at different times of the year modified sampling approaches may be required.

6. STATISTICAL STUDY

A study was made using 1990 data from the Kinnersley Manor monitoring station. Detailed results of this study are given in Appendix 1 but the main points to emerge were:

a) It is not possible to use "sampling window" data to estimate the 95%ile value for dissolved oxygen. This is due to the effect of photosynthesis on D.O. which leads to low D.O. between the hours of 0400 and 0800 hours.

b) A large number of randomly taken spot samples is required to obtain a reasonable estimate of the 95%ile for dissolved oxygen and ammonia, e.g. for D.O. 975 samples per year are required in order to be 95% confident of being within 10% of the true 95%ile. Similarly, for ammonia the required number of samples is 600. Even to represent the mean quality adequately requires over 400 samples a year.

c) If sampling is done within the normal sampling window, then weekly sampling is the only fequency which gives reasonable accuracy of the true mean quality. This estimates the means for all determinands to within 10% with a probability greater than 0.8.

The conclusions of this study were based on one monitoring station for one year. Further work is being done to assess the general applicability of these conclusions in space and time.

7. DISCUSSION

When rivers were grossly polluted and effluent was of very poor quality, it was unnecessary to employ sophisticated monitoring techniques and spot sampling was not only simple but also effective. The present position is entirely different however, and modern environmental protection measures require very sophisticated techniques for supplying sound and reliable data. These techniques must be applied reasonably; consideration must be given to economic costs. It is not justifiable, for example, to install AQMS at every routine sampling point in the catchment.

The previous sections in this report have attempted to demonstrate some of the problems that can occur by relying on spot sample data and it is possible that much interpretative and modelling work may have been damaged by the use of this inadequate data. If progress is to be made, then extensive modifications are required to our monitoring strategy.

It is of fundamental importance to establish the objectives of a sampling programme at the outset. Different objectives require different sampling strategies and it may not always be possible to have one programme to suit all needs. Four of the principal requirements of the NRA sampling programme are:

a) To provide data that can be used to obtain an accurate assessment of the 95%ile value for compliance assessment purposes with river standards and with consent conditions;

b) To provide data from which it is possible to detect significant long term changes in quality;

c) To provide data to determine the impact of discharges on the receiving watercourses so that appropriate consent conditions can be set, (with or without the use of models);

d) To compare rivers from region to region and nationally.

8. NEW APPROACHES TO MONITORING

Previous sections in this report have demonstrated some of the shortcomings of the existing system. There is a need to match the monitoring requirement to the practical resource limitation which make it rather difficult to accommodate programmes which involve many hundreds of random spot samples per site.

There are, however, a number of ways in which improvements can be made.

a) Compliance Assessment

The principal requirement is to have the ability to be confident of identifying the 95%ile of various chemical parameters with reasonable precision, since standards are set on this basis.

A study of the Kinnersley Manor AQMS data reveals that the lowest 10% of all D.O. values occur almost exclusively under certain well defined limits of time of day, water temperature and river flow. Equally, there are other occasions when it can be confidently predicted that D.O. levels will be high.

It is therefore feasible to concentrate sampling effort at certain times in order to detect the required percentile value. For example, if samples are taken at times when the lowest 10% are expected, then it could be estimated that the 5% D.O. is the median of these samples.

The situation with regard to ammonia values is similar but is more closely related to sewage works performance. In order to confidently identify the true 95%ile ammonia value it would be necessary to sample the river at times when effluent quality was known to be poor. This might seem crude, but there is more chance of estimating the 5% this way than in the current spot sampling programme.

b) Trend Detection

Because of the quality variations that are caused by climatic conditions and the influence of diel patterns, it is necessary to specify quite precisely which particular trend is of interest.

For example, it is quite common for trends to emerge that are simply due to different types of weather pattern, i.e. hot or wet summers.

In order to avoid these problems it would be preferable to eliminate as many variables as possible by sampling always at the same time of day and under the same conditions of river flow and water temperature. Relatively few samples would be required each year for this purpose.

c) Impact of discharges on watercourses

Because of the diel variation in effluent quality and variable times of travel to sampling points, it is really necessary to undertake intensive surveys to understand the impact of discharges on watercourses.

d) Comparisons between regions

This requirement, although important for the NRA as a means of generating national statistics, should be regarded as a simple arbitrary measure of quality. It is not easily compatible with the other, more scientific, requirements and is best kept as a separate objective using whatever system is nationally agreed. By adopting this approach it is possible to have a clear, simple system without introducing any of the complexities previously discussed.

9. CONCLUSIONS

a) The existing system of chemical spot sampling does not provide reliable data for compliance assessment purposes and quality trend detection. The data base derived from spot samples also falls far short of the requirements for mathematical modelling and catchment control purposes for consent setting.

b) Because of resource implications it will never be possible to provide totally comprehensive data for all rivers and effluents.

c) It is possible, however, to devise forms of intelligent systematic sampling which can provide satisfactory data within certain confidence and precision levels.

d) These new approaches to sampling could be introduced on a limited trial basis with a view to evolving new strategies for the future.

APPENDIX 1

A1 DATA DESCRIPTION

The 1990 data from the Automatic Monitoring Station on the River Mole at Kinnersley Manor were used in the study. The data were verified using graphs of the station output to show up irregularities. However, due to there being over 8000 data cases for the year (24 x 365 = 8760) it is unlikely that they would have caused any significant problems. The data set consists of hourly samples taken by the monitor and as such was regarded as a census representation of the quality of the river ie. the target population.

The data used consisted of measured readings for dissolved oxygen, temperature and ammoniacal nitrogen; and un-ionised ammonia calculated using pH in conjunction with the latter two measured determinands.

Four analyses were undertaken. These were simple random sampling from all data to determine a suitable sample size to achieve a certain level of precision; a comparison of 24 hour and sampling window data; sampling from within the 0900-1500 window; and a comparison of sampling at 0900 and 1400. Each will be described in turn.

A2 SIMPLE RANDOM SAMPLING FROM ALL THE DATA

Using all 8000 data values, a computer program was written to take samples of sizes 10, 20, 25, 50, 75, 100, 200, 300, 500 and 1000 totally at random. The means were then calculated for each sample and similarly percentiles were calculated for samples of sizes 50, 75, 100, 150, 200, 250, 300, 400, 500 and 1000. Large sample sizes were used to estimate percentiles by the Weibull method avoiding the problems associated with parametric methods of estimation, necessary when sample sizes are less than fifty. This process of sampling and estimation was carried out 1000 times to increase accuracy.

These statistics were used in a regression analysis to determine the sample size necessary to achieve a desired level of accuracy when estimating the population statistics from a sample. Also a normal approximation (since the data set was large) for sample size, based on the width of the confidence interval about the mean, was made for comparison with the regression.

The results of the two methods give in table 1 were largely similar. The table shows the number of samples needed to be 95% sure that the sample statistic is no more than 5, 10, or 20 percent away from the population statistic. For instance 50 random samples of DO have to be taken to be 95% sure that the sample mean is no more than 10% away from the true mean. Similarly for the 5th percentile 975 random samples have to be taken to be 95% sure the sample 5th percentile is no more than 10% away from the population 5th percentile.

It can be seen from this table that for the sample means of un-ionised ammonia and ammonia, more samples are necessary than for DO or temperature. To be 95% sure that the sample mean for ammonia is no more than 10% away from the population mean 400 samples have to be taken and correspondingly for un-ionised ammonia, 475 are necessary.

When percentiles were considered the sample sizes for ammonia and DO increased, but for the other determinands no calculations were made. It is likely that since un-ionised ammonia is correlated with ammonia the number of samples necessary will be of the same order as that for ammonia. No sample sizes were calculable for temperature because the probability of the sample 95th percentile being more than 10% away from the population 95th percentile was very close to zero for all samples. It therefore seems safe to assume that a sample of size 10 is needed to achieve 95% certainty that the sample statistic is no more than 5% away from the population statistic.

A3 COMPARISON OF 24 HOUR AND SAMPLING WINDOW DATA

Means and percentiles were calculated for both all 8000 data cases and all the data from the standard sampling window ie. all samples taken between 0900 and 1500, inclusive, on a weekday. The results (Table 2) were on the whole reasonably similar except that the 5th percentile for DO was higher in the sampling window, possibly demonstrating the effects of the eutrophic nature of the Mole at Kinnersley Manor (ie. DO higher due to photosynthesis in daytime).

Statistical tests showed that this difference in DO was the only significant difference between the sampling window data and all 24 hours data. Since DO is critical though this difference is important. Regarding the other determinands though, it is correct to say that random sampling from within the sampling window, provided the sample size is great enough, will be representative of the 24hr period as a whole. So to take a sample, of size as specified within A2, at random within the sampling window will represent the true picture of river quality for un-ionised ammonia, ammonia and temperature.

A4 SAMPLING FROM WITHIN THE 0900-1500 WINDOW

A similar program to that used in A2 was adapted to simulate random quarterly, monthly, fortnightly and weekly sampling within the sampling window (ie. one at random from the first quarter, one from the second etc.). The means were calculated for 1000 such samples and compared with the means for all 24hr data. The same measures of accuracy as in A2 were calculated (Table 3) showing that as expected from the results of A2 and A3 the level of accuracy achieved by these methods is quite low. Even when sampling weekly the probability that the sample means of ammonia and un-ionised ammonia are more than 10% different to the population mean is 0.1 ie. if ten rivers are sampled weekly the ammonia and un-ionised ammonia means for one of the rivers will be more than 10% away from the true figure.

Similarly a comparison of the quarterly and monthly accuracies shows that apart from temperature there is not much advantage is sampling monthly rather quarterly. So for the Mole at Kinnersley Manor to increase the sampling from 4 to 12 samples a year will not necessarily increase the accuracy of the estimate.

The dissolved oxygen component of Table 3 is rather odd. As the sampling frequency was increased it was expected that the accuracy of the sample statistics would increase. The converse was true for DO % saturation when A=0.5. The quarterly sample mean had a probability of 0.53 of being 5% away from the true mean whilst the weekly sample mean had a corresponding probability of 0.71. For A=0.10 or 0.20 though the accuracy increased as sample size was increased, as expected.

This suggests that more frequent sampling detects the more extreme DO values but these values are not extreme enough to 'bias' the sample statistics when less than 10% accuracy is required.

A5 COMPARISON OF 0900 AND 1400 SAMPLING

In this exercise only the samples taken at 0900 and 1400 hours during weekdays were considered thus simulating a sampling officers scheme of sampling. The means and percentiles for these times were compared with the 24 hour means (Tables 4 & 5) and with each other.

The only significant differences were in dissolved oxygen saturation. None of the three schemes were statistically comparable on this determinand but the other three determinands could be correctly represented by sampling at 0900 or 1400 every weekday.

When sampling once a week at these times (Table 6) the 0900 sample represented the mean DO and temperature well and the 1400 sample represented the mean un-ionised ammonia, temperature and ammoniacal nitrogen similarly so. The appropriate percentiles for each determinand were also estimated showing similar accuracy as for the means for the 1400 sample whilst the 0900 sample only represented the temperature 95th %-ile with any reasonable accuracy.

So in comparing the quality results obtained at these two times the photosynthetic nature of the Mole is again emphasised, demonstrating that random spot sampling will not detect the true pattern of dissolved oxygen concentration.

TABLE 1 SAMPLE SIZES FOR A SPECIFIED PRECISION

$$\text{Probability}\left\{ \left| \frac{\text{Sample Statistic} - \text{Population Statistic}}{\text{Population Statistic}} \right| > A \right\} = 0.05$$

		A = 0.05	A = 0.1	A = 0.2
MEANS	UN-IONISED AMMONIA	>1000 (2041)	475 (510)	125 (128)
	TEMPERATURE	125 (174)	25 (44)	10 (11)
	DISSOLVED OXYGEN SATURATION	175 (225)	50 (55)	10 (14)
	AMMONIACAL NITROGEN	1000 (1714)	400 (429)	100 (107)
95%-ILES	UN-IONISED AMMONIA	-999	-999	-999
	TEMPERATURE	10	-999	-999
	DISSOLVED OXYGEN SATURATION(*)	>1000	975	400
	AMMONIACAL NITROGEN	-999	700	150

-999 not calcuable by this method.

(.) refers to normal approximation method of calculation of sample size.
(*) 5th rather than 95th %-ile is reported for DO % Sat.

TABLE 2 WATER QUALITY STATISTICS FOR KINNERSLEY MANOR AQMS 1990

DETERMINAND	ALL DATA		SAMPLING WINDOW		TEST RESULTS	
	MEAN	95%-ILE	MEAN	95%-ILE	KS	MW
UN-IONISED AMMONIA	0.2073	0.7140	0.2001	0.6977	✓	✓
TEMPERATURE	12.81	19.60	12.64	19.40	✓	✓
DO (%SAT) (*)	46.10	14.00	44.52	23.00	X	X
AMMONIACAL NITROGEN	2.66	8.37	2.54	8.07	✓	✓

SAMPLING WINDOW - All samples taken between 0900 and 1500 on Monday to Friday (inclusive)

KS - KOLMOGOROV-SMIRNOV test. This tests the shape of the distributions of the two populations.

MW - MANN-WITNEY test. This tests the medians of the two populations ie. tests centre of two populations.

X - populations differ.

✓ - populations are the same.

(*) 5th rather than 95th%-ile is reported for % sat.

TABLE 3 ACCURACY OF SPOT SAMPLING WITHIN SAMPLING WINDOW

Probability{| Sample mean - Population Mean|/Population Mean > A} (%)

Sampling Scheme	Det.	A = 0.05	A = 0.10	A = 0.20
Quarterly	UN-I	37.2	34.0	27.4
	TEMP	32.2	15.1	0.9
	%SATN	53.6	41.0	18.0
	AMM.NIT	37.5	34.4	28.6
Monthly	UN-I	39.1	32.6	23.0
	TEMP	4.2	0.0	0.0
	%SATN	58.7	32.5	3.5
	AMM.NIT	37.5	30.1	18.4
Fortnighly	UN-I	37.7	26.6	12.9
	TEMP	4.0	0.0	0.0
	%SATN	59.3	20.5	0.1
	AMM.NIT	34.5	25.0	10.6
Weekly	UN-I	29.9	15.2	3.2
	TEMP	0.0	0.0	0.0
	%SATN	71.1	7.7	0.0
	AMM.NIT	25.8	13.2	2.1

TABLE 4 COMPARISON OF SAMPLING AT 0900 AND 1400. AND 24 HOURS DATA

	POPULATION STATISTICS (24 hours)		0900 STATISTICS		1400 STATISTICS	
DETERMINAND	MEAN	95TH%-ILE	MEAN	95TH%-ILE	MEAN	95TH%-ILE
UN-IONISED AMMONIA	0.2073	0.7140	0.2026	0.7406	0.199	0.674
TEMPERATURE	12.81	19.61	12.34	19.00	12.80	19.60
OXYGEN %SAT (*)	46.10	14.00	43.46	15.55	53.19	31.05
AMM.NIT.	2.66	8.37	2.67	8.88	2.50	7.27

(*) 5th rather than 95th%-ile is reported for % Sat.

TABLE 5 STATISTICAL SIGNIFICANCE TEST RESULTS FOR THE COMPARISONS OF TOTAL POPULATION. 0900 AND 1400 SAMPLES

		0900 SAMPLES		1400 SAMPLES	
		KS	MW	KS	MW
ALL DATA	UN-IONISED AMM.	✓	✓	✓	✓
	AMMONIA	✓	✓	✓	✓
	DO (% SAT)	X	X	X	X
	TEMPERATURE	✓	✓	✓	✓
0900 SAMPLES	UN-IONISED AMM.			✓	✓
	AMMONIA			✓	✓
	DO (%SAT)			X	X
	TEMPERATURE			✓	✓

KS - KOLMOGORON-SMIRNOV TEST) X - populations different
MW - MANN-WITNEY TEST) ✓ - populations same

ALL DATA - ALL 8760 SAMPLES
0900 SAMPLES - ALL 365 SAMPLES AT 0900
1400 SAMPLES - ALL 365 SAMPLES AT 1400

TABLE 6 COMPARISON OF WEEKLY SAMPLING AT 0900 AND 1400 WITH ALL 24 HOURS DATA

PROBABILITY {|(SAMPLE STATISTIC-POPULATION STATISTIC)/POPN STATISTIC|>A} (%)

SAMPLE TIME	DETERMINAND	A = 0.05	A = 0.10	A = 0.20
0900	UN-I AMM.	52.3 (27.2)	29.0 (21.8)	4.2 (13.2)
	TEMP.	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	%SAT.	0.0 (53.6)	0.0 (39.8)	0.0 (6.7)
	AMM.NIT.	67.5 (41.2)	41.7 (29.7)	11.1 (14.2)
1400	UN-I AMM.	36.3 (24.3)	10.6 (12.3)	0.2 (1.9)
	TEMP.	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	%SAT.	100.0 (100.0)	99.7 (100.0)	0.5 (100.0)
	AMM.NIT.	16.0 (0.0)	2.2 (0.0)	0.0 (0.0)

(.) refer to 95%-ile comparisons (5th for DO % Sat.)

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APPENDIX 1

A1 DATA DESCRIPTION

The 1990 data from the automatic monitoring station on the River Mole at Kinnersley Manor were used in the study. The data were verified using graphs of the station output to show up irregularities. However, due to there being over 8000 readings for the year (24 x 365 = 8760) it is unlikely that they would have caused any significant problems. The data set consists of hourly samples taken by the monitor and as such was regarded as a census representation of the quality of the river i.e. the target population.

The data used consisted of measured readings for dissolved oxygen, temperature and ammoniacal nitrogen; and un-ionised ammonia calculated using pH in conjunction with the latter two determinands.

Four analyses were undertaken. These were simple random sampling from all data to determine a suitable sample size to achieve a certain level of precision; a comparison of 24 hour and sampling window data; sampling from within the 0900 - 1500 window; and a comparison of sampling at 0900 and 1400. Each will be described in turn.

A2 SIMPLE RANDOM SAMPLING FROM ALL THE DATA

Using all 8000 data values, a computer program was written to take samples of sizes 1, 2, 3, 4, 5, 10, 15, 20, 30, 40, 50, 75, 100, 150, 200, 250, 300, 400, 500, 1000, 1250, 1500, 1750, 2000, 2500 and 3000. The means were calculated for each sample and percentiles were calculated for the larger sample sizes (>50) using the Weibull method. The problems associated with parametric methods of estimating percentiles were thus avoided. This process of sampling was repeated 1000 times to ensure consistency.

These statistics were used in a regression analysis to determine the sample size necessary to achieve a desired level of accuracy when estimating the population statistics from a sample. Also a normal approximation (using the central limit theorem) for sample size, based on the width of the confidence interval about the mean, was made for comparison with the regression.

The results of the two methods given in Table 1 were largely similar. The table shows the number of samples needed to be 95% sure that the sample statistic is no more than 5, 10, or 20 percent away from the population statistic. For instance 76 random samples of d.o. have to be taken to be 95% sure that the sample mean is no more than 10% away from the true mean. Similarly for the 5th percentile 1863 samples have to be taken to be 95% sure the sample 5th percentile is no more than 10% away from the population 5th percentile.

It can be seen from this table that for the sample means of un-ionised ammonia and ammoniacal nitrogen, more samples are necessary than for D.O. or temperature. To be 95% sure that the sample mean for ammonia is no more than 10% away from the population mean 565 samples have to be taken and correspondingly for un-ionised ammonia, 669 are necessary.

When percentiles were considered the sample sizes for temperature remained largely the same but for the other determinands they increased. It is interesting to note that for both D.O. and un-ionised ammonia a sample size of 3000 was not sufficient to estimate the population percentiles to within 5%. This amounts to almost 10 samples a day !

A3 COMPARISON OF 24 HOUR AND SAMPLING WINDOW DATA

Means and percentiles were calculated for both all 8000 data cases and all the data from the standard sampling window i.e. all samples taken between 0900 and 1500, inclusive, on weekdays. The results (Table 2) were on the whole not noticeably different, but the sampling window quality is higher than that for 24 hours data. The D.O. 5th percentile demonstrated the greatest difference, highlighting the eutrophic nature of the Mole (i.e. D.O. higher due to photosynthesis in the daytime).

Statistical tests showed that this difference in D.O. and the difference in the ammoniacal nitrogen were significant. Thus no matter how many samples are taken during the sampling window the population statistics for these two determinands will not be estimated with any precision. For the other two determinands though, provided enough samples are taken (see Table 1) sampling from within the sampling window will allow the population statistics to be estimated accurately.

A4 SAMPLING FROM WITHIN THE 0900 - 1500 WINDOW

A similar program to that used in A2 was adapted to simulate random quarterly, 4-weekly, fortnightly and weekly sampling within the sampling window (i.e. one at random from the first quarter, one from the second, etc.). The means were calculated for 1000 such samples and compared with the means for all 24 hours data. The same measures of accuracy as in A2 were calculated (Table 3) showing that as expected from the results of A2 and A3 the level of accuracy achieved by these methods is quite low. Even when sampling weekly the probability that the sample mean of ammonia is more than 10% different to the population mean is greater than 0.4 i.e.if the Mole was sampled at Kinnersley Manor once a week over a ten year period and the means calculated for each of those years, four of the values obtained would be more than 10% away from the population means as far as ammoniacal nitrogen is concerned. Thus four years of sampling could be said to have been wasted.

Similarly a comparison of the quarterly and 4-weekly accuracies shows that at the 10% accuracy level only the estimation of temperature can be said to have improved, by increasing the sampling frequency. So the extra expense of sampling monthly rather than quarterly may not always be justified.

The dissolved oxygen component of Table 3 is rather odd. As the sampling frequency was increased it was expected that the accuracy of the sample statistics would increase. The converse was true for D.O. when A = 0.5. The 4-weekly accuracy was 61.5% whilst those for the fortnightly and weekly schemes were 65.6% and 71.2%, respectively. For A = 0.10 and A = 0.20 though the accuracy increased as the sampling frequency increased, as expected.

This suggests that more frequent sampling detects the more extreme D.O. values but these values are not extreme enough to 'bias' the sample statistics when less than 10% accuracy is required.

A5 COMPARISON OF 0900 AND 1400 SAMPLING

In this exercise only the samples taken at 0900 and 1400 hours during weekdays were considered thus simulating a sampling officers scheme of sampling. The means and percentiles for these times were compared with the 24 hour statistics and with each other (Tables 4 & 5).

The only significant differences were in dissolved oxygen. None of the three schemes were statistically comparable on this determinand but the other three determinands could be correctly represented by sampling at 0900 or 1400 every weekday.

When sampling once a week at these times (Table 6) the 0900 sample represented the mean temperature well and the mean D.O. reasonably so while the 1400 sample represented the mean temperature well and the un-ionised ammonia reasonably so. The appropriate percentiles for each determinand were also estimated showing much poorer accuracy for all determinands except for temperature at both times.

So in comparing the quality results obtained at either of these times with the population results the photosynthetic nature of the Mole, and the variability of its quality are again emphasised. This demonstrates that the present system of spot sampling is not sufficient enough to describe the water quality at Kinnersley Manor.

TABLE 1 - SAMPLE SIZES FOR A SPECIFIED PRECISION

$$\text{probability}\left(\left|\frac{\text{sample statistic - population statistic}}{\text{population statistic}}\right| > A\right) = 0.05$$

	DETERMINANDS	A = 0.05	A = 0.10	A = 0.20
MEANS	UN-IONISED AMMONIA	1807 (2313)	669 (578)_	148 (145)
	TEMPERATURE	173 (155)	43 (39)	10 (10)
	DISSOLVED OXYGEN	212 (225)	76 (56)	16 (14)
	AMMONIACAL NITROGEN	1842 (2257)	565 (564)	148 (141)
%ILES	UN-IONISED AMMONIA	>3000	1859	594
	TEMPERATURE	120	43	13
	DISSOLVED OXYGEN	>3000	1863	686
	AMMONIACAL NITROGEN	2908	983	396

( ) Central limit theorem calculations of sample size

5th %-ile reported for D.O. saturation

TABLE 2 - WATER QUALITY STATISTICS FOR KINNERSLEY MANOR 1990

	ALL DATA		SAMPLING WINDOW		TESTS	
DETERMINAND	MEAN	%-ILE	MEAN	%-ILE	KS	MW
UN-IONISED AMMONIA	0.22	0.83	0.21	0.76	Y	Y
TEMPERATURE	12.81	19.60	12.64	19.40	Y	Y
DISSOLVED OXYGEN	46.07	14.00	49.44	23.00	X	X
AMMONIACAL NITROGEN	2.91	9.53	2.68	8.73	X	X

SAMPLING WINDOW = all samples taken between 0900 and 1500 inclusive, on weekdays only.

KS = KOLMOGOROV-SMIRNOV test, a test of the shape of the distributions of the populations.

MW = MANN-WITNEY test, a test of the medians of the populations.

X = populations differ.

Y = populations the same.

5th percentile reported for D.O. % saturation.

TABLE 3 - ACCURACY OF SPOT SAMPLING WITHIN THE SAMPLING WINDOW

$$\text{probability}\left(\left|\frac{\text{sample statistic - population statistic}}{\text{population statistic}}\right| > A\right)$$

	DETERMINAND	A = 0.05	A = 0.10	A = 0.20
QUARTERLY	UN-IONISED AMMONIA	94.4	87.8	75.2
	TEMPERATURE	58.9	29.3	1.1
	DISSOLVED OXYGEN	75.0	51.7	20.0
	AMMONIACAL NITROGEN	91.9	86.8	73.9
4-WEEKLY	UN-IONISED AMMONIA	86.5	74.3	50.1
	TEMPERATURE	61.0	0.0	0.0
	DISSOLVED OXYGEN	61.5	29.5	2.6
	AMMONIACAL NITROGEN	86.2	73.4	47.5
FORTNIGHTLY	UN-IONISED AMMONIA	79.7	61.7	30.6
	TEMPERATURE	0.6	0.0	0.0
	DISSOLVED OXYGEN	65.6	20.1	0.0
	AMMONIACAL NITROGEN	79.2	60.9	30.5
WEEKLY	UN-IONISED AMMONIA	65.5	35.7	5.8
	TEMPERATURE	0.0	0.0	0.0
	DISSOLVED OXYGEN	71.2	11.9	0.0
	AMMONIACAL NITROGEN	66.7	40.9	7.3

TABLE 4 - COMPARISON OF SAMPLING AT 0900 HOURS, 1400 HOURS, AND ALL DATA.

	POPULATION STATISTICS		0900 STATISTICS		1400 STATISTICS	
	MEAN	%-ILE	MEAN	%-ILE	MEAN	%-ILE
UN-IONISED AMMONIA	0.22	0.83	0.21	0.87	0.21	0.80
TEMPERATURE	12.81	19.60	12.34	19.00	12.80	19.60
DISSOLVED OXYGEN	46.07	14.00	43.44	15.65	53.00	31.20
AMMONIACAL NITROGEN	2.91	9.53	2.92	10.06	2.63	8.03

5th percentile reported for D.O. % saturation.

TABLE 5 - STATISTICAL SIGNIFICANCE TEST RESULTS FOR THE COMPARISON OF 24 HOURS DATA, 0900 AND 1400 SAMPLE.

		0900 SAMPLES		1400 SAMPLES	
		KS	MW	KS	MW
24 HOURS	UN-IONISED AMMONIA	Y	Y	Y	Y
	TEMPERATURE	Y	X	Y	Y
	DISSOLVED OXYGEN	X	X	X	X
	AMMONIACAL NITROGEN	Y	Y	Y	Y
0900 DATA	UN-IONISED AMMONIA			Y	Y
	TEMPERATURE			Y	Y
	DISSOLVED OXYGEN			X	X
	AMMONIACAL NITROGEN			Y	Y

KS = KOLMOGOROV-SMIRNOV test, a test of the shape of the distributions of the populations.
MW = MANN-WITNEY test, a test of the medians of the populations.
X = populations differ.
Y = populations the same.
5th percentile reported for D.O. % saturation.

TABLE 6 COMPARISON OF WEEKLY SAMPLING AT 0900 AND 1400 WITH 24 HOURS DATA

$$\text{probability}\left(\left|\frac{\text{sample statistic - population statistic}}{\text{population statistic}}\right| > A\right)$$

	DETERMINAND	A = 0.05	A = 0.10	A = 0.20
0900	UN-IONISED AMMONIA	62.1 (72.7)	32.1 (59.1)	4.8 (30.3)
	TEMPERATURE	0.0 (21.0)	0.0 (21.0)	0.0 (0.0)
	DISSOLVED OXYGEN	93.0 (72.9)	93.0 (72.9)	0.0 (0.0)
	AMMONIACAL NITROGEN	73.9 (84.2)	73.9 (84.2)	13.1 (31.9)
1400	UN-IONISED AMMONIA	50.7 (94.0)	50.7 (94.0)	0.2 (47.2)
	TEMPERATURE	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
	DISSOLVED OXYGEN	100.0 (100.0)	100.0 (100.0)	0.6 (100.0)
	AMMONIACAL NITROGEN	83.5 (100.0)	83.5 (100.0)	1.2 (74.3)

( ) refer to percentile comparisons (5th for D.O.)