



Field Comparison of Optical and Clark Cell Dissolved Oxygen Sensors in the Tualatin River, Oregon, 2005

By Matthew W. Johnston and John S. Williams

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Conversion Factors

Multiply	By	To obtain
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)

Acknowledgments

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Abstract

Comparison of two Clark cell type dissolved oxygen sensors with three optical sensors in the Tualatin River, Oregon, indicated that the optical sensors were less prone to fouling drift and calibration drift. In two cleanings and calibrations over the 3-week study, the Clark cells exhibited fouling drifts ranging from 0.17 to 0.37 mg/L (milligrams per liter) and calibration drifts ranging from -0.22 to 0.03 mg/L. The optical sensors had fouling drifts ranging from 0 to 0.02 mg/L and calibration drifts ranging from -0.09 to 0.02 mg/L after 2–3 weeks of deployment. Measurements by the Clark cell and optical sensors compared well to each other and to point measurements of oxygen concentration using the Winkler method, indicating that the optical sensors were as accurate as the Clark cell sensors under the study conditions.

Introduction

The U.S. Geological Survey monitors dissolved oxygen (DO) concentration in the Tualatin River, west of Portland, Oregon, as part of a long-term assessment of the water quality of the river. (A description of the study can be found at <http://or.water.usgs.gov/tualatin/>) The Tualatin River study deploys polarographic, Clark cell type DO sensors as components of multiparameter datasondes that contain sensors for DO, temperature, pH, specific conductance, and turbidity.

Clark cell sensors measure DO indirectly through an electrochemical reaction. The tip of the sensor contains a positive electrode (cathode) and a negative electrode (anode) connected electrically by a saturated electrolyte solution, all covered by a permeable Teflon membrane. Oxygen molecules dissolved in the water pass through the membrane and are chemically reduced within the sensor, generating an electrical current that is proportional to the oxygen concentration in the water. The current is converted to a DO concentration that is either displayed on a meter or stored as data for later retrieval.

Clark cell DO sensors have been used for decades and provide accurate and precise DO data; however, they have drawbacks: (1) Clark cell units can require frequent calibration and maintenance. (2) Because oxygen is consumed at the surface of the membrane, water in that vicinity must be moving to obtain good measurements; in slow-moving water or in protective housings, mechanical stirring is necessary for most models, although YSI, Inc., has developed a technology that reportedly eliminates the need for stirring (http://www.act-us.info/Download/Do_Evaluations/ACT_VS04-04_YSI_DO.pdf, accessed March 3, 2006). (3) The Teflon membrane can be punctured by aquatic insects, improper handling, and waterborne debris. (4) Fouling of the membrane by algae and fine waterborne materials can significantly affect measurement quality; some units employ an automatic wiper to alleviate this problem.

Optical DO sensors are a relatively new technology that can potentially reduce operating costs as a result of less-frequent required calibration and maintenance. Optical DO sensors have a tip coated on the inside with a thin layer of oxygen-sensitive fluorescent dye. A light-emitting diode (LED) shines blue light on the dye layer, causing the dye to emit red fluorescent light that travels to a photodetector. Oxygen diffusing into the sensor tip interferes with the light emitted by the dye, reducing the intensity of the light emitted, the amount of time the dye fluoresces, and the amount of time between blue light emission and

red light response. This phenomenon is known as “quenching.” The degree of quenching is directly related to oxygen concentration, and different brands of oxygen sensors use different physical aspects of quenching to calculate DO concentration in water.

From September 14, 2005, through October 7, 2005, the USGS conducted a comparison of three models of optical DO sensors and two Clark cell sensors at an existing continuous water-quality monitoring site in the Tualatin River near Oswego Dam at river mile 3.4 (fig. 1). The purpose of the study was to compare calibration drift—the tendency of instrument readings to diverge from the true value over time—and fouling drift—deviation in readings due to an accumulation on the sensor of algae and/or other organic and inorganic material in the water column—in the two types of sensors. The site was chosen because of the potential for sensor fouling in the Tualatin River at that time of the year and because the site already had two Clark cell sensors deployed there.

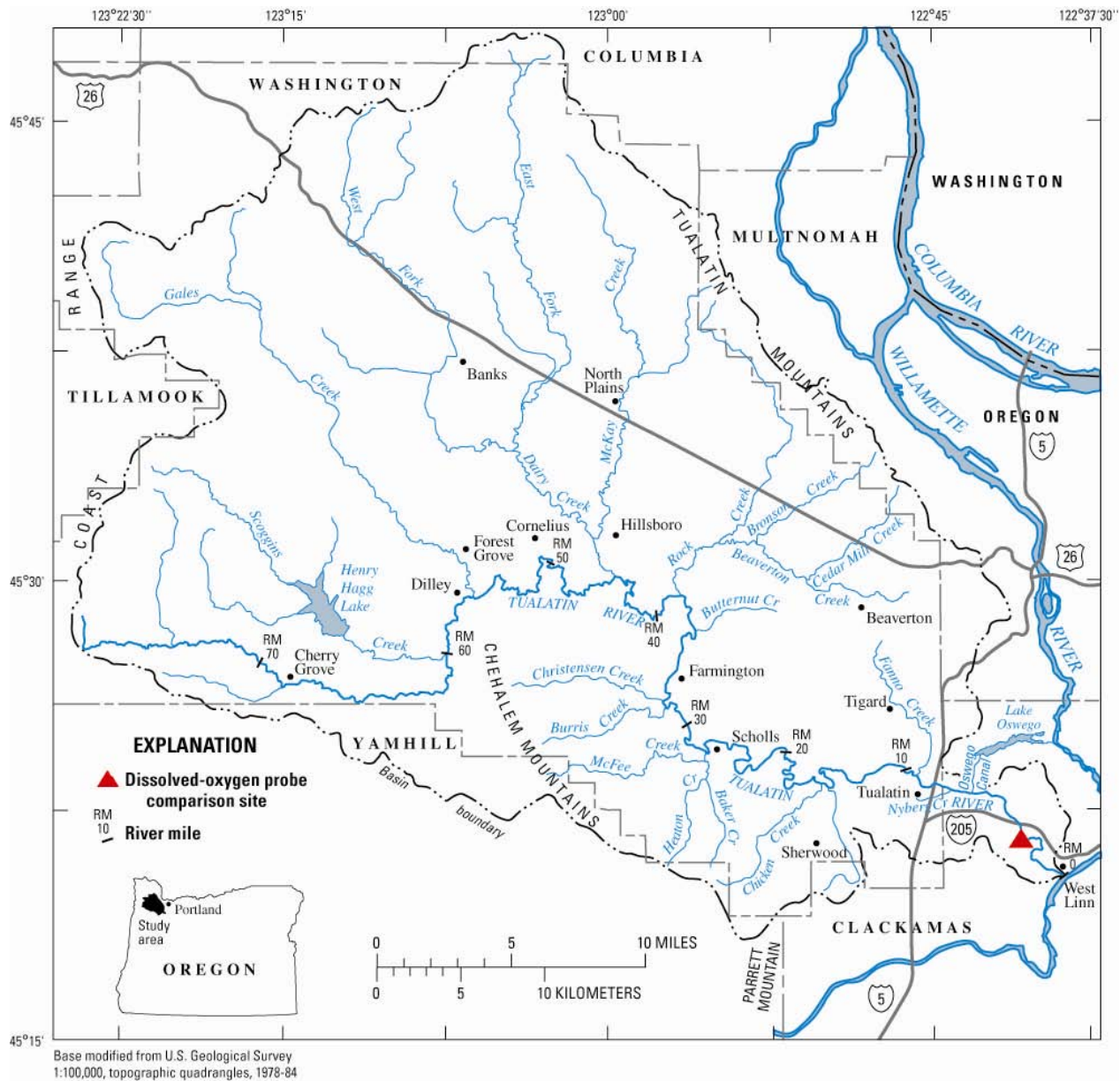


Figure 1. Tualatin River Basin, showing location of dissolved oxygen sensor comparison study.

Methods

The oxygen sensors assessed in this study were components of multiparameter datasondes. The datasonde models and their DO sensor type were:

- YSI 6600EDS (Rapid Pulse™ Clark cell sensor with automatic wiper), already deployed as part of monitoring program (<http://www.ysi.com/extranet/EPGKL.nsf/447554deba0f52f2852569f500696b21/5adb2bc006585c2c85256bb50067bf19!OpenDocument>, accessed March 3, 2006)
- YSI 600XLM (Rapid Pulse Clark cell sensor without wiper), already deployed as part of monitoring program ([http://www.ysi.com/extranet/EPGKL.nsf/447554deba0f52f2852569f500696b21/8db42369ec1b6e3a85256cef00562ec6/\\$FILE/600XL%20600XLM%200103%20E55.pdf](http://www.ysi.com/extranet/EPGKL.nsf/447554deba0f52f2852569f500696b21/8db42369ec1b6e3a85256cef00562ec6/$FILE/600XL%20600XLM%200103%20E55.pdf), accessed March 3, 2006)
- Hach® Hydrolab® MS5 (LDO™ optical sensor), deployed September 14, 2005 (http://www.hydrolab.com/products/ldo_sensor.asp, accessed March 3, 2006)
- In-Situ Troll™ 9000 (RDO™ optical sensor), deployed September 16, 2005 (http://www.in-situ.com/In-Situ/Products/TROLL9500/TROLL9500_RDO.html, accessed March 3, 2006)
- YSI 6600 (ODO optical sensor with wiper—still in development at the time of this study), deployed September 22, 2005

The sondes were housed in perforated PVC pipe at a depth of 2 feet. The three sondes containing the optical DO sensors logged data internally once every hour, on the hour, while the two sondes containing the Clark cell sensors collected data through a Campbell CR-10 data logger at the same time interval. Data collected on the CR-10 is telemetered via cell phone and displayed at <http://or.water.usgs.gov/tualatin/monitors/>. Data from the optical sensors were manually downloaded to a laptop computer at the end of the deployment period.

The two Clark cell sensors were cleaned and calibrated on August 31, prior to the study, and on September 16 and 28, during the study. The optical DO sensors were calibrated at deployment, cleaned on October 6, and recalibrated on October 7, at the end of the study period. The two Clark cell sensors were calibrated in a water-saturated-air (100% relative humidity) chamber (Radtke and others, 1998), whereas the optical sensors were calibrated in a chamber filled with air-saturated water per the manufacturers' protocols. The YSI ODO sensor could not be calibrated to the reference value for air-saturated water at ambient temperature and barometric pressure; however, the probe reading differed from the reference value by only 0.08 mg/L (milligrams per liter), probably less than the inherent error of the calibration method. The final data set was corrected for the 0.08 mg/L difference. At the time of this test, the YSI ODO sensor was still in development, and we do not presume that the calibration problem experienced during this test extends to the production version.

Two types of shifts (corrections) were applied to the data, a cleaning shift and a calibration shift. The cleaning shift is applied as a result of decreased probe performance as the probe becomes coated with algae and fine suspended material from the river. This shift is determined by observing the DO concentration, as measured by the DO sensor, before and after cleaning the probe. This difference is applied to the data set and prorated back to a difference of 0 mg/L at the time of the previous cleaning. The calibration shift is applied to the data set in the same way, but the shift is determined by observing the DO reading in a water-saturated-air or air-saturated-water chamber (depending on the sensor type) and noting the difference between that value and the 100% saturation value.

Because the DO concentration in a stream can vary over a relatively short time, a calibrated backup sensor typically is deployed while the primary sensor is being cleaned to measure DO changes that might

occur between when the primary sensor is withdrawn from the stream for cleaning and when it is placed back in the stream after cleaning, a process that takes only a few minutes. The difference in the reading before and after cleaning is corrected by the amount of change detected by the backup sensor as follows:

$$(DO_{pa} - DO_{pb}) - (DO_{ba} - DO_{bb}) \quad (1)$$

where DO_{pa} is the reading of the primary DO sensor after cleaning,

DO_{pb} is the reading of the primary DO sensor before cleaning,

DO_{ba} is the reading of the backup DO sensor after cleaning, and

DO_{bb} is the reading of the backup DO sensor before cleaning.

A backup sensor was deployed during cleaning only for the Clark cells sensors, not for the optical sensors; however, the site's permanent monitor showed no significant change in the DO concentration in the river during the cleaning operation for the optical sensors, so the general result of the comparison was not affected.

Winkler DO analyses (Radtke and others, 1998) were performed on September 30 and October 6 to provide a standard against which to measure DO sensor performance. Samples for the Winkler analysis were collected at the same depth as the test probes were deployed.

Results

Data completeness was generally good; however, the Hydrolab MS5 LDO optical sensor lost data between 9-27-2005 and 9-30-2005 due to battery failure caused by an overly long warmup period. The YSI 6600EDS and YSI 600XLM Clark cells had a few missing values on 9-16-2005 and 9-28-2005 due to a calibration visit. The Troll 9000 RDO and YSI 6600 ODO optical sensors had no missing data.

Results of the comparison are shown in figures 2–7 and tables 1–5. The Clark Cell sensors required larger shifts to the data than the optical sensors because of both calibration drift (–0.22 to 0.03 mg/L) and fouling drift (0.17 to 0.37 mg/L). The ranges of calibration and fouling drift for the optical sensors at the conclusion of the test were –0.09 to 0.02 mg/L and 0.00 to 0.02 mg/L, respectively. Fouling due to algal growth was substantial on all sensors.

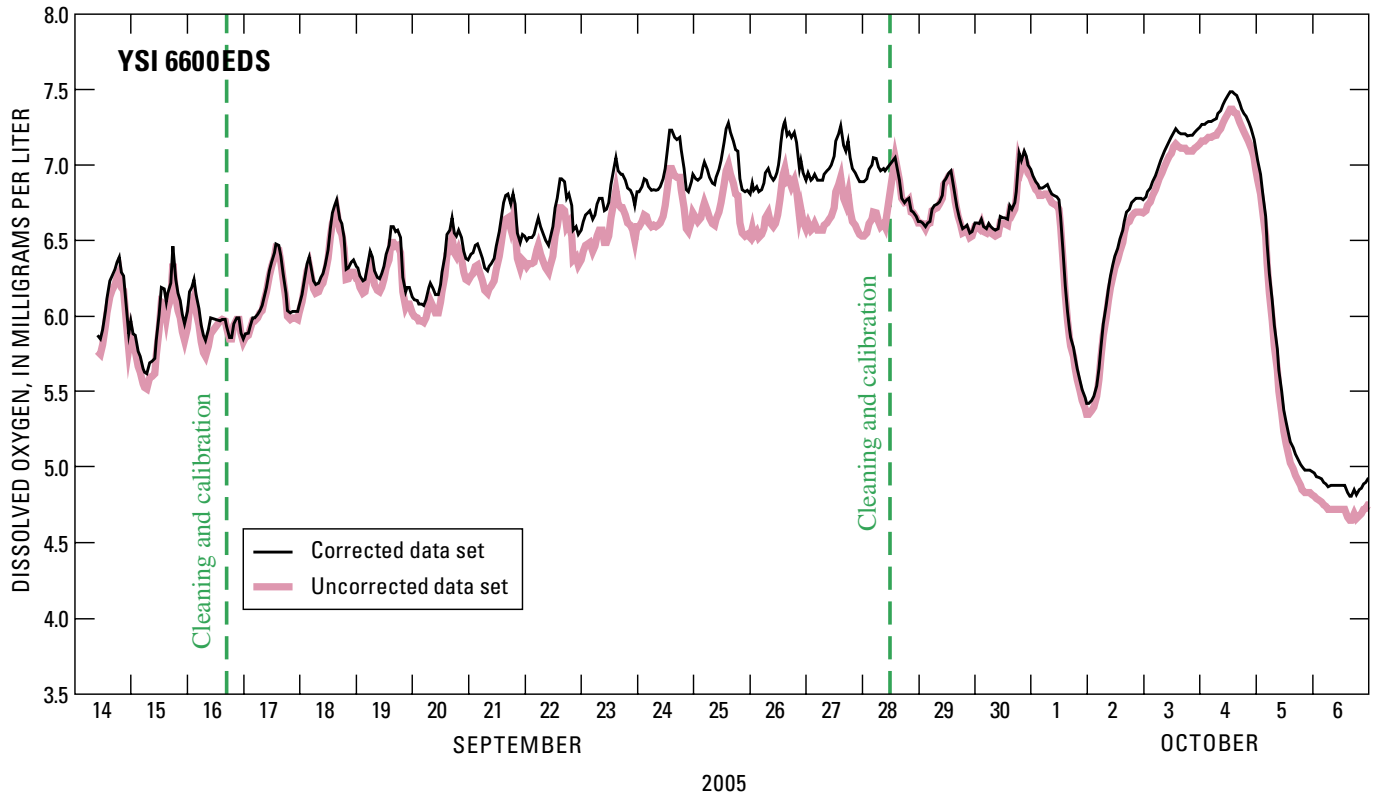


Figure 2. Uncorrected and corrected dissolved oxygen concentration data from the YSI 6600EDS Clark cell dissolved oxygen sensor.

Table 1. Cleaning- and calibration-correction data for the YSI 6600EDS Clark cell dissolved oxygen sensor

[Dissolved oxygen (DO) concentrations are in milligrams per liter. **Value for saturated air**, DO concentration in water-saturated air at ambient water temperature and barometric pressure; --, not applicable]

Date	Cleaning					Calibration		
	Before cleaning		After cleaning		Fouling drift correction	Value for saturated air	Meter reading	Calibration drift correction
	Primary sensor	Backup sensor	Primary sensor	Backup sensor				
08-31-2005	--	--	--	--	--	8.95	8.95	--
09-16-2005	5.95	6.18	6.14	6.04	0.33	9.98	10.20	-0.22
09-16-2005	--	--	--	--	--	9.98	9.98	--
09-28-2005	6.59	6.98	6.88	6.93	0.34	9.29	9.26	0.03
09-28-2005	--	--	--	--	--	9.29	9.29	--
10-12-2005	6.60	7.49	6.88	7.40	0.37	10.11	10.20	-0.09

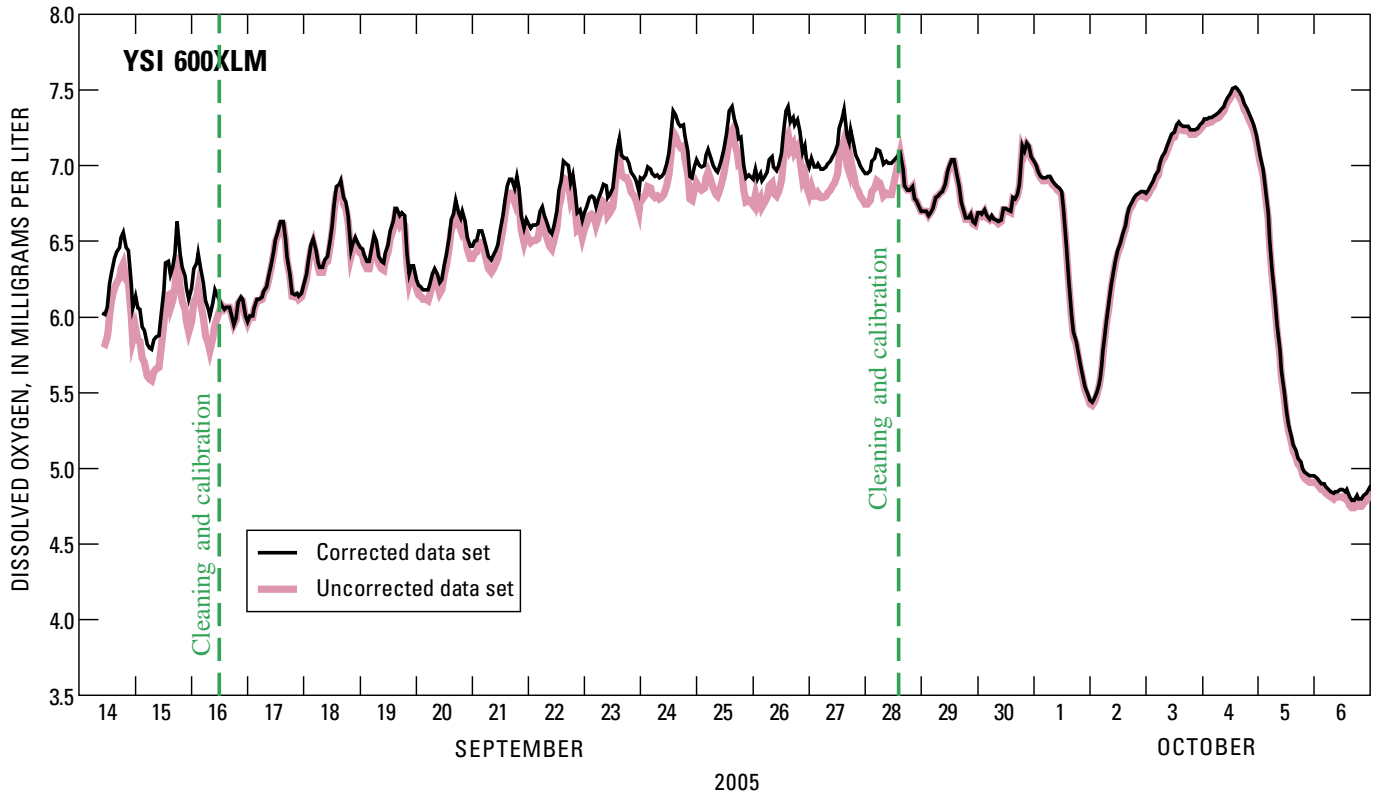


Figure 3. Uncorrected and corrected dissolved oxygen concentration data from the YSI 600XLM Clark cell dissolved oxygen sensor.

Table 2. Cleaning- and calibration-correction data for the YSI 600XLM Clark cell dissolved oxygen sensor

[Dissolved oxygen (DO) concentrations are in milligrams per liter. **Value for saturated air**, DO concentration in water-saturated air at ambient water temperature and barometric pressure; --, not applicable]

Date	Cleaning					Calibration		
	Before cleaning		After cleaning		Fouling drift correction	Value for saturated air	Meter reading	Calibration drift correction
	Primary sensor	Backup sensor	Primary sensor	Backup sensor				
08-31-2005	--	--	--	--	--	8.82	8.82	--
09-16-2005	6.01	6.16	6.19	6.04	0.30	9.90	9.97	-0.07
09-16-2005	--	--	--	--	--	9.93	9.93	--
09-28-2005	6.82	6.97	7.13	6.93	0.35	9.49	9.63	-0.14
09-28-2005	--	--	--	--	--	9.52	9.52	--
10-12-2005	6.73	7.47	6.83	7.40	0.17	10.06	10.15	-0.09

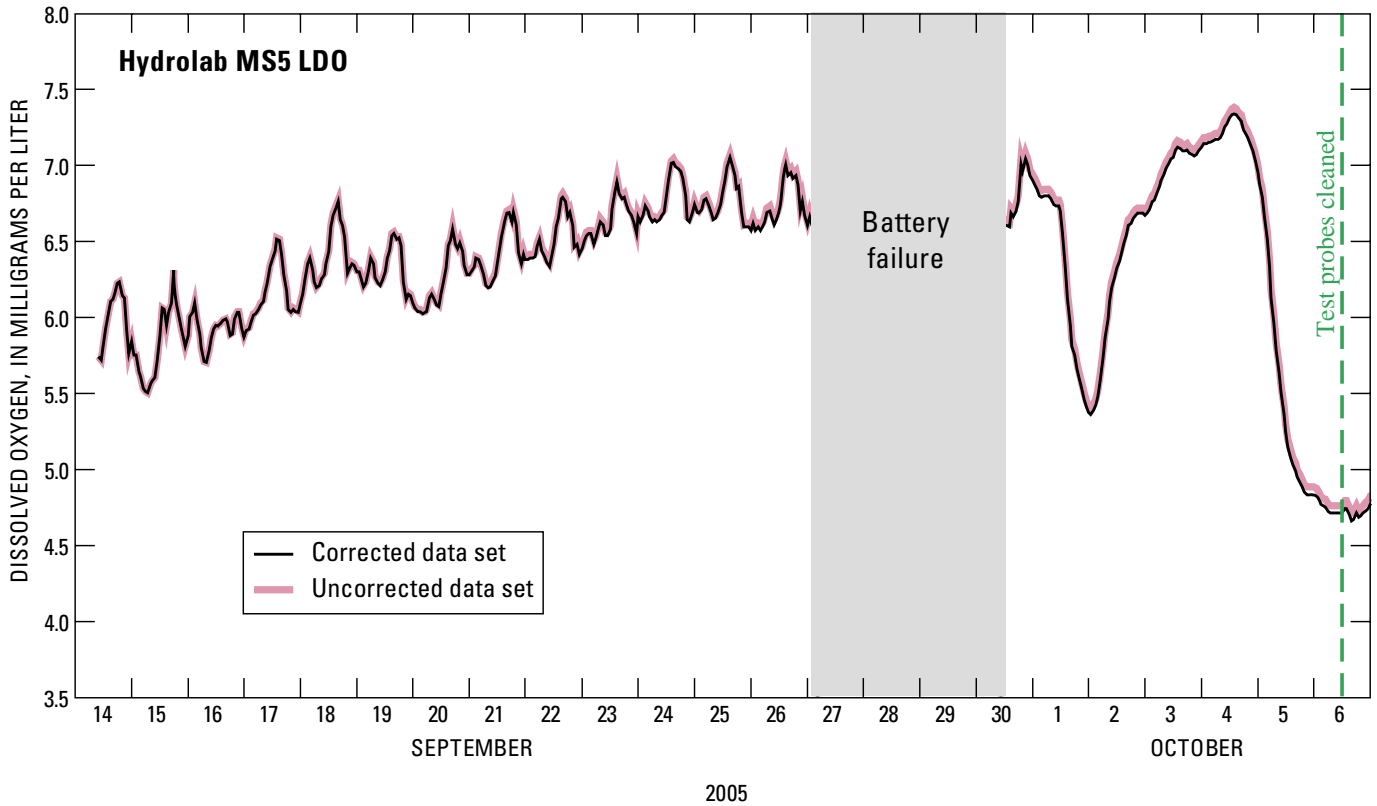


Figure 4. Uncorrected and corrected dissolved oxygen concentration data from the Hydrolab MS5 LDO optical dissolved oxygen sensor.

Table 3. Cleaning- and calibration-correction data for the Hydrolab MS5 LDO optical dissolved oxygen sensor

[Dissolved oxygen (DO) values are in milligrams per liter. **Value for saturated water**, DO concentration in air-saturated water at ambient water temperature and barometric pressure; --, not applicable]

Date	Cleaning			Calibration		
	Before cleaning	After cleaning	Fouling drift correction	Value for saturated water	Meter reading	Calibration drift correction
09-14-2005	--	--		8.74	8.74	--
10-06-2005	4.76	4.78	0.02	--	--	--
10-07-2005	--	--	--	8.56	8.65	-0.09

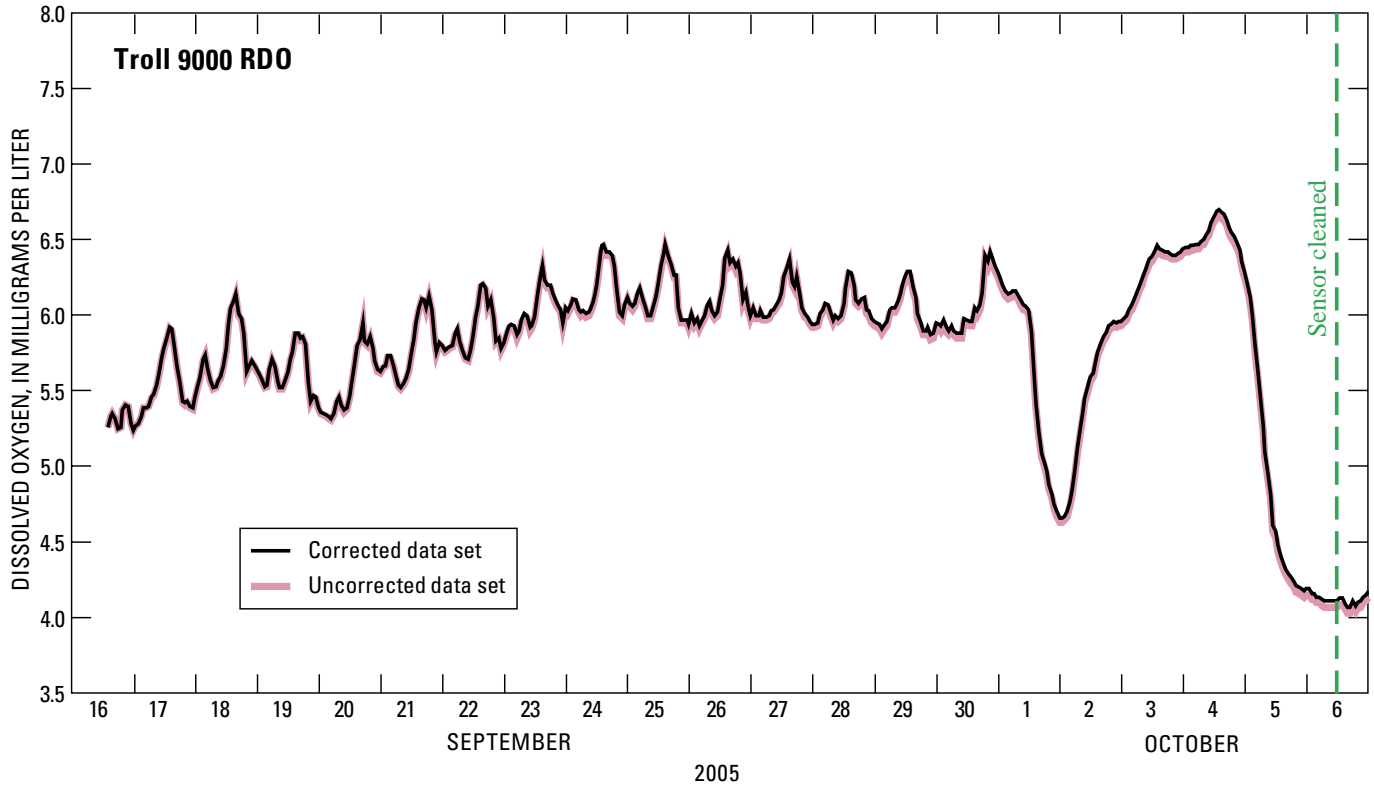


Figure 5. Uncorrected and corrected dissolved oxygen concentration data from the Troll 9000 RDO optical dissolved oxygen sensor.

Table 4. Cleaning- and calibration-correction data for the Troll 9000 RDO optical dissolved oxygen sensor

[Dissolved oxygen (DO) values are in milligrams per liter. **Value for saturated water**, DO concentration in air-saturated water at ambient water temperature and barometric pressure; --, not applicable]

Date	Cleaning			Calibration		
	Before cleaning	After cleaning	Fouling drift correction	Value for saturated water	Meter reading	Calibration drift correction
09-16-2005	--	--		8.81	8.81	--
10-06-2005	4.07	4.09	0.02	--	--	--
10-07-2005	--	--	--	8.73	8.71	0.02

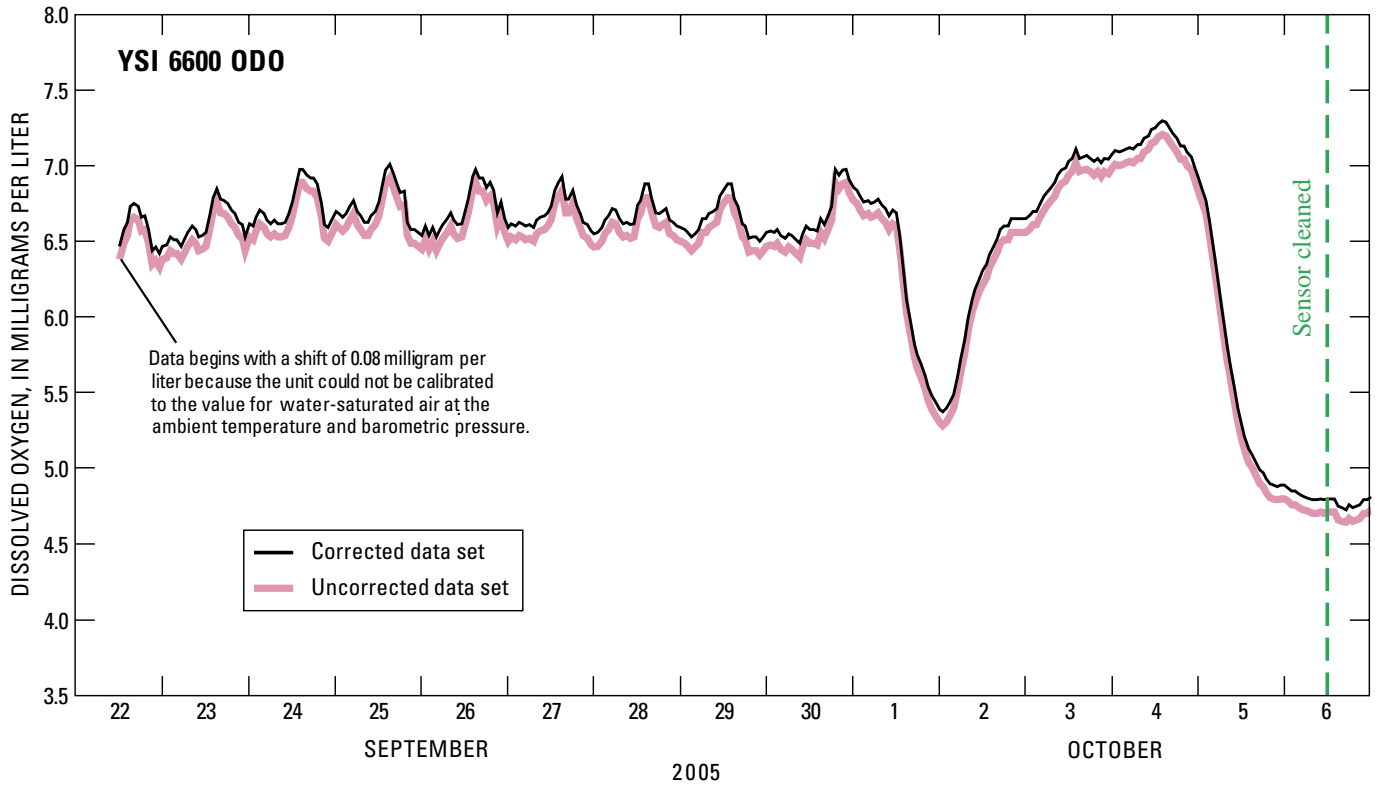


Figure 6. Uncorrected and corrected dissolved oxygen concentration data from the YSI 6600 ODO optical dissolved oxygen sensor.

Table 5. Cleaning- and calibration-correction data for the YSI 6600 ODO optical dissolved oxygen sensor

[Dissolved oxygen (DO) values are in milligrams per liter. **Value for saturated water**, DO concentration in air-saturated water at ambient water temperature and barometric pressure; --, not applicable]

Date	Cleaning			Calibration		
	Before cleaning	After cleaning	Fouling drift correction	Value for saturated water	Meter reading	Calibration drift correction
09-22-2005	--	--	--	8.68	8.60	0.08 ^a
10-06-2005	4.71	4.71	0.00	--	--	--
10-07-2005	--	--	--	8.60	8.50	0.10 ^b

^a Sensor could not be calibrated to the reference value for air-saturated water at ambient temperature and barometric pressure.

^b Actual correction is 0.02 mg/L when initial calibration discrepancy is subtracted.

All of the sensors recorded fine- and large-scale hourly and daily variations in the DO concentration at the river test site (fig. 7), as well as two large concentration swings caused by low-DO plumes on October 1–2 and October 5–7 that resulted from storm runoff. Values from the Troll 9000 RDO were

generally about one-half milligram per liter less than those from the other optical units. The values recorded by the Clark cell sensors were generally slightly higher than those from the optical sensors. Concentrations from the Winkler analyses fell midway between the concentrations recorded by the Troll 9000 RDO and those from the other sensors; thus, all of the units had similar accuracy relative to the reference standard of the Winkler analysis.

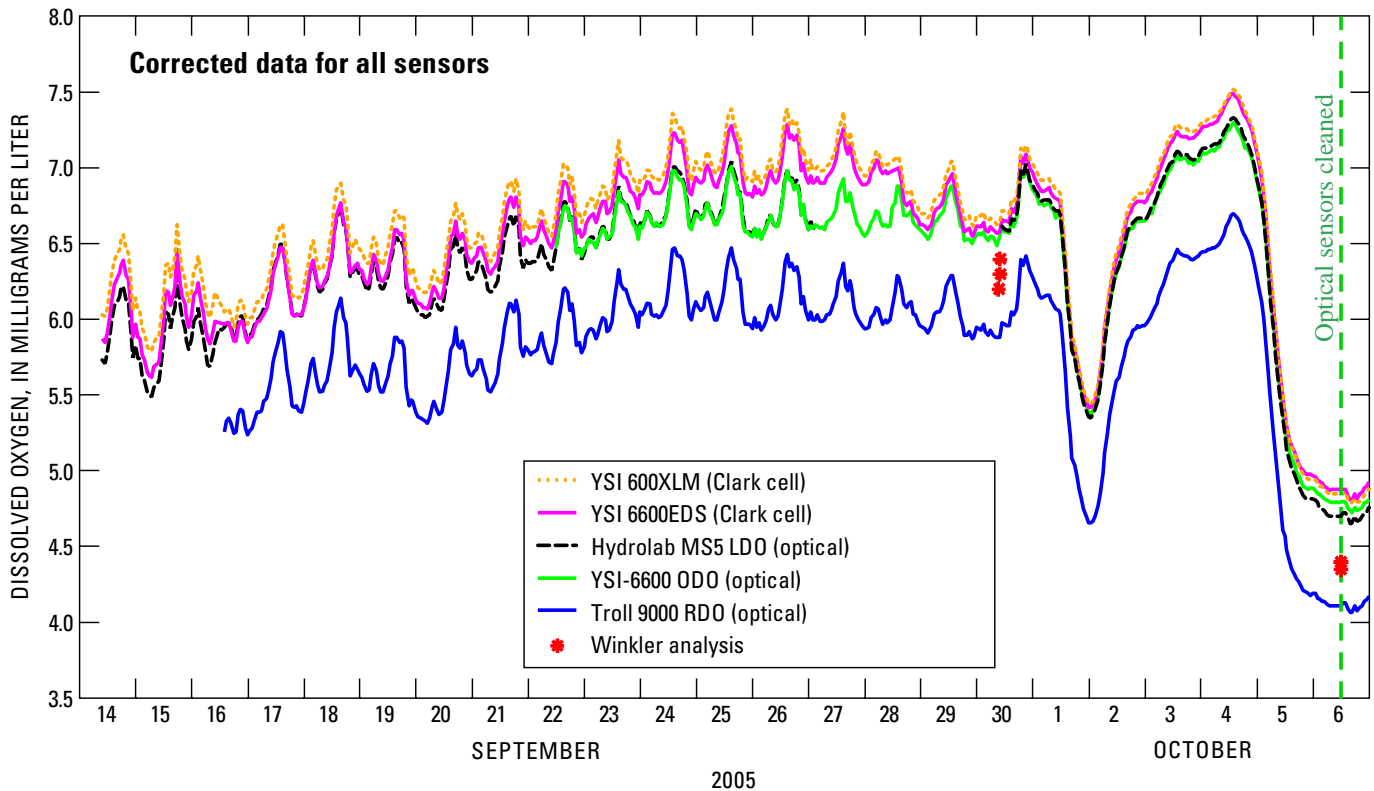


Figure 7. Dissolved oxygen concentration data from the five sensors in the comparison study and results of Winkler analyses.

Discussion

The results of this comparison study indicate that the optical sensors had accuracies similar to those of the Clark cells but were less prone to decreasing accuracy over time caused by fouling and calibration drift. Note, however, that this comparison used only single optical-sensor units from each manufacturer and consequently could not measure variation within brands. Therefore, the performance of each instrument in the comparison might not be indicative of the performance that can be expected from off-the-shelf units from each manufacturer. Further testing will be required to confirm that optical sensors routinely outperform Clark cells with regard to drift and thus require less-frequent servicing, a cost savings.

Another USGS study (Fulford and others, 2005) found that drifts due to fouling were similar between the two types of sensors in a study conducted in a brackish-water, estuarine environment for a longer time period, 30 days; the sensors were not serviced during the test. Other comparisons (Alliance for Coastal Technologies, 2005) have found, similar to this one, that the optical sensors were less prone to fouling drift and required less-frequent calibration.

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