Appendix 7. Laboratory Comparison between StablCal and multiple lots of Polymer Turbidity Standard using natural sediment and water (from the Neosho River at Neosho Rapids, Kansas, U.S. Geological Survey [USGS] station number 07182390) at the Kansas Water Science Center Laboratory, Lawrence, Kansas on September 7, 2017

Comparison Description

Station name: Kansas Water Science Center laboratory, Lawrence, Kansas.

Equipment: Two Yellow Springs Instrument (YSI) EXO water-quality monitors, one equipped with two YSI EXO turbidity sensors calibrated in polymer standard and one equipped with one YSI EXO turbidity sensor calibrated in StablCal standard were deployed in a laboratory turbidity testing apparatus for comparison between the standards. (See "Performance Evaluation Tests," "Laboratory Tests," p. 7 of main report, for a full description of laboratory methods.) The Hach model 2100AN laboratory turbidimeter with a flow-through cell was used as a reference to measure the turbidity in the apparatus bucket every 15 minutes before adding more sediment. No datum corrections were applied to either dataset.

Testing material and water: Sediment and water from Neosho River at Neosho Rapids, Kansas (U.S. Geological Survey [USGS] station number 07182390).

Calibration standard used: One sensor was calibrated with Hach StablCal turbidity standard and two sensors calibrated with YSI polymer standard.

Laboratory comparison date: September 7, 2017.

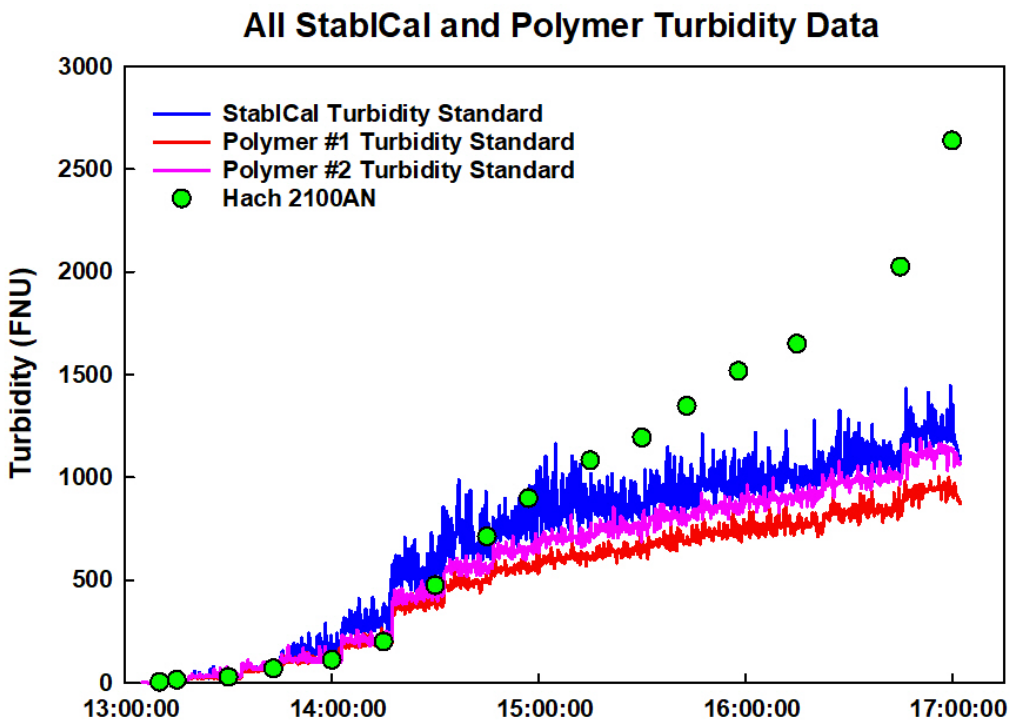
Datasets

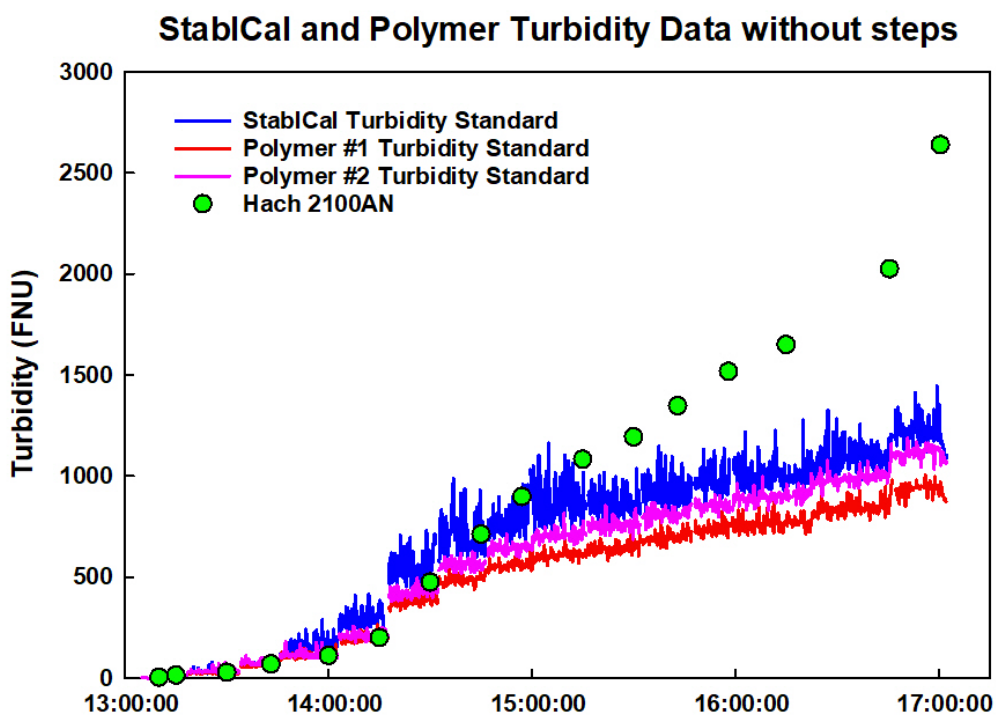
All data were collected using U.S. Geological Survey [USGS] protocols (U.S. Geological Survey, variously dated) and are published in King (2021). Data were edited to remove periods where material was added to the testing apparatus, leaving the steady-state data for analysis.

Polymer Standard Identification

	124 FNU Lot Number	1,010 FNU Lot Number
Polymer #1	17H798860	17H797418
Polymer #2	17E796816	17E794976

Time Series


All StablCal and Polymer Turbidity Data
StablCal Turbidity Standard
Polymer #1 Turbidity Standard
Polymer #2 Turbidity Standard
Hach 2100AN
Turbidity (FNU)
3000
2500
2000
1500
1000
500
0
13:00:00
14:00:00
15:00:00
16:00:00
17:00:00


StablCal and Polymer Turbidity Data without steps
StablCal Turbidity Standard
Polymer #1 Turbidity Standard
Polymer #2 Turbidity Standard
Hach 2100AN
Turbidity (FNU)
3000
2500
2000
1500
1000
500
0
13:00:00
14:00:00
15:00:00
16:00:00
17:00:00

Statistical Analyses - StablCal and Polymer #1 Data

Slope comparison

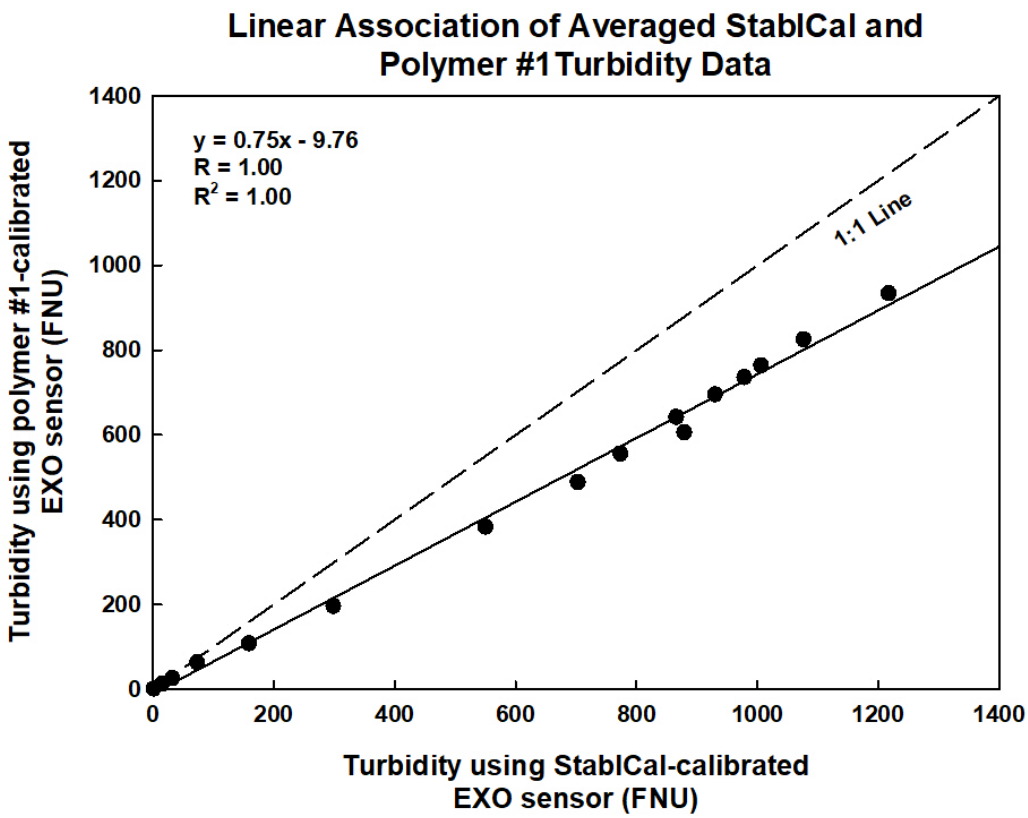
The following is a summary of final regression analysis for sensor-measured turbidity from one YSI EXO turbidity sensor calibrated by using StablCal turbidity standard and one YSI EXO turbidity sensor calibrated by using polymer #1 turbidity standard at the Kansas Water Science Center laboratory, Lawrence, Kansas, on September 7, 2017; the data used in the final regressions were averages of turbidity for each step, each of which had a duration of approximately 15 minutes once the sensor had stabilized:

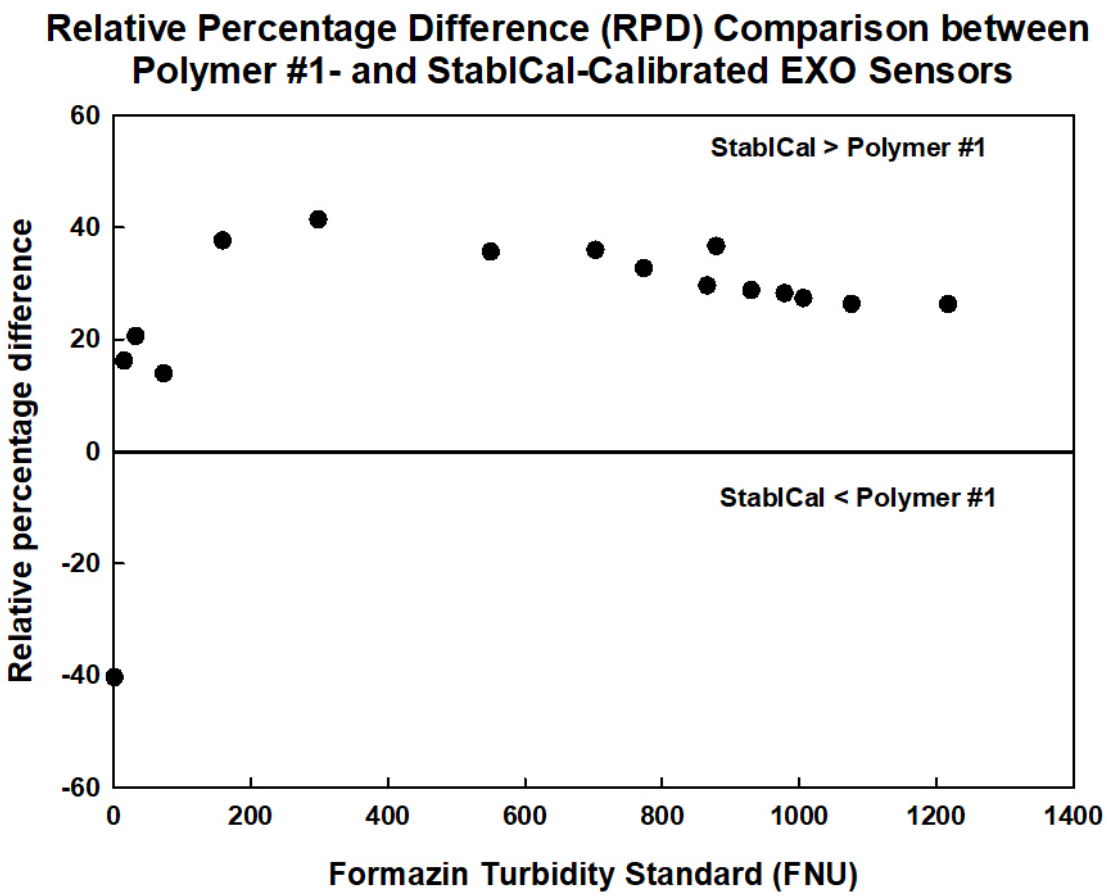
$$y = 0.75x - 9.76$$

where

y = turbidity measured with polymer #1-calibrated EXO sensor (FNU)

x = turbidity measured with StablCal-calibrated EXO sensor (FNU).





Wilcoxon Signed-Rank Test for StablCal and Polymer #1 Data

SigmaPlot Statistical Output:

Normality Test (Shapiro-Wilk): Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
StablCal	16	0	738.304	94.309	966.350
Polymer #1	16	0	522.257	74.623	726.275

W= -134.000 T+ = 1.000 T-= -135.000
Z-Statistic (based on positive ranks) = -3.464
P(est.) = <0.001 P(exact)= <0.001

The change that occurred with the treatment is greater than would be expected by chance; there is a statistically significant difference (P = <0.001).

R Statistical Output:

```
Wilcoxon Signed-Rank test with continuity correction

data:  StablCal and Polymer #1
V = 135, p-value = 6.104e-05
alternative hypothesis: true location shift is not equal to 0
95 percent confidence interval:
 109.9402 232.6727
sample estimates:
(pseudo)median
      146.2001
```

Summary of Results

There is a strong linear association between measurements made with the two sensors (R = 1.00). Relative percentage difference ranged from 14 to 41 percent (median: 29 percent; mean: 30 percent). The data did not pass the Shapiro-Wilk test for normality ($P<0.05$); therefore, a Wilcoxon signed-rank test was performed. The difference between median values for the StablCal- and polymer #1-calibrated EXO sensors was statistically significant ($P<0.05$).

Statistical Analyses - StablCal and Polymer #2 data

Slope comparison

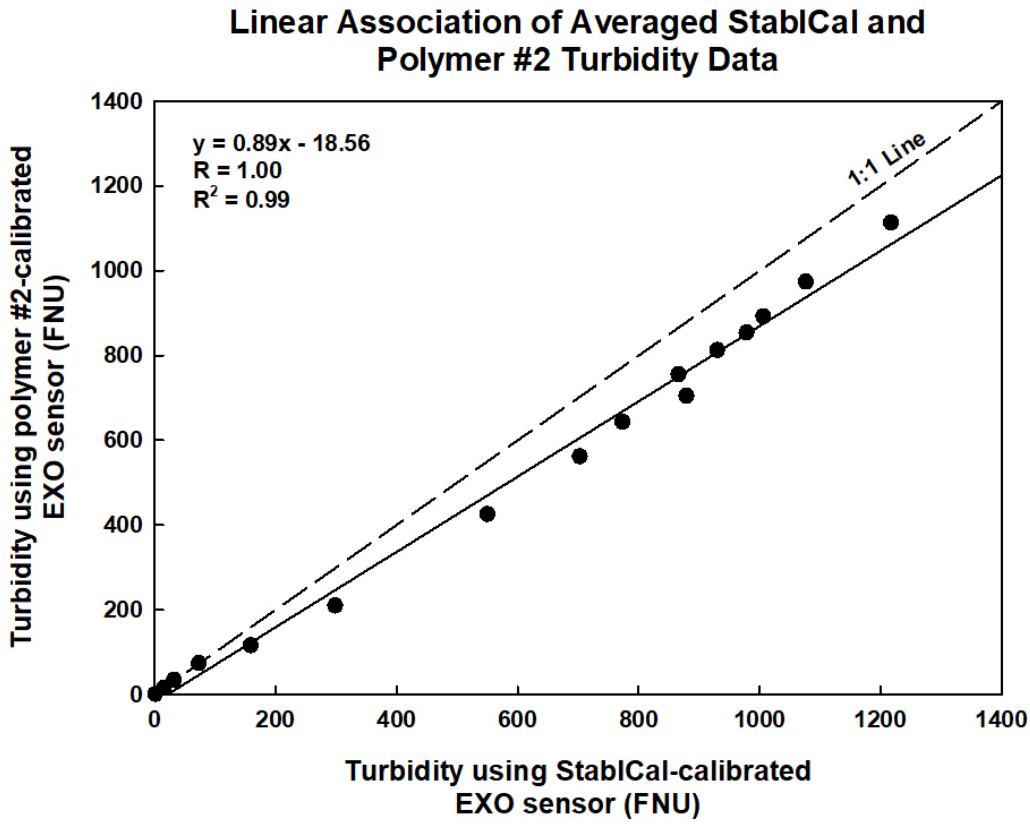
The following is a summary of final regression analysis for sensor-measured turbidity from one YSI EXO turbidity sensor calibrated by using StablCal turbidity standard and one YSI EXO turbidity sensor calibrated by using polymer #2 turbidity standard at the Kansas Water Science Center laboratory, Lawrence, Kansas, on September 7, 2017; the data used in the final regressions were averages of turbidity for each step, each of which had a duration of approximately 15 minutes once the sensor had stabilized:

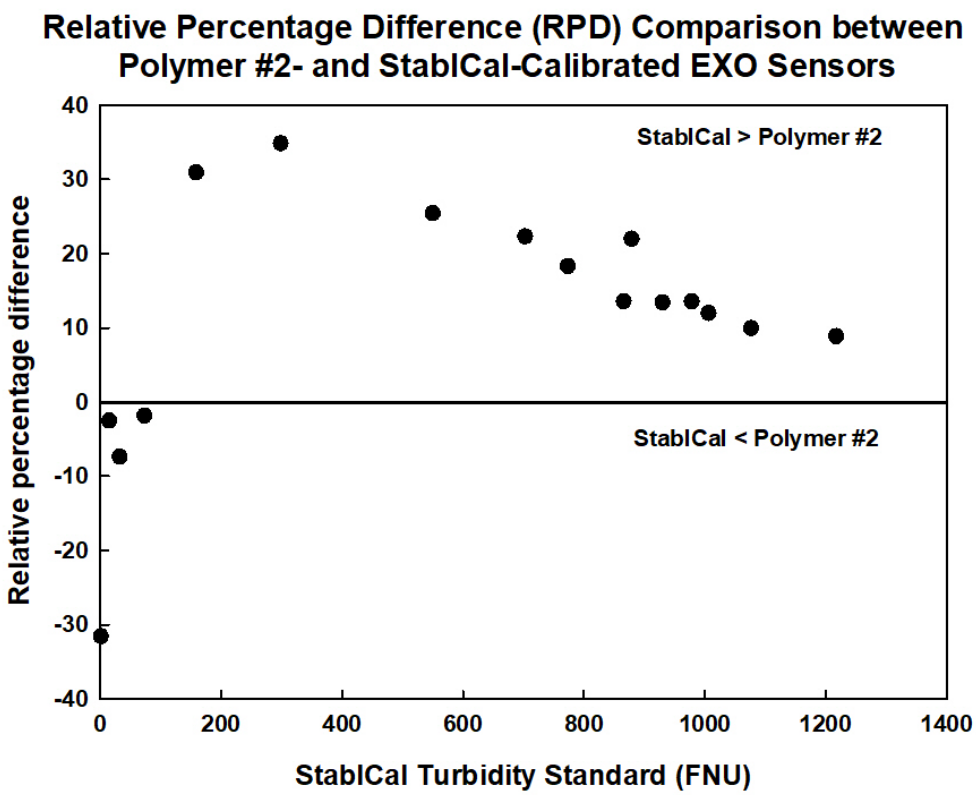
$$y = 0.89x – 18.56$$

where

y = turbidity measured with polymer #2-calibrated EXO sensor (FNU)

x = turbidity measured with StablCal-calibrated EXO sensor (FNU).


Linear Association of Averaged StablCal and
Polymer #2 Turbidity Data
y = 0.89x - 18.56
R = 1.00
R2 = 0.99
1:1 Line
Turbidity using polymer #2-calibrated
EXO sensor (FNU)
Turbidity using StablCal-calibrated
EXO sensor (FNU)
0
200
400
600
800
1000
1200
1400



Wilcoxon Signed-Rank Test for StablCal and Polymer #2 Data

SigmaPlot Statistical Output:

Normality Test (Shapiro-Wilk): Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
StablCal	16	0	738.304	94.309	966.350
Polymer #2	16	0	602.826	84.690	843.876

W= -116.000 T+ = 10.000 T-= -126.00
0
Z-Statistic (based on positive ranks) = -2.999

P(est.) = 0.003 P(exact)= 0.001

The change that occurred with the treatment is greater than would be expected by chance; there is a statistically significant difference (P = 0.001).

R Statistical Output:

```
Wilcoxon Signed-Rank test with continuity correction

data:  StablCal and Polymer #2
V = 126, p-value = 0.001312
alternative hypothesis: true location shift is not equal to 0
95 percent confidence interval:
  54.8821 120.4898
sample estimates:
(pseudo)median
      87.74091
```

Summary of Results

There is a strong linear association between measurements made with the two sensors (R = 1.00). Relative percentage difference ranged from 2 to 35 percent (median: 14 percent; mean: 17 percent). The data did not pass the Shapiro-Wilk test for normality ($P<0.05$); therefore, a Wilcoxon signed-rank test was performed. The difference between median values for the StablCal- and polymer #2-calibrated EXO sensors was statistically significant ($P<0.05$).

Statistical Analyses – Polymer #1 and Polymer #2 Data

Slope comparison

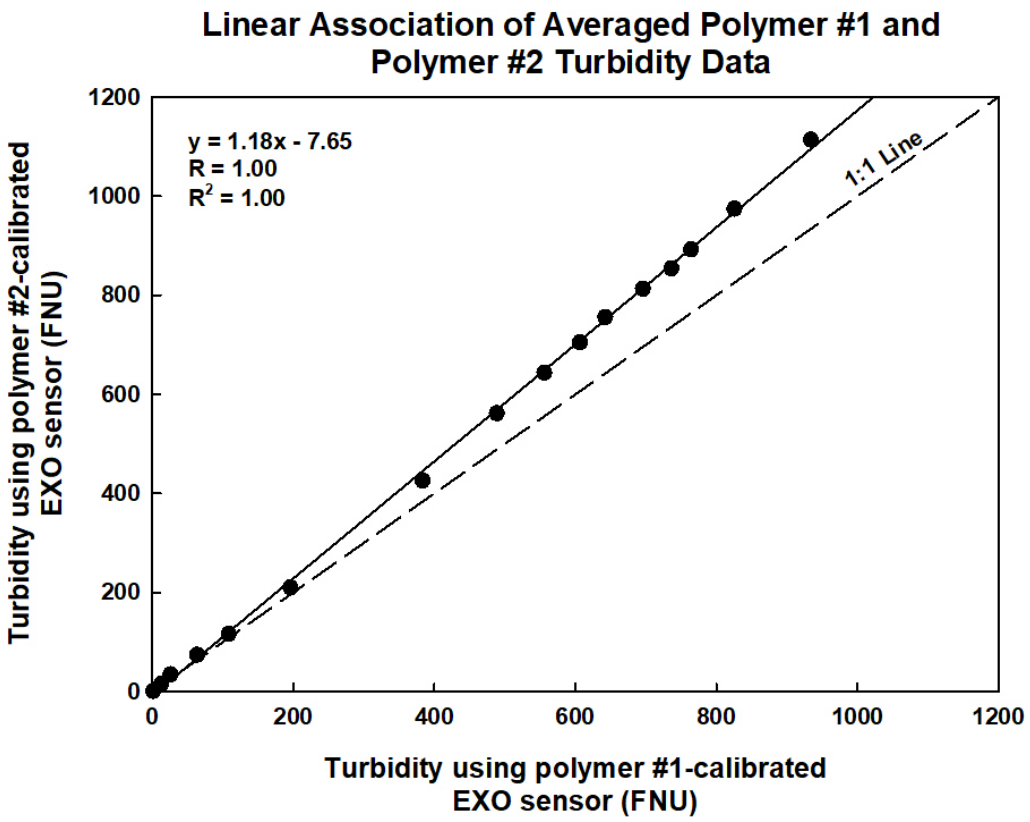
The following is a summary of final regression analysis for sensor-measured turbidity from one YSI EXO turbidity sensor calibrated by using polymer #1 turbidity standard and one YSI EXO turbidity sensor calibrated by using polymer #2 turbidity standard at the Kansas Water Science Center laboratory, Lawrence, Kansas, on September 7, 2017; the data used in the final regressions were averages of turbidity for each step, each of which had a duration of approximately 15 minutes once the sensor had stabilized:

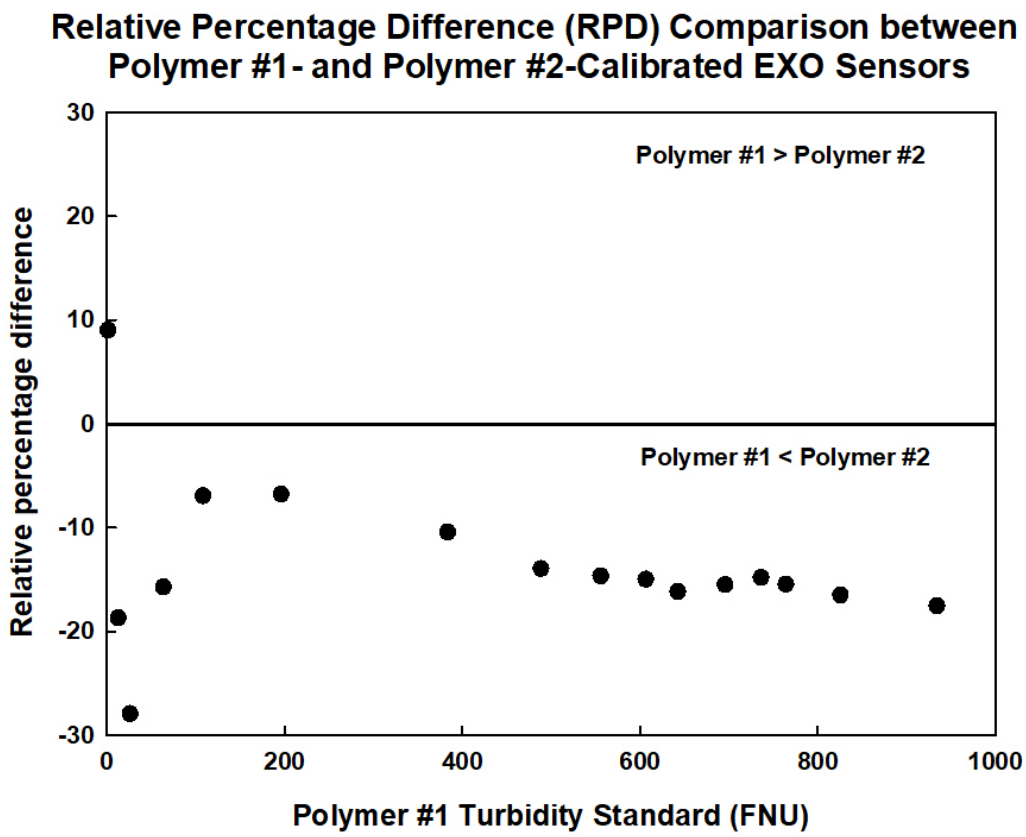
$$y = 1.18x – 7.65$$

where

y = turbidity measured with polymer #2-calibrated EXO sensor (FNU)

x = turbidity measured with polymer #1-calibrated EXO sensor (FNU).


Linear Association of Averaged Polymer #1 and Polymer #2 Turbidity Data
y = 1.18x - 7.65
R = 1.00
R2 = 1.00
1:1 Line
Turbidity using polymer #2-calibrated EXO sensor (FNU)
Turbidity using polymer #1-calibrated EXO sensor (FNU)
0
200
400
600
800
1000
1200



Paired t-test for Polymer #1 and Polymer #2 Data

SigmaPlot Statistical Output:

Normality Test (Shapiro-Wilk): Passed (P = 0.077)

Paired t-test:

Treatment Name	N	Missing	Mean	Std Dev	SEM
Polymer #1	16	0	440.127	326.305	81.576
Polymer #2	16	0	511.938	385.339	96.335
Difference	16	0	-71.810	59.725	14.931

t = -4.809 with 15 degrees of freedom.

95 percent two-tailed confidence interval for difference of means: -103.635 to -39.985

Two-tailed P-value = 0.000230

The change that occurred with the treatment is greater than would be expected by chance; there is a statistically significant change (P = <0.001)

One-tailed P-value = 0.000115

The sample mean of treatment Polymer 2 exceeds the sample mean of treatment Polymer 1 by an amount that is greater than would be expected by chance, rejecting the hypothesis that the population mean of treatment Polymer 1 is greater than or equal to the population mean of treatment Polymer 2. (P = <0.001)

Power of performed two-tailed test with alpha = 0.050: 0.994

Power of performed one-tailed test with alpha = 0.050: 0.998

Summary of Results

There is a strong linear association between measurements made with the two sensors (R = 1.00). Relative percentage difference ranged from 7 to 28 percent (median: 15 percent; mean: 15 percent). The data passed the Shapiro-Wilk test for normality (P=0.077); therefore, a paired t-test was performed. The difference between mean values for the polymer #1- and polymer #2-calibrated EXO sensor was statistically significant (P<0.05).

Statistical Analyses - StablCal and Hach 2100AN Data

Slope comparison

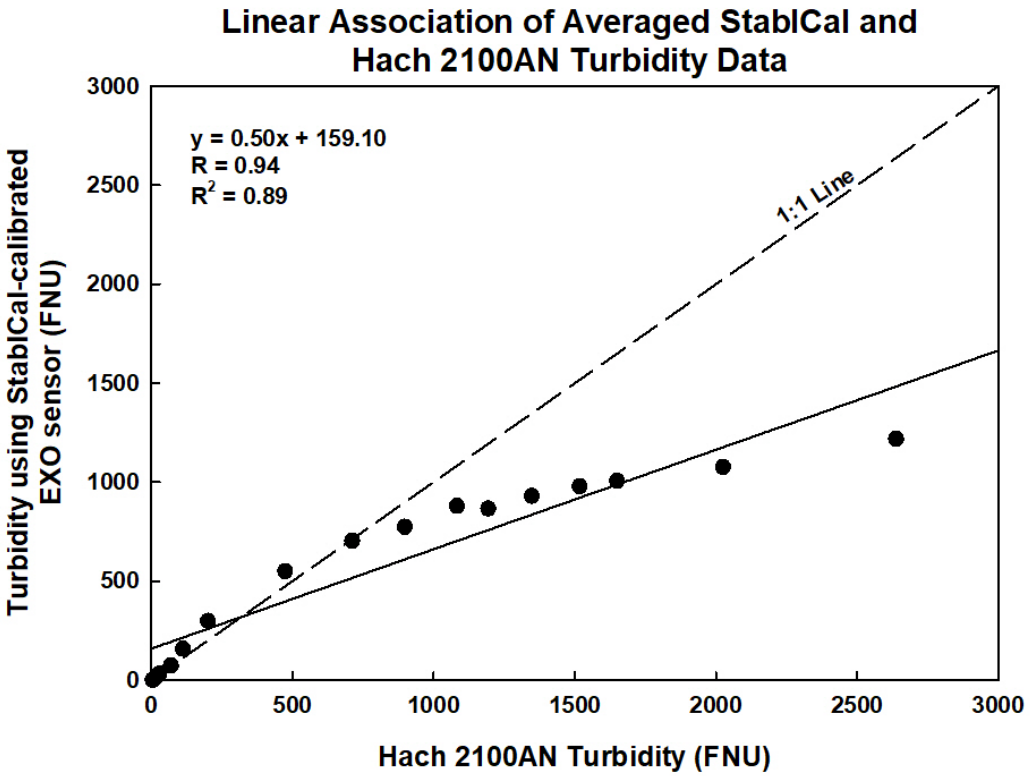
The following is a summary of final regression analysis for sensor-measured turbidity from one YSI EXO turbidity sensor calibrated by using StablCal turbidity standard and the Hach 2100AN laboratory turbidimeter at Kansas Water Science Center laboratory, Lawrence, Kansas, on September 7, 2017; the data used in the final regressions were averages of turbidity for each step, each of which had a duration of approximately 15 minutes once the sensor had stabilized:

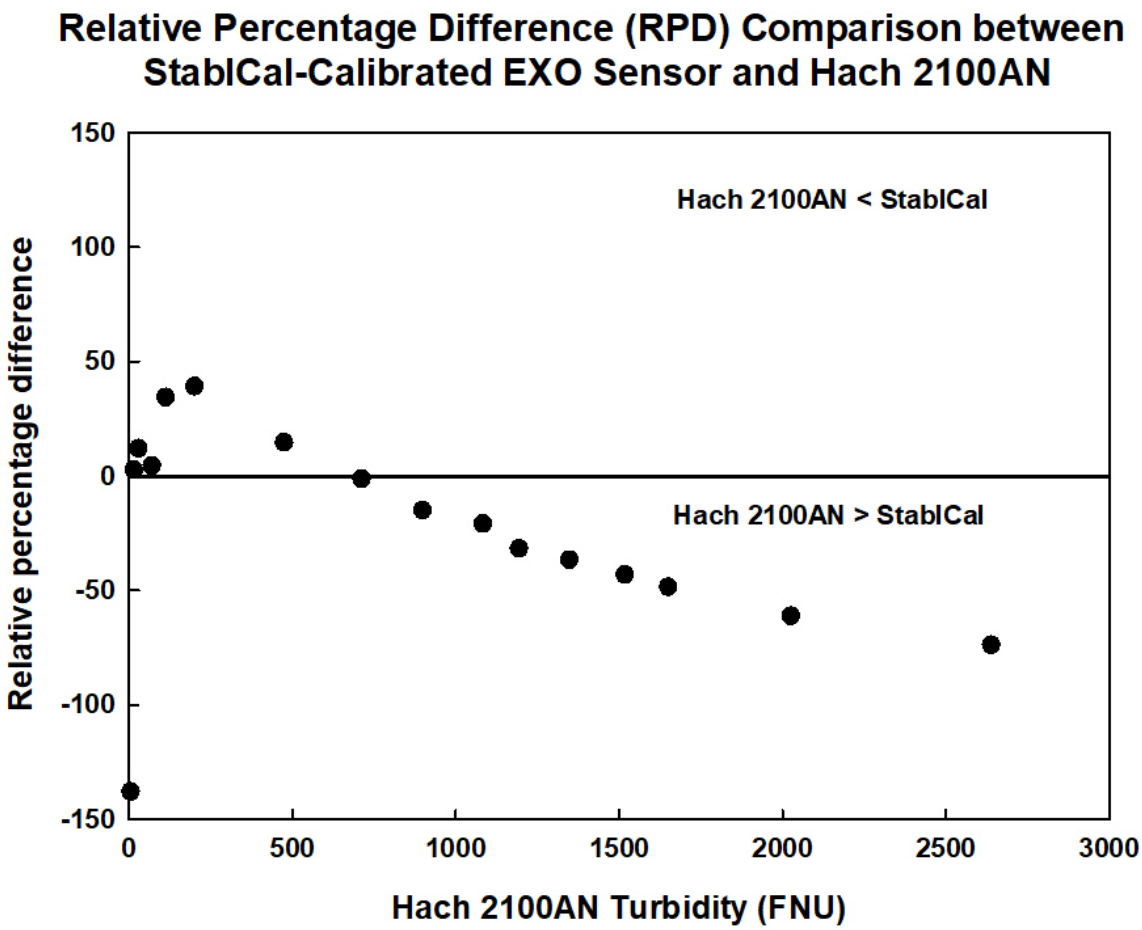
$$y = 0.50x + 159.10$$

where

y = turbidity measured with StablCal-calibrated EXO sensor (FNU)

x = turbidity measured with Hach 2100AN turbidimeter (FNU).


Linear Association of Averaged StablCal and
Hach 2100AN Turbidity Data
y = 0.50x + 159.10
R = 0.94
R2 = 0.89
1:1 Line
Turbidity using StablCal-calibrated
EXO sensor (FNU)
Hach 2100AN Turbidity (FNU)
0
500
1000
1500
2000
2500
3000



Wilcoxon Signed-Rank Test for StablCal and Hach 2100AN Data

SigmaPlot Statistical Output:

Normality Test (Shapiro-Wilk): Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Hach 2100AN	16	0	804.750	80.238	1475.000
StablCal	16	0	738.304	94.309	966.350

W= -82.000 T+ = 27.000 T-= -109.000

Z-Statistic (based on positive ranks) = -2.120

P(est.) = 0.036 P(exact)= 0.034

The change that occurred with the treatment is greater than would be expected by chance; there is a statistically significant difference (P = 0.034).

R Statistical Output:

```
Wilcoxon Signed-Rank test with continuity correction

data:  Hach 2100AN and StablCal
V = 109, p-value = 0.03354
alternative hypothesis: true location shift is not equal to 0
95 percent confidence interval:
   1.785954 478.299815
sample estimates:
(pseudo)median
      207.8856
```

Summary of Results

There is a strong linear association between measurements made with the two sensors (R = 0.94). Relative percentage difference ranged from 3 to 138 percent (median: 33 percent; mean: 36 percent). The data did not pass the Shapiro-Wilk test for normality (P<0.05); therefore, a Wilcoxon signed-rank test was performed. The difference between median values for the StablCal-calibrated EXO sensor and Hach 2100AN was statistically significant (P<0.05).

Statistical Analyses – Polymer #1 and Hach 2100AN Data

Slope comparison

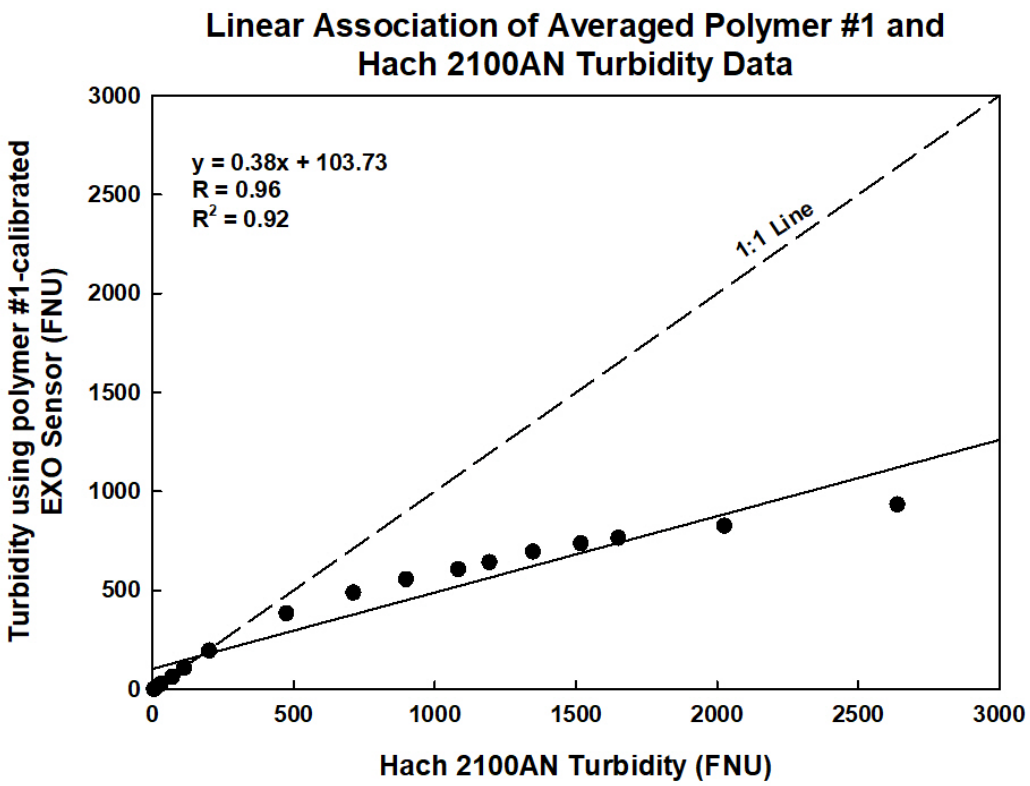
The following is a summary of final regression analysis for sensor-measured turbidity from one YSI EXO turbidity sensor calibrated by using polymer #1 turbidity standard and the Hach 2100AN laboratory turbidimeter at the Kansas Water Science Center laboratory, Lawrence, Kansas, on September 7, 2017; the data used in the final regressions were averages of turbidity for each step, each of which had a duration of approximately 15 minutes once the sensor had stabilized:

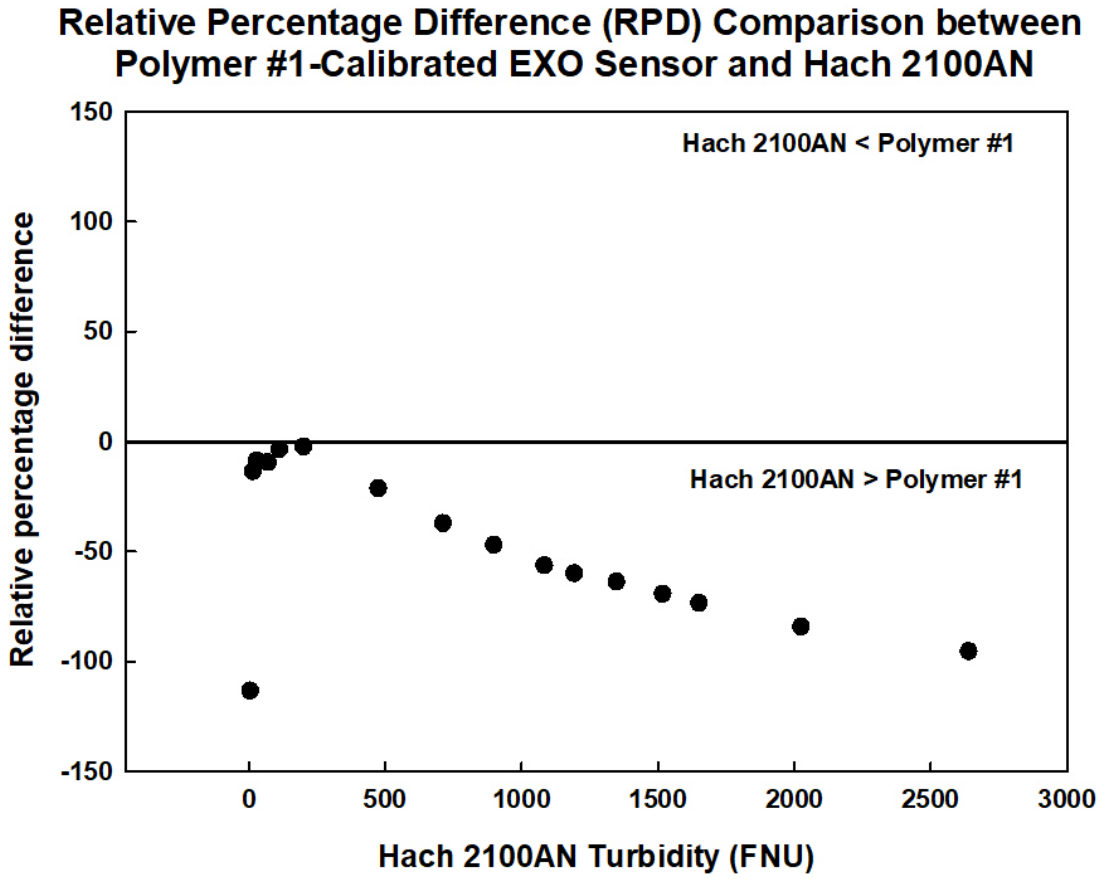
$$y = 0.38x + 103.73$$

where

y = turbidity measured with polymer #1-calibrated EXO sensor (FNU)

x = turbidity measured with Hach 2100AN turbidimeter (FNU).


Linear Association of Averaged Polymer #1 and
Hach 2100AN Turbidity Data
y = 0.38x + 103.73
R = 0.96
R2 = 0.92
1:1 Line
Turbidity using polymer #1-calibrated
EXO Sensor (FNU)
Hach 2100AN Turbidity (FNU)
0
500
1000
1500
2000
2500
3000



Wilcoxon Signed-Rank Test for Polymer #1 and Hach 2100AN Data

SigmaPlot Statistical Output:

Normality Test (Shapiro-Wilk): Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Hach 2100AN	16	0	804.750	80.238	1475.000
Polymer #1	16	0	522.257	74.623	726.275

W= -136.000 T+ = 0.000 T-= -136.000

Z-Statistic (based on positive ranks) = -3.516

P(est.) = <0.001 P(exact)= <0.001

The change that occurred with the treatment is greater than would be expected by chance; there is a statistically significant difference (P = <0.001).

R Statistical Output:

```
Wilcoxon Signed-Rank test with continuity correction

data:  Hach and Polymer
V = 136, p-value = 3.052e-05
alternative hypothesis: true location shift is not equal to 0
95 percent confidence interval:
 112.6660 711.0986
sample estimates:
(pseudo)median
      389.0634
```

Summary of Results

There is a strong linear association between measurements made with the two sensors (R = 0.96). Relative percentage difference ranged from 2 to 113 percent (median: 52 percent; mean: 47 percent). The data did not pass the Shapiro-Wilk test for normality ($P<0.05$); therefore, a Wilcoxon signed-rank test was performed. The difference between median values for the polymer #1-calibrated EXO sensor and Hach 2100AN was statistically significant ($P<0.05$).

Statistical Analyses - Polymer #2 and Hach 2100AN Data

Slope comparison

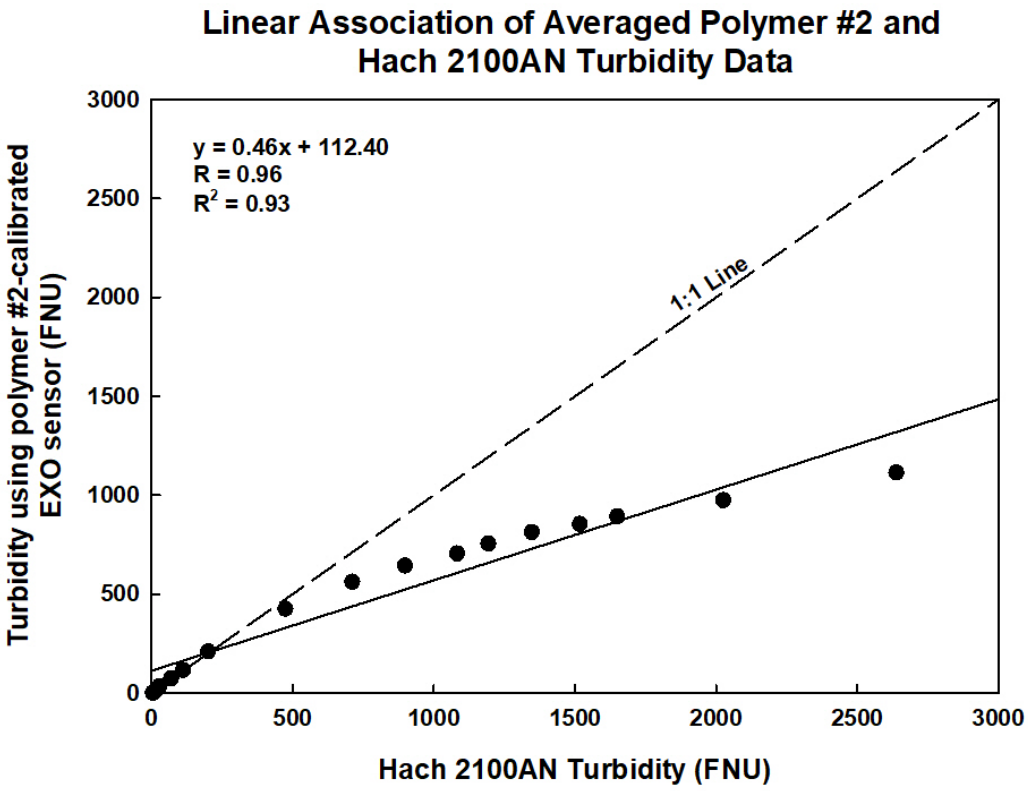
The following is a summary of final regression analysis for sensor-measured turbidity from one YSI EXO turbidity sensor calibrated by using polymer #2 turbidity standard and the Hach 2100AN laboratory turbidimeter at Kansas Water Science Center laboratory, Lawrence, Kansas, on September 7, 2017; the data used in the final regressions were averages of turbidity for each step, each of which had a duration of approximately 15 minutes once the sensor had stabilized:

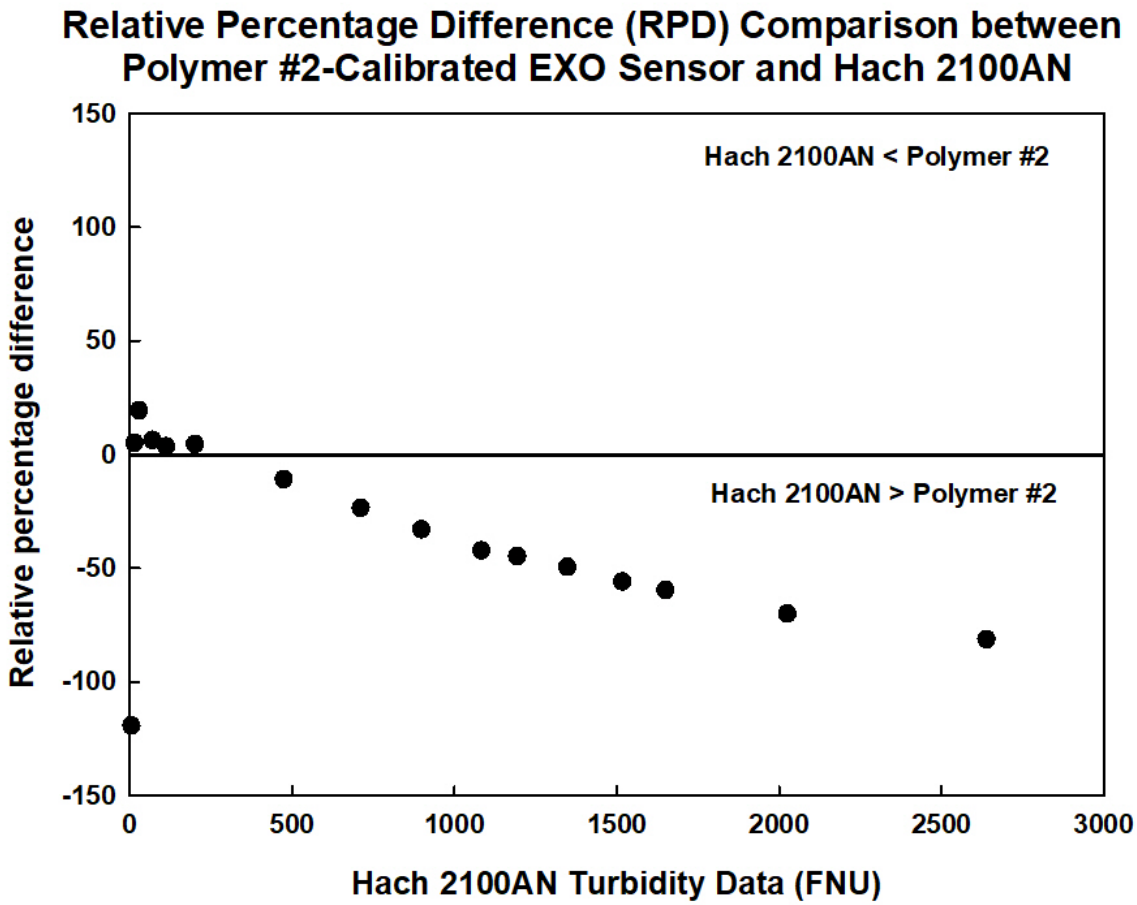
$$y = 0.46x + 112.40$$

where

y = turbidity measured with polymer #2-calibrated EXO sensor (FNU)

x = turbidity measured with Hach 2100AN turbidimeter (FNU).


Linear Association of Averaged Polymer #2 and
Hach 2100AN Turbidity Data
y = 0.46x + 112.40
R = 0.96
R² = 0.93
1:1 Line
Turbidity using polymer #2-calibrated
EXO sensor (FNU)
Hach 2100AN Turbidity (FNU)
0
500
1000
1500
2000
2500
3000



Wilcoxon Signed-Rank Test for Polymer #2 and Hach 2100AN Data

SigmaPlot Statistical Output:

Normality Test (Shapiro-Wilk): Failed (P < 0.050)

Group	N	Missing	Median	25%	75%
Hach 2100AN	16	0	804.750	80.238	1475.000
Polymer 2	16	0	602.826	84.690	843.876

W= -98.000 T+ = 19.000 T-= -117.000

Z-Statistic (based on positive ranks) = -2.534

P(est.) = 0.012 P(exact)= 0.009

The change that occurred with the treatment is greater than would be expected by chance; there is a statistically significant difference (P = 0.009).

R Statistical Output:

```
Wilcoxon Signed-Rank test with continuity correction

data:  Hach and Polymer
V = 117, p-value = 0.009186
alternative hypothesis: true location shift is not equal to 0
95 percent confidence interval:
  71.78448 597.68616
sample estimates:
(pseudo)median
      304.6786
```

Summary of Results

There is a strong linear association between measurements made with the two sensors (R = 0.96). Relative percentage difference ranged from 4 to 119 percent (median: 38 percent; mean: 39 percent). The data did not pass the Shapiro-Wilk test for normality (P<0.05); therefore, a Wilcoxon signed-rank test was performed. The difference between median values for the polymer #2-calibrated EXO sensor and Hach 2100AN was statistically significant (P<0.05).

Selected References

Cleveland, W.S., 1979, Robust locally weighted regression and smoothing scatterplots: Journal of the American Statistical Association, v. 74, no. 368, p. 829–836.

Helsel, D.R., and Hirsch, R.M., 2002, Statistical methods in water resources—Hydrologic analysis and interpretation: U.S. Geological Survey Techniques of Water-Resources Investigations, book 4, chap. A3, 522 p. [Also available at https://doi.org/10.3133/twri04A3.]

King, L.R., 2021, Laboratory and field data for selected turbidity standard and sensor comparisons, October 2014 to September 2017: U.S. Geological Survey Data Release, https://doi.org/10.5066/P9EVSDHH.

U.S. Geological Survey, variously dated, The national field manual for the collection of water-quality data: U.S. Geological Survey Techniques and Methods, book 9, chaps A1–A10. [Also available at https://water.usgs.gov/owq/FieldManual/.]