

National Evaluation Centre

**EVALUATION OF AN
ELE/pHOX SUB-LOGGER
SUBMERSIBLE
WATER QUALITY MONITOR**

National Rivers Authority

National Evaluation Centre Manager
National Rivers Authority
February 1995



NRA

*National Centre
for
Instrumentation
and
Marine Surveillance*

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THE EVALUATION OF AN ELE\pHOx SUB-LOGGER
SUBMERSIBLE WATER QUALITY MONITOR

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Evaluation
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THE EVALUATION OF AN ELE/pHOx SUB-LOGGER SUBMERSIBLE WATER QUALITY MONITOR

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EXECUTIVE SUMMARY

This report describes the evaluation of an ELE\pHOx Sublogger water quality logger. It is designed for field use in fresh or saline water to measure dissolved oxygen, temperature, conductivity, pH, and turbidity.

The instrument was supplied with developmental software, which caused a number of problems.

The D/O readings changed by up to 14% saturation with different flow rates and the temperature, pH, and D/O probes were all affected by temperature.

The response times of the conductivity, pH, and D/O sensors were consistently less than 1 minute and the instrument is strongly built.

As with all field instruments careful maintenance and calibration is required before deployment in the field, but the size of the logger and the software made accurate calibration difficult to achieve.

1. INTRODUCTION

There are currently a number of submersible water quality meters in use by the NRA and there is now a need to understand how environmental factors affect the reliability and accuracy of data obtained. In order to gain some information about the precision and operational limits of a ELE\pHOx sublogger in natural waters a series of tests were carried out on an instrument obtained from the manufacturer.

The instrument is a multi-parameter meter which directly measures temperature, dissolved Oxygen, pH, conductivity and turbidity. Conductivity is used to derive a value for salinity. The dissolved oxygen (%sat) is used to calculate the oxygen concentration as mg/l.

The instrument was tested over 6 months at the NRA evaluation centre at Fobney Mead and its facilities at Lea Marston and Crossness. The test program was agreed to by the NRA regions and by pHOx ltd.

The test findings are presented in sections 2 and 4. In section 2 the results are summarised along with comments about operation and construction, and the implications for use are given. Section 4 contains detailed test results after some initial data analysis. The test methods are outlined in section 5. If more information is required then the authors can be contacted at :

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2. MAJOR FINDINGS

2.1 Implications for use

The results of these tests can be used to estimate the accuracy and uncertainty which can be expected from this instrument during normal use.

pH	< ± 0.3
D/O	±10% to ±15%
Temperature	< ± 1.0°C

The conductivity reading can not be fairly estimated because of the lack of a reliable calibration during the test, and the turbidity can not be estimated because of the deep silting which occurred.

The pH value has been obtained from the drift test results by comparison with the laboratory values. The temperature uncertainty is caused by the calibration errors observed during the temperature test. The D/O uncertainty is estimated from the flow and temperature effects.

Changes of flow and temperature both caused large errors in some of the sensors primarily the D/O sensor. This has been reflected in the uncertainty estimates because of the differences in conditions between calibration and deployment which will occur.

The size of the logger and the current software make it difficult to calibrate accurately.

2.2 Instrument performance

Water Flow Rate

The instrument was rigidly mounted vertically and horizontally in the flow tank at Fobney Mead and subjected to different water flow speeds. The logger readings were recorded both directly and using the logging facility. Samples were taken throughout the test for analysis of pH and conductivity. The tank was continuously aerated to maintain 100% saturation, and the temperature was measured with a hand held thermometer.

The results show that there is no significant flow effect on temperature, pH, or conductivity.

The D/O sensor is affected in a manner similar to a normal non-stirred probe both when operated on-line, and when logging. The difference in reading between zero flow and 0.33 m/s (maximum flow) was up to 14%. This can lead to significant errors if the instrument is calibrated in air and used in still water, or if it is calibrated in still aerated water and used in flowing water.

The turbidity readings are not shown since they increased steadily throughout the test from 0 to 250 FTU, we believe that this may be due to the formation of bubbles on the optical surfaces.

Logger orientation had no significant effect at 0.33 m/s (maximum flow)

Water temperature

The instrument was placed in a tank of stirred water and the temperature was increased through the steps shown below. A sample was taken at each temperature for laboratory analysis to provide reference information.

All sensors were affected by the water temperature. The error in D/O reading changed from -2.9% at 9.9°C to -30.0% at 45.4°C. This is a change of approximately -0.6% per °C and could generate a maximum error of 12% if the instrument was calibrated in a laboratory at 23°C then used in a river at 3°C.

The temperature reading error changed from -0.1°C at 1.8°C to +1.0°C at 40.3°C. This is a change of approximately +0.02°C per °C. This was compared against an electronic thermometer which has been calibrated against a mercury column thermometer with a traceable calibration of ±0.05°C.

The pH difference changed from -0.2 at 1.8°C to +0.5 at 40.3°C. This is a change of approximately 0.01 units per °C.

The Turbidity difference changed from -2 FTU at 20.1°C to +36 FTU at 45.4°C however this is probably due to the formation of air bubbles on the optical surfaces as the temperature increased.

The conductivity sensor could not be tested since a software problem made it impossible to calibrate the probe adequately.

Accuracy

The accuracy of the dissolved oxygen and conductivity probes were tested directly, and the accuracy of the temperature probe was tested in the temperature test. The accuracy of the pH and turbidity probes can be inferred from the drift tests.

Dissolved Oxygen : The Instrument reading was within the reference uncertainty at 100% and 70.7%. At $41.5 \pm 2\%$ an error of +3.1% was observed - the instrument readings were 42.5 and 44.6%, and at $152.3 \pm 8\%$ an error of -10.1% was observed - the instrument readings were 142.7% and 147.5%.

Conductivity : This test was not completed because of a software fault in the logger.

Temperature : Errors of up to 1.0°C were observed. (See Temperature test).

Response time

The instrument was transferred quickly from between solutions with different concentrations close to the lower and upper end of the measuring ranges. The response time values represent the time taken for the instrument to complete 90% of the step change. The D/O, pH, and conductivity sensors were tested.

The test was carried out before and after the estuarine drift test and all three sensors had responses of less than 1 minute on each occasion.

Fresh water Fouling and Drift

The temperature and pH readings were within the uncertainties of the laboratory readings during the test at Lea Marston.

The Sublogger D/O readings fell to less than 20% after 8 days which is probably due to a layer of anaerobic silt which built up in the tank and covered the sensor and cleaning brush. The Winkler analysis showed that the D/O values remained above 50% (4 mg/l). The instrument was later tested at Fobney Mead for 2 weeks and the D/O readings were stable for the first five days. After that time the readings increased to over 200% indicating that the probe had failed.

At Lea Marston the sublogger conductivity reading varied between 700 and 900 $\mu\text{S}/\text{cm}$ and the laboratory values were between 900 and 1000 $\mu\text{S}/\text{cm}$. The difference may be caused by different temperature corrections. The laboratory results are given as conductivity at 20°C . There was no information available about any temperature correction applied by the sublogger.

At the end of the test a large amount of silt had built up on all upper surfaces and the cleaning brush had weed growing on it.

Estuarine Fouling and drift

The instrument was deployed at the floating water quality monitor moored in the Thames at Crossness from 21/3 to 11/4/94. Samples were taken from a nearby pier and the laboratory data shows a good correlation with the instrument. Where laboratory data is not available the results are consistent with the known water quality of that part of the Thames reflecting the normal tidal cycle, and are consistent with other instruments deployed at the same time.

The Conductivity readings recorded were corrupted by a software fault in the instrument which occurred when the values changed from the low range to the high range. The salinity readings are calculated from the high range conductivity readings and were consistent with the known water quality.

The response times of the pH, conductivity, and D/O sensors all seemed to

improve during the test, however this may not be significant since the responses before the test were all less than 1 minute.

The instrument proved to be very robust during the test as the sensors were unaffected and the test was completed when one of the supporting ropes parted allowing it to move a knock into the side of the barge. A foam mat had been wrapped around the sublogger but this was lost allowing some surface damage. (The instrument was initially suspended from the side of the station by two ropes during the test to prevent it from swinging.)

2.3 Comments on use, construction, and documentation

The sublogger is approximately 820 mm long, 190 mm diameter, and 15.2 kg mass. It is strongly made with an outer case of plastic coated steel and is very robust. The sensors are protected by a wire cage. During normal operation there is no need to open the instrument, since it has a rechargeable battery, therefore the internal layout was not inspected.

It is powered by a high capacity rechargeable battery which would probably last many months between charges. Neither the battery limits nor the data storage limits were encountered during the tests.

Calibration of the various sensors was difficult. Because of its size and weight the logger is awkward to manoeuvre between wash and calibration solutions, and requires large quantities of reference grade solutions to calibrate accurately. This may be made easier by some form of calibration cup.

The calibration settings of every sensor could be easily changed. This is useful for the D/O and pH sensors, but could cause problems with temperature and conductivity sensors which could be factory set should be stable in normal use.

The instrument software provided for on-line operation and for logging was an incomplete developmental package and was very poor. On-line data display used the 'esc' key to move between determinants, but also used the 'esc' key to enter the calibration routine. This made it possible to change the calibration settings of any parameter inadvertently. The logger did not record any '0' values in the spreadsheet, a common reading for turbidity. This caused all the subsequent data to be placed in the wrong columns when transferred for analysis, leading to much laborious editing of the data.

No manual was available for the sublogger.

2.4 Manufacturer's comments

ELE pH0x Systems Division Ltd provided the following comments on this report:

"1. The unit, whilst produced as a pre-production prototype, will probably undergo some further development partly based on this report.

2 The software used for both programming and down loading data is known to be less than satisfactory. It is due for replacement in January [1995] and is currently on schedule.

We trust that these modifications will significantly improve the use ability and await the final report with interest."

3. DETAILS OF INSTRUMENT EVALUATED

The instrument tested was loaned to the NRA by the manufacturer for the duration of the evaluation. It was a pre-production model which had been used as a display and demonstration model. It was fitted with separate sensors for Dissolved Oxygen, Temperature, pH (with a separate reference), and Turbidity.

Instrument	pHOx Sublogger
Sensors fitted	D/O; Temperature; Turbidity; pH with separate reference; Conductivity
Serial Number	Not located
Overall Length (approximate)	820 mm
Maximum Diameter (approximate)	190 mm
Mass (approximate)	15.2 kg
Manufacturer	ELE International Ltd pHOX Systems Division Eastman Way Hemel Hempstead Herts. HP2 7HB
	Tel : 0442 218355
	Fax : 0442 252474

4. TEST RESULTS

Water Flow Rate

The instrument was rigidly mounted in the flow tank at Fobney Mead and subjected to different water flow speeds. Samples were taken throughout the test for analysis of pH and conductivity. The tank was continuously aerated to maintain 100% saturation, and the temperature was measured with a hand held thermometer.

The results shown in table 1 are quoted as differences between the sample values and the instrument readings to remove any bulk changes and highlight the effect of flow on the instrument.

The results show that there is no significant flow effect on temperature, pH, or conductivity. The D/O sensor is affected in a manner similar to a normal non-stirred probe. The turbidity readings are not shown since they increased steadily throughout the test from 0 to 250 FTU; we believe that this may be due to the formation of bubbles on the optical surfaces.

Table 1 : Effect of water flow rate

Water Flow rate m/s	Reading Difference (pHOx - reference)			
	Temp °C	pH	D/O %sat	Conductivity @ 20°C µS/cm
off	+0.4	+0.3	-16.2	-35
0.04	+0.3	+0.3	- 6.8	-36
0.11	+0.3	+0.3	- 4.9	-38
0.16	+0.3	+0.3	- 4.3	-39
0.23	+0.3	+0.3	- 4.0	-40
0.29	+0.3	+0.3	- 3.5	-38
0.33 (max)	+0.3	+0.4	- 3.4	-37
0.33 (max)	+0.2	+0.2	- 3.4	-42
0.24	+0.2	+0.3	- 3.8	-42
0.19	+0.3	+0.3	- 4.3	-42
0.13	+0.3	+0.3	- 4.9	-39
0.09	+0.3	+0.3	- 5.8	-36
0.04	+0.3	+0.3	- 8.0	-38
off	+0.4	+0.3	-17.5	-40

Table 2 shows the values obtained when the logger was logging at 1 minute intervals for 10 minutes at maximum flow then at zero flow. The water was continuously aerated during the test. (The pH sensor was out of calibration during the test). The results confirm the on-line results and show that the temperature, pH, turbidity, and conductivity are not affected, but the D/O is affected.

Table 2 : Effect of flow when logging

Water Flow rate m/s	pHOx reading - Average logged value				
	Temp °C	pH	D/O %sat	Turb. FTU	Conductivity @ 20°C µS/cm
0.33	6.8	8.9	96.9	0	340
off	6.8	8.8	85.2	0	340

Table 3 shows the results of an extra check made to see if orientation in a flowing stream affected the readings. There was no significant change in the readings.

Table 3 : Effect of logger orientation

Logger orientation	pHOx reading - Average logged value				
	Temp °C	pH	D/O %sat	Turb. FTU	Conductivity @ 20°C mS/cm
vertical	10.7	8.1	98.0	0	1.12
horizontal sensors upstream	10.6	8.1	97.0	0	1.12
horizontal sensors downstream	10.5	8.1	95.6	0	1.11
vertical	10.4	8.1	96.2	0	1.11

Water temperature

The instrument was placed in a tank of stirred water and the temperature was increased through the steps shown below. A sample was taken at each temperature for laboratory analysis to provide reference information.

The results shown in table 4 are quoted as differences between the sample values and the instrument readings to remove any bulk changes and highlight the effect of temperature on the instrument. All sensors were affected by the water temperature, however the turbidity changes are probably due to the formation of air bubbles on the optical surfaces as the temperature increased.

Conductivity values are not given since a software problem made it impossible to calibrate the probe adequately

Table 4 : Effect of temperature

Water Temp. °C	Reading Difference (pHOx - Reference)			
	Temp °C	pH	D/O %sat	Turbidity
1.8	-0.1	-0.2	-4.1	-3
9.9	+0.4	0.0	-2.9	-3
20.1	+0.7	+0.3	-6.9	-2
30.4	+0.9	+0.2	-13.0	+13
40.3	+1.0	+0.5	-20.9	+26
45.4	+0.9	+0.2	-30.0	+36

Accuracy : Dissolved Oxygen

The instrument was placed in different solutions with known % saturation of dissolved oxygen. The uncertainty of the reference values is $\pm 2\%$ sat or $\pm 5\%$ of reading (ie 41 ± 2 %sat, see section 5 for a full list).

Table 5 : Dissolved Oxygen Accuracy

Reference value % saturation	Instrument reading %sat.	
	increasing	decreasing
41.5	42.5	44.6
70.7	70.5	71.3
100	98.1	100.4
152.3	142.7	147.5

Accuracy : Conductivity

The results of this test are not given because a software fault made it impossible to adequately calibrate the instrument before the test.

Response time

The instrument was transferred quickly from between solutions with different concentrations close to the lower and upper end of the measuring ranges. The response time values represent the time taken for the instrument to complete 90% of the step change. The D/O, pH, and conductivity sensors were tested.

The test was carried out before and after the estuarine drift test. Tables 6 and 7 show that all three sensors had responses of less than 1 minute, which improved after the drift test.

Table 6 : Response times (10/3/94 : Before visit to Crossness)

Sensor (step change)	Response time	
	rising	falling
Conductivity (5 to 10850 $\mu\text{S}/\text{cm}$)	17 sec	52 sec
pH (4.0 to 9.9)	26 sec	14 sec
DO (6 to 100%) : (14/3/94)	31 sec	19 sec

Table 7 : Response times (15/4/94 : After visit to Crossness)

Sensor (step change)	Response time	
	rising	falling
Conductivity (47 to 10200 $\mu\text{S}/\text{cm}$)	< 4 sec	<14 sec
pH (4.0 to 9.9)	< 6 sec	< 6 sec
DO (4 to 100%) : (19/4/94)	<20 sec	<17 sec

Fresh water Fouling and Drift

The following graphs show the data recorded by the instrument when it was deployed at Lea Marston from 10/6 to 1/7/94. The probes were calibrated by the manufacturer prior to deployment, and the D/O probe was calibrated according to the manufacturer's instructions at the start of the test.

Laboratory data from analysis of water samples has been plotted where available and shows a reasonable correlation for the temperature and ph readings.

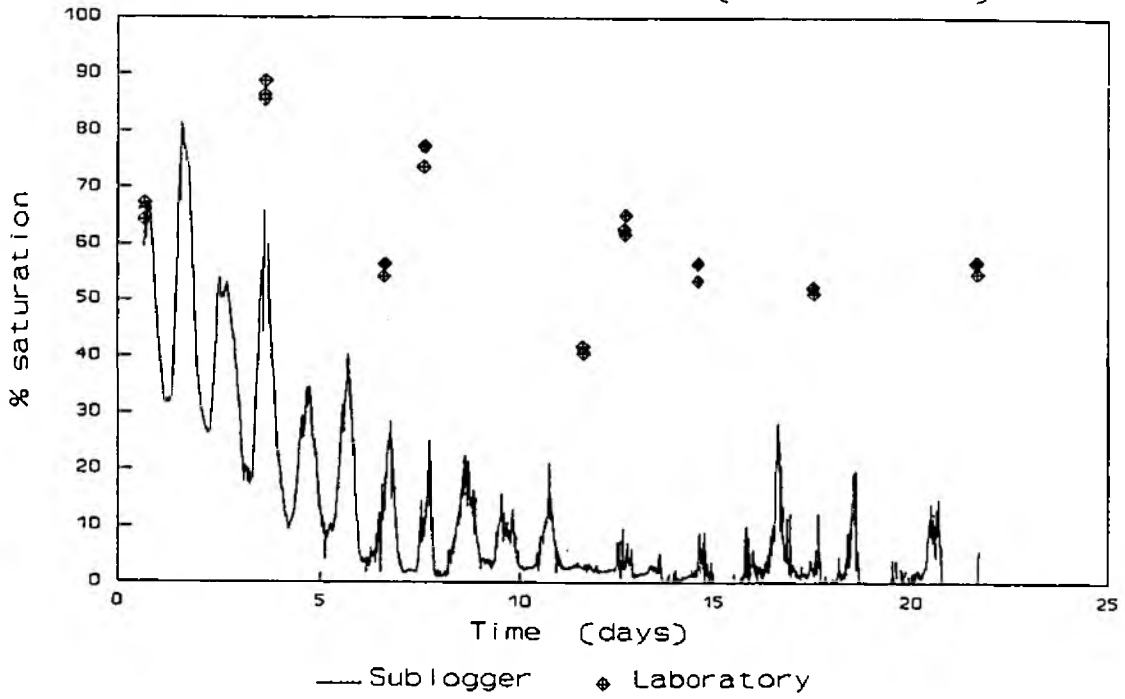
The differences in the conductivity reading between the laboratory and the sublogger may be caused by different temperature corrections. The laboratory results are given as conductivity at 20°C. There was no information available about any temperature correction applied by the sublogger.

The errors in the Sublogger D/O readings are probably due to a layer of anaerobic silt which built up in the tank and may have covered the sensor and cleaning brush. The instrument was later tested at Fobney Mead for 2 weeks.

At the end of the test a large amount of silt had built up on all upper surfaces and the cleaning brush had weed growing on it.

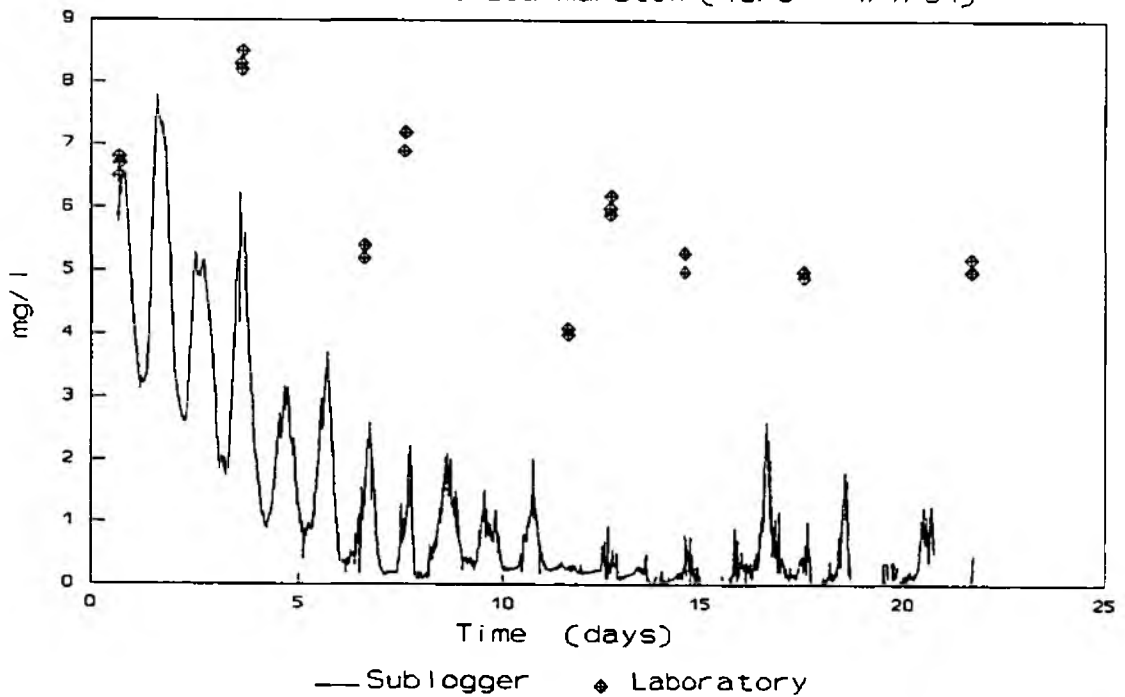
Dissolved Oxygen %sat

Drift test at Lea Marston (10/6 - 1/7/94)



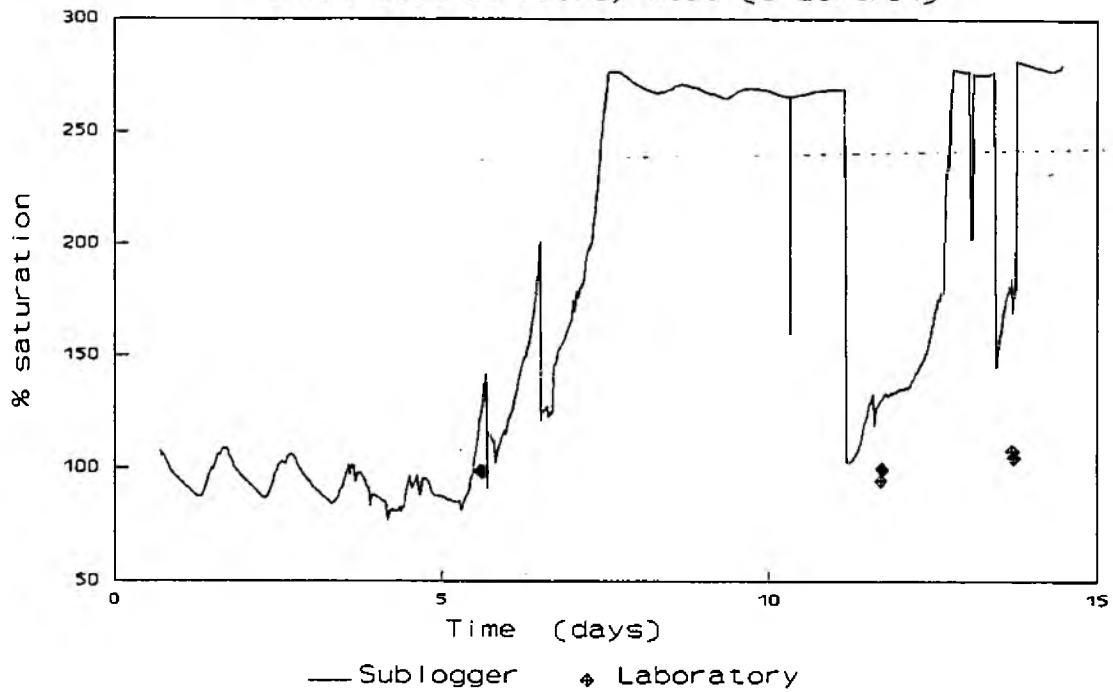
Dissolved Oxygen mg/l

Drift test at Lea Marston (10/6 - 1/7/94)



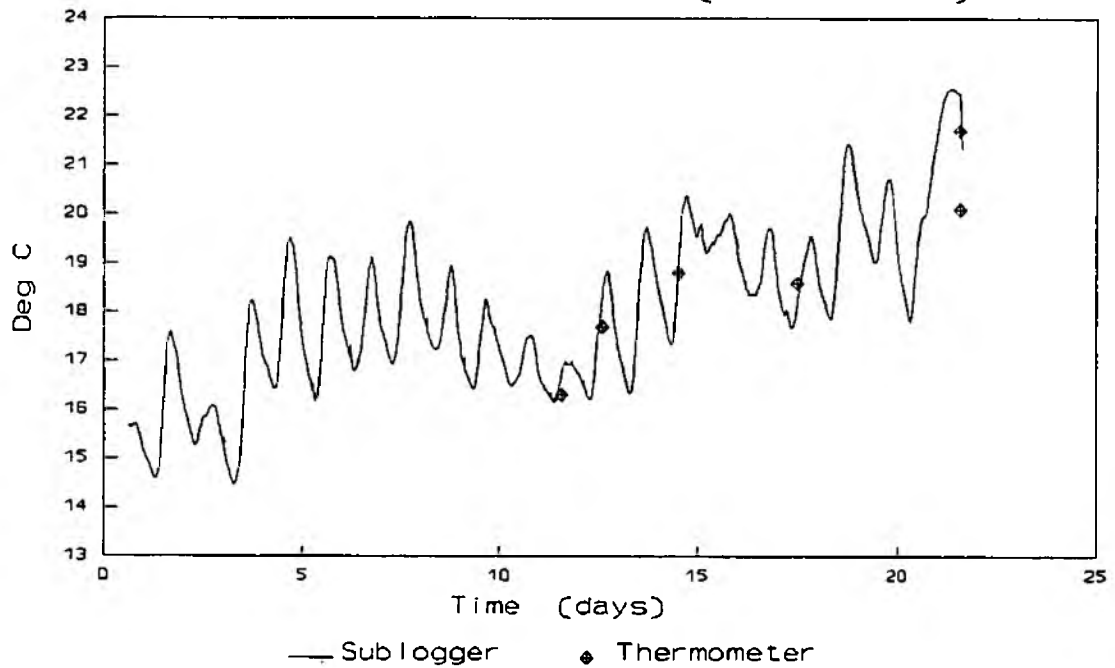
Dissolved Oxygen %sat

Drift test at Fobney Mead (9-23/9/94)



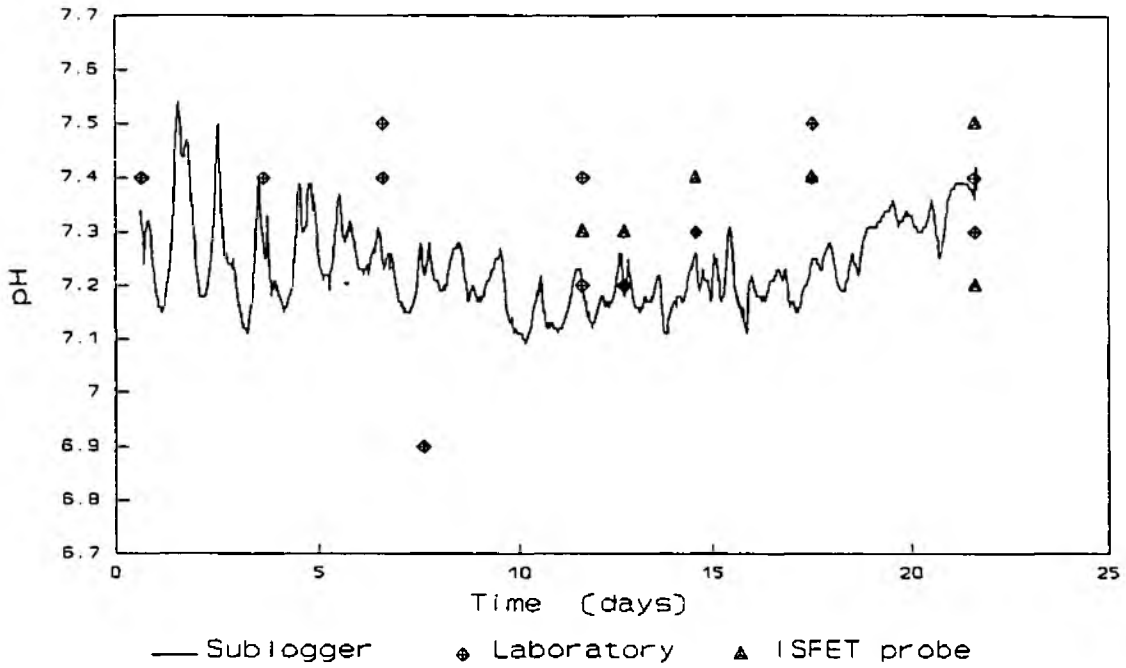
Temperature

Drift test at Lea Marston (10/6 - 1/7/94)



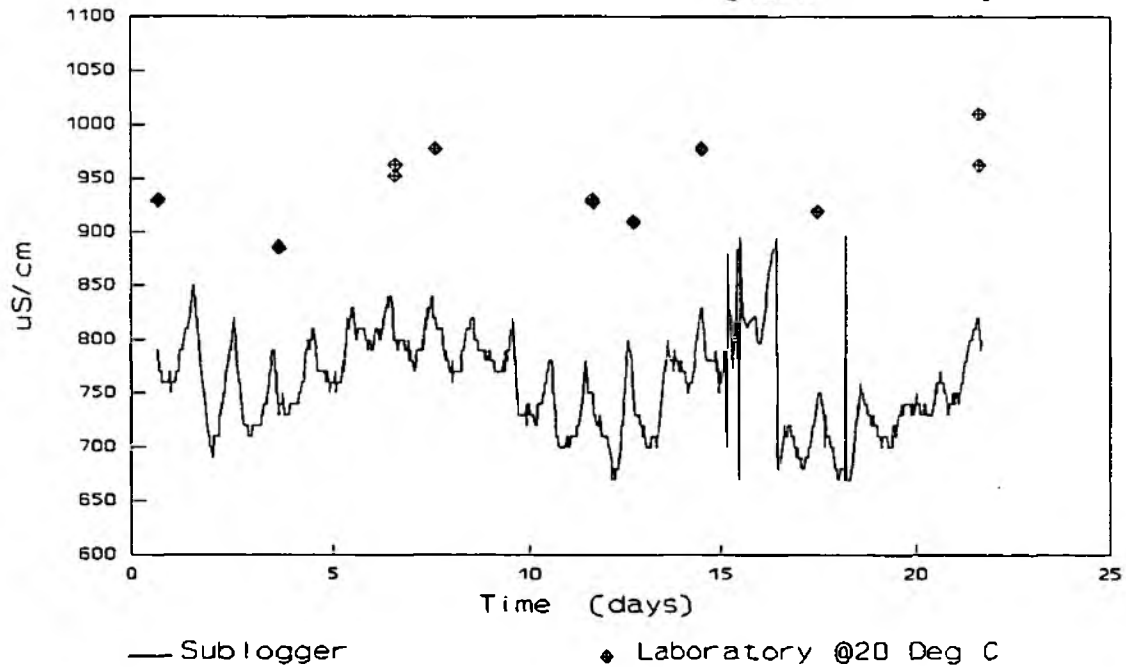
pH

Drift test at Lea Marston (10/6 - 1/7/94)



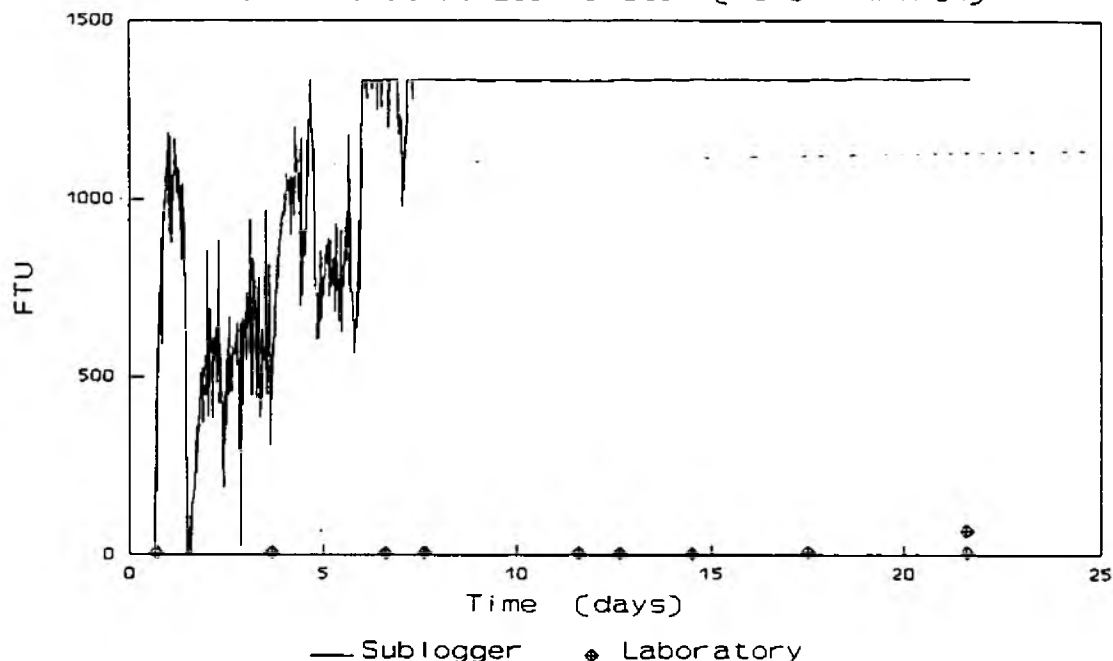
Conductivity

Drift test at Lea Marston (10/6 - 1/7/94)



Turbidity

Drift test at Lea Marston (10/6 - 1/7/94)



Estuarine Fouling and drift

The following graphs show the data recorded by the instrument when it was deployed at the floating water quality monitor moored in the Thames at Crossness from 21/3 to 11/4/94.

Samples were taken from a nearby pier and the laboratory data has been plotted where available and shows a good correlation with the instrument. The data clearly shows the tidal cycles and where laboratory data is not available the results are consistent with the known water quality of that part of the Thames. The results are also consistent with other instruments deployed at the same time.

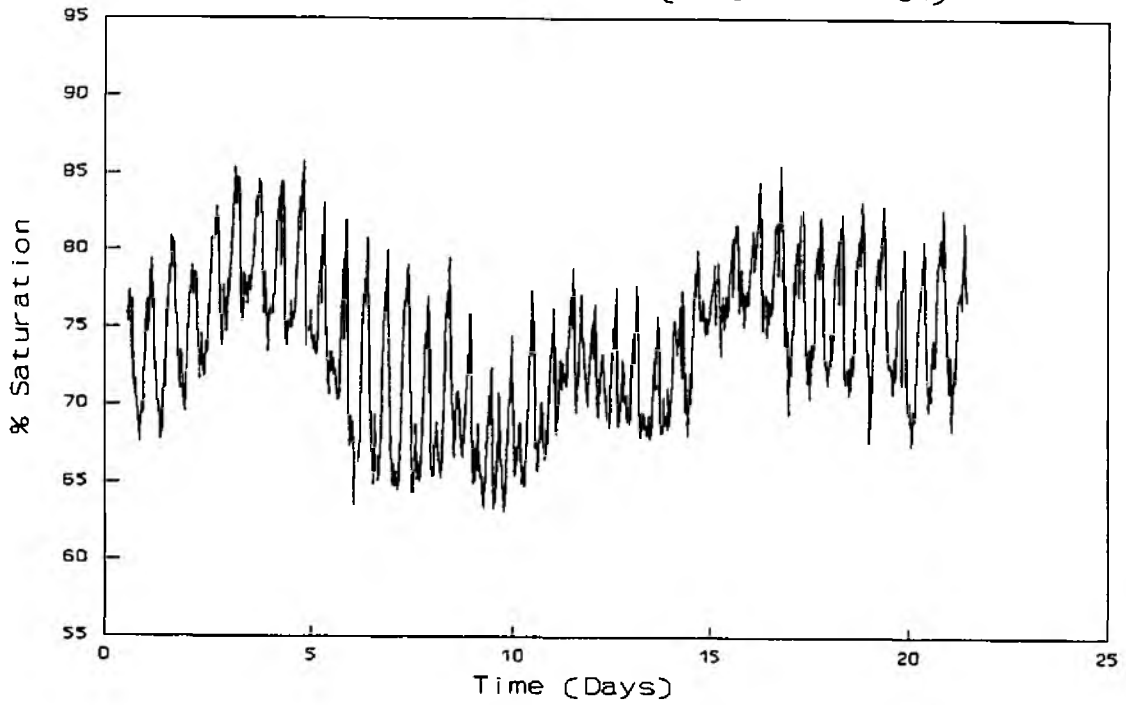
The Conductivity results are not given because the data was corrupted by a software fault in the instrument. The salinity readings are calculated from the conductivity high range and are shown.

The response times of the pH, conductivity, and D/O sensors all seemed to improve during the test, however this may not be significant since the responses before the test were all less than 1 minute.

The instrument proved to be very robust during the test since one of the supporting ropes parted allowing it to swing into the side of the barge. Foam matting had been wrapped around it which was lost allowing some surface damage, but the sensors were unaffected and the test was completed.

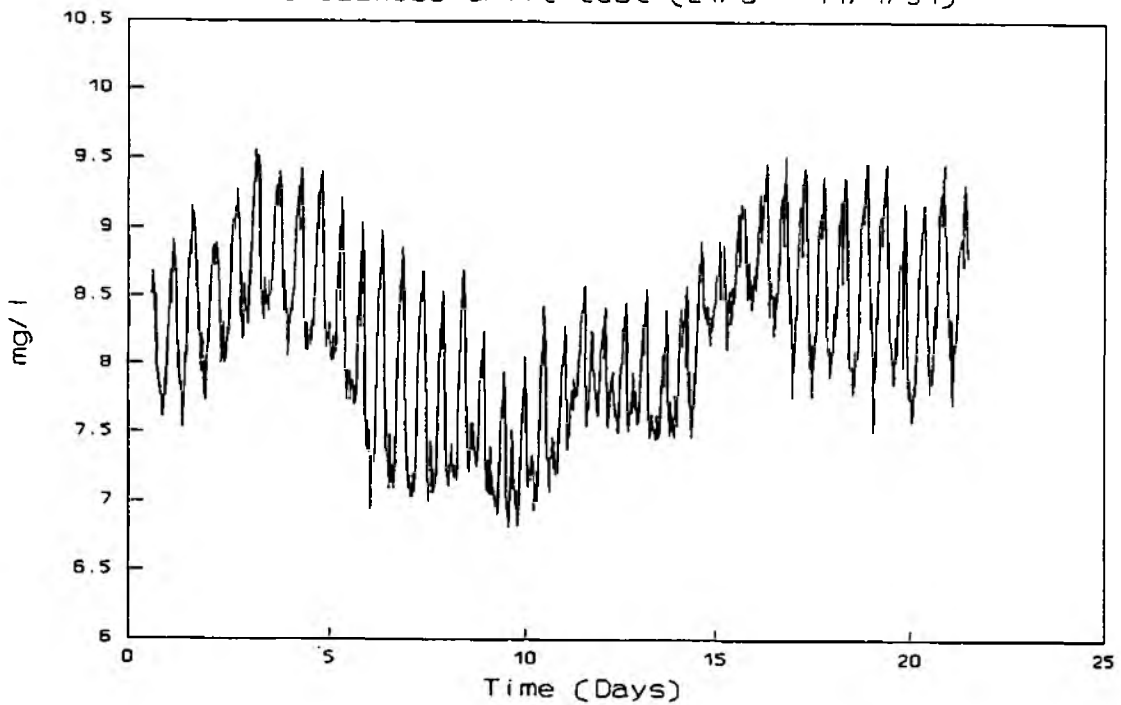
Dissolved Oxygen %sat

Crossness drift test (21/3 - 11/4/94)



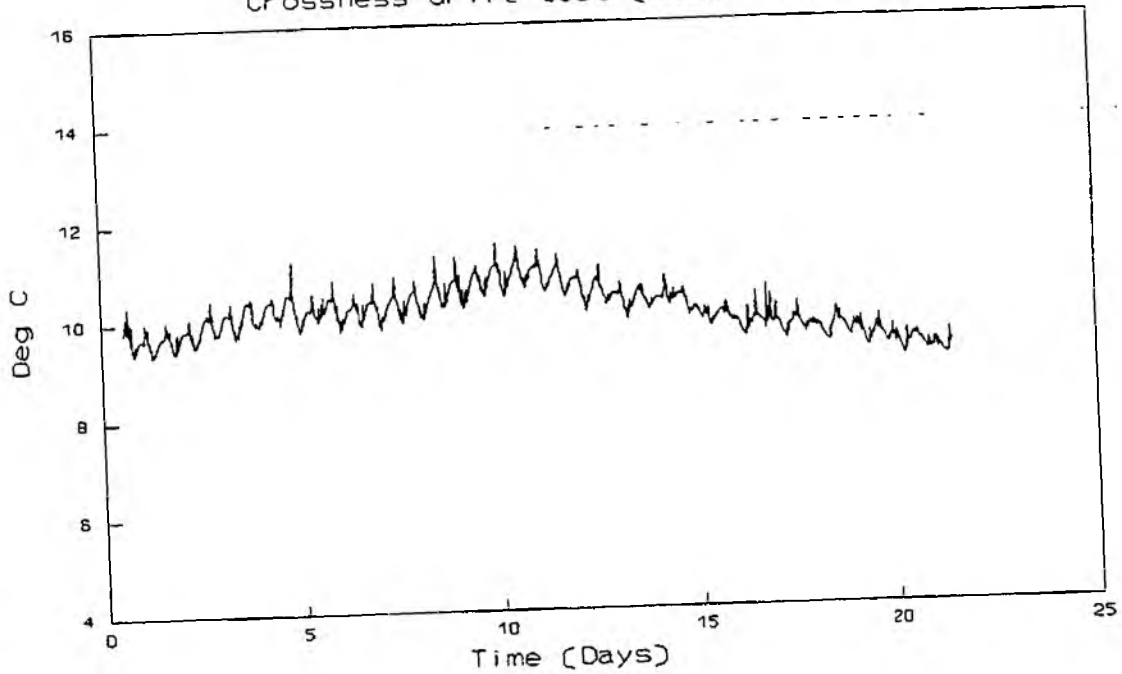
Dissolved Oxygen mg/l

Crossness drift test (21/3 - 11/4/94)



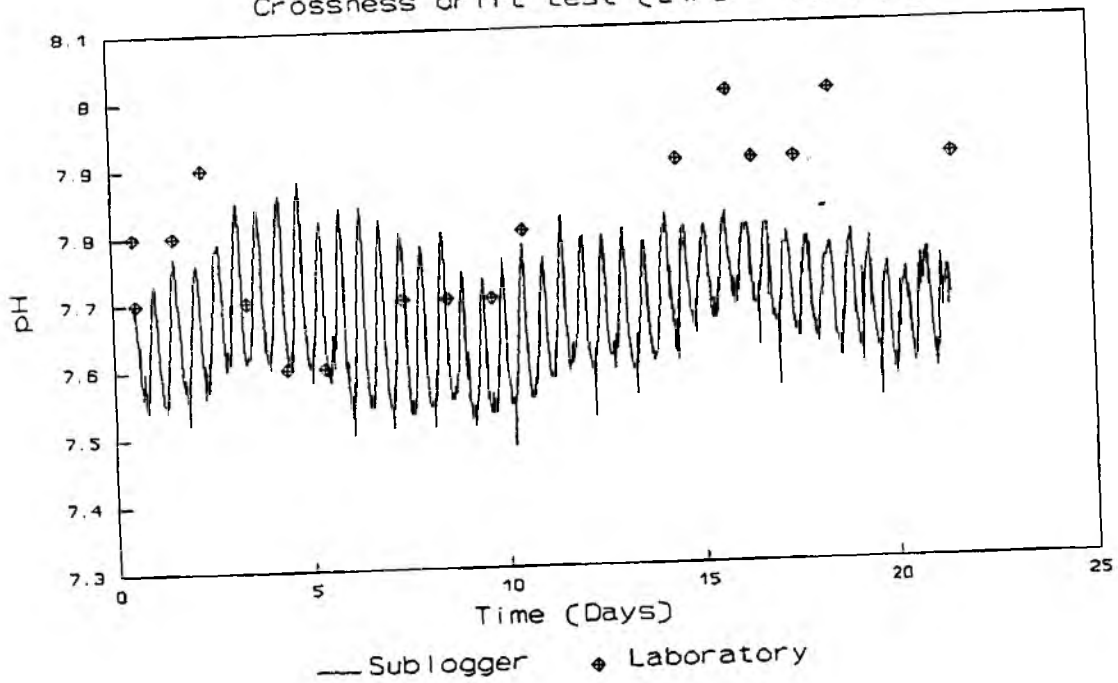
Temperature

Crossness drift test (21/3 - 11/4/94)



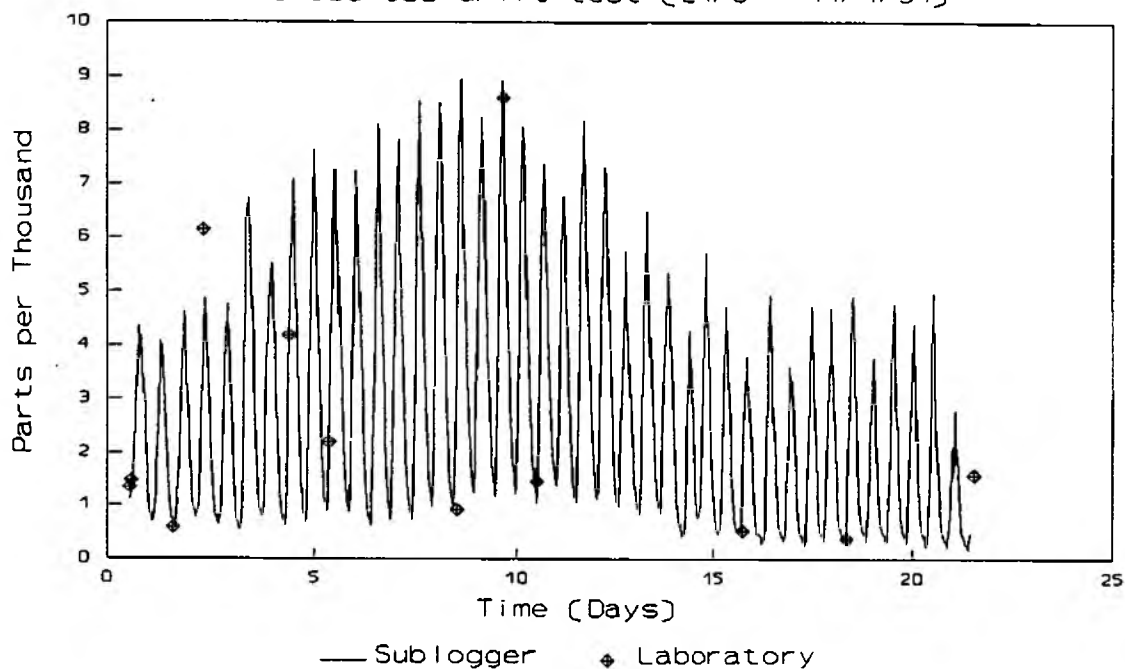
pH

Crossness drift test (21/3 - 11/4/94)



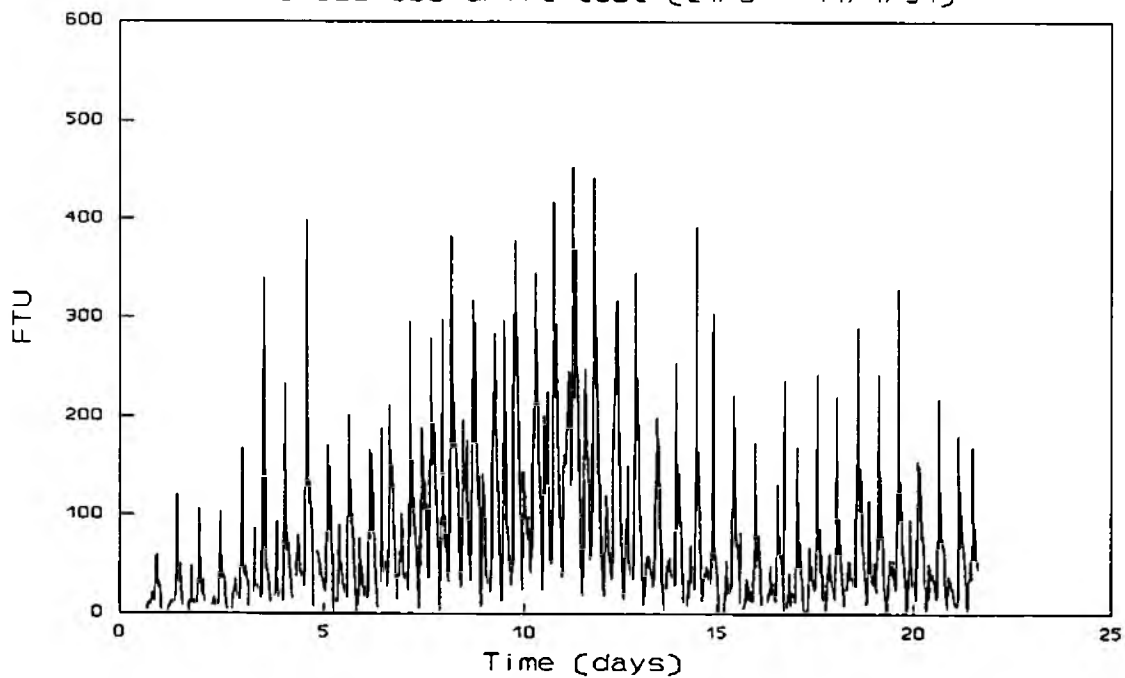
Salinity

Crossness drift test (21/3 - 11/4/94)



Turbidity

Crossness drift test (21/3 - 11/4/94)



5. TEST PROCEDURES

Flow rate

The instrument was calibrated according to manufacturer's instructions then clamped rigidly in a large flow tank filled with river water. It was positioned vertically with the sensors and the lower half immersed, and was connected to a computer for continuous operation.

The water in the tank was continuously aerated to maintain the oxygen level at 100% saturation and samples were taken regularly during the test for analysis of the pH and conductivity. The depth was constant and the temperature was checked using a thermometer. The flow speed was increased in steps to 0.37 m/s (as measured by an electromagnetic flow meter) then decreased stepwise to 0.0 m/s. The instrument parameters were allowed to stabilise at each speed before being recorded.

The effect of the instrument orientation was checked at maximum flow with the instrument mounted vertically, and horizontally facing upstream and downstream.

When logging the cleaning brush is designed to stir the water around the D/O probe. This was tested by leaving the instrument logging independently taking 1 reading per minute in maximum flow for approximately 10 minutes and in zero flow for approximately 10 minutes.

Water temperature

The instrument was calibrated according to manufacturer's instructions. It was then placed in a tank of stirred river water and connected to a computer for continuous operation. The water temperature was increased stepwise from 1.8 to 45.4°C and allowed to stabilise for at least 30 minutes at each temperature before the instrument readings were noted. The level of dissolved oxygen was fixed by continuous aeration, the depth was constant, and pH and conductivity were measured in samples taken at each temperature.

Response times

The response times of the instrument sensors was tested by transferring the instrument from water near the minimum of the measuring range to water near the maximum of the range. Instrument readings were recorded at regular intervals after the step change and a graph of reading against time was used to calculate the response time (time to complete 90% of the step change). This test was carried out before and after the fouling and drift tests.

Fresh water Fouling and Drift

The instrument was calibrated by the manufacturer. It was then immersed in water from the river Tame for 3 weeks at Lea Marston. The trend in levels of D/O, temperature, pH, conductivity, NH₃ and turbidity of the water were monitored using the standard Severn-Trent region monitoring station. The instrument was checked three times each week and a number of samples were taken for laboratory analysis at each visit. The level of fouling was assessed after the test.

Estuarine Fouling and Drift

The instrument was calibrated according to manufacturer's instructions. It was then subjected to estuarine conditions for three weeks at the Thames monitoring station moored at Crossness. The trend in levels of D/O, temperature and conductivity were monitored using standard water quality instruments, and samples were regularly taken for analysis from a nearby pier.

Accuracy

The accuracy of each sensor was checked separately in the following way.

The Oxygen was checked by placing the instrument in five tanks bubbled with five different oxygen/nitrogen mixtures to give known %saturation levels at 2 ± 2 , 41.5 ± 2 , 70.7 ± 4 , 100, 152.3 ± 8 , 194.3 ± 10 , from calibrated cylinders. The water in each tank was stirred by a submersible pump, but because of its size the instrument tended to obstruct the flow.

The Conductivity accuracy was tested by placing the instrument in the following solutions with known conductivities : De-ionised water , 100 ppm NaCl ($210 \mu\text{S/cm}$), 200 ppm NaCl ($415 \mu\text{S/cm}$), 0.1 M KCl ($12900 \mu\text{S/cm}$), and 0.5 M KCl ($58640 \mu\text{S/cm}$).

The accuracy of the pH, turbidity, and temperature sensors were not tested directly because of practical and software difficulties, but can be inferred from other tests.

6. REFERENCES

DMP : Water Logger Mk IV with Modem Facility Manual

A Chappell : Test protocol for Submersible water quality meters

BSI : BS6068:section 2.15 (1986) Determination of dissolved oxygen - electrochemical probe method.

Standard Methods for the Examination of Water and Wastewater (1989)

ACKNOWLEDGEMENTS

Thanks must be given to the pollution staff at Crossness, the Laboratory staff at Fobney Mead, and to ELE-PHOx for loan of the instrument.

APPENDIX : CALCULATIONS AND REFERENCE MEASUREMENTS

Dissolved Oxygen

For mg/l values the reference measurements are made by Winkler titration. The uncertainty is assumed to be ± 0.5 mg/l from observation.

For %sat values the water is aerated to 100%, or to other values, by bubbling air or Oxygen\Nitrogen certified mixtures through river water. The uncertainty is approximately $\pm 5\%$ of reading.

Temperature

The reference measurements were made using mercury in glass thermometer calibrated traceable to national standards. The total uncertainty is taken as $\pm 0.1^\circ\text{C}$.

pH

The pH is compared against laboratory measurements made using an automated CSP pH meter. During the drift test the readings were confirmed by comparison with the monitor panel and a portable ISFET pH meter calibrated before each use. The traceable uncertainty is $\pm 20\%$ of reading.

Conductivity

The conductivity is compared against laboratory measurements made using an automated CSP conductivity meter. The laboratory readings were given as conductivity at 20°C , this adjusted to 25°C for comparison with the instrument values using a temperature coefficient for the water of 1.91% per $^\circ\text{C}$. The traceable uncertainty of the laboratory values is $\pm 20\%$ of reading.

Salinity

The salinity values of sea and estuarine water were calculated from laboratory measurements of chloride in samples submitted for analysis by the following relationship:

$$\text{SALINITY} = \text{CHLORIDE} \times 1.80655$$

Turbidity

Turbidity was measured in the laboratory using a Hach 2000 turbidimeter and in the field with a pH0x 7501 turbidimeter. These results were used to check the values obtained in the tests.