

**A comparison between two methods of dissolved oxygen  
measurement in rivers**

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**Dani Church  
Claire Bennett**

**Environment Protection Assistant,  
Environment Protection Officer**

**Environment Services (Norfolk and Suffolk)**



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# A Comparison between two methods of dissolved oxygen measurement in rivers.

**By Dani Church EPA and Claire Bennett EPO, Norwich**

## **1. Introduction**

A comparison of the Winkler chemical test and the meter field test in Norfolk and Suffolk has been made to see if there is a difference between the two techniques. Data from 11 sites, 1 Norfolk, 10 Suffolk was investigated for the period 1991 – 1998 (although the data from 1998 is incomplete.) The meters currently used for dissolved oxygen (DO) meter field tests, WTWs, were recently employed in August 1997. Previous to this, PHOX and JENWAY meters were used. The report aims to answer the following questions.

1. Is there a significant difference between Winkler and field measurements.
2. Is there any obvious discrepancy for certain types of readings?
3. Has there been any improvement since the introduction of WTWs?
4. Have the different measurement techniques changed the RE compliance?
5. How we will continue to regulate DO measurement techniques in the future?

A detailed summary of all data is given in appendix A.

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**2. Is there a significant difference between Winkler and field meter measurements?**

A *t*-test<sup>1</sup> for matched pairs was performed on the data testing the hypothesis 'there is no significant difference between the two DO measurement techniques'. A comparison of differences prior to and after the introduction of WTW meters was also made. Table 1 below summarises the results found. If the resulting *t* value exceeded the  $p=0.1$  significance level value quoted in the *t*-distribution table<sup>1</sup> the hypothesis was rejected and it was concluded that there was a significant difference between the two techniques.

**Table 1.0 Summary of paired *t*-test analysis on Winkler results and DO field meter results for Norfolk and Suffolk.**

Hypothesis: There is no significant differences between the paired data sets.	R04BFS202571	R04BFBAT070	R04BFBLLY010	R04BFDEEB030	R04BFDVOV060	R04BFFVMD030	R04BFGIP010	R04BFGIP205	R04BFOAE047	R04BFWAY116B	R04BFWNG040
	Whole period	A	R	R**	R	R*	R**	R	R	R	A
Period prior WTWs	A	R	R	R	A	R	A	R		A	A
Period using WTWs	A	A	A	A	A	R***	A	R		A	A

Key to table:

A – Hypothesis accepted

R – Hypothesis rejected

\* rejected at  $p = 0.1$  level

\*\* rejected at  $p = 0.05$  level

\*\*\* rejected at  $p = 0.02$  level

The single Norfolk site, R04BFS202571 River Yare Rail Bridge, D/S Harford Tip, showed no significant difference between the two techniques whilst at 5 of the 10 Suffolk sites prior to the introduction of WTW meters a significant difference between the two techniques was found.

**3. Has there been any improvement since the introduction of WTWs**

There was a significant improvement in the similarity of readings at 3 of the 10 Suffolk sites after the introduction of the new WTW meters.

The apparent improvement in the DO results after the introduction WTW meters may be because they are more user friendly, i.e. there is no requirement for the user to manually scale the WTW meters unlike the PHOX meters.

**4. Obvious discrepancies noticed for certain types of readings.**

To enable a quick evaluation of differences between data sets to be made, the ratio between Winkler and field meter data for MEAN, MAX, and MIN statistics were calculated. This was calculated by dividing the field meter result by the Winkler result.

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Therefore, when the two results are the same the ratio will be 1. Table 1.1 summarises the MIN, MAX and MEAN ratios recorded at each site.

**Table 1.1 Ratios of MIN, MAX and MEAN results of Winklers and Field meters.**

	R04BFS202571	R04BFBAT070	R04BFBLY010	R04BFDEB030	R04BFDOV060	R04BFFYN030	R04BFGIP010	R04BFGIP205	R04BFOAE047	R04BFWAV116B	R04BFWNG040
MIN	0.99	0.94	1.25	0.50	0.85	1.2	0.91	0.33	0.9	14.3	1.39
MAX	0.92	1.00	0.76	0.87	0.41	0.91	0.54	0.65	0.54	0.95	0.75
MEAN	1.00	0.9	0.96	0.92	0.94	0.96	0.93	0.89	0.92	1.01	0.97

For the MIN ratios, the values are generally close to or greater than 1 possibly indicating that the Winklers technique measures to a lower percent saturation accurately than the field meters. The biggest deviation from 1 is 14.3, but this is due to the Winkler DO reading being 1, creating a large value for the ratio even though there is not a big difference between the values. The MAX ratio values are close to 1 or less than 1 possibly indicating that the Winklers technique records to a higher percent saturation than the field meters. This may explain why the MEAN of the ratios of the two methods are always close to 1. These results suggest that the field meters are able to record within a smaller range of oxygen saturation than the Winklers technique and not at very low or high saturations.

### 5.0 Have the different measurement techniques affected the RE compliance?

The optimistic 10 percentile values were calculated in the same manner used for compliance reporting for both the Winkler and field meter data over three year periods. The results were then examined to see if the differences in measuring techniques could have affected RE compliance at any sites. Table 1.3 shows those results where the method used may have wrongly resulted in compliance or non-compliance with the RE target.

**Table 1.3 Potential RE Target failures due to differences in measuring techniques. (Grey highlights indicate a failure against a target)**

Site	Date range	RE Target	Field Meter	Winkler
R04BFDOV060	1992 - 1994	60%	59.04	63.04
	1994 - 1996	60%	59.68	62.79
	1996 - 1998	60%	60.53	41.578
R04BFGIP205	1994 - 1996	70%	64.42	74.22
R04BFWNG040	1995 - 1997	60%	57.37	61.01

It is interesting to note that when data is extracted for use in the RE compliance computer program the following order of preference is used at each site in terms of which results are used for calculation.

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- 1) DO % Sat (Winkler)
- 2) DO % Sat Field (meter)
- 3) DO mg/l (Winkler)
- 4) DO mg/l Field (meter)

For example, when a DO% Sat (Winkler) result is present for a sample point, this will be used for the RE compliance calculations. If this is not present the program then looks for a DO % Sat Field measurement and so on.

From this report it is obvious that there are discrepancies between the results using the different methods, therefore if the results from one method are used and the result is inaccurate it could lead to a site incorrectly passing or failing its RE target.

However, 48 of the 53 pairs of observations (90.5%) did agree on the RE target being passed or failed. In only 1 of the 53 pairs of observations (1.8%) did the Winkler result fail the RE compliance target when the field meter result did not. 4 of the 53 observations (7.5%) failed the RE target by the field meter results. The passing or failing of an RE target is an important criteria for river compliance reporting. Differences between the two techniques have resulted in a 9% discrepancy in terms of RE compliance. This has been found to occur in more than one three year period at only one site, R04BFDOV060, whilst at the other two sites it has occurred only over one three year period. This is illustrated in Table 1.4 below.

**Table 1.4 Summary of differences in compliance found between the two techniques**

Period	Number of sites showing a difference in compliance.	Percentage(%)
1991-1993	0	100
1992-1994	1	90.9
1993-1995	0	100
1994-1996	2	81.8
1995-1997	1	90.9
1996-1998	1	90.9

Given the small sample number is difficult to scale up to assess the implications on a catchment scale. However, it would seem to indicate that the use of field meters for assessing RE compliance has probably only resulted in a different assessment of RE compliance having occurred in a small number of cases in any given three year period.

### 6. How will we continue to regulate DO measurement techniques in the future?

This report illustrates that there are obvious errors involved with the two DO measuring techniques that need to be identified and minimised as far as possible. A recent Agency report<sup>2</sup> has found that meters are more accurate than Winklers provided they are calibrated and used correctly. Errors are mainly incurred for the Winkler results via sampling and analytical techniques such as filling the bottles correctly,

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addition of the correct amount of chemicals to fix the oxygen and laboratory analysis. Errors in field meter results may be due to sampler error by incorrect use of the meter, misinterpreting meter readings, incorrect calibration, flow, temperature and meter drift.

No continuous record of field meter calibration has previously been kept, so it was not possible to comment on the accuracy of the meters. A calibration sheet has now been compiled and distributed to all staff using DO field meters. This sheet must be completed each time the meter is used or at least once a week so that a record of calibration and drift of the meter can be monitored. A member of staff from each team will ensure all meters have a monthly check done, regenerate probes if necessary and a quarterly summary report will be compiled. This will ensure all meters have been calibrated properly and are in good working order.

The number of Winkler tests in Norfolk has been significantly increased so that there is now a Winkler test done at one routine monitoring point every month on each main river along with the field meter test. All staff performing Winkler tests must be fully trained in the correct procedures on filling the bottles to minimise erroneous results. An ongoing quarterly summary of the data will be compiled so that the results from each method can be continuously monitored and cross referenced with samplers calibration records.

### **References**

- <sup>1</sup> *'Practical Statistics for Field Biology', section 16.13 pages 176 and 210.*  
*Jim Fowler and Lou Cohen,*
- <sup>2</sup> *D/O Meter Evaluation Summary Report – April 1998*  
*A J Chappell*

# Appendix A

**R04BFBAT070**

River Bat at B1113 Road Bridge  
NGR 08000 55900

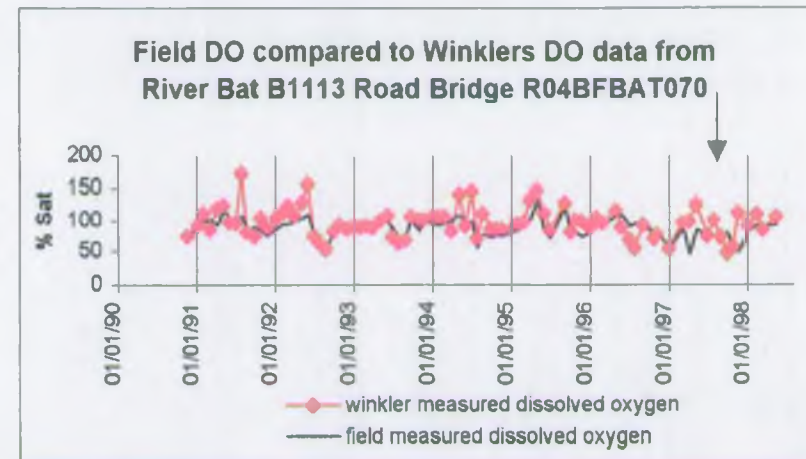
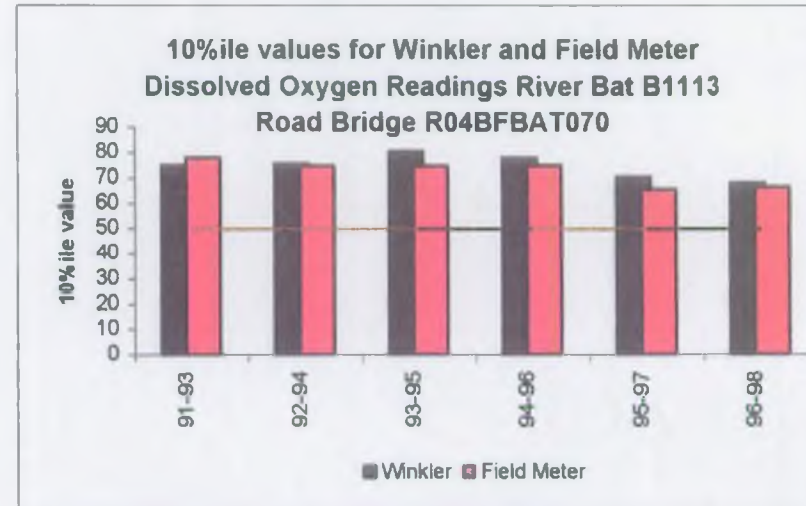
RE Target: 4  
DO Target: 50

	Winkler analysis result	Field meter reading	Ratio
	% SATN	% SATN	
N	84.0	84.0	1.00
MIN	48.9	46.0	0.94
MAX	173.0	173.0	1.00
MEAN	96.5	87.2	0.90
STD DEV	23.4	15.8	0.68

		Sig/Non Sig
r <sup>2</sup> value for whole period	0.370	NS
r <sup>2</sup> value prior to WTW (7/97)	0.458	NS
r <sup>2</sup> value after WTW (7/97 onwards)	0.052	NS

**Optimistic 10 percentile values**

Date range	Winkler	Field Meter
91-93	75.256	78.278
92-94	75.918	75.096
93-95	80.767	75.029
94-96	78.222	75.135
95-97	70.762	65.876
96-98	68.516	66.760





# Appendix A

R04BFBL010

River Blyth - Halesworth Thoroughfare  
NGR 38600 77600

RE Target: 3  
DO Target: 60

	Winkler analysis result	Field meter reading	Ratio
	% SATN	% SATN	
N	89.0	89.0	1.00
MIN	39.2	49.0	1.25
MAX	151.0	115.0	0.76
MEAN	88.6	84.6	0.96
STD DEV	18.8	11.8	0.63

r<sup>2</sup> value for whole period

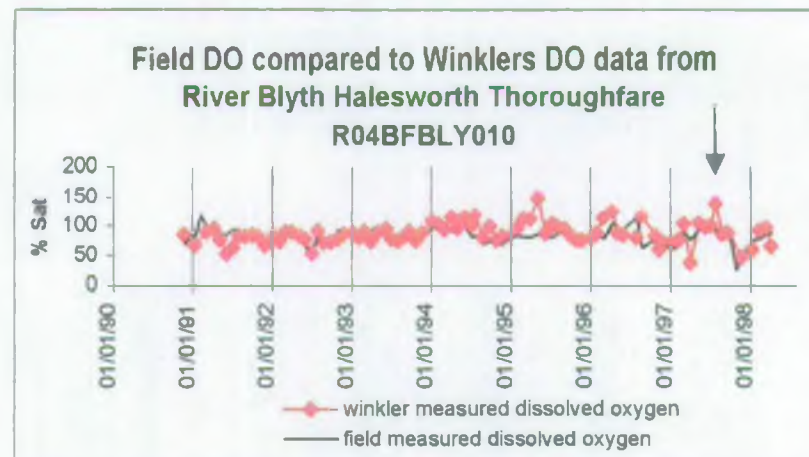
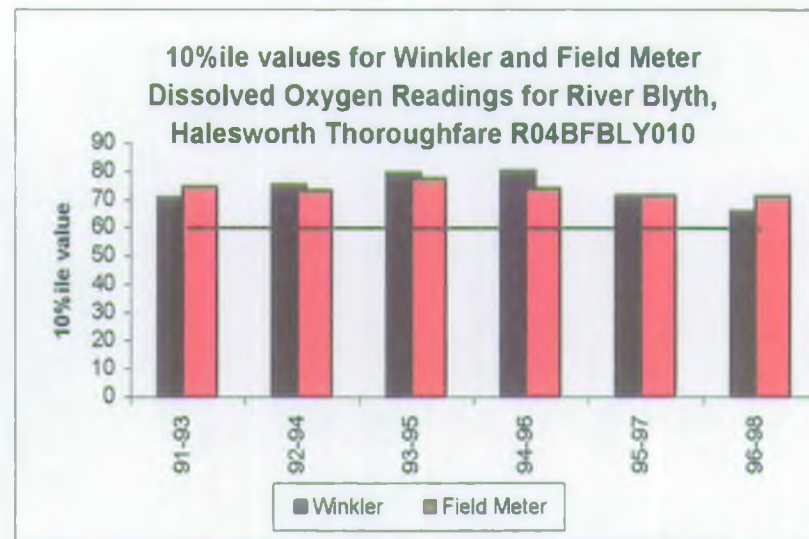
		Sig/Non Sig
r <sup>2</sup> value for whole period	0.169	NS
r <sup>2</sup> value prior to WTW (7/97)	0.089	NS
r <sup>2</sup> value after WTW (7/97 onwards)	0.422	NS

r<sup>2</sup> value prior to WTW (7/97)

r<sup>2</sup> value after WTW (7/97 onwards)

### Optimistic 10 percentile values

Date range	Winkler	Field Meter
91-93	71.258	74.794
92-94	75.592	73.769
93-95	79.908	77.817
94-96	80.622	74.469
95-97	71.934	71.885
96-98	66.329	71.611



**R04BFDEB030**

River Deben - Brandeston Bridge, Cretingham  
NGR 23800 60300

RE Target: 2  
DO Target: 70

	Winkler analysis result	Field meter reading	Ratio
	% SATN	% SATN	
N	89.0	89.0	1.00
MIN	21.2	10.5	0.50
MAX	187.0	162.0	0.87
MEAN	84.6	77.5	0.92
STD DEV	28.4	22.5	0.79

r<sup>2</sup> value for whole period

0.54 NS

r<sup>2</sup> value prior to WTW (7/97)

0.57 NS

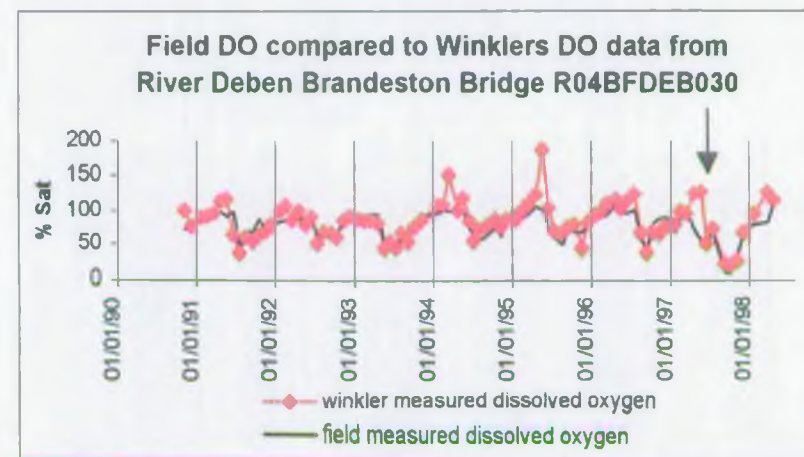
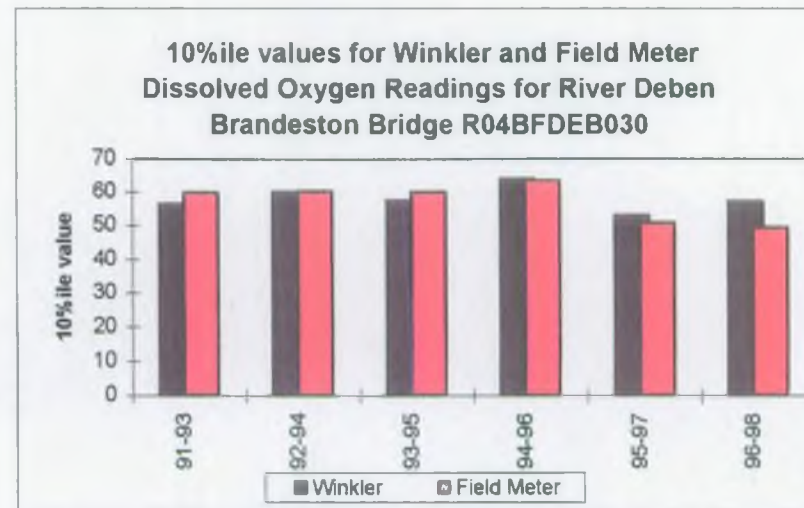
r<sup>2</sup> value after WTW (7/97 onwards)

0.58 S

Sig/Non Sig

**Optimistic 10 percentile values**

Date range	Winkler	Field Meter
91-93	58.471	59.958
92-94	60.176	60.408
93-95	57.631	60.091
94-96	64.357	63.587
95-97	53.264	50.959
96-98	57.360	49.663



Appendix A

R04BFDOV060

River Dove - Abbey Bridge, Eye  
NGR

RE Target: 3  
DO Target: 60

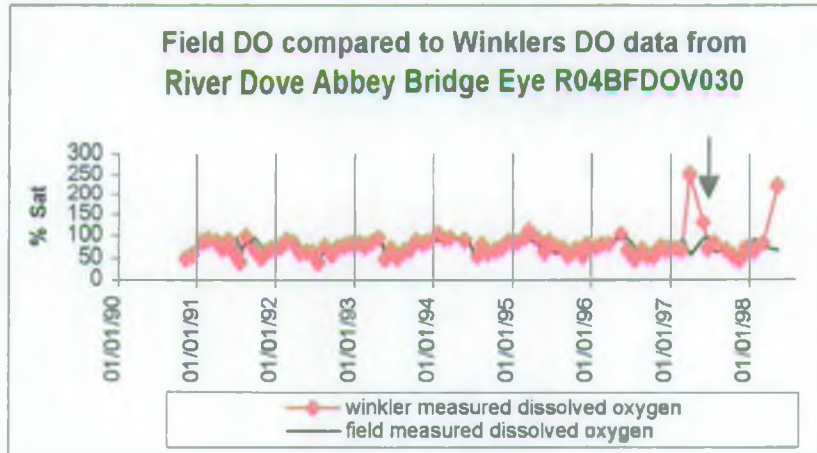
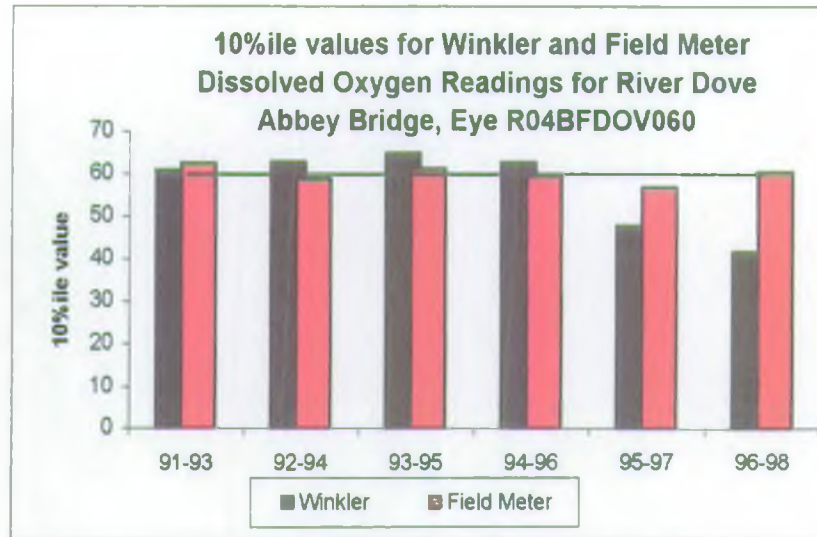
	Winkler analysis result	Field meter reading	Ratio
	% SATN	% SATN	
N	87.0	87.0	1.00
MIN	42.3	36.0	0.85
MAX	256.0	104.0	0.41
MEAN	80.1	75.2	0.94
STD DEV	30.4	16.4	0.54

Sig/Non Sig

$r^2$ value for whole period	0.051	NS
$r^2$ value prior to WTW (7/97)	0.476	NS
$r^2$ value after WTW (7/97 onwards)	0.021	NS

Optimistic 10 percentile values

Date range	Winkler	Field Meter
91-93	61.107	62.724
92-94	63.044	59.041
93-95	65.072	61.410
94-96	62.789	58.677
95-97	47.838	56.864
96-98	41.578	60.533



**R04BFFYN030**

River Fynn - Playford Bridge  
NGR21500 47700

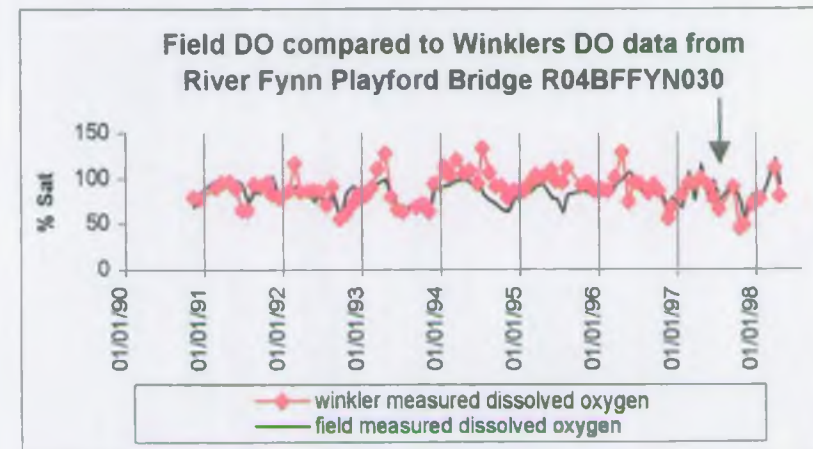
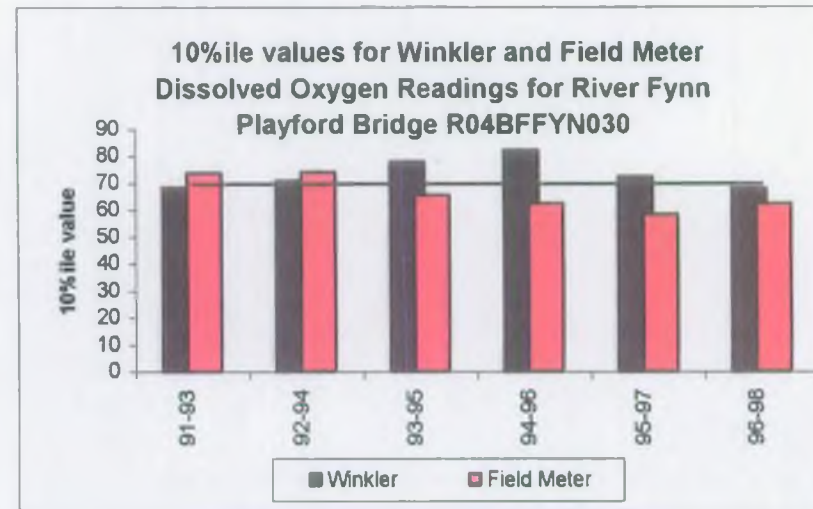
RE Target: 2  
DO Target: 70

	Winkler analysis result	Field meter reading	Ratio
	% SATN	% SATN	
N	88.0	88.0	1.00
MIN	46.5	56.0	1.20
MAX	134.0	122.0	0.91
MEAN	88.5	84.6	0.96
STD DEV	17.1	12.9	0.75

	Sig/Non Sig	
r <sup>2</sup> value for whole period	0.290	NS
r <sup>2</sup> value prior to WTW (7/97)	0.271	NS
r <sup>2</sup> value after WTW (7/97 onwards)	0.500	S

**Optimistic 10 percentile values**

Date range	Winkler	Field Meter
91-93	68.814	74.182
92-94	71.228	74.409
93-95	78.357	65.961
94-96	82.476	62.815
95-97	72.750	68.820
96-98	68.243	62.448



Appendix A

**R04BFGIP010**

River Gipping - Haughley Street, Old Newton  
NGR 04500 60400

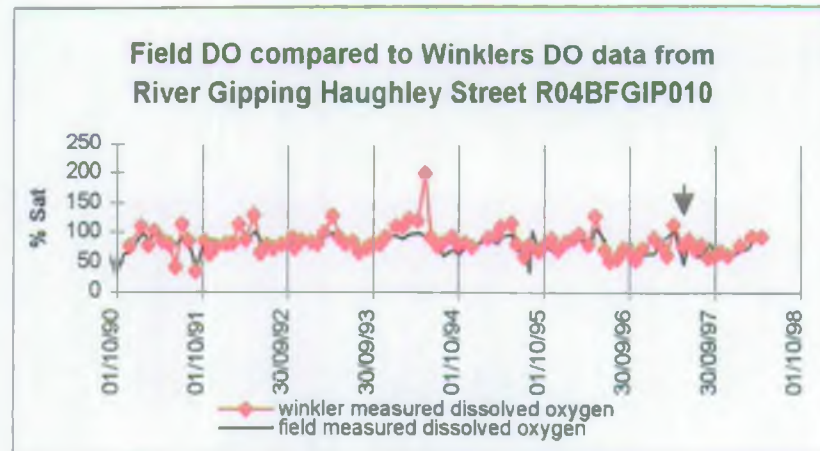
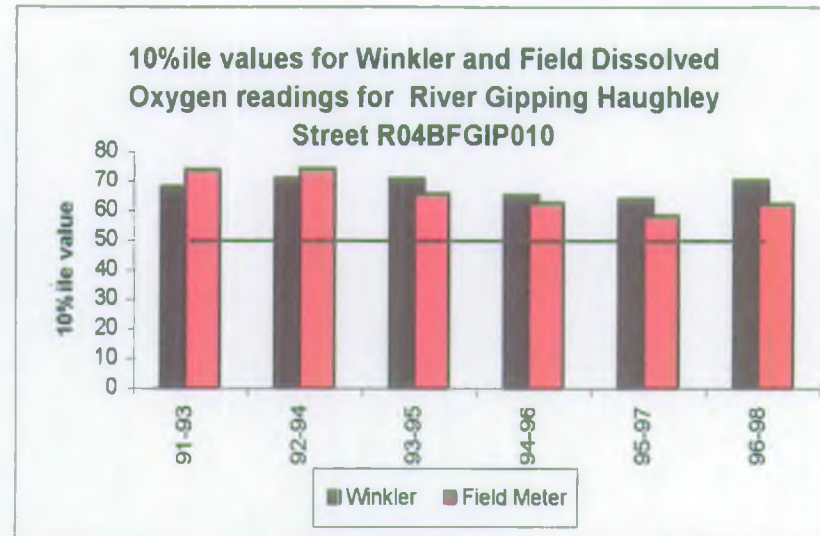
RE Target: 4  
DO Target: 50

	Winkler analysis result	Field meter reading	Ratio
	% SATN	% SATN	
N	90.0	90.0	1.00
MIN	37.4	34.0	0.91
MAX	201.0	108.0	0.54
MEAN	86.8	80.3	0.93
STD DEV	22.5	14.7	0.65

	Sig/Non Sig	
r <sup>2</sup> value for whole period	0.380	NS
r <sup>2</sup> value prior to WTW (7/97)	0.410	NS
r <sup>2</sup> value after WTW (7/97 onwards)	0.230	S

**Optimistic 10 percentile values**

Date range	Winkler	Field Meter
91-93	68.315	74.182
92-94	71.101	74.409
93-95	70.930	65.961
94-96	65.329	62.815
95-97	64.195	58.620
96-98	70.454	62.448



**R04BFGIP205**

River Gipping D/S Norwich Rail Bridge  
NGR TM14200 45000

RE Target: 2  
DO Target: 70

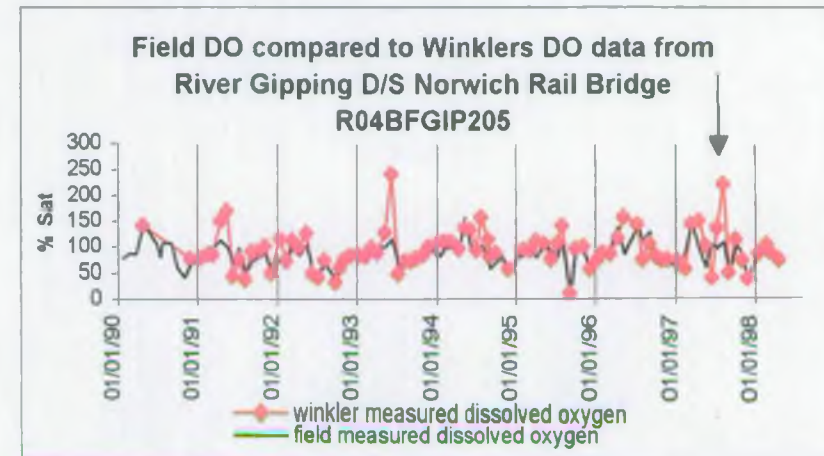
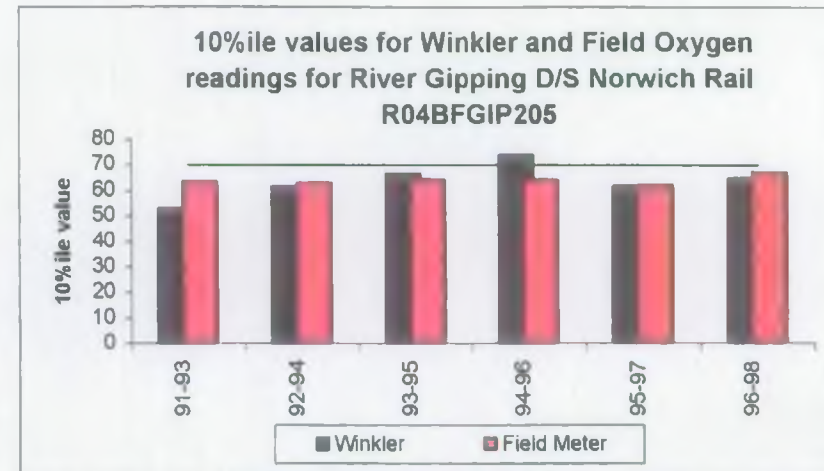
	Winkler analysis result	Field meter reading	Ratio
	% SATN	% SATN	
N	90.0	90.0	1.00
MIN	14.0	4.6	0.33
MAX	244.0	158.0	0.65
MEAN	97.5	86.9	0.89
STD DEV	37.2	24.9	0.67

Sig/Non Sig

r <sup>2</sup> value for whole period	0.460	NS
r <sup>2</sup> value prior to WTW (7/97)	0.520	NS
r <sup>2</sup> value after WTW (7/97 onwards)	0.535	S

**Optimistic 10 percentile values**

Date range	Winkler	Field Meter
91-93	53.145	63.703
92-94	61.801	63.437
93-95	66.643	64.387
94-96	74.224	64.422
95-97	62.037	62.227
96-98	64.783	67.122



**R04BFOAE047**

**Butley River - Butley Mill  
NGR TM38500 51700**

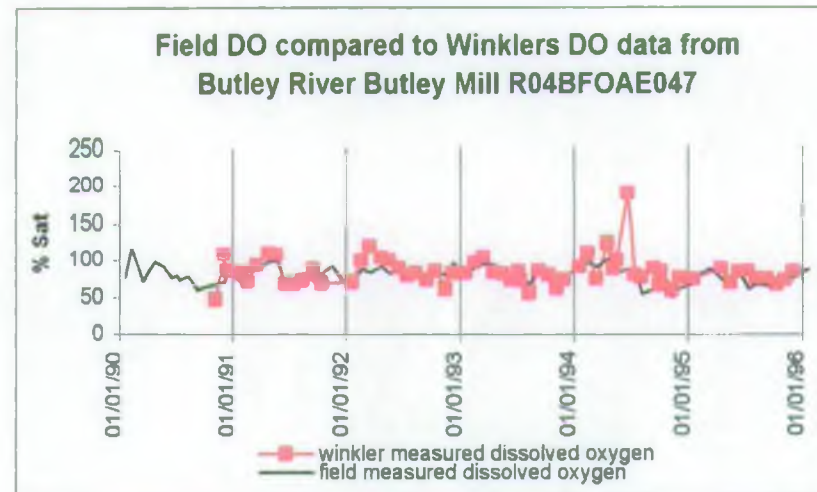
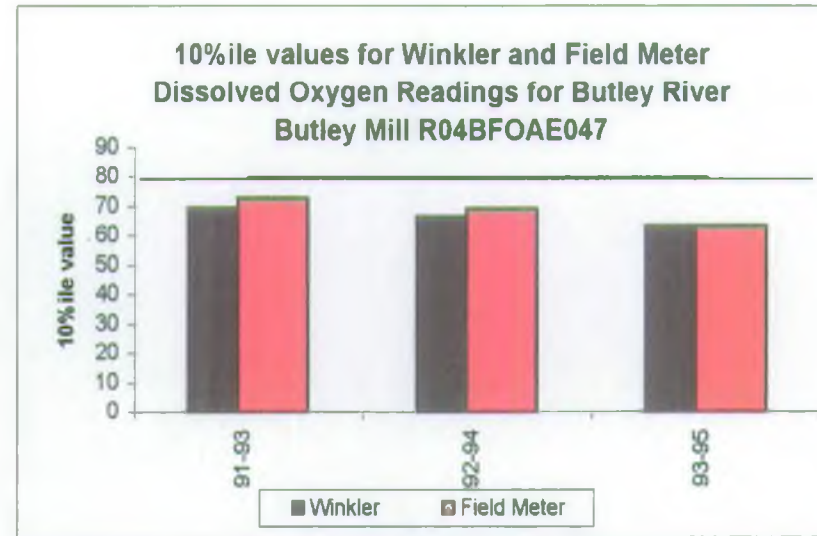
**RE Target: 1  
DO Target: 80**

	Winkler analysis result	Field meter reading	Ratio
	% SATN	% SATN	
N	61.0	61.0	1.00
MIN	55.7	50.0	0.90
MAX	193.0	104.0	0.54
MEAN	86.4	79.5	0.92
STD DEV	20.4	12.7	0.62

	Sig/ Non Sig	
r <sup>2</sup> value for whole period	0.228	NS
r <sup>2</sup> value prior to WTW (7/97)	0.228	NS

**Optimistic 10 percentile values**

Date range	Winkler	Field Meter
91-93	69.786	73.143
92-94	66.732	69.391
93-95	63.726	63.785



R04BFS202571

River Yare - Rail Bridge D/S Harford tip

NGR TG:22720:05190

RE Target:

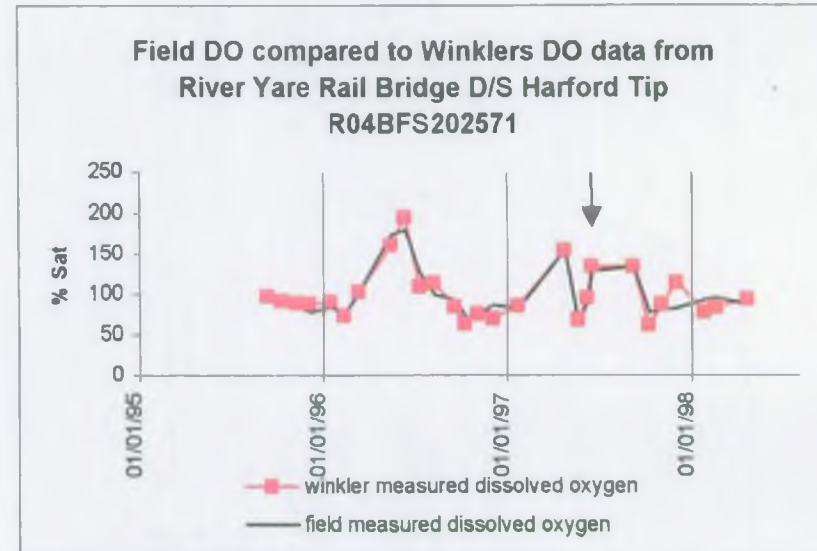
DO Target:

	Winkler analysis result	Field meter reading	Ratio
	% SATN	% SATN	
N	30.0	30.0	1.00
MIN	62.5	62.0	0.99
MAX	196.0	180.0	0.92
MEAN	99.8	99.3	1.00
STD DEV	30.3	28.9	0.95

	Sig/Non Sig	
r <sup>2</sup> value for whole period	0.915	S
r <sup>2</sup> value prior to WTW (7/97)	0.769	S
r <sup>2</sup> value after WTW (7/97 onwards)	0.796	S

**Optimistic 10 percentile values**

Date range	Winkler	Field Meter
95-97	72.875	72.427
96-98	70.011	71.731





**R04BFWAV116B**

River Waveney - Dukess Bridge

NGR

RE Target:

DO Target:

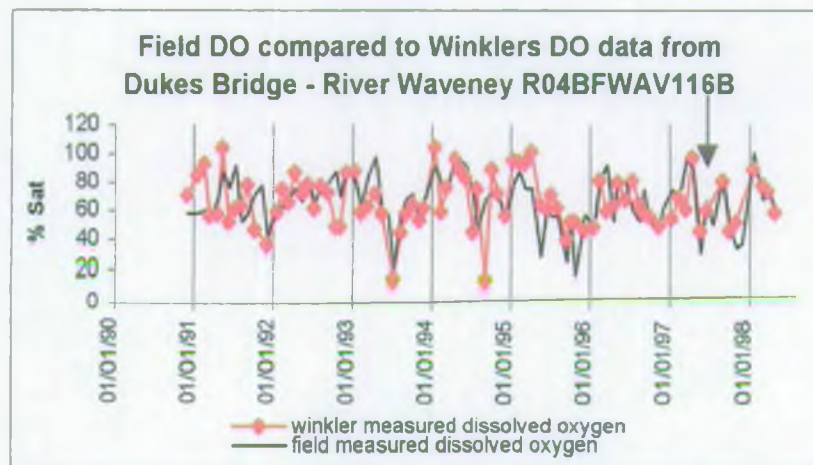
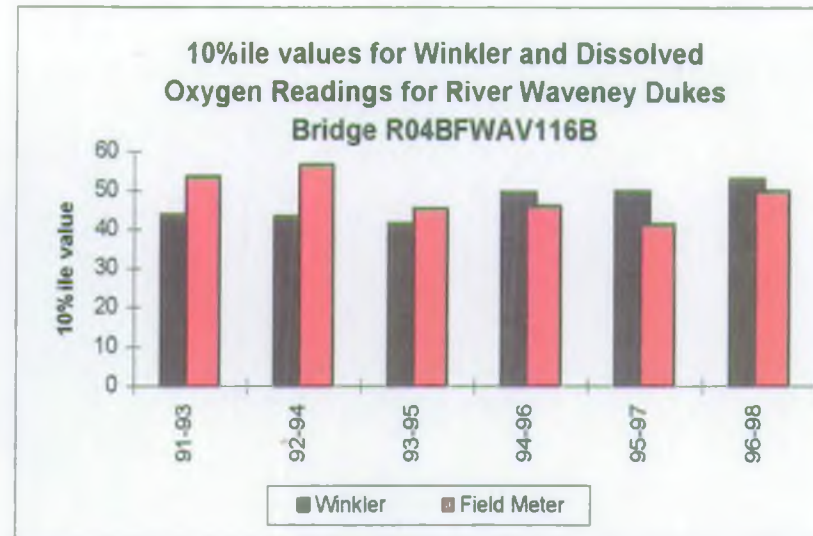
	Winkler analysis result	Field meter reading	Ratio
	% SATN	% SATN	
N	87.0	87.0	1.00
MIN	1.0	14.3	14.30
MAX	105.0	100.0	0.95
MEAN	66.5	67.2	1.01
STD DEV	19.5	18.1	0.93

Sig/Non Sig

$r^2$ value for whole period	0.297	NS
$r^2$ value prior to WTW (7/97)	0.260	NS
$r^2$ value after WTW (7/97 onwards)	0.560	NS

**Optimistic 10 percentile values**

Date range	Winkler	Field Meter
91-93	43.866	53.883
92-94	43.562	56.855
93-95	41.741	45.760
94-96	49.937	46.482
95-97	50.176	41.568
96-98	53.516	50.419



**R04BFWNG040**

River Wang - Hill Farm Bridge  
NGR TM:4610077900

RE Target: 3  
DO Target: 60

	Winkler analysis result	Field meter reading	Ratio
	% SATN	% SATN	
N	89.0	89.0	1.00
MIN	29.5	41.0	1.39
MAX	134.0	100.0	0.75
MEAN	76.5	73.9	0.97
STD DEV	16.3	13.7	0.84

		Sig/Non Sig
r <sup>2</sup> value for whole period	0.31	NS
r <sup>2</sup> value prior to WTW (7/97)	0.26	NS
r <sup>2</sup> value after WTW (7/97 onwards)	0.42	NS

**Optimistic 10 percentile values**

Date range	Winkler	Field Meter
91-93	60.497	65.819
92-94	60.232	63.176
93-95	65.606	63.604
94-96	65.651	62.909
95-97	61.014	57.379
96-98	57.201	54.589

