123 Main Street
White Plains, New York 10601
914 681.6200

NewYorkPower Authority

January 19, 1994

Mr. William Stiedle
New York State Department of
Environmental Conservation
Region No. 3
21 South Putt Corners Road
New Paltz, New York, 10601

Re: SPDES Modification Request Indian Point Unit No.3
(I.D. No. NY 000 4472) Continuous Chlorine Analyzer

Dear Mr. Stiedle:

In accordance with additional requirement No. 10 of the SPDES permit issued for the Indian Point Unit No.3 Nuclear Power Plant the Authority is submitting the attached report detailing the analysis of the suitability of continuous chlorine monitoring for compliance purposes. This report was compiled by the chemistry department at Indian Point Unit No.3.

The current instrument installed at Indian Point Unit No.3 has been in place since 1988. From the installation to the present time the unit has experienced numerous problems and shortcomings. The environment where installation of this equipment takes place, is severe and other operational problems tend to compound both the reliability and operational characteristics of the analyzer.

As part of this submission the Authority requests that the monitoring frequency be changed to include grab sampling in lieu of the continuous monitoring, and that this grab sampling be conducted in accordance with the conditions as defined by footnote "r" which states "Grab samples shall be taken at least once daily during low level service water chlorination...". In addition, the Authority requests that grab sampling during periods of condenser chlorination be substituted for continuous monitoring as found in footnote "q".

If you have any questions please contact John Kahabka at (914) 681-6308.

John W. Blake, Ph.D.
Director
Environmental Division

260006

cc: Mr. Paul Kolakowski NYSDEC

U.S. Nuclear Regulatory Commission
ATTN: Document Control Desk
Mail Station PI-137
Washington, DC 20555

IE23.

Mr. Thomas T. Martin
Regional Administrator
Region I
U.S. Nuclear Regulatory Commission
475 Allendale Road
King of Prussia, Pennsylvania 19406-1415

EVALUATION OF THE ORION MODEL 1770 CHLORINE ANALYZER

at The Indian Point 3
Nuclear Generating
Station.

List of References:

1. Evaluation of the Orion 1770 continuous Chlorine Monitor by Consolidated Edison Company of New York, Inc Sept 1985

2. Testing of ON-LINE RESIDUAL CHLORINE ANALYZERS
   S.G. Nutt and W. W. Schuk
   Canviro Consultants Ltd
   Water Engineering Research Laboratory
   July 24,1985

3. Zebra Mussel Control- Chlorination Monitoring
   Ontario Hydro December 1990

LIST OF ATTACHMENTS:

1. Manual Chlorine Titration Result minus Orion 1770 Result bar graph

2. Chlorine Manual vs Titration raw data graph

3. Statistical analysis t-test

4. Raw data tables including difference values

The State Pollution Discharge Elimination System (SPDES) permit for Indian Point 3 Nuclear Power Generating Station requires that a continuous chlorine mcnitor be installed in the discharge canal for total residual chlorine. A monitor has been installed since March of 1988. Several deficiencies have been observed since initial installation. This study presents the New York Power Authority's evaluation of the data collected, which compares the results of the continuous monitor to the grab sampling program. The data indicates that the monitor, an Orion model 1770, cannot be operated reliably, accurately and economically at the Indian Point 3 Generating Station.

The New York Power Authority installed, operated and evaluated an Orion 1770 since March of 1988. The initial installation utilized an Orion sample delivery system. Grab samples were collected from the sample line provided on the Orion 1770 and analyzed using the DPD FAS Titrimetric Method. Samples were collected from this location in order to provide a true comparison of results. In July of 1991, after replacing multiple sample and reagent pumps as well as electronic packages, a New York Power Authority designed sample delivery system was installed. This system operated with fewer complications.

The data evaluation comparing the Orion 1770 to the grab samples analyzed commenced in November of 1991 and lasted into July 1994. Included on the following pages are graphic representations of the collected data. These conclusions are based on that data:

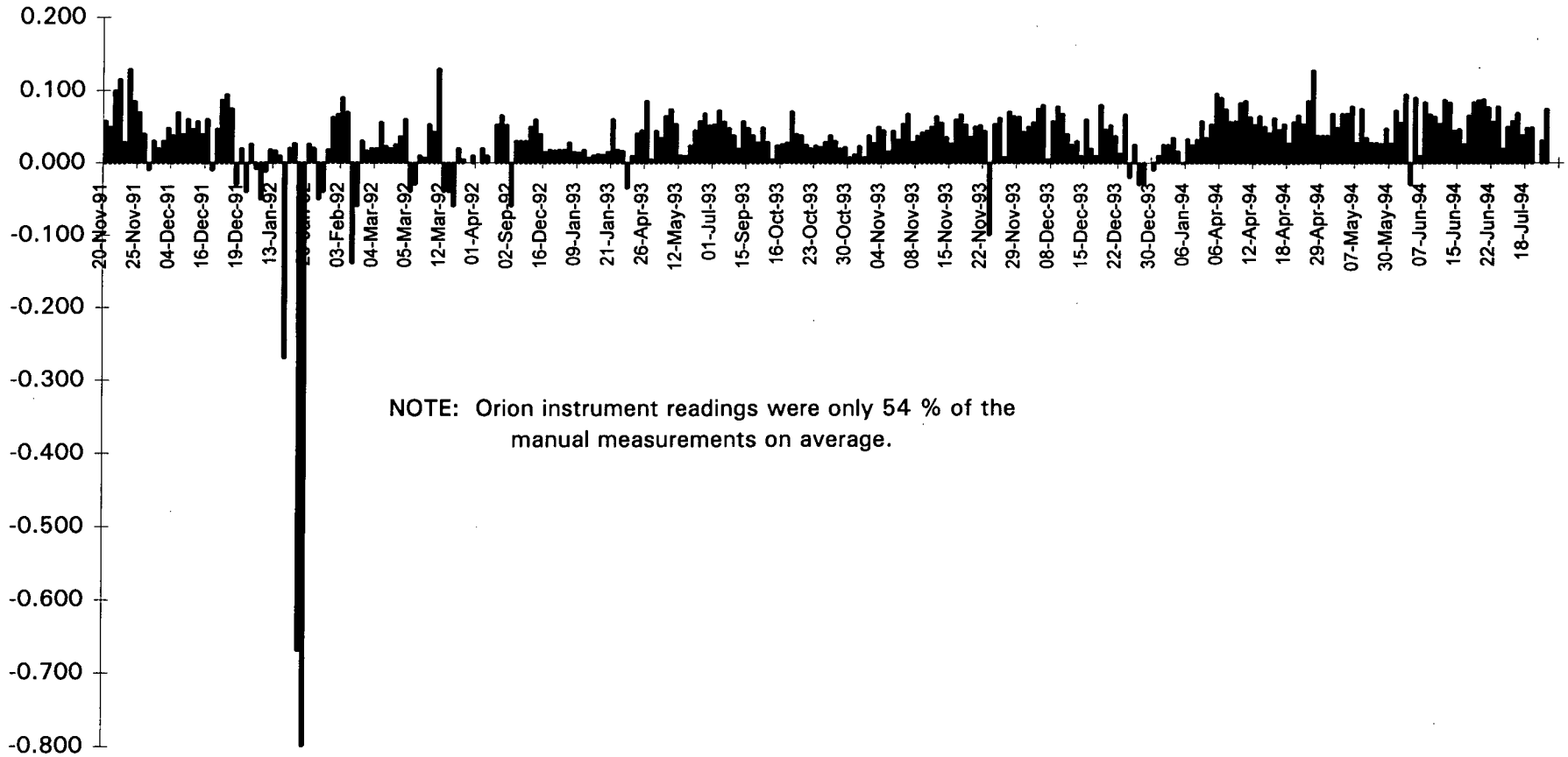
- The Orion 1770 data collected over the 2 year period was statistically different from the grab sample results.
- The Orion 1770 showed a negative bias averaging 45% over the period tested.
- For weeks at a time the instrument readings were less than the lowest mark (0.001 ppm) while manual measurements indicated >.01 ppm.
- The Orion 1770 produced unreliable, inaccurate results for the period reviewed.

Further investigation revealed that other companies have tested the Orion 1770 and similar results were obtained. These documents are listed in the references of this study.

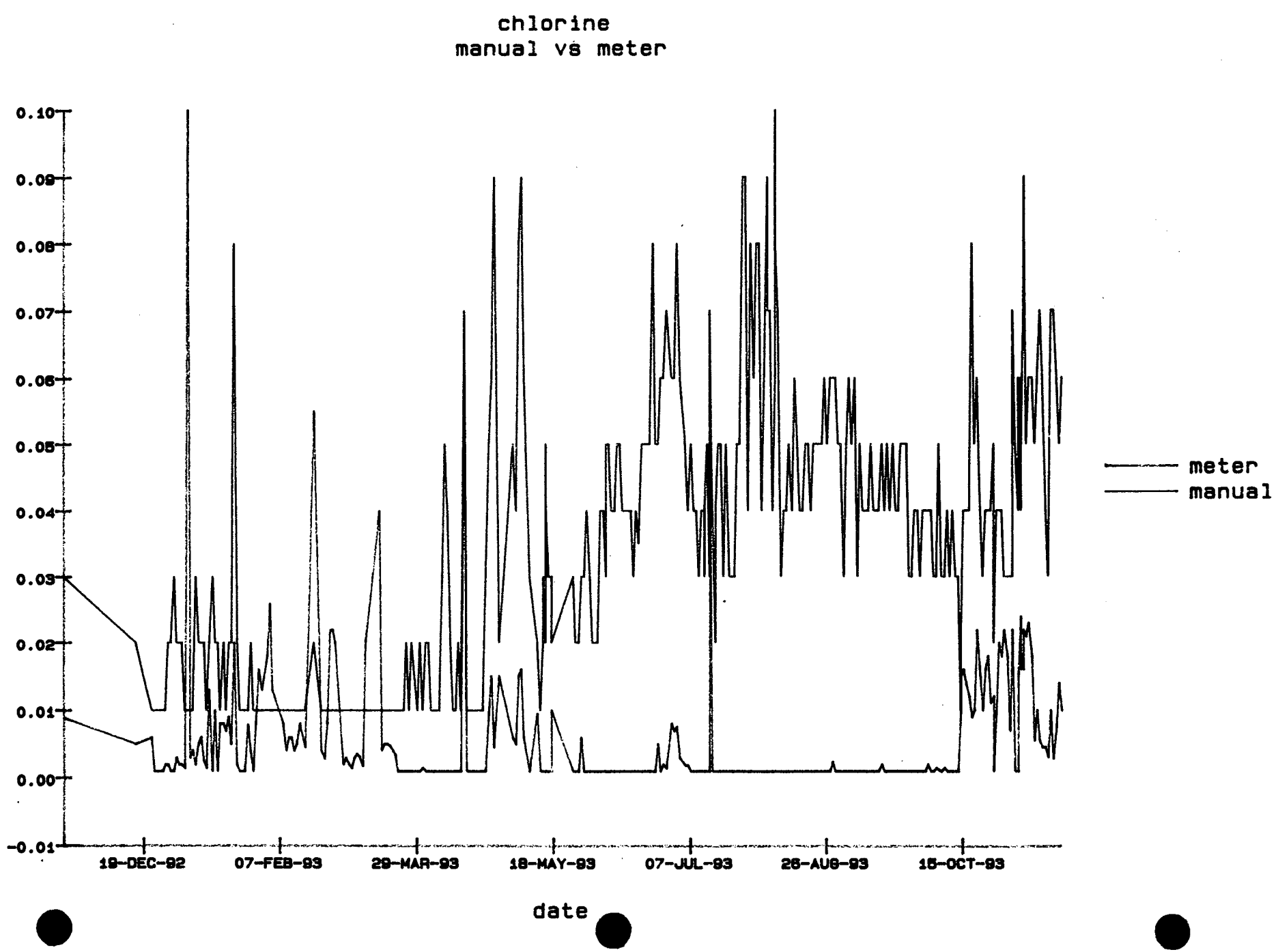
Conclusion and Recommendations

The Orion 1770 continuous TRC monitor cannot be operated reliably, accurately and economically at Indian Point 3 Generating Station. Accordingly, The New York Power Authority recommends that the SPDES permit requirements for continuous chlorine monitoring be replaced with site specific grab sampling programs to be mutually agreed on with the New York State Department of Environmental Conservation. Such programs should provide for representative compliance monitoring without being unduly burdensome.

Manual Titration Minus Orion Instrument Reading (ppm)



NOTE: Orion instrument readings were only 54 % of the manual measurements on average.


chlorine
manual vs meter
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
-0.01
conc
18-DEC-92
07-FEB-93
29-MAR-93
18-MAY-93
07-JUL-93
26-AUG-93
15-OCT-93
date
meter
manual

Method Comparison: Manual Chloride Titration vs. Chlorine Instrument

Data analysis performed by R. Cullen, September 2, 1994

A t-test was done on the paired data below based on Section 5.2.4 from the book Practical Statistics for Analytical Chemists by Robert L. Anderson.

The t-test will be used to test the null hypothesis that there is no statistically significant difference between the values generated by either analytical method.

$M := READPRN(chlor4_{dat})$

Column 0 represents manual titration results
Column 1 represents instrument results
Column 2 represents the manual result minus the instrument result

Only the first 17 data points are displayed.

$M =$

	0	1	2
0	0.08	0.022	0.058
1	0.08	0.03	0.05
2	0.14	0.04	0.1
3	0.15	0.035	0.115
4	0.03	0.001	0.029
5	0.14	0.011	0.129
6	0.17	0.085	0.085
7	0.17	0.1	0.07
8	0.14	0.1	0.04
9	0.11	0.12	-0.01
10	0.16	0.13	0.03
11	0.19	0.17	0.02
12	0.19	0.16	0.03
13	0.05	0.002	0.048
14	0.04	0.002	0.038
15	0.12	0.05	0.07
16	0.08	0.04	0.04

$n := length(M^{<2>})$ $n = 296$ # of samples

$df := n - 1$ $df = 295$ degrees of freedom

$i := 0..295$

$d := M^{<2>}$ assigns the variable d to col 2 of matrix

$d_{avg} := mean(d)$

$d_{avg} = 0.031$

calculates the average difference between data pairings

$$s_d := \sqrt{\frac{\sum_{i=0}^{295} (d_i)^2 - \frac{\left(\sum_{i=0}^{295} d_i\right)^2}{n}}{n-1}}$$

calculates the standard deviation of the differences between the pairs of observations

$s_d = 0.074$

$t := \frac{d_{avg}}{s_d} \cdot \sqrt{n}$ $t = 7.127$ calculates the t-value for the data differences

t(.05/2,295) = 1.96 This is the critical t-value for a two tailed test with alpha of 0.05 and 295 degrees of freedom. Since the critical t-value is exceeded, we reject the null hypothesis and conclude that the two methods give different chlorine concentrations.

The following 296 data points were extracted from the original 629 point data set. The extraction criteria eliminated data points where the instrument values were 0.001 ppm or less and/or manual titration values were 0.010 ppm or less.

These values were selected because they represent the minimum detectable for each method.

Indian Point 3 Discharge Canal Chlorine Measurements

Date	Instrument (ppm)	Manual Titration (ppm)	Manual minus Instrument (ppm)			
20-Nov-91	0.022	0.080	0.058			
20-Nov-91	0.030	0.080	0.050			
21-Nov-91	0.040	0.140	0.100			
21-Nov-91	0.035	0.150	0.115			
21-Nov-91	0.001	0.030	0.029			
25-Nov-91	0.011	0.140	0.129			
25-Nov-91	0.085	0.170	0.085			
25-Nov-91	0.100	0.170	0.070			
25-Nov-91	0.100	0.140	0.040			
27-Nov-91	0.120	0.110	-0.010			
27-Nov-91	0.130	0.160	0.030			
27-Nov-91	0.170	0.190	0.020			
27-Nov-91	0.160	0.190	0.030			
27-Nov-91	0.002	0.050	0.048			
04-Dec-91	0.002	0.040	0.038			
04-Dec-91	0.050	0.120	0.070			
04-Dec-91	0.040	0.080	0.040			
04-Dec-91	0.060	0.120	0.060			
04-Dec-91	0.003	0.050	0.047			
05-Dec-91	0.003	0.060	0.057			
05-Dec-91	0.150	0.190	0.040			
16-Dec-91	0.030	0.090	0.060			
16-Dec-91	0.130	0.120	-0.010			
18-Dec-91	0.003	0.050	0.047			
18-Dec-91	0.003	0.090	0.087			
18-Dec-91	0.005	0.100	0.095			
18-Dec-91	0.005	0.080	0.075			
19-Dec-91	0.100	0.070	-0.030			
19-Dec-91	0.130	0.150	0.020			
19-Dec-91	0.100	0.060	-0.040			
09-Jan-92	0.004	0.030	0.026			
09-Jan-92	0.058	0.050	-0.008			
09-Jan-92	0.110	0.060	-0.050			
09-Jan-92	0.082	0.070	-0.012			
09-Jan-92	0.012	0.030	0.018			
13-Jan-92	0.003	0.020	0.017			
13-Jan-92	0.120	0.130	0.010			
13-Jan-92	0.410	0.140	-0.270			
13-Jan-92	0.010	0.030	0.020			

Indian Point 3 Discharge Canal Chlorine Measurements						
Date	Instrument (ppm)	Manual Titration (ppm)	Manual minus Instrument (ppm)			
15-Jan-92	0.003	0.030	0.027			
15-Jan-92	0.850	0.180	-0.670			
15-Jan-92	0.980	0.180	-0.800			
20-Jan-92	0.004	0.030	0.026			
20-Jan-92	0.140	0.160	0.020			
20-Jan-92	0.110	0.060	-0.050			
20-Jan-92	0.110	0.070	-0.040			
03-Feb-92	0.002	0.020	0.019			
03-Feb-92	0.007	0.070	0.063			
03-Feb-92	0.003	0.070	0.067			
03-Feb-92	0.010	0.100	0.090			
13-Feb-92	0.100	0.170	0.070			
13-Feb-92	0.200	0.060	-0.140			
13-Feb-92	0.160	0.100	-0.060			
13-Feb-92	0.170	0.200	0.030			
13-Feb-92	0.004	0.020	0.017			
04-Mar-92	0.020	0.040	0.020			
04-Mar-92	0.030	0.050	0.020			
04-Mar-92	0.010	0.066	0.056			
04-Mar-92	0.007	0.030	0.023			
04-Mar-92	0.010	0.030	0.020			
05-Mar-92	0.005	0.030	0.025			
05-Mar-92	0.004	0.040	0.036			
05-Mar-92	0.080	0.140	0.060			
05-Mar-92	0.130	0.090	-0.040			
05-Mar-92	0.130	0.100	-0.030			
05-Mar-92	0.080	0.090	0.010			
05-Mar-92	0.023	0.030	0.007			
12-Mar-92	0.007	0.060	0.053			
12-Mar-92	0.007	0.050	0.043			
12-Mar-92	0.050	0.180	0.130			
12-Mar-92	0.210	0.170	-0.040			
12-Mar-92	0.200	0.160	-0.040			
12-Mar-92	0.200	0.140	-0.060			
12-Mar-92	0.020	0.040	0.020			
26-Mar-92	0.015	0.020	0.005			
26-Mar-92	0.200	0.200	0.000			
26-Mar-92	0.090	0.100	0.010			
01-Apr-92	0.080	0.080	0.000			
02-Apr-92	0.050	0.070	0.020			
24-Apr-92	0.070	0.080	0.010			
25-Apr-92	0.070	0.070	0.000			
24-Jul-92	0.002	0.055	0.053			
24-Jul-92	0.005	0.070	0.066			
24-Jul-92	0.003	0.055	0.053			

Indian Point 3 Discharge Canal Chlorine Measurements						
Date	Instrument (ppm)	Manual Titration (ppm)	Manual minus Instrument (ppm)			
02-Sep-92	0.130	0.070	-0.060			
02-Sep-92	0.050	0.080	0.030			
02-Sep-92	0.050	0.080	0.030			
02-Sep-92	0.050	0.080	0.030			
02-Sep-92	0.060	0.110	0.050			
02-Sep-92	0.040	0.100	0.060			
02-Sep-92	0.020	0.060	0.040			
16-Dec-92	0.005	0.020	0.015			
28-Dec-92	0.002	0.020	0.018			
31-Dec-92	0.003	0.020	0.017			
01-Jan-93	0.002	0.020	0.018			
02-Jan-93	0.002	0.020	0.018			
07-Jan-93	0.002	0.030	0.028			
08-Jan-93	0.005	0.020	0.015			
09-Jan-93	0.006	0.020	0.014			
10-Jan-93	0.003	0.020	0.018			
12-Jan-93	0.013	0.020	0.007			
14-Jan-93	0.010	0.020	0.010			
17-Jan-93	0.008	0.020	0.012			
19-Jan-93	0.009	0.020	0.011			
20-Jan-93	0.005	0.020	0.015			
21-Jan-93	0.020	0.080	0.060			
22-Jan-93	0.002	0.020	0.018			
27-Jan-93	0.004	0.020	0.016			
19-Feb-93	0.055	0.020	-0.035			
15-Apr-93	0.060	0.070	0.010			
24-Apr-93	0.009	0.050	0.041			
25-Apr-93	0.015	0.060	0.045			
26-Apr-93	0.005	0.090	0.086			
28-Apr-93	0.015	0.020	0.005			
03-May-93	0.006	0.050	0.044			
04-May-93	0.005	0.040	0.035			
05-May-93	0.015	0.080	0.065			
06-May-93	0.016	0.090	0.074			
07-May-93	0.006	0.060	0.054			
12-May-93	0.010	0.020	0.011			
17-May-93	0.010	0.020	0.010			
28-May-93	0.006	0.030	0.024			
25-Jun-93	0.005	0.050	0.045			
27-Jun-93	0.002	0.060	0.058			
28-Jun-93	0.002	0.070	0.069			
30-Jun-93	0.008	0.060	0.052			
01-Jul-93	0.007	0.060	0.053			
02-Jul-93	0.008	0.080	0.073			
03-Jul-93	0.003	0.060	0.057			

Indian Point 3 Discharge Canal Chlorine Measurements						
Date	Instrument (ppm)	Manual Titration (ppm)	Manual minus Instrument (ppm)			
05-Jul-93	0.002	0.050	0.048			
06-Jul-93	0.002	0.040	0.038			
14-Jul-93	0.050	0.070	0.020			
28-Aug-93	0.002	0.060	0.058			
15-Sep-93	0.002	0.050	0.048			
02-Oct-93	0.002	0.040	0.038			
05-Oct-93	0.002	0.030	0.029			
06-Oct-93	0.001	0.050	0.049			
08-Oct-93	0.002	0.030	0.029			
14-Oct-93	0.015	0.020	0.005			
15-Oct-93	0.016	0.040	0.024			
16-Oct-93	0.014	0.040	0.026			
17-Oct-93	0.012	0.040	0.028			
18-Oct-93	0.009	0.080	0.071			
19-Oct-93	0.010	0.050	0.040			
20-Oct-93	0.022	0.060	0.038			
21-Oct-93	0.015	0.040	0.025			
22-Oct-93	0.010	0.030	0.020			
23-Oct-93	0.016	0.040	0.024			
24-Oct-93	0.018	0.040	0.022			
25-Oct-93	0.011	0.040	0.029			
26-Oct-93	0.012	0.050	0.038			
27-Oct-93	0.010	0.040	0.030			
28-Oct-93	0.020	0.040	0.020			
29-Oct-93	0.018	0.040	0.022			
30-Oct-93	0.022	0.030	0.008			
31-Oct-93	0.018	0.030	0.012			
01-Nov-93	0.007	0.030	0.023			
02-Nov-93	0.022	0.030	0.008			
02-Nov-93	0.022	0.060	0.038			
02-Nov-93	0.022	0.050	0.028			
02-Nov-93	0.020	0.070	0.050			
04-Nov-93	0.015	0.060	0.045			
05-Nov-93	0.024	0.040	0.016			
05-Nov-93	0.016	0.060	0.044			
05-Nov-93	0.018	0.050	0.032			
06-Nov-93	0.016	0.070	0.054			
06-Nov-93	0.022	0.090	0.068			
07-Nov-93	0.021	0.050	0.029			
08-Nov-93	0.023	0.060	0.037			
09-Nov-93	0.018	0.060	0.042			
10-Nov-93	0.006	0.050	0.045			
11-Nov-93	0.010	0.060	0.050			
12-Nov-93	0.006	0.070	0.065			
13-Nov-93	0.005	0.060	0.056			

Indian Point 3 Discharge Canal Chlorine Measurements						
Date	Instrument (ppm)	Manual Titration (ppm)	Manual minus Instrument (ppm)			
14-Nov-93	0.005	0.040	0.036			
15-Nov-93	0.003	0.030	0.027			
16-Nov-93	0.010	0.070	0.060			
17-Nov-93	0.003	0.070	0.067			
18-Nov-93	0.007	0.060	0.053			
19-Nov-93	0.014	0.050	0.036			
20-Nov-93	0.010	0.060	0.050			
21-Nov-93	0.008	0.060	0.052			
22-Nov-93	0.006	0.050	0.044			
23-Nov-93	0.130	0.030	-0.100			
24-Nov-93	0.007	0.060	0.054			
25-Nov-93	0.018	0.080	0.062			
26-Nov-93	0.012	0.020	0.008			
27-Nov-93	0.010	0.080	0.071			
28-Nov-93	0.006	0.070	0.065			
29-Nov-93	0.007	0.070	0.064			
30-Nov-93	0.022	0.065	0.043			
01-Dec-93	0.020	0.070	0.050			
02-Dec-93	0.014	0.070	0.056			
03-Dec-93	0.025	0.100	0.075			
04-Dec-93	0.020	0.100	0.080			
06-Dec-93	0.025	0.030	0.005			
08-Dec-93	0.022	0.080	0.058			
09-Dec-93	0.032	0.110	0.078			
10-Dec-93	0.032	0.100	0.068			
11-Dec-93	0.060	0.100	0.040			
12-Dec-93	0.065	0.090	0.025			
13-Dec-93	0.070	0.100	0.030			
14-Dec-93	0.080	0.090	0.010			
15-Dec-93	0.020	0.080	0.060			
16-Dec-93	0.080	0.100	0.020			
17-Dec-93	0.080	0.090	0.010			
18-Dec-93	0.030	0.110	0.080			
19-Dec-93	0.004	0.050	0.046			
20-Dec-93	0.028	0.080	0.052			
21-Dec-93	0.013	0.050	0.037			
22-Dec-93	0.032	0.045	0.013			
23-Dec-93	0.003	0.070	0.067			
24-Dec-93	0.100	0.080	-0.020			
25-Dec-93	0.075	0.100	0.025			
26-Dec-93	0.090	0.060	-0.030			
28-Dec-93	0.100	0.070	-0.030			
29-Dec-93	0.050	0.050	0.000			
30-Dec-93	0.060	0.050	-0.010			
31-Dec-93	0.030	0.040	0.010			

Indian Point 3 Discharge Canal Chlorine Measurements						
Date	Instrument (ppm)	Manual Titration (ppm)	Manual minus Instrument (ppm)			
01-Jan-94	0.045	0.070	0.025			
02-Jan-94	0.035	0.060	0.025			
03-Jan-94	0.055	0.090	0.035			
04-Jan-94	0.024	0.040	0.016			
05-Jan-94	0.021	0.020	-0.001			
06-Jan-94	0.017	0.050	0.033			
07-Jan-94	0.025	0.050	0.025			
01-Apr-94	0.018	0.050	0.032			
02-Apr-94	0.022	0.080	0.058			
03-Apr-94	0.025	0.060	0.035			
04-Apr-94	0.007	0.060	0.054			
05-Apr-94	0.014	0.110	0.096			
06-Apr-94	0.010	0.100	0.090			
07-Apr-94	0.006	0.080	0.075			
07-Apr-94	0.003	0.060	0.057			
08-Apr-94	0.002	0.060	0.058			
09-Apr-94	0.007	0.090	0.083			
10-Apr-94	0.004	0.090	0.086			
11-Apr-94	0.007	0.070	0.064			
12-Apr-94	0.007	0.060	0.053			
13-Apr-94	0.005	0.070	0.065			
14-Apr-94	0.010	0.060	0.050			
15-Apr-94	0.008	0.050	0.042			
15-Apr-94	0.008	0.070	0.062			
16-Apr-94	0.004	0.050	0.046			
17-Apr-94	0.007	0.060	0.054			
18-Apr-94	0.003	0.030	0.028			
19-Apr-94	0.003	0.060	0.057			
20-Apr-94	0.004	0.070	0.066			
21-Apr-94	0.006	0.060	0.054			
25-Apr-94	0.004	0.090	0.086			
27-Apr-94	0.002	0.130	0.128			
28-Apr-94	0.002	0.040	0.038			
29-Apr-94	0.002	0.040	0.038			
30-Apr-94	0.002	0.040	0.038			
01-May-94	0.002	0.070	0.069			
03-May-94	0.001	0.050	0.049			
04-May-94	0.002	0.070	0.068			
05-May-94	0.002	0.070	0.068			
06-May-94	0.002	0.080	0.078			
07-May-94	0.002	0.030	0.028			
08-May-94	0.005	0.080	0.075			
09-May-94	0.005	0.040	0.035			
14-May-94	0.002	0.030	0.028			
15-May-94	0.002	0.030	0.028			

Indian Point 3 Discharge Canal Chlorine Measurements						
Date	Instrument (ppm)	Manual Titration (ppm)	Manual minus Instrument (ppm)			
16-May-94	0.004	0.030	0.027			
29-May-94	0.003	0.050	0.048			
30-May-94	0.003	0.030	0.027			
31-May-94	0.008	0.080	0.073			
01-Jun-94	0.004	0.060	0.056			
02-Jun-94	0.015	0.110	0.095			
03-Jun-94	0.120	0.090	-0.030			
04-Jun-94	0.020	0.110	0.090			
05-Jun-94	0.070	0.080	0.010			
07-Jun-94	0.006	0.090	0.084			
08-Jun-94	0.023	0.090	0.067			
09-Jun-94	0.006	0.070	0.064			
10-Jun-94	0.006	0.060	0.054			
11-Jun-94	0.003	0.090	0.087			
12-Jun-94	0.006	0.090	0.084			
14-Jun-94	0.005	0.050	0.045			
15-Jun-94	0.004	0.050	0.047			
16-Jun-94	0.004	0.030	0.026			
17-Jun-94	0.005	0.070	0.066			
18-Jun-94	0.006	0.090	0.084			
19-Jun-94	0.004	0.090	0.087			
20-Jun-94	0.002	0.090	0.088			
21-Jun-94	0.003	0.080	0.077			
22-Jun-94	0.003	0.060	0.057			
30-Jun-94	0.002	0.080	0.078			
05-Jul-94	0.030	0.050	0.020			
06-Jul-94	0.040	0.090	0.050			
12-Jul-94	0.002	0.060	0.058			
16-Jul-94	0.001	0.070	0.069			
17-Jul-94	0.002	0.040	0.039			
18-Jul-94	0.002	0.050	0.049			
18-Jul-94	0.001	0.050	0.049			
Average	0.037	0.068	0.031			
Std Dev	0.087	0.038	0.074			